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ACETYLENE EQUIVALENTS IN CYCLOADDITION REACTIONS

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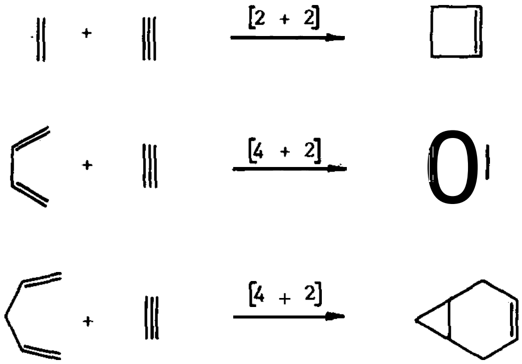
CONTENTS

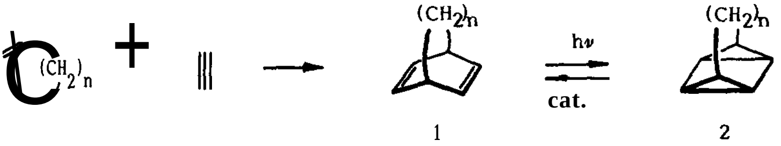
Acetylene is a poor dienophile reacting only with difficulty either thermally with dienes to give products derived from (4 + 2)-cycloaddition or photochemically with olefins to form (2 + 2)-cycloaddition products.[1-7] Nonetheless many compounds formally derived from acetylene cycloadditions are useful intermediates and/or interesting molecules. In fact, as represented in Scheme 1, cyclobutene, 1,**4-cyclohexadiene** and **bicyclo[4.1.0]hept-3-ene** may be regarded as formal cycloaddition products of acetylene to ethylene, **1,3-** and 1,**4-butadiene** respectively.

Of particular interest is the synthesis of molecules derived from the cycloaddition of acetylene to cyclic **1,3-dienes** (Scheme 2). The forced configuration imposed by the polycyclic skeleton results in interactions between the orbitals of the **1,4-diene,** causing these systems to exhibit peculiar behaviour and reactivity. An example is given by the photochemical intramolecular (2 + 2)-cycloaddition of norbornadiene **(1)** (n = 1 in Scheme 2) to the strained quadricyclane (2). This reaction is being actively investigated as a way of solar energy storage since quadricyclane may be catalytically reverted back to norbornadiene with evolution of **heat.**[8]

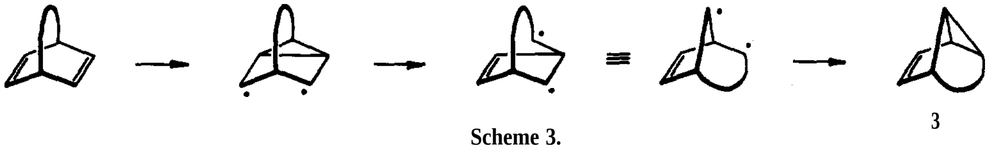
Another important characteristic of monocyclic or polycyclic **1,4-dienes** is the so called di-z-methane or Zimmermann rearrangement.' This process may be in competition with the **afore** mentioned intramolecular (2 + **2)-cycloaddition,** depending on the structural characteristic of the given molecule. As illustrated in Scheme 3 for a bicyclic diene this rearrangement affords **vinyl-**



Scheme 1.



Scheme 2.

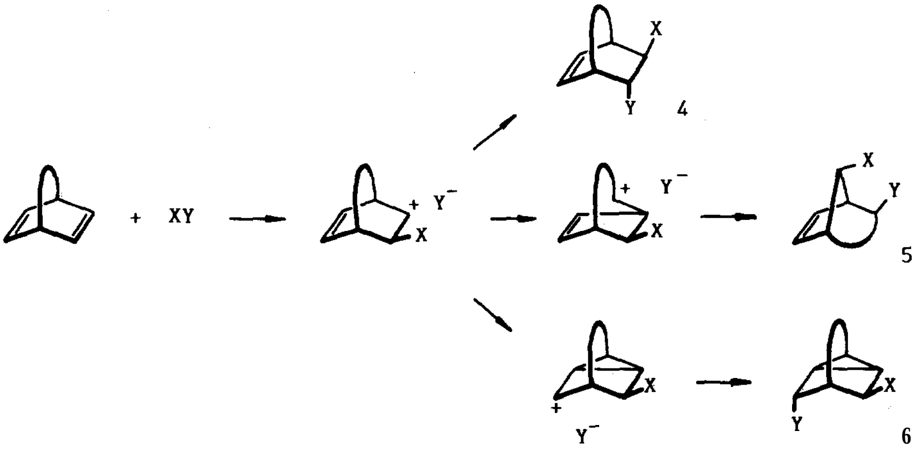


Scheme 3.

cyclopropanes 3 through postulated diradical intermediates. This photorearrangement remains a fertile field of mechanistic studies.

Polycyclic 1,4-dienes are also good ligands for transition metals and a large number of studies in this field has appeared in the literature. This property is also related to the geometry of the two double bonds in the molecule. Some of the complexes show antitumoral activity.

The addition of electrophiles to the double bonds of these polycyclic systems usually occurs with skeletal modification. Wagner-Meerwein rearrangement of the intermediate carbocation can be competitive with the formation of the unrearranged product (4) and the nortricyclane type product (6) (Scheme 4).



Scheme 4.

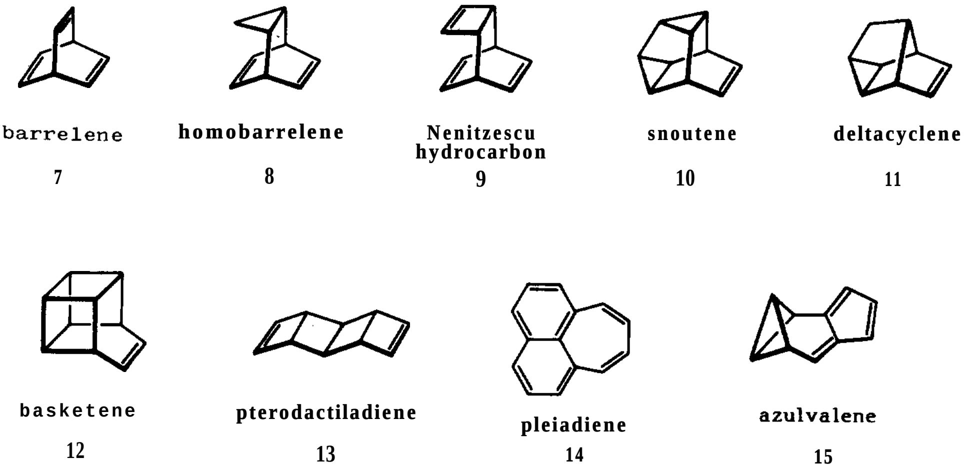
Furthermore the synthesis of individually important molecules such as those illustrated in Scheme 5 entails at least one step in which an acetylene has been introduced in a cycloaddition reaction.

On the other hand cyclobutenes and bicyclo[4.1.0]hept-3-enes, formally derived by (2 + 2) and homo (4 + 2) additions of acetylene to an olefin or a 1,4-diene, are equally important. An example is given by the oxa-di-π-methane rearrangement of systems such as **16** (Scheme 6) that can be obtained through cycloaddition of an acetylene synthon to a cyclic enone (several examples are reported in the following sections). The tricyclic systems thus obtainable have a ketone group which can be subjected to further modification. Cyclobutenes are also useful starting materials for the preparation of cyclic 1,3-dienes via the route shown in Scheme 7.

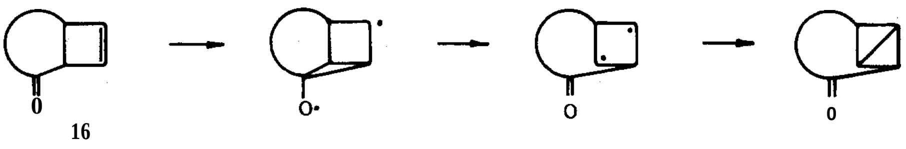
As anticipated, since acetylene itself is practically unreactive in cycloaddition, a variety of acetylene equivalents in cycloaddition reactions have been devised by several authors. Reasons for these synthetic efforts lie also in part on the safety hazard of handling gaseous acetylene at the high reaction temperatures and pressures that are normally required. A good acetylene equivalent can be defined as a reactive dienophile whose adducts can be readily converted to olefins. This concept is illustrated for a 1,3-diene in Scheme 8.

The available methods for the insertion of an ethylenic bridge by cycloaddition reactions are reviewed and the effectiveness and limitations of each procedure evaluated to give an overview on the methodologies available to meet this synthetic challenge.

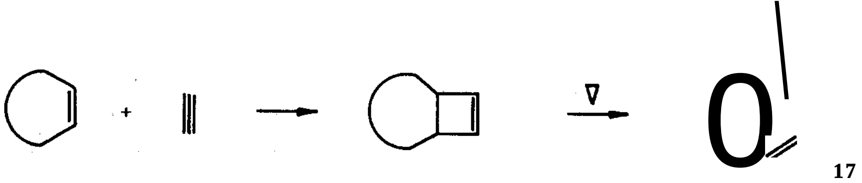
Significative examples where the adduct between 1,3-dienes and the acetylene equivalent is reduced to a saturated (substituted) cyclohexane and then eliminated to a cyclohexene (Scheme 8) will be also discussed. In this case the acetylene synthon is actually an ethylenic one but *the*



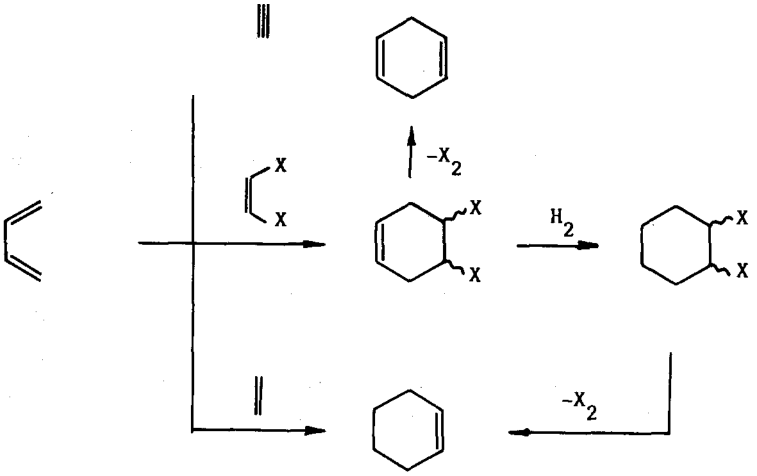
Scheme 5.



Scheme 6.



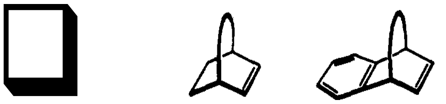
Scheme 7.



Scheme 8.

unsaturation has been introduced with the dienophile. However, as shown in Scheme 8, the crucial step is the introduction of an acetylene equivalent.

As in most of the cases the conversion of the initially obtained product to the "formal acetylene cycloadduct" amounts to the creation of an unsaturated centre, two types of acetylene adducts must be considered. In one case (type A) no reactive double bonds are present in the vicinity of the forming olefinic bond, while in the other (type B) a 1,4-diene is being formed. As will become clear later, while it is relatively easy to synthesize molecules of type A, many more difficulties may be encountered in the preparation of dienes of type B. Indeed thermolytic procedures for



type A molecules

type B dienes

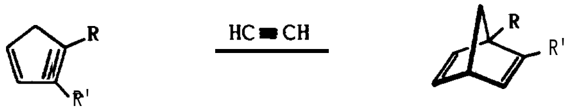
preparing dienes of type B are in general of little use since the retro Diels-Alder process is often the predominant reaction path. Furthermore the formation of lactones is frequently observed when the elimination step deals with endo carboxylic acids. These facts limit the number of mild and effective acetylene synthons and make more valuable those which are able to afford type B dienes. The present review will give them special emphasis.

The layout of the sequence of reagents was dictated in general by the method of removal of the functionalized groups leading to the formation of the carbon–carbon double bond. Thus, reagents necessitating oxidative processes are followed by those in which no change in net oxidation state is observed and then by those in which a reductive treatment is necessary. However, since in many instances this formulation cannot be observed, priority was given to the type of synthon.

CYCLOADDITION OF ACETYLENE

A few examples of acetylene cycloaddition will be discussed in this section mostly to define the limit of reactivity of the parent molecule. However, it has to be pointed out that most chemical laboratories lack the sophisticated equipment required to work under the forcing conditions needed, if the necessary safety requirements are obeyed. Nonetheless procedures involving gaseous acetylene are of importance in industrial processes for the preparation of large amounts of special chemicals.

Norbornadiene **(1)** can be obtained in 64% yield via (4 + 2)-cycloaddition of acetylene to cyclopentadiene at 280-300” and 10-12 atm.[10] These drastic conditions are effective also for the preparation of the methyl substituted norbornadienes 18 and **19**.[11]

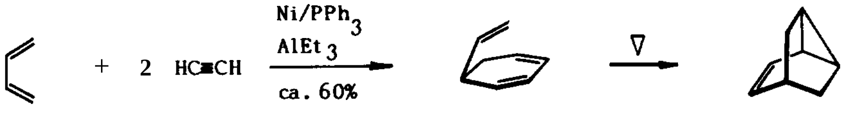


(eq. 1)

R=H R'=Me
R=Me R'=H

18 R=H R'=Me
19 R=Me R'=H

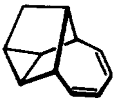
Non-cyclic dienes show a lower reactivity towards acetylene and a metal catalyst is necessary. These reactions have been already discussed in several reviews’-’ and we shall present here only a few representative examples. Acetylene and **1,3-butadiene** afford, in the presence of a catalyst, the tricyclic hydrocarbon **20**[12] (eqn 2).



20

(eq. 2)

Also homo-(4 + **2)-cycloadditions** have been reported and sometimes the structure of the products depends upon the nature of the catalyst. For example, acetylene with norbornadiene mediated by **$Co(acac)_3/Et_2AlCl$/bis(1,2-diphenylphosphino)ethane** produces **deltacyclene (11)**[13] while 21 is obtained when **$Ni(Co)_2(PPh_3)_2$** 22 is **used.**[14]



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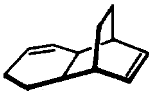
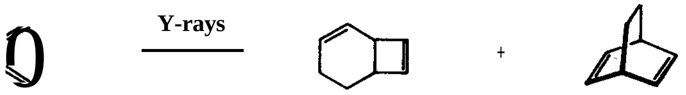


23

Cyclohexadiene, the higher **homologue** of cyclopentadiene, but not as reactive, marks the borderline of reactivity of acetylene with cyclic dienes. In fact it does not **cycloadd** with acetylene, preferring to dimerize to the tricyclic hydrocarbon 23. In this case the conjugated double bond of **cyclohexadiene** is a stronger **dienophile** than acetylene. The cycloaddition can however be promoted by **γ-radiation,**[15] to afford the (2 + **2)-** and the (4 + **2)-cycloaddition** products 24 and 25 (eqn 3).



(eq. 3)

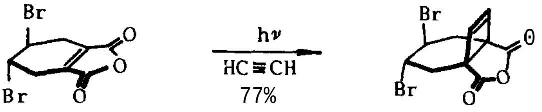
24 (27.5%) 25 (1.5%)

Photochemical (2 + **2)-cycloadditions** of acetylene are indeed possible but they are **almost** exclusively limited to cyclic **enones.** A pertinent example is the formation of 26 reported by Murata et *al.*[16] which is a key step for the preparation of the interesting ketone 27 (eqn 4).

26 27

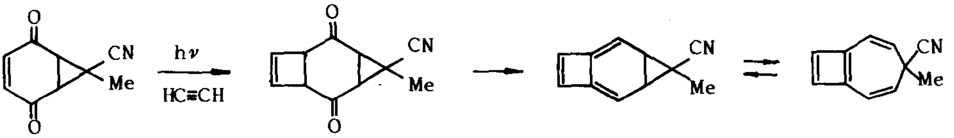
(eq. 4)

Propellane **28** has been prepared by this direct route and has been used in cycloreversion studies by **Maier**[17] (eqn 5).


28

(eq. 5)

The effect on the norcaradiene-cycloheptatriene equilibrium caused by the introduction of a cyclobutadiene in 29 has been recently studied.‘* The required starting material was made available by photochemical cycloaddition of acetylene to the homoquinone 30 (eqn 6).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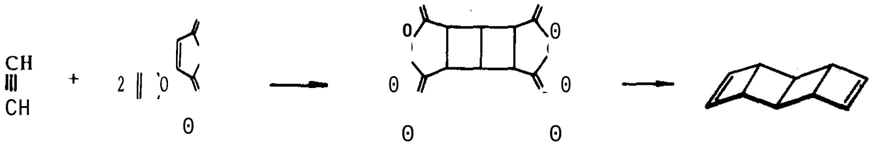
29

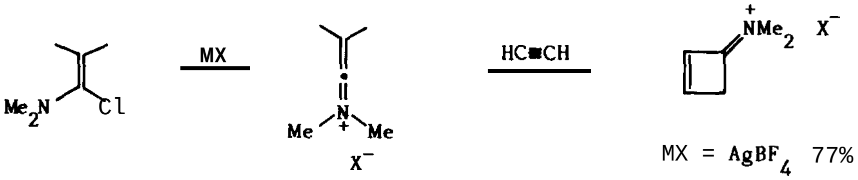
(eq. 6)

The interesting hydrocarbon pterodactyladiene 13 was prepared by Martin” through double addition of **maleic** anhydride to acetylene and subsequent manipulation of the **adduct** (eqn 7).


13

(eq. 7)

A rare example of cycloaddition of acetylene to a differently activated double bond has been reported by Ghosez et *al.* (eqn 8).[20] Other similar reactions have been reported by the Ghosez group.


(eq. 8)

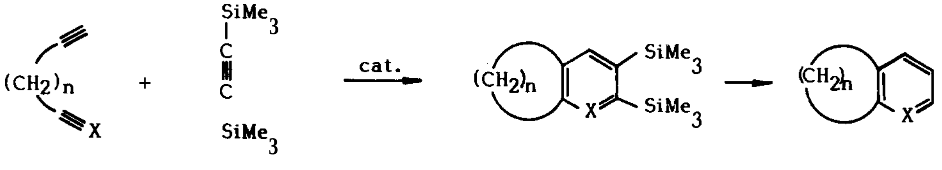
MX = $AgBF_4$ 77%
= $ZnCl_2$ 80%

A class of acetylene equivalents that must be included in the section of the parent one is that of the silyl derivatives.[21] These acetylenes should not have much different reactivity toward cycloaddition but they are much safer and easier to handle. Some examples of cycloaddition of silyl derivatives have been **reported**[22] (eqn 9).


(eq. 9)

X = H 87%
= Cl 93%
= F polymers

As expected the trichlorosilyl derivative is more reactive. However the **adduct** was not protodesilyated to norbornadiene. The doubly-substituted silylacetylene 31 has proved useful in the following **cycloadditions**[23] (eqn 10).

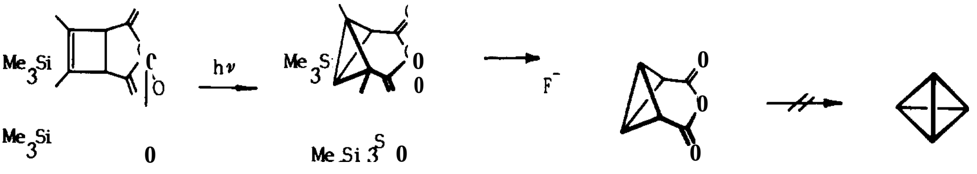


(eq. 10)

X = CH or N 31

The reaction, as in the case of the parent acetylene, is catalyzed by a cobalt complex. The same reaction works with cyano derivatives with the ultimate formation of pyridines.[24]

Disilylacetylene 31 has also been successfully photochemically cycloadded to a number of enone-type alkenes.[25,26] The maleic anhydride adduct was further transformed into the polycyclic anhydride **32**.[27] Photoexcitation in an argon matrix at 10 K did not afford tetrahedrane (eqn 11) but cyclobutadiene instead.



(eq. 11)

32

α,β-UNSATURATED DICARBOXYLIC ACIDS AND DERIVATIVES

Maleic anhydride is one of the most widely used dienophiles owing to its high C=C reactivity given by the cis-locked conformation and by its thermal stability that allows reactions also at high temperature; Indeed most dienes have been added to maleic anhydride.[28] The cycloadducts can be hydrolyzed to the corresponding cis-dicarboxylic acids under standard hydrolysis conditions. Since the diacid is usually poorly soluble in aqueous solvents, a base-acid sequence affords crystalline products in high yields.

Obviously the dicarboxylic compounds correspond to the cycloaddition product of maleic acid to the same diene; however maleic anhydride is generally used in preference in standard synthetic procedures both for the higher reactivity and for the low solubility of maleic acid in the standard solvents used for Diels-Alder reactions. The selected examples reported here are subdivided according to the methods of decarboxylation; hence decarboxylative procedures dealing with diacids may refer to adducts obtained by both methods. Furthermore since no special stereoselectivity is observed in the decarboxylation, the adducts obtained from fumaric acid cycloaddition are also included in this section.

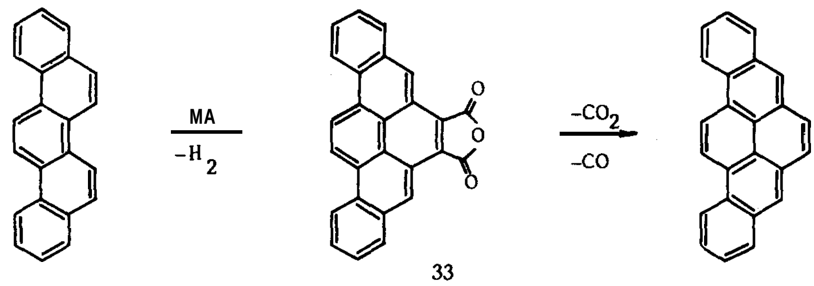
The already high reactivity of α,β-unsaturated dicarboxylic acid and derivatives can be further improved by complexation with Lewis acids such as $AlCl_3$. It follows that this class of compounds presents one of the highest reactivity in cycloaddition so that they may define the limit of reactivity of a diene. Unfortunately, as will become apparent later, there are limitations in the subsequent transformation of the adducts to dienes. This explains why substantial efforts to find easier and more effective methods of decarboxylation have been expended by several laboratories recently.

(a) *Direct decarboxylation of maleic anhydride cycloadducts*

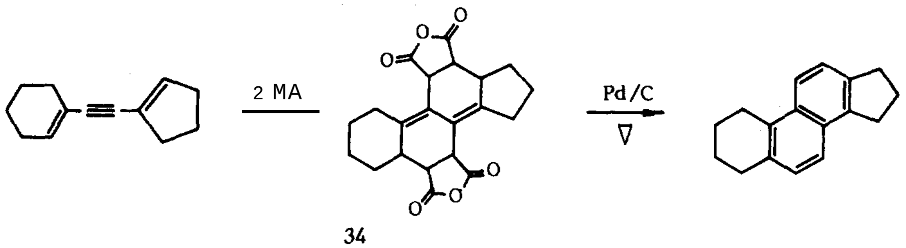
Thermolysis. Thermal decarboxylation rarely gives good results unless particularly stable products are to be formed. This is especially the case of the synthesis of aromatic compounds, but since the Diels-Alder reaction does not lead directly to aromatic molecules, dehydrogenating catalysts are often helpful.

Indeed compounds of type 33 (eqn 12) decarboxylate with ease[29] as shown also by the following representative examples[30–31] (eqn 13, 14). Another interesting example is given by the photochemical cycloaddition of dibromomaleic anhydride 36 to N-phenyl pyrrole 37[32] (eqn 15).

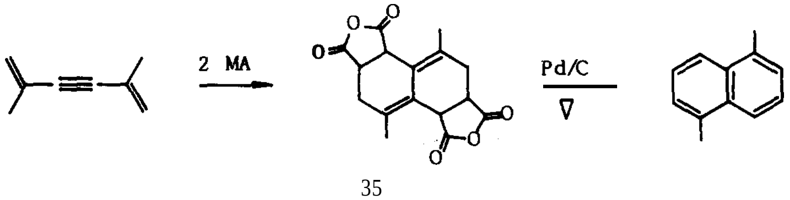
Photolysis. Photoelimination of CO, and CO is a possible, but relatively unexploited, procedure for the formation of the required double bond from maleic anhydride cycloadducts. A represen-



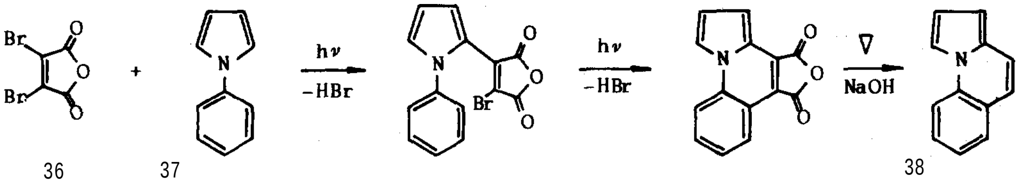
(eq. 12)



(eq. 131

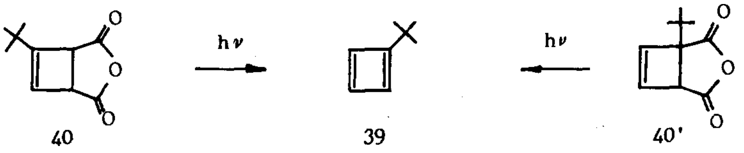


(eq. 14)



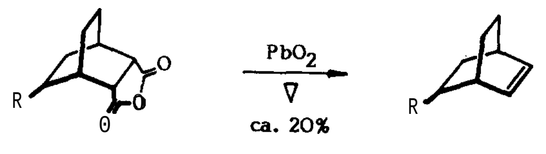
(eq. 15)

tative example is given by the matrix isolation of cyclobutadienes[33] as shown in eqn (16). This topic has been reviewed by Maier.[34]



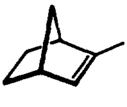
(eq. 16)

With lead dioxide. The original method reported by Doering *et al.*[35] has proved successful only for some saturated cycloadducts of type A (eqn 17). The same authors later reported difficulties in reproducing the results and a specially prepared PbO_2 was needed to give consistent yields of about 19%.[36] This method has been used only in a few other cases as for example in the synthesis of aposantene (42) which was obtained in 15% yield.[37]



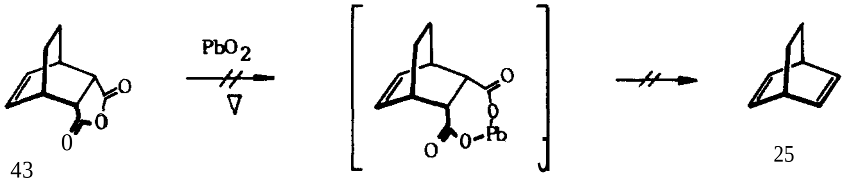
41 R = H, OMe, CO_2Me

(eq. 17) ;



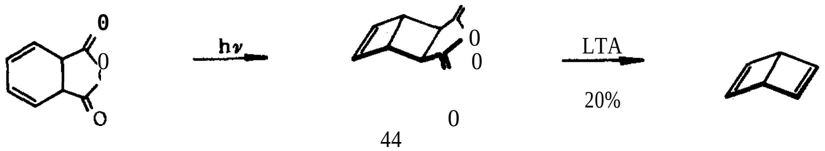
42

It is likely that the high temperatures required for the reaction promote retro-Diels-Alder processes rather than the desired decarboxylation in type B dienes. This was confirmed by the observation by Hine ***et al.*** who were unsuccessful in the preparation of 25 from 43 via the planned sequence illustrated in eqn **18.**[38]



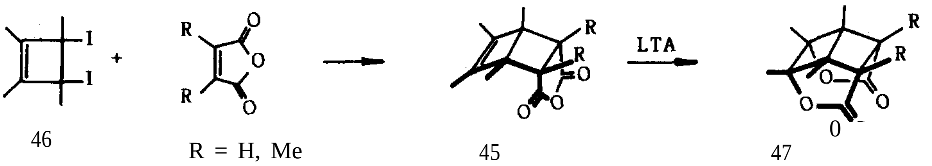
43 25 (eq. 18)

With lead tetraacetate (LTA). This widely used synthetic methodology is usually applied to the dicarboxylic acids (see later), however, some example are reported in which the maleic anhydride cycloadduct is subjected to oxidation directly. Van **Tamelen** and **Carty**[39] obtained Dewar-benzene for the first time by this procedure (eqn 19).



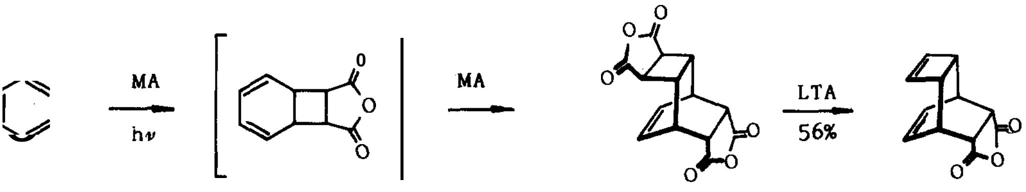
44 (eq. 19)

Yields were usually low and only the exo isomer underwent decarboxylation. In fact the van **Tamelen** exo-anhydride 44, obtained through an internal (2 + 2)-cycloaddition process yielded Dewar benzene whereas the Criegee **endo-anhydride** 45, obtained from cycloaddition of maleic anhydride to the cyclobutadiene derived from 46, did not decarboxylate in the lead tetraacetate reaction” (eqn 20). The **endo** position of the anhydride ring favours in these cases lactonization with the oppositely placed double bond giving 47.



46 R = H, Me 45 47 (eq. 20)

An atypical example is that of the maleic anhydride cycloadduct of benzene **48**. This double **adduct,** that is obtained photochemically through the reaction reported in eqn **(21),** decarboxylates even better as the dianhydride than as the tetracarboxylic **acid.**[41] As pointed out by the same authors, the product obtained corresponds to the maleic anhydride cycloadduct of **cy**clooctatetraene.

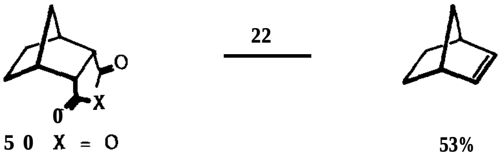


48 49 (eq. 21)

From this and the previous examples it seems that the oxidative decarboxylation **affects** only anhydrides bonded to a four membered ring while it is **uneffective** with those bonded to larger rings. This statement has, however, to be tested by a larger number of examples.

With organometailic complexes. The most effective direct transformation of maleic anhydride cycloadducts into the corresponding **olefin** is best achieved by the use of the nickel complex

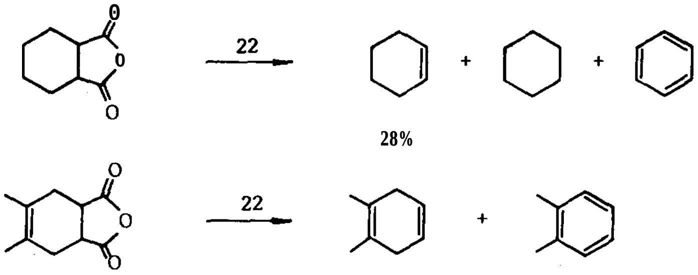
$Ni(CO)_2(PPh_3)_2$ 22. The potentiality of this decarboxylative procedure in the preparation of formal acetylene **adducts** through addition of maleic anhydride was first realized by Trost." This method has subsequently found application in several synthetic processes. In the original procedure both the oxa- and the thia-anhydride have been tested and a slight advantage for the latter was noticed. For example norbornene was obtained either from **50** or from **51** (eqn 22).



(eq. 22)

50 X = O — 53%
51 X = S — 56%

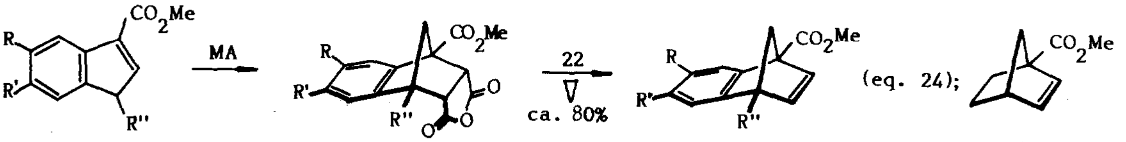
The reaction is rather limited in monocyclic systems because secondary products are also formed, sometimes in predominant yield, as illustrated in the following examples (eqn 23).



1%

(eq. 23)

An early application of this method was the regiospecific synthesis of **benzonorbornadienes**[43] that took advantage of the ability of maleic **anhydride to** react even with indenes, trapping the **iso-**indene present in small amount at high temperature. It should be pointed out that maleic anhydride or **(*E*)-1,2-bis(phenylsulfonyl)ethylene** (see later) are the only dienophiles capable of reacting in this way with indenes. The synthesis is illustrated in eqn 24. Yields are fairly good especially considering that other decarboxylative methods work very poorly. **Grunewald**[44] was able to optimize this reaction to 91% yield in the preparation of the bridgehead substituted norbornene **52**.

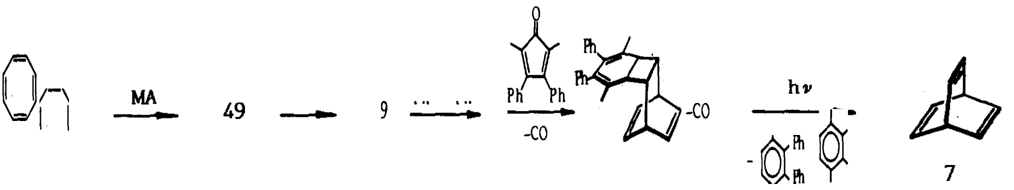


(eq. 24);

52

R= OMe R'=R"= H
R=R"= H R'= OMe
R=R"= H R'= OMes
R=R'= H R"= OMe

$Ni(CO)_2(PPh_3)_2$ 22 is also effective for the synthesis of the Nenitzescu hydrocarbon 9 (the formal addition product of acetylene with the valence isomer of cyclooctatetraene) that can be obtained in two steps in *ca* 70% yield." As shown in eq. 25, hydrocarbon 9 can be used in a rather convenient synthesis of barralene 7. An-overall yield of 24% starting from cyclooctatetraene has been reported.[45]

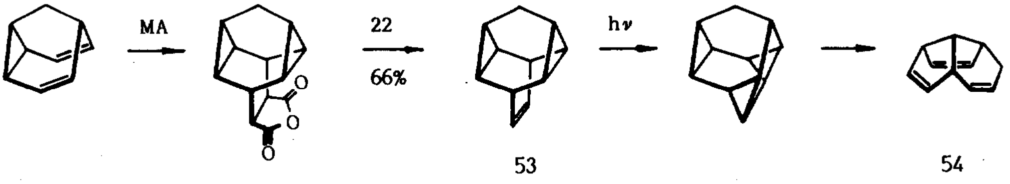


7

(eq. 25)

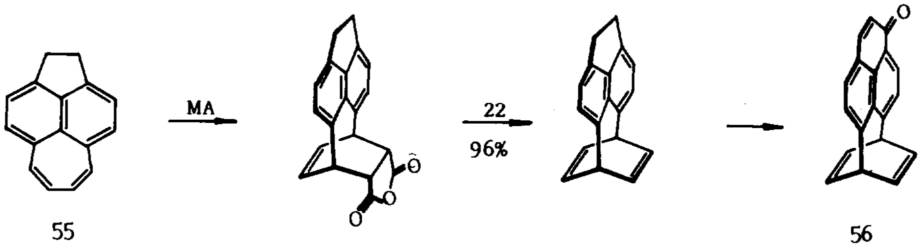
overall 21%

A synthesis of the homo-snoutene 53 devised by de **Meijere**[46,47] makes use of this method (eqn 26). Also in this case the reported yields are quite good. 53 was then photorearranged to homo-triquinacene 54 in a reaction similar to the rearrangement of snoutene to triquinacene (see later).



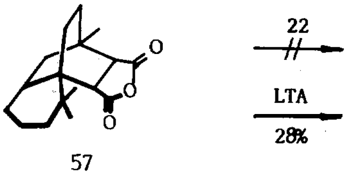
(eq. 26)

A recent example that demonstrates the efficiency of this method is the one reported by Murata *et al.*” The cycloadduct of maleic anhydride with acepleiadiene 55 was decarboxylated in practically quantitative yield. The **adduct** was then transformed in several subsequent steps to the desired molecule 56, which has been used for electron delocalization studies (eqn 27).



(eq. 27)

The present methodology, however, cannot be applied in all cases. For example, it has been reported that 57 failed to give the corresponding olefin and the lead tetraacetate method had **to be** used, with the production of 58 in 28% **yield**[49] (eqn 28).

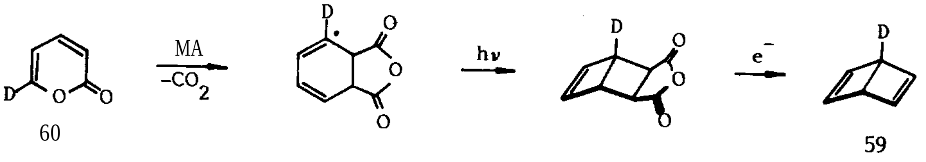


(eq. 28)

In conclusion this method, when applicable, represents the best synthetic procedure for the transformation of maleic anhydride cycloadducts. The main limitations in its application are related to the high reaction temperature (*ca* 200”) which often causes the formation of side products of retro-Diels-Alder processes.

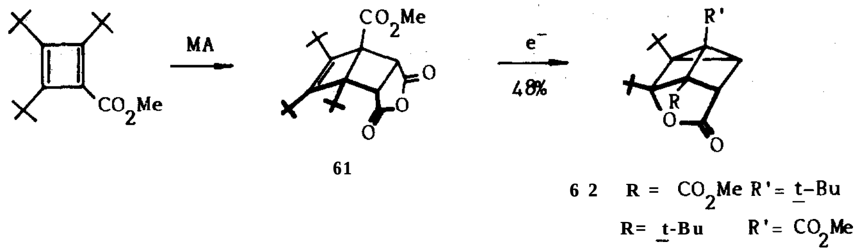
With ***anodic*** *processes.* Electrochemical methods are usually applied to the dicarboxylic acids in aqueous solutions of triethylamine or pyridine, but in only a few cases has the maleic anhydride cycloadduct been used directly.

An example of this procedure is the preparation of the Dewar benzene 59 used for subsequent electrochemical **studies.**[50] The synthesis is illustrated in eqn (29) starting from the deuterated a **-pyrone** 60.



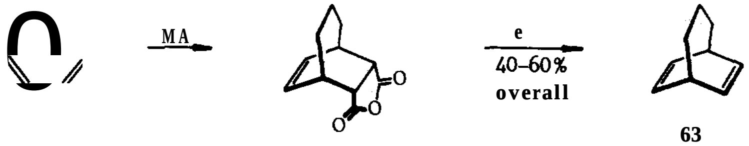
(eq. 29)

The electrochemical oxidation yields are often satisfactory, in spite of the harshness of the reaction conditions. The related anhydride 61, however, does not afford on electrochemical oxidation the corresponding diene but the **lactone 62**[51] (eqn 30).



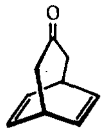
(eq. 30)

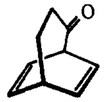
A synthesis of **bicyclo[3.2.2]dienes**[52] (eqn 31) is also relevant. It should be noticed that only carboxylic acid derivatives or **(*E*)-1,2-bis(phenylsulfonyl)ethylene** are dienophiles strong enough



(eq. 31)

to react with cycloheptadienes. As reported in the same paper, this procedure has proved useful also for the synthesis of the interesting ketones 6466.


64

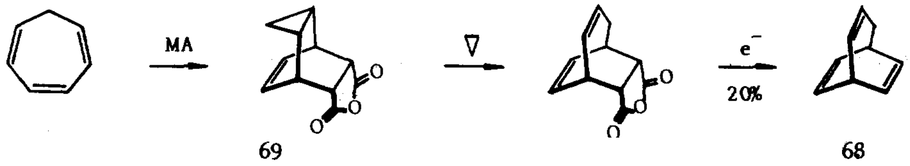

65


66


67

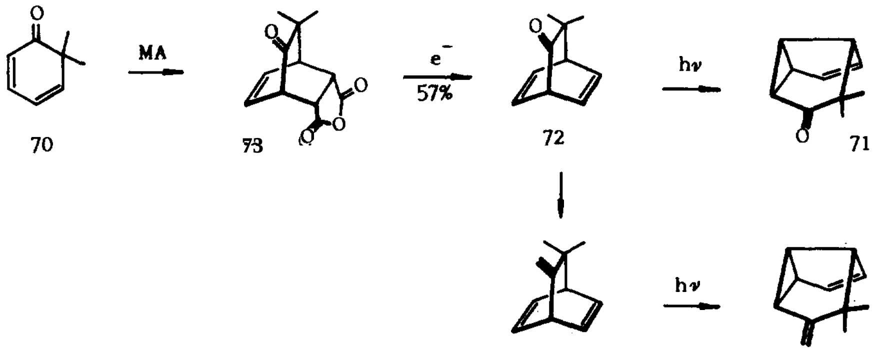
Improvement in the preparation of these dienes and additional examples using **$Ni(CO)_2(PPh_3)_2$** 22 as decarboxylating agent with yields up to **92–97%** has been described.” It is to be noted that the higher homologue of 63, i.e. 67, had to be prepared through alternative routes due to the unreactivity of **1,3-cyclooctadiene** with most of the **C=C** dienophiles.

Triene **68** may be prepared starting from ketone 66 but a more direct method has been reported as illustrated in eqn 32.” Triene **68** corresponds to the (4 + 2)-cycloaddition product of acetylene



(eq. 32)

to the tropilidene form of cycloheptatriene. Ketone 71 was prepared via **oxa-di-π-methane** rearrangement of diene 72 efficiently obtainable from the anhydride 73 with this **technique**[56,57] (eqn 33).

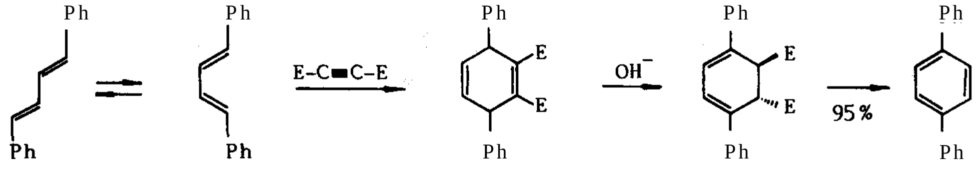


(eq. 33)

(b) ***Decarboxylation of fumaric and maleic acid cycloadducts***

As previously discussed cis-dicarboxylic acid adducts are derived from the addition of a maleic acid derivative such as the ester or maleic anhydride itself followed by hydrolysis, while a fumaric acid adduct is prepared from fumaric acid itself or its diester followed by hydrolysis.

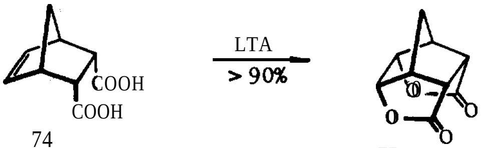
With potassium ferricyanide. The oxidative decarboxylation that makes use of this reagent appears to be limited to the synthesis of polyphenyls (eqn *34).* Fieser and Haddadin[58] reinvestigated this strategy and reviewed the literature of pertinent work.



(eq. 34)

$E = -CO_2Et$

With lead tetraacetate. To overcome the difficulties and low yields obtained with the lead dioxide procedure of Doering, Grob *et al.*[59,60] published a method in 1958 based on the use of lead tetraacetate as oxidant with much improved yields. This method later found wide application to a large number of decarboxylations[61] of which the more significant are mentioned here. The lead tetraacetate procedure cannot be applied to the synthesis of type B dienes from endodicarboxylic acids since lactones are usually obtained instead of decarboxylated products. For example, if the diacid 74 is treated with lead tetraacetate under the usual decarboxylative conditions, the dilactone 75 is obtained rather than norbornadiene 1.[62,63] The occurrence of this reaction is probably due to the electrophilic interaction of the lead acetate with the double bond and subsequent ring closure (eqn 35).

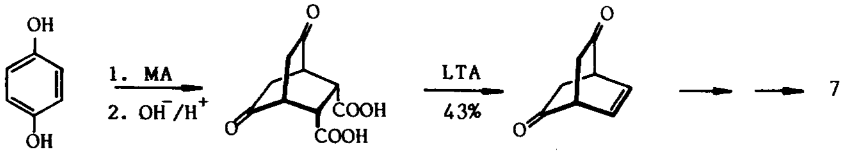


74 75

(eq. 35)

With the [2.2.2] systems the reaction is also feasible, and it is observed in low yields. Nenitzescu has reported that the synthesis of tricyclic hydrocarbon 9[64] and barrelene 7[65] can be accomplished by lead tetraacetate decarboxylation. It seems likely that the geometry of the molecule in the [2.2.2] system is such that the two double bonds are a little further apart so that the possibility of interaction of the carboxylic groups with the double bond is weaker. Because of the fairly low yields and the availability of several alternative methods, the preparation of either 9 or 7 via thisprocedure is not useful.

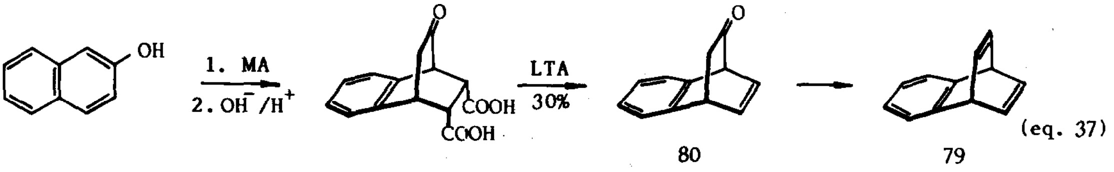
One of the most interesting approaches to barrelene 7 is that proposed by Jefford.[66] His procedure is based on the transformation of the diketone 76, prepared for the first time by Grob[67] and later with improved yields by de Meijere,[68] from the inexpensive hydroquinone as shown in eqn (36). In two subsequent steps, described later, 76 is converted into barrelene 7 in 11% yield.



78 77 76

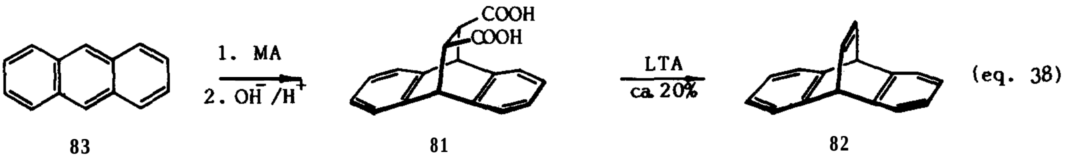
(eq. 36)

The benzohomologue of barrelene, the hydrocarbon 79, was prepared in a similar way from *β*-naphthol[69–72] (eqn 37). However, yields of 80 are poor due to the concomitant formation of a

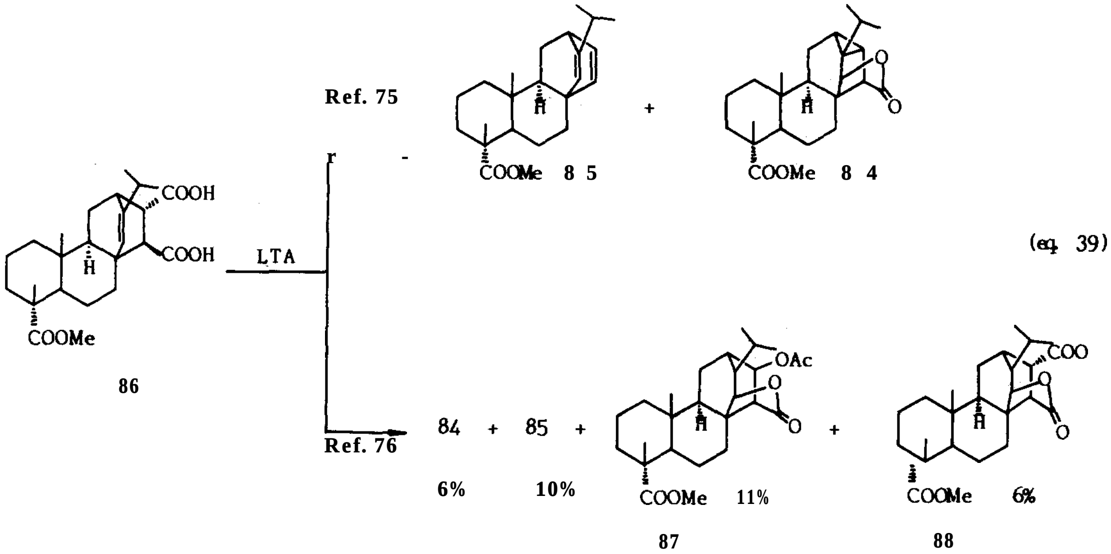


lactone in the decarboxylative step. The more direct approach to 79 through direct decarboxylation of the maleic anhydride **adduct** of naphthalene,[73] has not yet been reported although it appears to be a reasonable approach. Alternative syntheses of 79 have been **reported.**[74]

The next higher benzo-homologue, dibenzobarrelene 82, which corresponds to the acetylene **adduct** to anthracene, can also be prepared through a similar route using the maleic anhydride cycloadduct of anthracene **83**[59,69a] (eqn 38).

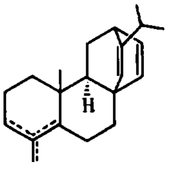


These latter cases corresponds to type A dienes. Examples in which this technique has been used to prepare type B dienes are more unusual. An interesting example is that illustrated in eqn **(39),** in which the outlined sequence has been applied for the synthesis of the levopimaric acid-acetylene cycloadduct in one of the early stages of the synthesis of more complex natural products. Two research groups reported almost simultaneously the same reaction. Some minor discrepancies may be due to small differences in the reaction conditions and could be. regarded as evidence of the temperamental nature of the reaction. Zalkow and **Brannon**[75] reported the formation of only the lactone **84** and the diene 85 starting from 86 while Ayer and **McDonald**[76] observed the formation of four products (eqn 39). The **first** authors reported also the synthesis of the related compound 89. Similarly ketones **90**[77] were synthesized in studies related to the synthesis of atisine. A further

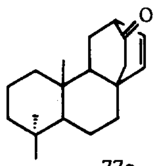


application of this procedure to the synthesis of the natural product aphidicolin has recently been reported. This makes use of the formal acetylene **adduct 91.**[78]

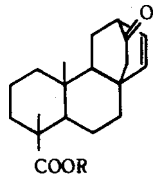
A more in depth study on the potentiality of the maleic anhydride-lead tetraacetate **decarboxylation** sequence is that pursued by Wolinsky and **Cimarusti**[69a] who **carefully** scrutinized the best conditions for the decarboxylative step. They could determine that oxygen, which is



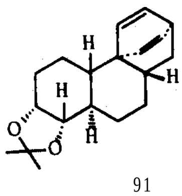
89



90[77a]

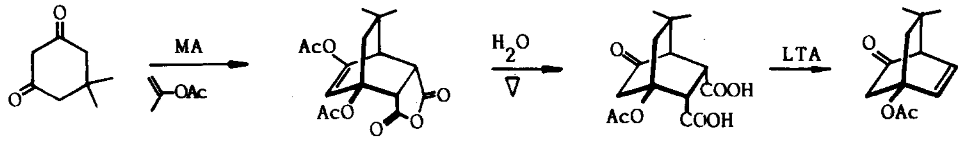


90'[77b]

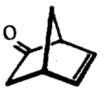


91

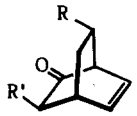
detrimental in **monodecarboxylations,**[78] is helpful in bisdecarboxylations, considerably improving the yields. The reactions investigated included, among others, maleic anhydride addition to cyclic **1,3-diketones** in the presence of isopropenyl acetate (eqn 40). As represented in detail in eqn (40) for dimedone. the related olefins shown below have also been prepared in yields of *ca* 50–70%.[69]



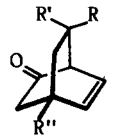
(eq. 40)



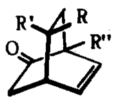
92



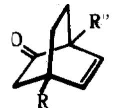
93 R=R'= H
R=H R'=Me
R=i-propenyl
R'= H



R=R'= H R''= Me
R=R'=Me R''= H
R= H R'=R''= Me
R=R'=R''= Me
R=R'= Me R''=OAc



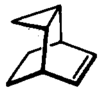
R=R''= H R'=Me
R=R' =Me R''=H
R=R'=R''= Me



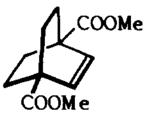
R=OAc R'=H
R=Me R'=i-Pr

Some other examples of the synthesis of type A olefins obtained in this way are shown below. The method is also suitable for the synthesis of **bicyclo[3.2.2]nonadienes 63.**[82]

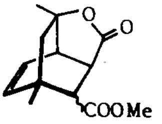
Ref. **80a**



Ref. 80b.c

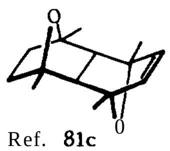


Ref. 81a



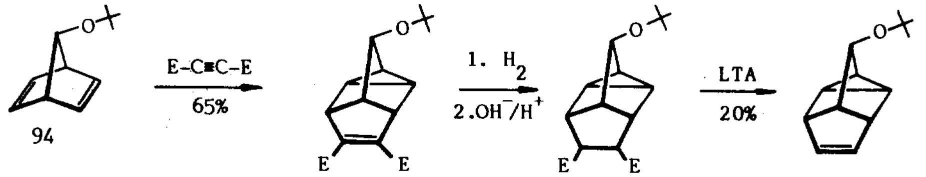
Ref. **81b**

Ref. 70



Ref. **81c**

Acetylenedicarboxylates are also useful acetylene equivalents since their **adducts** can be transformed into the same **adducts** derived from the addition of maleic acid. An interesting example is provided by the preparation by Schleyer and **Leone**[83] of substituted deltacyclenes, employed for the generation of the corresponding cation (eqn 41).



(eq. 41)

94

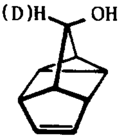
E=-COOMe

95

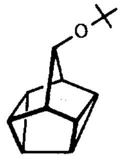
96

97

98



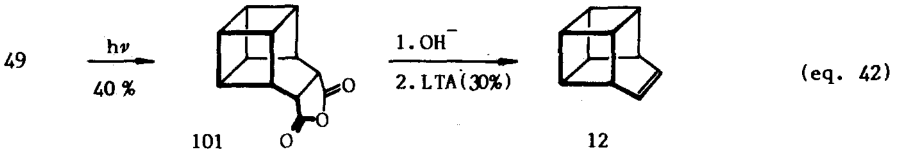
99



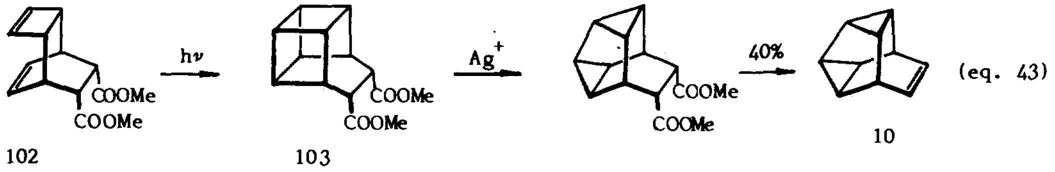
100

By the same route, these authors also obtained deltacyclenone 98, the alcohols 99 and the pentacyclic ether 100. The same procedure has later been applied by **Russell**[84] for the preparation of the parent hydrocarbon **11**.

The synthesis of other interesting hydrocarbons, for example basketene 12 and snoutene 10, have also been achieved via this route. Basketene, in fact, was first synthesized by **Masamune**[85] in the following way (eqn 42). Snoutene has been obtained by **Paquette**[86,88] and **Dauben**[87] via a structural modification of 103 mediated by silver ion (eqn 43).

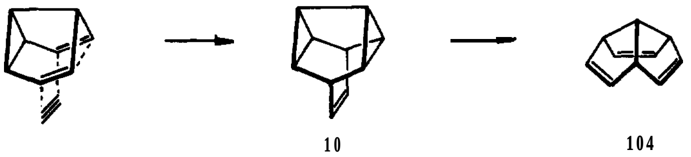


(eq. 42)



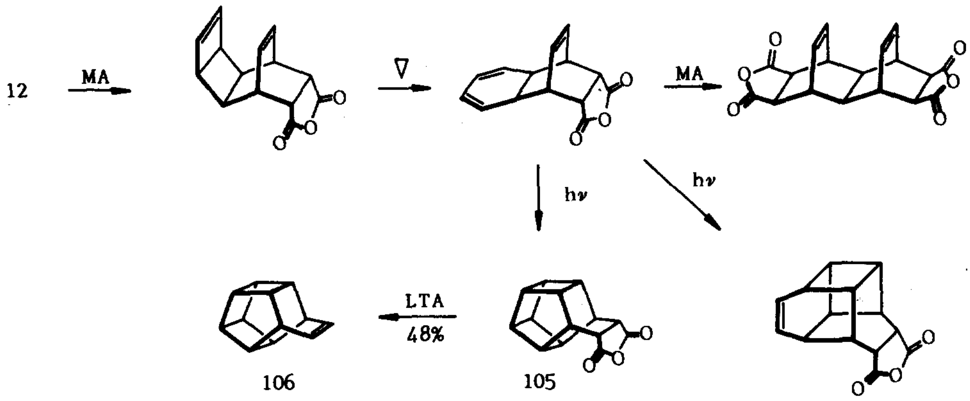
(eq. 43)

It should be noted that snoutene corresponds to the cycloaddition product of acetylene to semibullvalene (eqn 44). Snoutene **10** can also be converted, albeit in low yield, to triquinacene **104**.[89]



(eq. 44)

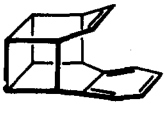
Basketene 101 may react further with **maleic** anhydride to give the set of products described in eqn (45).[90]



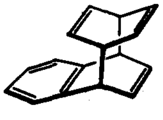
(eq. 45)

Anhydride **105** can be transformed by lead tetraacetate decarboxylation into the caged hydrocarbon 106. It is assumed that the other anhydrides of eqn (45) did not give the corresponding hydrocarbons.

The synthesis of the formal cycloadducts of benzene to naphthalene 107 and 108 has been achieved through lead tetraacetate decarboxylation of **109**.[91]



107



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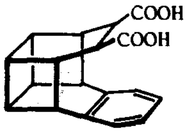
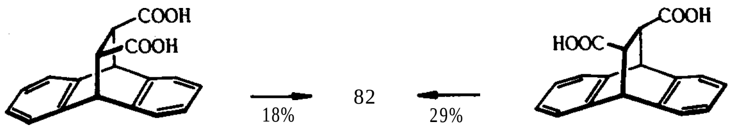


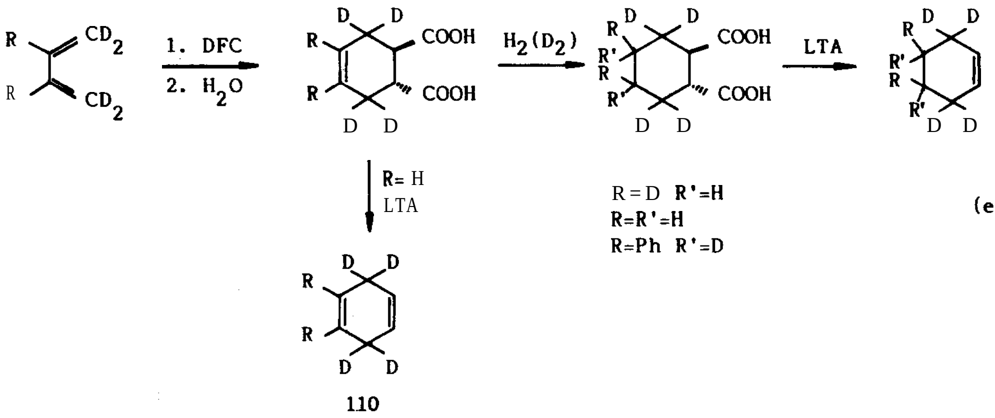
109

The lead tetraacetate decarboxylation is not stereospecific as shown by Corey” and subsequently confirmed by **Wolinsky**[69a] (eqn 46). **Wolfe**[93] in this context, studied the bisdecarboxylation of



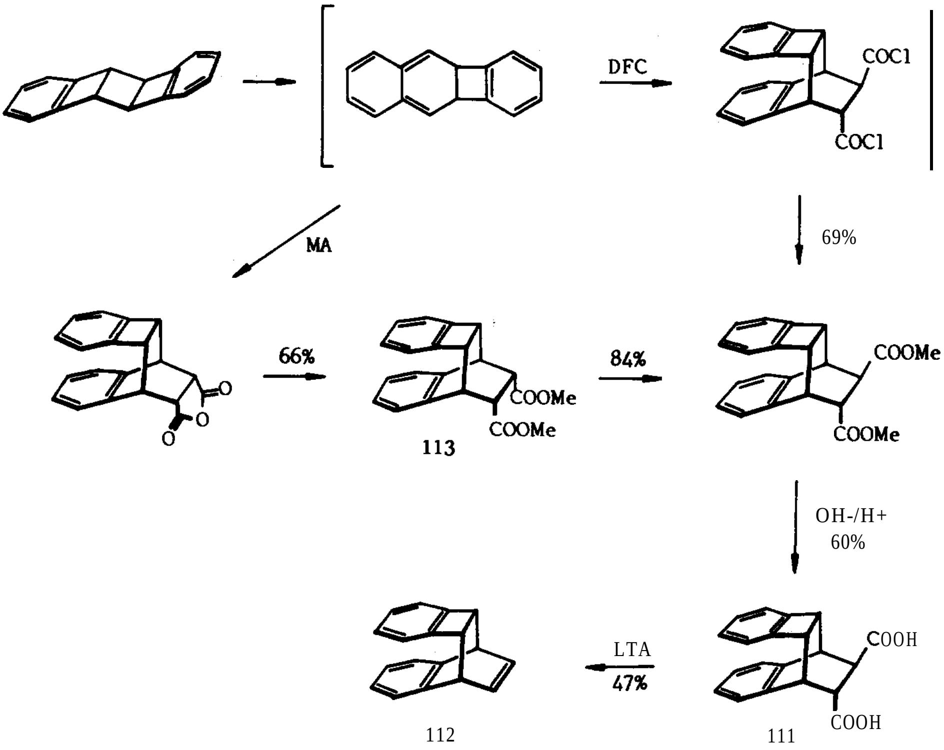
(eq. 46)

deuterated cyclohexadienes, and reported that the trans isomer (obtained via_ **cycloaddition/hydrolysis** of fumaroyl dichloride) is more efficiently transformed than the cis isomer (eqn 47).



(eq. 47)

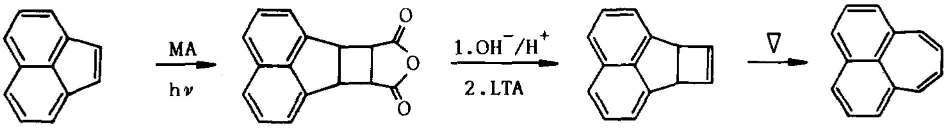
In a related example, the trans **adduct 111** was subjected to lead tetraacetate decarboxylation in the synthesis of hydrocarbon **112**[94] (eqn 48).



(eq. 48)

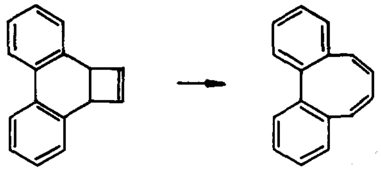
It should be noted that the cistrans isomerization from 113 makes trans isomers available from maleic anhydride cycloadducts.

In addition to the more classical (4 + 2)-cycloadditions the present procedure is also of great utility in the preparation of cyclobutenes via (2 + 2)-cycloaddition reactions. For example this method has been used for a convenient preparation of pleiadiene **14**[95,96] (eqn 49). Similarly the related molecules 115 and 116 have been synthesized."

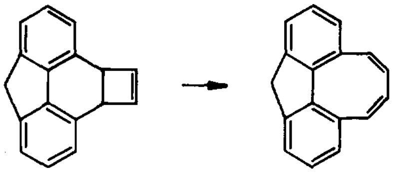


(eq. 49)

114 14

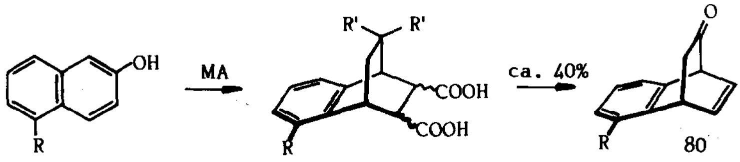


115



116

With anodicprocesses. The following procedure is perhaps the most efficient route for preparing type B dienes, although it requires equipment which is not always available in organic chemistry laboratories.[98] The method is an extension of the Kolbe electrolytic decarboxylation. Its application to dicarboxylic acids derived from cycloaddition of maleic anhydride or derivatives, was reported almost simultaneously by three laboratories.[99-101] Plieninger[99] carefully studied the electrochemical conditions for transforming the dicarboxylic acid 117 into the unsaturated compound **80**. The latter was subsequently transformed into more complex molecules.

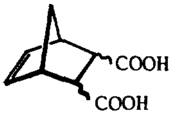


(eq. 50)

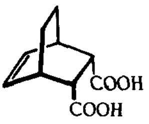
R= NO_2, H

117 R'=R'=O
R'=R'=-O-$(CH_2)_2$-O-

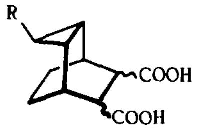
At about the same time van Tamelen et *al.*[100] and Dauben *et al.*[101] reported the synthesis of a number of dienes via this route. In every case the yields of unsaturated product were far better than those previously reported by other methods.



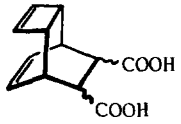
cis-endo 1%[101]
trans 7%[101]
cis-exo 15%[101]



48%[101]
40%[101]



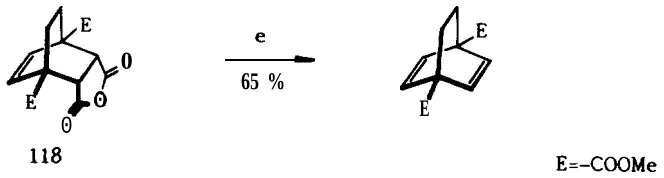
R=H cis-endo
35%[100] ; 36%[101]
R=H trans 45%[101]
R=CN cis-endo 48%[101]
R=COOEt cis-endo 40%[101]



cis-endo 37%[101]
trans 53%[101]

The electrolysis is usually conducted in aqueous pyridine in the presence of triethylamine. The conditions are however very drastic. Potentials of *ca* 100 V with initial current intensities of *ca* 1 amp have to be maintained for many hours and the heat evolved must be carefully eliminated by efficient cooling. Furthermore, and this is perhaps the most serious drawback of the method, the reaction cannot be carried out in a large scale.

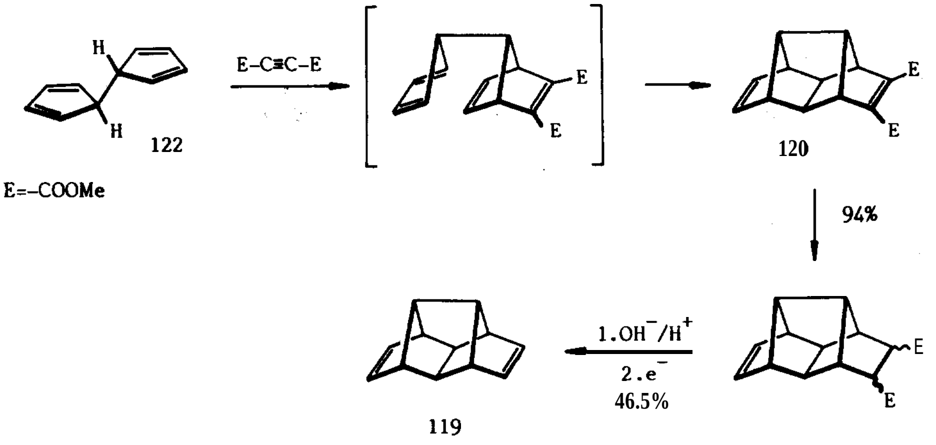
It was later discovered that addition of a small amount of **4-t-butylcatechol** increases the yield of diene from 30 to 60% in the decarboxylation of **118**[102] (eqn 51).



(eq. 51)

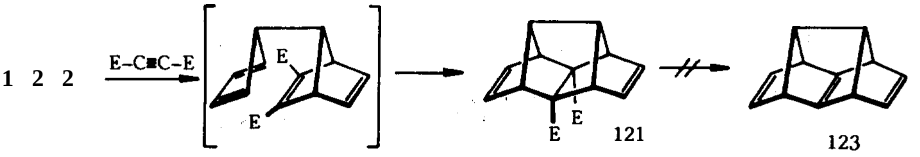
A further improvement was obtained by replacing the usual solvent system for this reaction with acetonitrile, water, pyridine or triethylamine. In this way the reaction time was decreased from 12 to 2 **h.**[102]

An interesting later application of this technique is represented by the synthesis of the hydrocarbon 119 obtained through addition of **dimethyl** acetylenedicarboxylate and subsequent manipulation of one of the resulting **adducts**[103,104] (eqn 52).



(eq. 52)

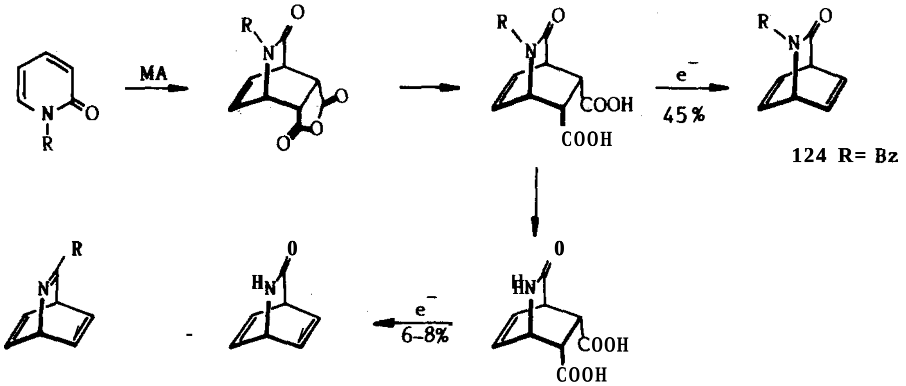
The other **adduct** 121 was used later, also by Paquette, in the synthesis of **dodecahedrane.**[105] Its decarboxylation to the very interesting but probably very unstable hydrocarbon 123 has not been reported (eqn 53).



(eq. 53)

Another recent application of this procedure has been reported by **Gompper**[106] for the preparation of the barrelene derivatives 124-126 (eqn 54). Attempts at the preparation of **2-azabicyclo[2.2.2]octatriene** 126 with lead dioxide, lead tetraacetate, or anodic oxidation all **failed.**[107]

The **2-oxa** analogue, **3-oxo-2-oxabicyclo[2.2.2]octa-5,7-diene (127),** is much more unstable. After intense investigation **Plieninger**[108] reached the conclusion that if it does exist, it is unstable above **0°.** His attempts ranged from anodic odixation to the t-butylperester decomposition either thermally or photochemically (eqn 55).

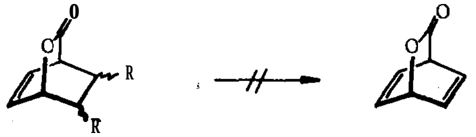


124 R= Bz

126

125

(eq. 54)



128

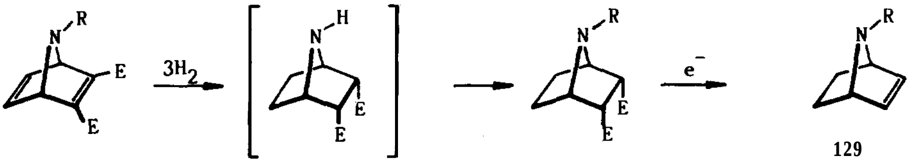
127

$R=-CO_3tBu$

$R=-COOH$, etc.

(eq. 55)

Decarboxylation by this method is also effective in the preparation of **7-substituted aza-norbornenes** **129**[109] (eqn 56). The **2-azasulfonylnorbornadiene** 131 has been prepared by



(eq. 56)

130 E=-COOH

R=-Bz

R=-COOEt

=-Tos

129

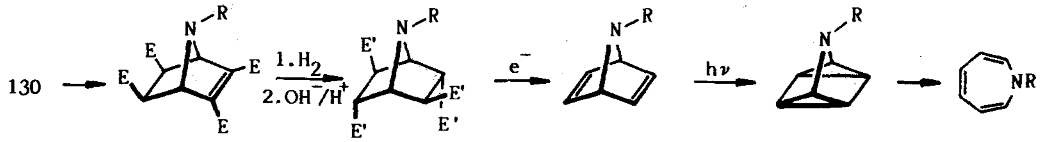
R=-COOEt

R=-Tos

R= H

R= Me

Prinzbach[110] by the ingenious synthesis illustrated in eqn (57). It served as a method to prepare azepine 133 through the quadricyclane 132. Furthermore compounds of type 8, 25, 134 and 135 were prepared by anodic decarboxylation and their **IP**[111] and NMR **spectra**[112] recorded.



131

132

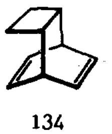
133

E=-COOMe

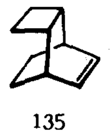
E'=-COOH

R=-Tos

(eq. 57)

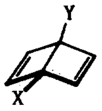


134



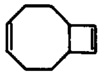
135

Cyclobutenes are also efficiently obtained through this route. Some examples of cyclobutenes derived by electrochemical decarboxylation of the corresponding diacids obtained through the maleic anhydride procedure are illustrated.

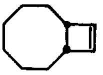


136

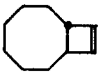
X=Y=H or hal



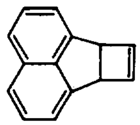
137



138



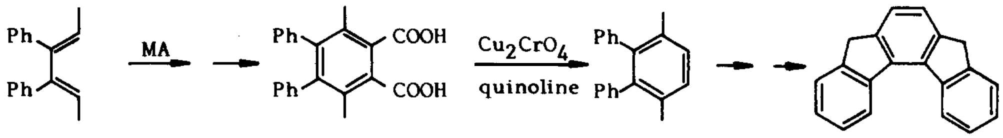
139



114[113]

With low valent copper and quinoline. Procedures involving copper as metal or low valent salts and oxides at high temperatures in quinoline have often found application for those systems able to survive the drastic conditions that have to be employed. It follows that examples are mainly found in the synthesis of aromatic rings through decarboxylation of phthalic acid derivatives. The following citations are illustrative.

Dihydro-5,8-indeno(2,1-c)fluorene 140 has been prepared via the use of maleic anhydride as the acetylene synthon following the route outlined in eqn (58).[115] The crucial decarboxylation was performed with copper **chromite** in quinoline.

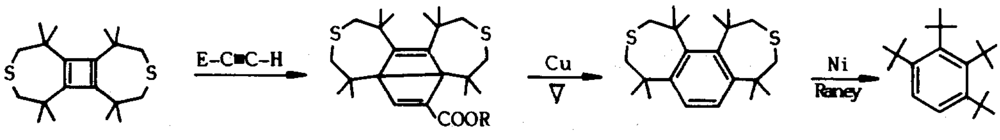


(eq. 58)

overall 8.2%

140

The very highly sterically congested **1,2,3,4-tetratertbutylbenzene** has recently been prepared by **Krebs**[116] with a clever procedure that started from the stable cyclobutadiene 141 and made use of methyl propiolate as the acetylene synthon. Copper powder was **sufficient** for the decarboxylative step.



(eq. 59)

141

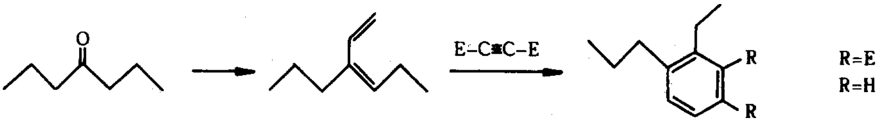
R=-Me

R=-H (48%)

64%

63%

Dimethyl acetylenedicarboxylate has been used by **Paquette**[117] as a reagent for the **benzo**-annulation of ketones. Via the sequence represented in eqn (60) for o-(n-propyl)ethyl benzene. The interesting hydrocarbons 142-144 have similarly been prepared using copper powder in quinoline in the decarboxylation step.

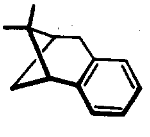


R=E
R=H

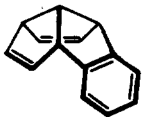
(eq. 60)

E=-COOMe

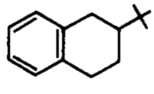
141



142

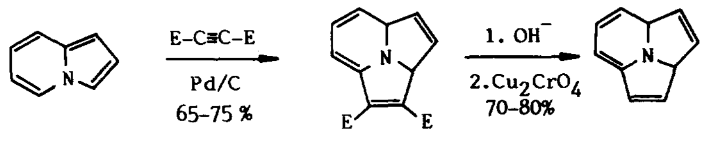


143

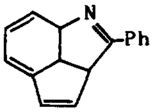


144

The interesting ring system of the amine 145 has been achieved by the Boekelheide group”* as shown in eqn (61). The formation of the cycloadduct from pyrrocoline and **dimethyl acetylenedicarboxylate** is unexpected on the basis of orbital symmetry considerations. The related compound 146 was similarly **obtained**[118c] but, in this case diphenyl ether was used instead of quinoline in the decarboxylative step.



(eq.61);

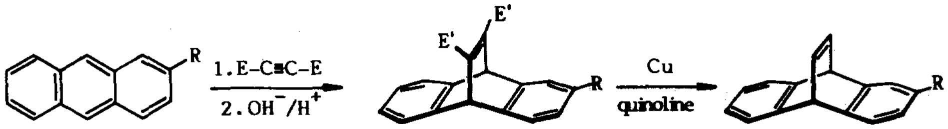


E=-COOMe

145

146

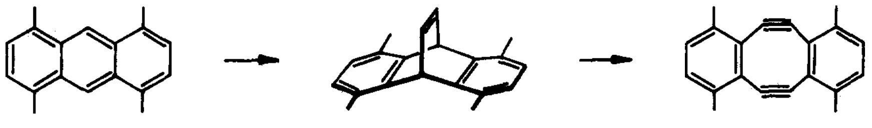
Figeys[119] prepared the dibenzobarrelenes 147 bearing substituents sensitive to other eliminative procedures in high yields by the treatment of the unsaturated dicarboxylic acid with copper in quinoline (eqn 62). This method has been recently **applied**[120] to the synthesis of the tetramethyl



(eq. 62)

147 R= Cl
82 R=H

derivative 148, in a key step for the preparation of the presumed planar eight-membered ring hydrocarbon 149 (eqn 63).

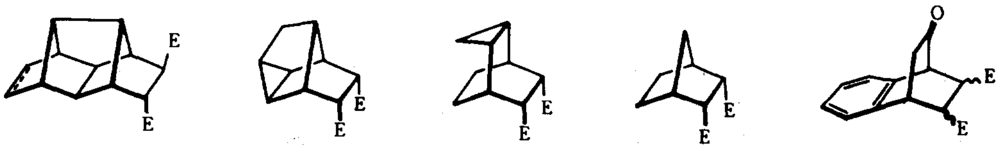


(eq. 63)

148

149

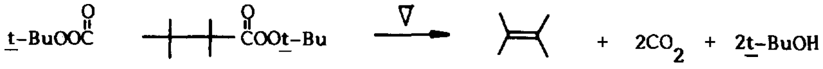
With cupric oxide. Paquette[121] devised a method for the decarboxylation of vicinal diacids that makes use of **CuO** in quinoline. This method gives improved yields in the decarboxylation of the following **adducts**. However, the use of the high temperatures (the necessity of using quinoline as



E=-COOH

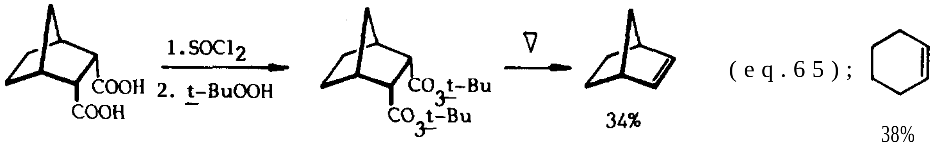
solvent is significant) makes this method useless for type B dienes or for compounds that may undergo alternative processes. Some compounds in which this procedure cannot be applied are the dicarboxylic acids derived from 69, **83** as well as others.

With t-butylperoxide decomposition. The method proposed by **Masamune**[122] has not found many applications despite the promising results reported in the initial communication. The basic idea was to use the known decomposition of t-butyl peroxyesters into carbon dioxide and t-butyl alcohol (eqn 64).



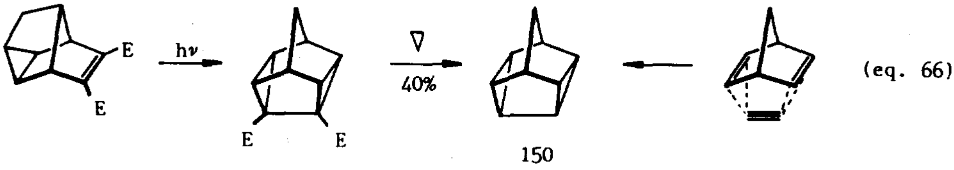
(eq. 64)

Norbomene and cyclohexene have been prepared according to the sequence illustrated in eqn (65) in 34 and 38% yields, respectively. However basketene could not be prepared in pure form



in this way since partial isomerization to the Nenitzescu hydrocarbon occurred, owing to the high temperatures required.

In an earlier paper Prinzbach[123] had used the di-t-butylperoxide decomposition in the synthesis of **pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane** (150). The synthesis started with the cycloaddition of acetylenedicarboxylic acid to norbornadiene giving 151 which by photochemical cycloaddition furnishes the cyclopropane derivative 151. This was decarboxylated as shown in eqn (66) 150 corresponds to the double homoaddition product of acetylene to norbornadiene.

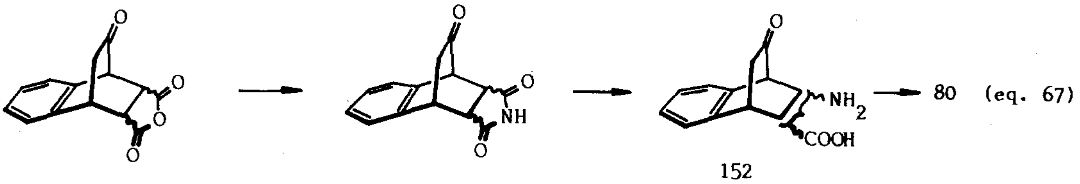


151 E=–COOH
=–COOMe
=–CO$_3$t–Bu

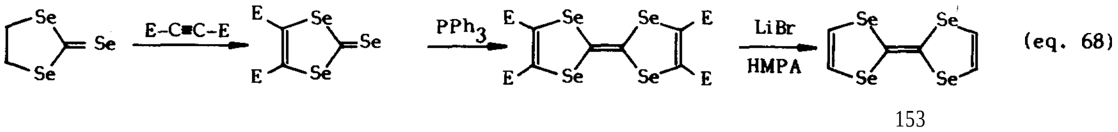
In this context, the radical decarboxylations studied by **Barton**[124] offer further reaction possibilities.

With miscellaneous methods. There are scattered reports in the literature on alternative methods that cannot be placed in the categories discussed thus far.

For example the diene **80** was obtained through the sequence outlined below (eqn **67).**[125] This method entails dediazodecarboxylation of the diazonium salt derived from 152. This route does not appear to have been applied in other synthetic sequences probably because of the easy incursion of side reactions.

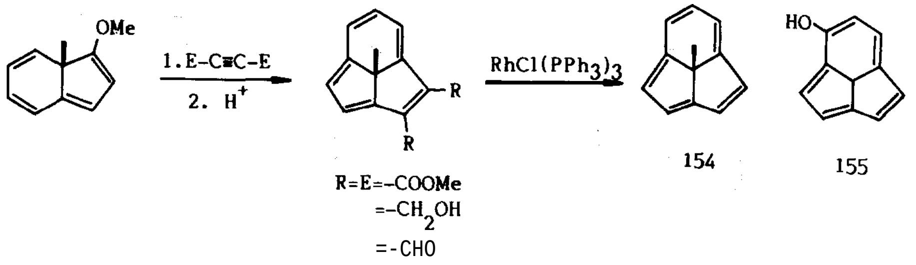


Another decarboxylative method of limited application makes use of **LiBr** in **HMPA**[126] (eqn *68).* It has been used for the preparation of 153.



E=–COOMe

Recent work by Rees and Gilchrist[127] leads to the ring system of 154 through the following reaction sequence (eqn 69). Similarly the alcohol 155 has been **reported.**[128]

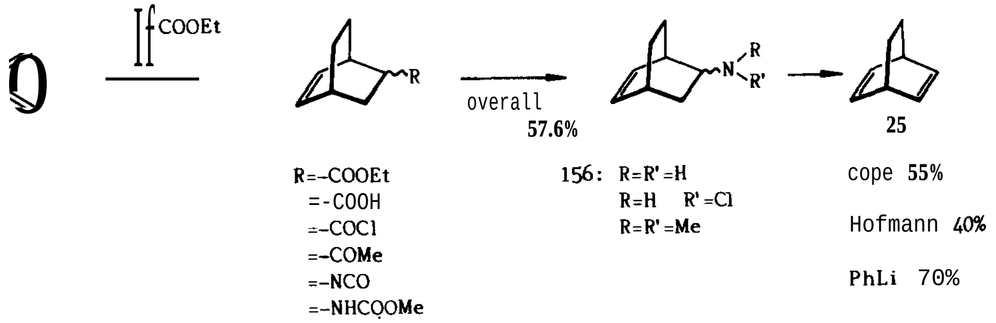


(eq.69)

ACRYLIC ACIDS AND DERIVATIVES

Acrylic acid derivatives are largely used as acetylenic synthons because their adducts can be degraded to olefins by standard chemical transformations. Despite the presence of only one electron withdrawing group this class of compounds usually presents a high reactivity that can be even enhanced by the use of Lewis acids as catalysts.[129] The only drawback of the present approach is the number of steps necessary for the elimination.

One of the first applications is that reported by Grob[130] for the synthesis of bicyclo[2.2.2]octa-2.6-diene (25). The ethyl acrylate adduct to 1,3-cyclohexadiene was, through Curtius rearrangement transformed into the amine 156 which, via Cope or Hofmann elimination gave the desired hydrocarbon 25. Alternatively a phenyllithium procedure is also reported (eqn 70).

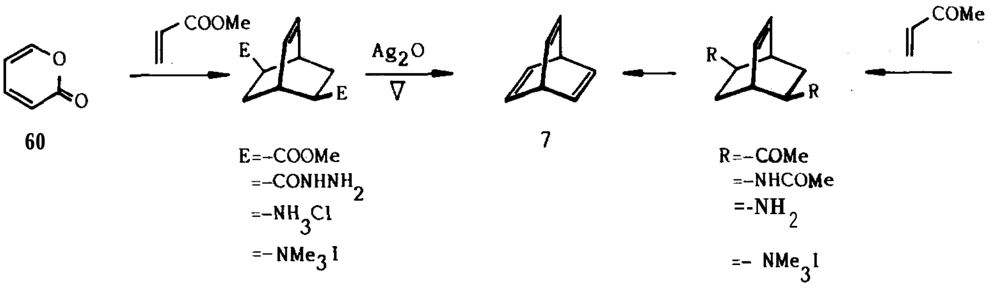


(eq. 70)

Other slight modifications of this reaction sequence have since appeared.[131] The amine intermediate 156 can also be conveniently prepared in two steps by cycloaddition of nitroethylene to 1,3-cyclohexadiene followed by reduction with iron and acetic acid.[132]

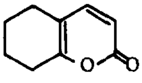
The completely unsaturated analogue of 25, that is barrelene 7, was for the first time prepared by this route by Zimmerman and Paufler.[133] The synthesis entailed double addition of methyl acrylate to a-pyrone 60, hydrazinolysis, diazotization and Hofmann elimination.

Alternatively the same authors proposed a sequence based on the addition of methyl vinyl ketone and subsequent transformation of the adduct (eqn 71). The overall yields of the two procedures are similar.

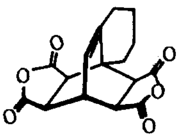


(eq. 71)

It is worthy of note that intensive attempts at the preparation of the barrelene 157 starting from the a-pyrone 158 through the cycloadducts 159 and 160 were uniformly unrewarding.[134] The preparation of 7 from the readily available 161[135] has not been reported.



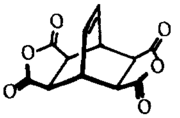
158



159

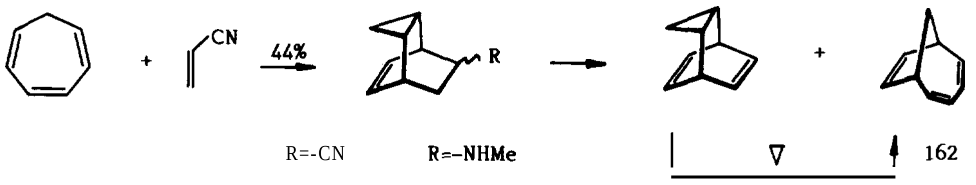
160 R=-COOEt
=-COOMe

157



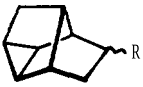
161

Homobarrelene 8 was also for the first time synthesized in a very similar **way.**[136] In this case acrylonitrile was used as the dienophile. It adds to cycloheptatriene in 44% yield. The sequence of reactions illustrated in eqn (72) was then necessary to lead to the desired product. The relatively high temperature necessary for the Hofmann elimination, however caused partial rearrangement of 8 to the **isomeric** hydrocarbon 162. It is important to notice **that** this hydrocarbon, as well as the lower homologue barrelene, gives photochemically, through a **di-π** -methane rearrangement, the fluxional molecule barbaralane. Similarly the higher homologue **bicyclo[4.2.2]decatetraene** affords bullvalene on irradiation.



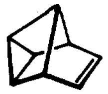
R=-CN R=-NHMe
=-COOH =-NMe$_3$I
=-CHO =-NMe$_3$OH
=-NHCOOMe

Two different methods for the conversion of the **nitrile** 163, obtained through **homo**-Diels-Alder cycloaddition of acrylonitrile to norbornadiene have been **reported**[137] (eqn 73).



163

$\xrightarrow[\text{route b: 32\%}]{\text{route a: 22\%}}$ 11 $\xrightarrow{h\nu}$ 150 (eq. 73);



164

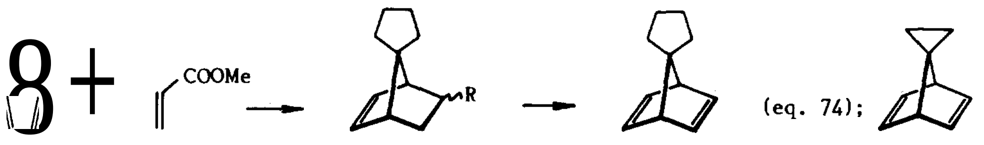
Route a: R=-CN → -CONH$_2$ → -NHMe → -NMe$_3$OH → 11
Route b: R=-CN → -COOH → -OCOMe → 11

The authors prefer the second route for its simplicity and yield. The lower homologue 164 has also been **prepared**[138] but via a route that does not involve acetylene synthons. It corresponds to the homo-cycloadduct of acetylene to Dewar benzene.

The acrylate route followed by Cope or Hofmann elimination can be also used for the synthesis of norbornadiene.“’ Although the parent molecule is commercially available, this procedure may be useful when substituted norbornadienes are desired.

An example that shows the potential of this method is represented by the synthesis of the norbornadiene derivative 165. Its synthesis was not successful with the one reported for 166. However, as in the preceding example, either Cope or Hofmann elimination furnished the diene 165 in poor **yield**[140] (eqn 74).

The synthesis of bicyclic dienes with a bridging unit of more than two carbons is somewhat limited by the low reactivity of monocyclic dienes with more than six carbon atoms. Acrylic acid derivatives are among the few dienophiles which do react with dienes of this class as for example cycloheptadiene. **Bicyclo[3.2.2]nonadiene** 63 was in fact synthesized from the **adduct** 167 through the sequence outlined below with some modification over the previous procedures to enhance the yields.[141]



(eq. 74);

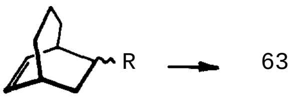
165

166

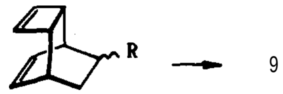
R=–COOMe
=–CONHNH$_2$
=–NHCOOMe
=–NHMe
=–NMe$_2$

Cope 20%
Hofmann 10%

A recently proposed route to the **Nenitzescu** hydrocarbon 9 makes **use**[142] of acryloyl chloride as dienophile because of the higher electron withdrawing ability of the chlorine atom and the consequent higher reactivity.

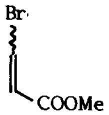


167 R =–COOEt
=–CONHNH$_2$
=–NHCOOMe
=–NHMe
=–NMe$_2$
=–NMe$_2$O

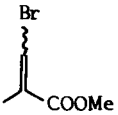


168 R =–COCl
=–NCO
=–NH$_2$
=–NMe$_2$
=–NMe$_2$O

***β*-Halogenoacrylic** acids 169 are, on the contrary, a group of acetylene synthons whose **adducts** can be easily transformed into the olefinic compound by simple treatment with alkali. **Roth**[143] reported for example the synthesis of the following compounds obtained through cycloaddition of 170.

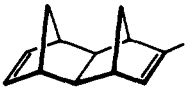


169

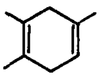


170

19'

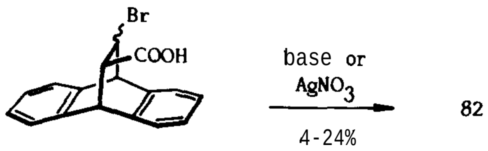


171



172

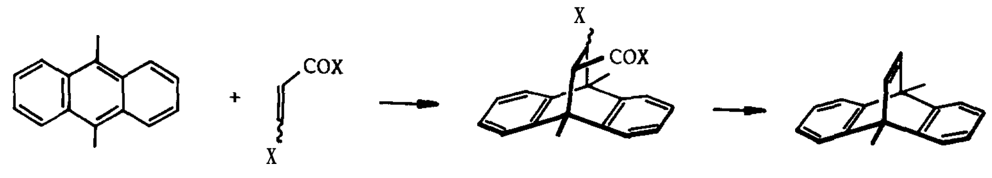
As usual **endo-adducts** are useless in this context since they lead to lactones. No problems are encountered in the elimination of 173 to form the type A olefin **82.**[144] Yields are, however, poor.



173

(eq. 75)

The development of cis- and **trans-*β*-haloacryloyl** chlorides as acetylene equivalents has been extensively studied in Coates' laboratory.[145] These reagents take advantage of the powerful activating effect of the acid halide functionality and of the relatively mild reductive fragmentation of the resulting ***β*-halocarbonylchloride adducts** with **$(PPh_3)_2Ni(CO)_2$** or with various forms of zinc (eqn 76).



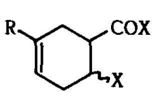
X= Hal

174

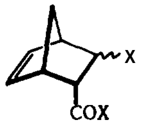
175

(eq.76)

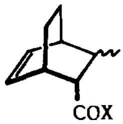
The best results are obtained with the inorganic complex (17–93% yield). Among the cases studied they reported the formation of acetylene adducts via the following synthetic intermediates (176178).



176



177

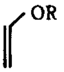


178

A route using β-chloroacrylic acid as the synthetic equivalent of acetylene was used for the preparation of 3,3,6,6-d$_4$-cyclohexadiene in 45% overall yields.[146]

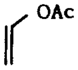
ENOL ETHER DERIVATIVES

This category includes dienophiles of type **179–181**. They react, as is well known, very poorly with typical dienes but are very reactive with inverse electron demand dienes such as 182. Their adducts eliminate with some difficulty in bicyclic systems. The cases in which they can be utilized are those where energy gain is achieved through, for example, aromatization.



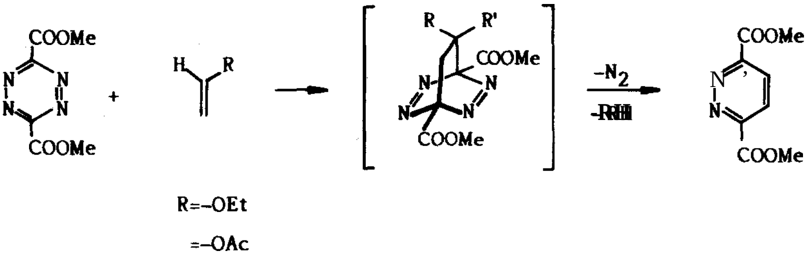
179

180



181

Indeed, Sauer[147] obtained good results with the Diels-Alder reaction of the tetrazene 182 (eqn 77). Similar results were obtained using 3,6-diphenyltetrazene.

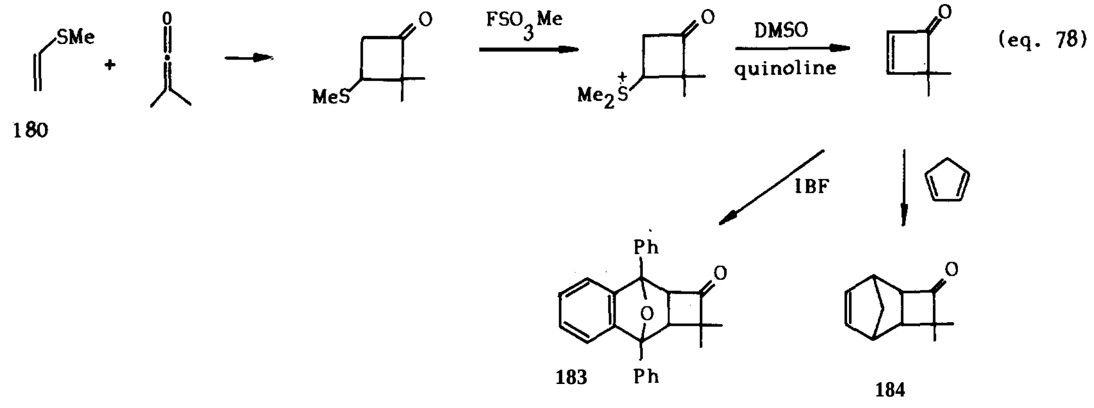


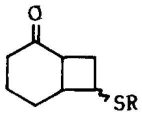
182

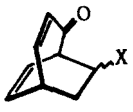
(eq. 77)

An application of the thioanalogue **180** in a cyclobutene synthesis was reported by Kelly and McNutt.[148] The complete sequence is shown in eqn (78). The cyclobutenone has also been cycloadded to form **183** and **184.**

Further examples have also been reported in the literature in which vinylsulfides have been added but the resulting cycloadducts were not transformed into the corresponding olefins. This is, however, a potentially very convenient method for the preparation of the corresponding unsaturated compounds. Other dienophiles of this type are discussed in the following paragraphs.




185^{149}


186^{150}

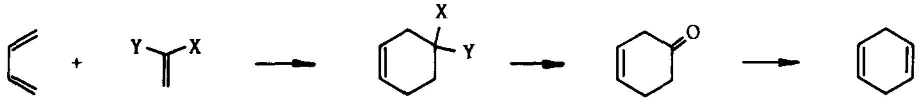

187^{150}

X=-SAr or -OAc

THROUGH FORMAL CYCLOADDITION OF KETENE

The following procedures deal with cycloaddition of a ketene followed by modification of the ketene cycloadduct to the corresponding olefin. If a (4 + 2) cycloaddition is desired a masked ketene has to be used since ketene itself preferably adds in a (2 + 2) fashion with 1,3-dienes. Since a recent review[151] on ketene synthons is available, this part of the problem will be only briefly discussed.

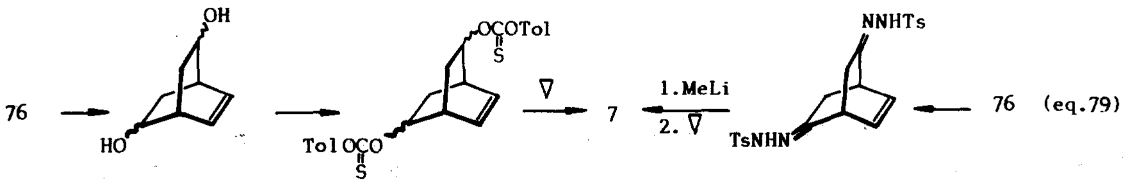
This strategy can be summarised as follows (Scheme 9).



Scheme 9.

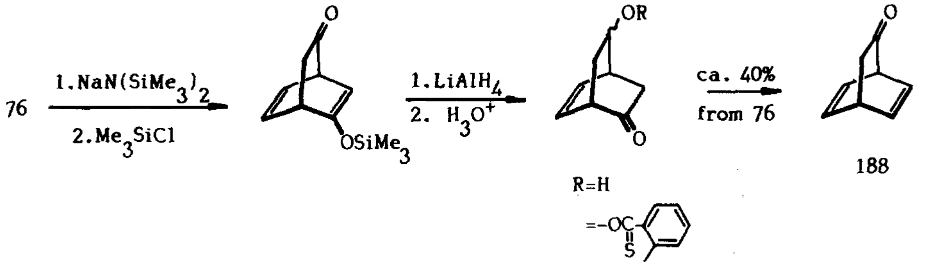
There are several ways to convert a ketone into the corresponding alkene by classical chemical reactions. The problem is whether they are feasible for the actual molecules in question.

One of the first reported cycloadditions of a ketene synthon is once again due to Alder et al., who used vinyl acetate.[152] Although they could prepare the corresponding alcohol, they were not interested in the dehydration step. Indeed the sequence passing through the alcohol as well as its obvious modifications like those via the acetate or tosylate were little used. A rare example in which a modified Chugaev method have been successfully employed is in the preparation of barrelene devised by de Meijere[153] and illustrated below with overall yields of 20% (eqn 79).

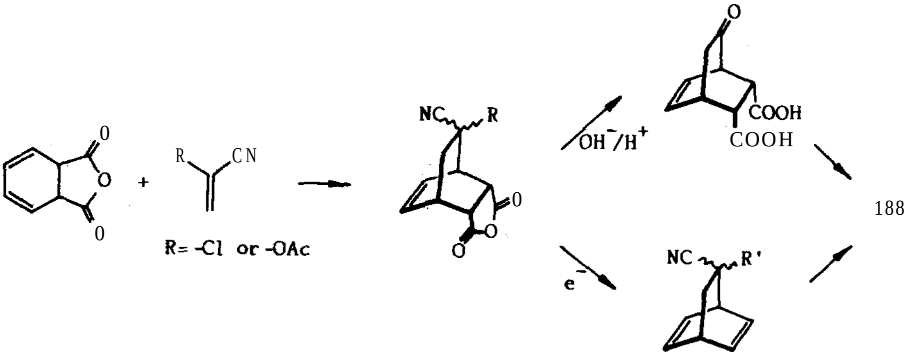


Jefford[154] reported. the preparation of the same compound, but using the **Bamford–Stevens** reaction for the transformation of the **diketone** 76 (eqn 79).

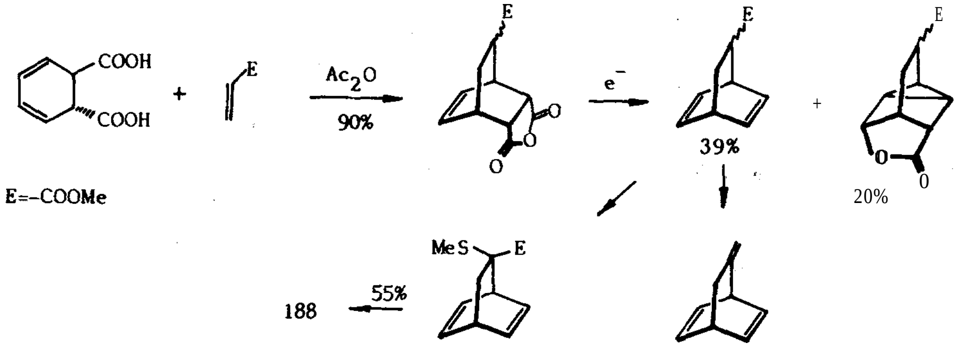
Using the same starting material **Gompper**[155] prepared the barrelenone **188**, with a similar procedure (eqn **80**) or via other routes (eqn **81, 82**).



(eq.80)[155]

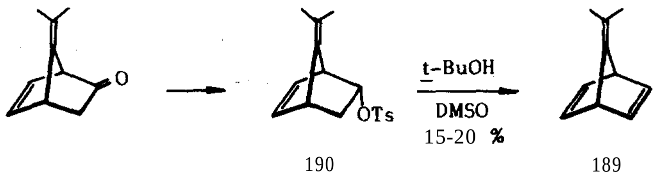


(eq. 81)[155]



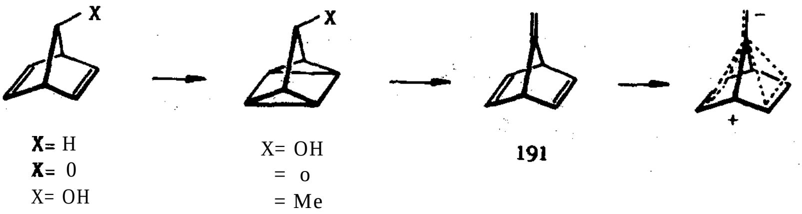
(eq. 82)[156]

Martin”' succeeded in the preparation of 7-isopropylidenenorbornadiene 189, which presents a high degree of cyclic homoconjugation, by **DMSO/t-BuOK** treatment of the **tosylate 190** (eqn 83).



(eq. 83)

The parent diene 191 was, however, prepared through a different route (eqn 84) which does not involve acetylene **synthons.**[158] Its high degree of polarization has been compared to

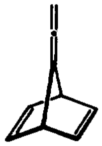


(eq. 84)

that of cycloheptafulvalene. The norbornadienes 166, 192 and 193 and the derived quadricyclanes have also been reported.[159]

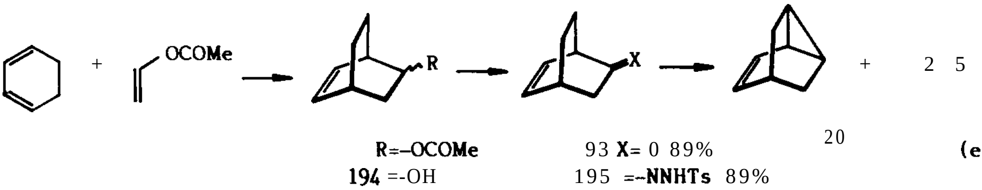
166

192



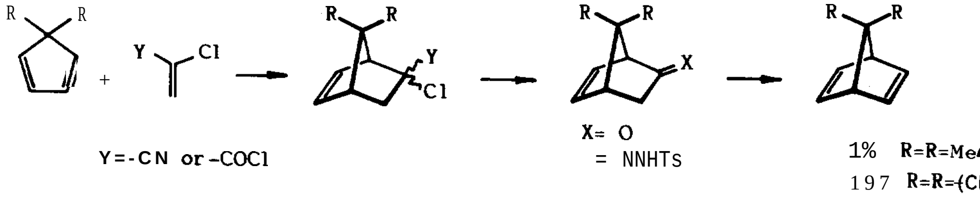
193

The method of choice to convert a formal ketene synthon to an acetylene synthon is that based on the reaction of the tosylhydrazone with an alkyllithium reagent.‘@’ If the sodium salt is used, this method may lead to the formation of side products if there are saturated carbons in the vicinity of the double bond which is being formed. This diversion is due to the possibility of an insertion reaction involving the intermediate carbene. For example, bicyclo[2.2.2]octa-2,6-diene 25 is not obtained through the decomposition of the tosylhydrazone sodium salt of 195 in synthetic useful yields. As reported by Grob[161a] the reaction gives mainly the tricyclic hydrocarbon 20. The lithium salt gives instead a 67% yield of the diene 25.[161b] The alcohol 194 dehydrates in the gas chromatograph giving the bicyclo[2.2.2]octa-2,5-diene 25.[161a]



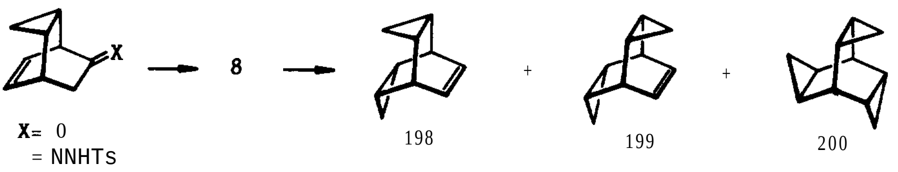
(eq. 85)

7,7-Dimethylnorbornadiene 1% and 7-spirocyclobutane norbornadiene 197 have been synthesised by Jefford[162] and de Meijere[163] respectively as shown in eqn (86). Since the authors chose this methodology to produce these molecules starting from precious starting dienes, this method is clearly one of the higher yielding procedures.



(eq. 86)

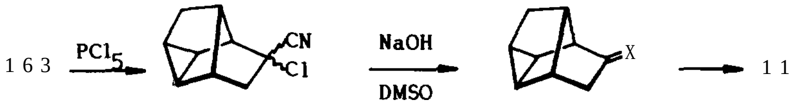
De Meijere[164] proposed a synthesis of the homo-barrelene 8 through the route of eqn (87); 8 was then cyclopropanated to the bis- and tris-homo-barrelenes 198–200, compounds that show an unexpected bridgehead reactivity.



(eq. 87)

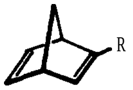
Hall[165] used acrylonitrile as homo-Diels-Alder dienophile and Freeman and Ball[166] used the product in the synthesis of deltacyclene 11 (eqn 88).

‘Recently the chiral hydrocarbons 1* and 25* have been synthesized via the tosylhydrazone route.[167] Their synthesis, however, did not utilize an acetylene synthon. It would be of great interest to have a chiral acetylene synthon available but studies of this objective are not available in the literature.

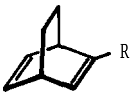


(eq. 88)

201 x= 0
= NNHTs



1*

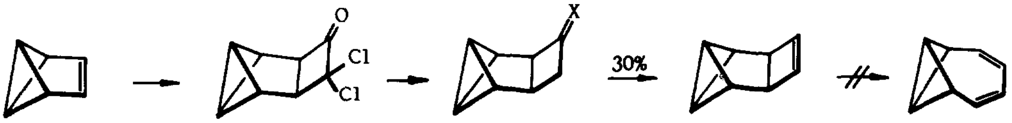


25*

R= **D**, Me

The most important applications of this method are in the synthesis of cyclobutenes, as ketenes undergo mainly (2 + **2)-cycloadditions**.

Dichloroketene, formed *in situ* by different methods, is one of the widely used ketenes. A recent review exhaustively covers this topic.[168] A representative example is that of **Meinwald**[169] who prepared the tetracyclic compound 202 by this procedure (eqn 89).



(eq. 89)

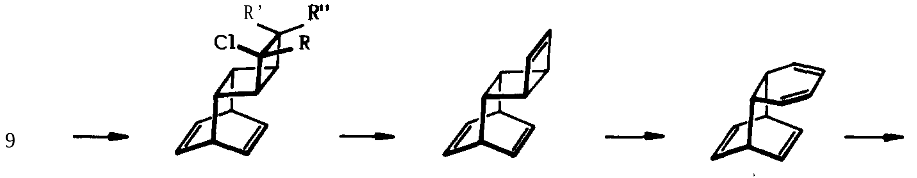
X= O 95%
= NNHTs 76%

202

203

The complexity and the strain of the molecule 202 are an indication of the mildness of the method and clearly emphasizes its potential. The related octavalene 203 is not obtainable by ring opening of 202, and it has been synthesized by Christl and **Lang**[170] only very recently.

An example in which the mesylate elimination was used is that reported by **Grimme** for the **synthesis** of the Diels-Alder self-adduct of benzene **204**[171] and the **benzene–naphthalene adduct.**[172] The entire sequence for the benzene dimer is reported in eqn (90).

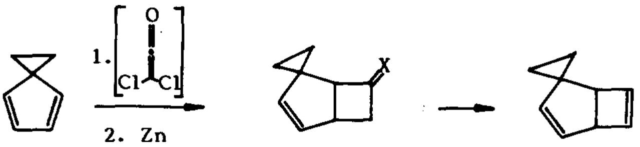


(eq.90)

R=Cl R'=R''=O
R= H R'=R''=O
R=R'=H R''=OH
R=R'= H R''=OMes

204

Although not yet reported in the literature, the potentially interesting molecule 205 could be prepared starting from the ketone 206 obtained through the dichloroketene addition to **spirocyclopentadiene.**[173]



(eq. 91)

206 X= 0
=NNHTs

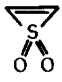
205

THREE MEMBERED RING REAGENTS

Compounds of type **207–210** might act as acetylene equivalents, if after cycloaddition, they can expel the functional fragment in form of a stable molecule. Indeed they all possess the attributes

207

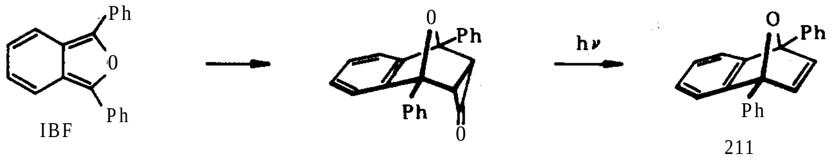
208



209

210

to be strong dienophiles, such as activation of the double bond by electron withdrawing groups and ring strain. A necessary requirement is that the unsaturated reagent loses the stable fragment less readily than the **adduct.** The limitation of these reagents are determined by the **difficulty** of preparation and low stability of the three membered ring heterocycle and hence the scope of the reaction is limited. A rare example is shown in eqn **(92).**[174]



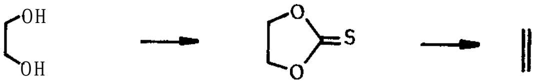
IBF

211

(eq. 92)

VINYLENE CARBONATE AND DERIVATIVES

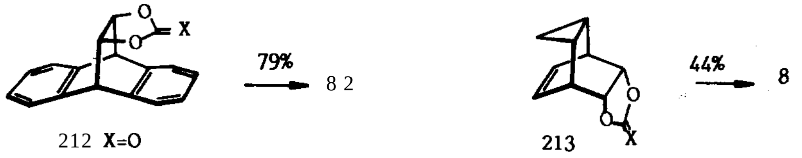
This method has attracted the interest of chemists after the Corey-Winter synthesis of olefins starting from **vicinal** diols through the corresponding **thionocarbonate.**[175]



(eq. 93)

After this **first** report a number of alternatives to the triphenylphosphine method have been **reported.**[176]

The present strategy makes use mainly of vinylene carbonate as an acetylene synthon because of its rather high reactivity.“’ One of the very first reports which covers the complete sequence is that by Daub *et al.*[178] who applied their method based on $Fe(CO)_5$ to reduce the thionocarbonates 212 and 213 (eqn 94). The yields for 8 have been subsequently optimized and the detailed procedure **reported.**[179]

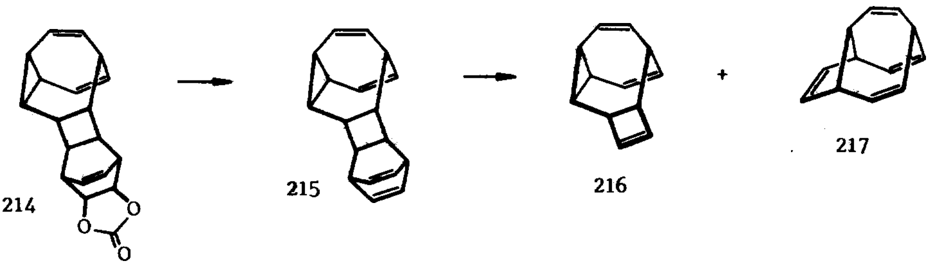


212 X=O
=S

213

(eq. 94)

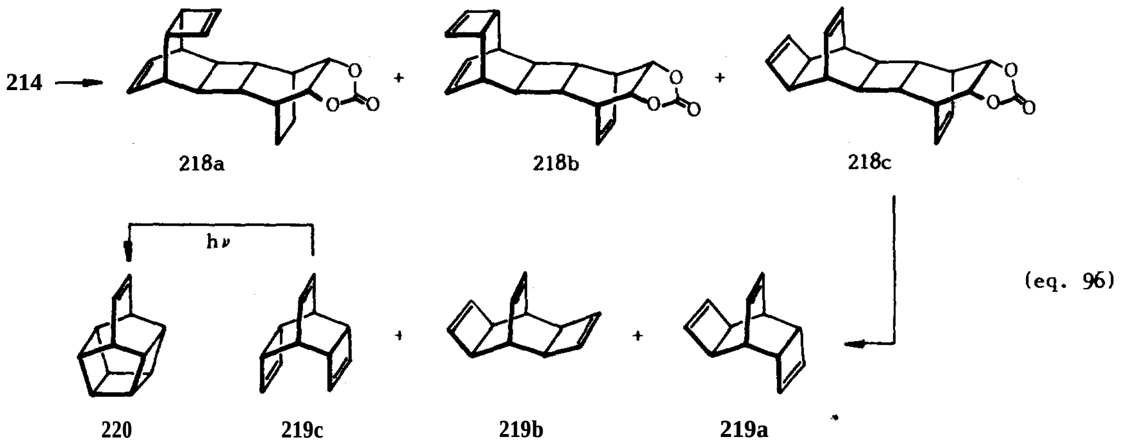
Cycloaddition of vinylene carbonate to cyclooctatetraene affords the intersting cycloadduct 214 that can be converted to the olefin 215 through this **procedure**[180] (eqn **95).Thermolysis** of the polycyclic triene 215 gives the two interesting $C_{12}H_{12}$ hydrocarbons 216 and 217.



214 215 216 217

(eq. 95)

The **adduct** 214 undergoes an interesting photochemical rearrangement to the carbonates 218 which can be converted to the corresponding **olefinic hydrocarbons.**[181] These may be pyrolyzed to 219; **219c** on further photocyclization generates the caged hydrocarbon 220 (eqn 96).

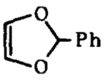


218a 218b 218c

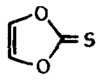
220 219c 219b 219a

(eq. 96)

Anderson and **Dewey**[182] reported for the **first** time the synthesis and the use of the derivatives **221 and 222**[183] as acetylene synthons. Differently substituted vinylethers are also available by similar **procedures.**[184]



221



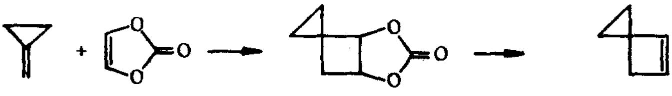
222

Except for these examples only a few other cases have been reported on the use of this class of compounds as acetylene synthons in (4 + **2)-cycloaddition.** Among them may be included the report by **Prinzbach**[185] on the synthesis of oxanorbomadiene 223, a valuable precursor of oxepine 224, through the **oxa-quadricyclane** 225 (eqn 97). The corresponding **thia-analogue** of 223, on the other hand, is not yet **known.**[186]

223 225 224

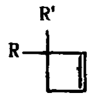
(eq.97)

This class of compounds is of great utility for the preparation of cyclobutenes via **photochemical** cycloaddition. The spirocyclobutene 226 was, for instance, prepared via this route as shown in eqn (98).[187] Similarly the other differently substituted cyclobutenes 227 have been **reported.**[188,189] On the other hand, the related **adducts 228–230** of vinylene carbonate to hydrocarbons have not yet been used as precursors of the corresponding **hydrocarbons.**[190]



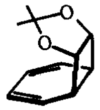
226

(eq. 98);

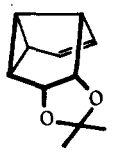


227

R=R'=H, Me
R=H R'=Me, Et. i-Pr, t-Bu



228



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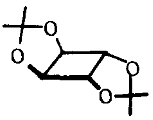
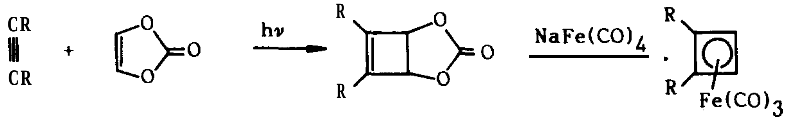


230

The **adduct** between acetylene and vinylene carbonate has been utilized to prepare **cy**clobutadienes 231 .[191] The dideutero analogue 232 was synthesized by **Carpenter**[192] in a study aimed at defining the conformation of cyclobutadienes in solution.



(eq. 99)

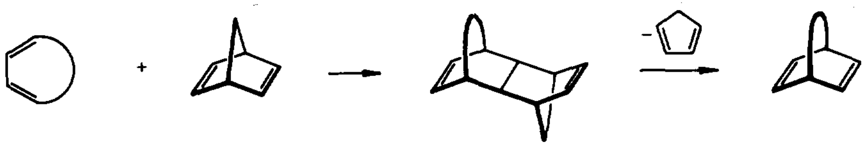
231: R=H 232: R=D

The halo-substituted vinylene carbonates have better cycloaddition properties, especially in photochemical processes. A fairly large number of cycloadducts are indeed **available**[193] but rarely, to date, have they been transformed to the corresponding olefins.

Several other procedures for the formation of olefins from vicinal diols have been reported so that the step involving the transformation to the thionocarbonate can be avoided. A very recent one is that reported by **Sharma**[194] with the use of chlorotrimethylsilane and sodium iodide. The Sharma paper reports a list of precedent methodologies for accomplishing this conversion. Other methods are **available.**[195]

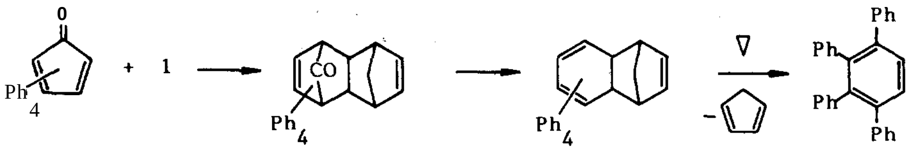
NORBORNADIENE AND QUADRICYCLANE

For a limited number of cases norbornadiene and quadricyclane can be classified as acetylene synthons. This reaction mode is very similar to the previously discussed examples but in these cases the departing molecule is cyclopentadiene, through a retro-Diels-Alder process. The pathway is illustrated in Scheme 10.



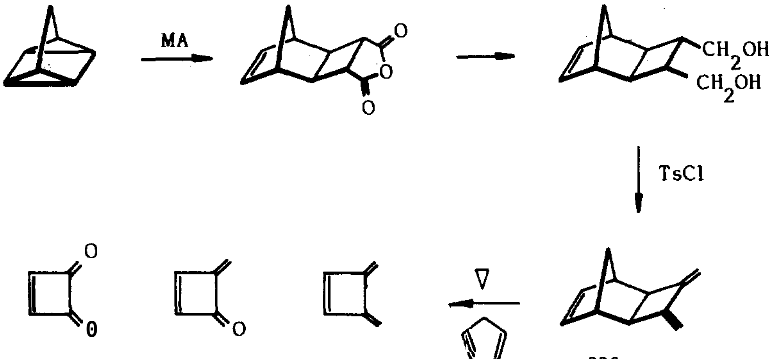
Scheme 10.

The **first** to achieve this strategy recognizing its potential as acetylene synthon, was MacKenzie.‘% The following equation shows one of his findings (eqn 100).



(eq. 100)

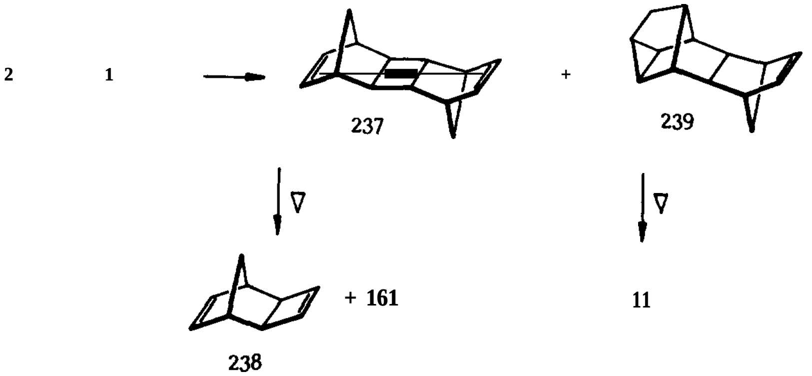
The use of this interesting approach has found some applications especially for those compounds that can be made through processes mediated by metals. No cases are reported in which the norbornadiene has been introduced thermally although the reaction is reasonably feasible with reactive dienes. Much more prone to cycloaddition is quadricyclane. For example it has been cleverly employed by **Martin**[197] in a synthesis of dimethylene-cyclobutene 233 (eqn 101). Similarly the other cyclobutanones 234 and 235 have been **prepared.**[198]



(eq. 101)

235 234 233 236

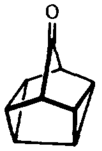
One of the early examples of the use of nonbornadiene as acetylene synthon has been reported by **Cannell.**[199] He used the norbornadiene dimer 237 and thermolyzed it to get a mixture of the two hydrocarbons 238 and 161 which were both unknown at that time. Similarly he obtained deltacyclene **11** from the pyrolysis of the **isomeric** norbornadiene dimer 239 (eqn 102).



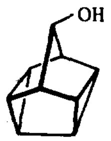
(eq. 102)

237 239 238

The synthesis of hydrocarbon 11 through the same sequence was simultaneously reported by **Katz.**[200] Deltacyclene prepared in 100 g quantities by a slight modification of this method served as the starting material for a number of related molecules including 240,241 and some deuterated **analogues.**[201] The solvolysis of the brosylate of **241** is 10^{10}–10^{12} times **faster** compared with that of the corresponding **7-norbornyl** deriyative because of the neighbouring group **participation** of the anti-cyclopropane rings.

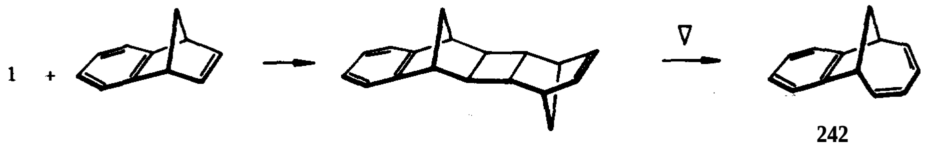


240



241

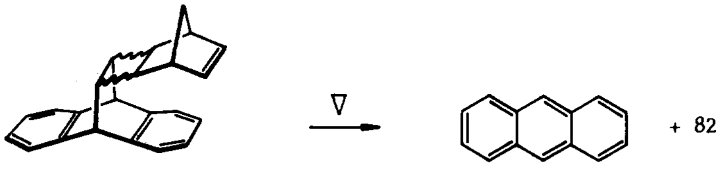
This reaction sequence did find some application for synthesis of more complex molecules as in the case of **242**[202] (eqn 103).



(eq. 103)

242

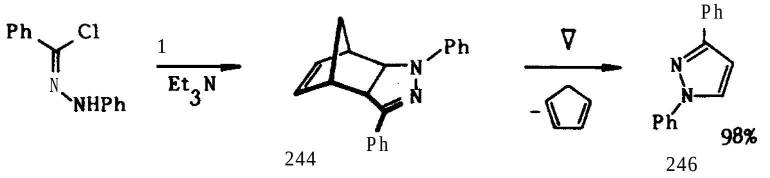
This synthetic sequence, however, does not provide a useful route for the preparation of dibenzobarrelene 82. In fact thermal transformation of the **adducts** 243 obtainable either from quadricyclane or from norbornadiene gives mixtures of the desired molecule 82 and **anthracene**[203,204] (eqn 104).



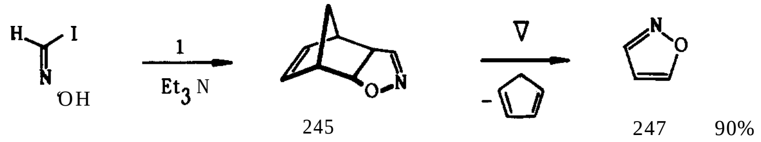
243

(eq. 104)

The products of **1,3-dipolar** cycloaddition to norbornadiene are often valuable precursors of five-membered heterocycles. Two examples are those with **diphenylnitrilimine**[205] and fulminic **acid**[206] **244** and 245. The first decomposes at 135” to give the pyrazoline **246,** the second at **140–160°** to give **isooxazole** 247. Both processes proceed with yields greater than 90%. The two heterocyclic products correspond with a **1,3-dipolar** cycloaddition to acetylene. Related to these reactions are many others which have already been **reviewed.**[207]



(eq. 105)



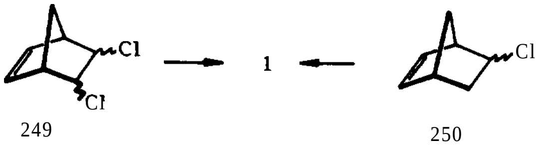
(eq. 106)

HALOGENATED OLEFINS

Compounds of the type **248** are **widely** used as acetylene synthons since the **adducts** are easily converted in high yields to the corresponding olefins by several standard methods.

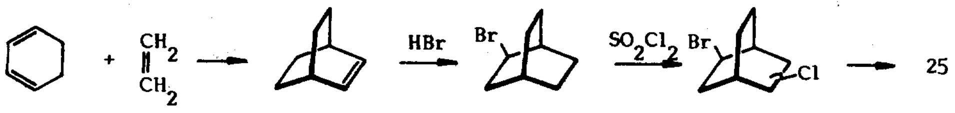
The cycloaddition of halogenated olefins to dienes has been widely investigated by Alder et ***al.*** However, they did not investigate the further dehalogenation step to the corresponding **olefin.**[208] This step was studied later on by Hine ***et al.***[37] who obtained the desired diene **1** by the use of **Mg/MgI$_2$**. The weaker **NaI** in acetone proved to be **uneffective** in these systems (eqn 107).

248 X= Cl, Br



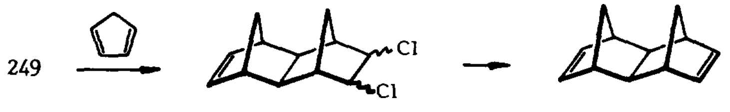
(eq. 107)

This strategy, however, as illustrated in the same paper, did not allow the synthesis of the higher homologous **bicyclo[2.2.2]octa-2,6-diene** 25, because dichloroethyiene does not cycloadd to **cy**clohexadiene. Another route to introduce halogens into the previously constructed skeleton had to be used, as illustrated in eqn (108).



(eq. 108)

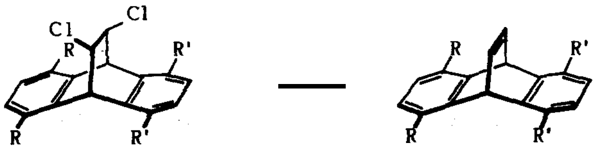
The product **251** of cyclopentadiene addition to 249 (arising in the cycloaddition of dichloroethylene to cyclopentadiene) has been dehalogenated (eqn 109) in a study intended to define the stereochemistry of addition of norbornadiene to cyclopentadiene.[209]



251

(eq. 109)

One of the best methods available for the preparation of the important dibenzobarrelene **82** is that described by Cristol.[210] The preparation involves dehalogenation of the dichloroethylene adduct to anthracene 252. In this synthesis, Zn/Cu couple[211] appears to be the reagent of choice in the dehalogenation step (eqn 110). A study has also been made by the Quast group[212] for the preparation of substituted dibenzobarrelenes which have been used in electrochemical studies.



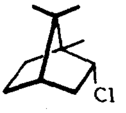
(eq. 110)

252	Zn/Cu	Na/i-PrOH
R=R'=H	98%	- -
R=H R'= OMe(88%)	77%	88%
R=R'=OMe (58%)	53%	48%

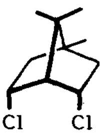
The applicability of these synthetic methods is seriously limited by the drastic conditions required for the cycloaddition of these poorly reactive olefins. In fact the preparation of the molecules thus far discussed requires thick-walled sealed tubes or autoclaves at temperatures as high as 180–200° for several hours with the inevitable formation of by-products.

An example in which the limitations of this approach are evident is that of the reaction with S-substituted cyclopentadienes. In fact while Alder *et al.*[213,214] succeeded in the synthesis of the norbornadiene **166**, Wilcox *et al.*[139] could not extend this procedure to the synthesis of the higher homologue **165.**

It has to be pointed out that, whereas dehalogenation is reasonably facile in these systems, dehydrohalogenation seems to be a much more difficult task. Especially unreactive are bornyl chlorides 253 and 254. For the preparation of the corresponding unsaturated compounds 255 and **256** specific reagents had to be devised.[215]



253



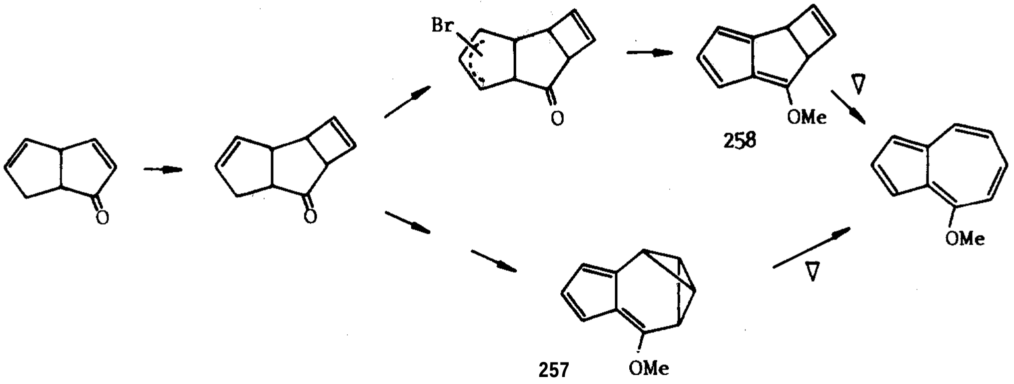
254


255

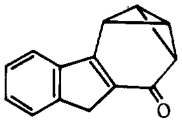

256

The use of halogenated olefins for the preparation of cyclobutenes through photochemical cycloaddition of dihalogenoethylenes is much more general[216,217] and examples of such methodology are often appearing in the literature. As in the case of the parent molecule, acetylene, the most common cases concern cycloaddition to enones.

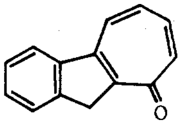
For instance Murata *et al.*[218] *very* recently introduced dichloroethylene photochemically in a key step for the preparation of 6-methoxyazulvalene 257 and 6-methoxy Dewar azulene **258**[218b] as illustrated in eqn (111). The procedure has been applied by the same authors to prepare the benzo-homologues 259 and **260**.[218c]



(eq. 111)

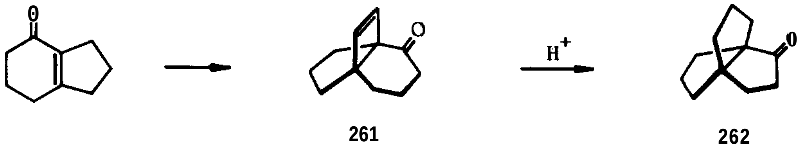


259



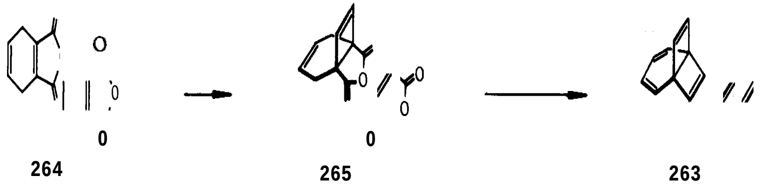
260

In another case, this sequence was used for the preparation of the propellane **261**.[219] Acid treatment gave 262 (eqn 112).

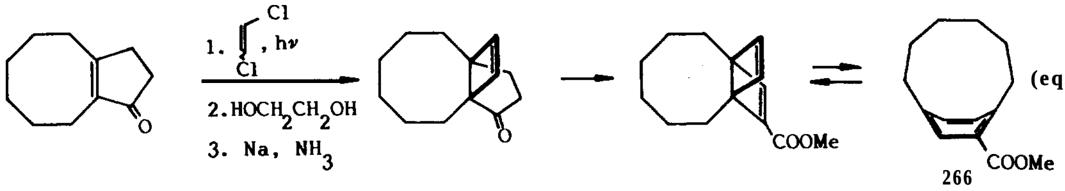


(eq. 112)

The interesting propellane 263 has been prepared by Tsuji et *al.*[220] The key step in the preparation is the cycloaddition of dichloroethylene to 264 (eqn 113). A similar route has very recently been reported for the preparation of the paracyclophane 266 that contains a highly deformed benzene **ring**.[221]

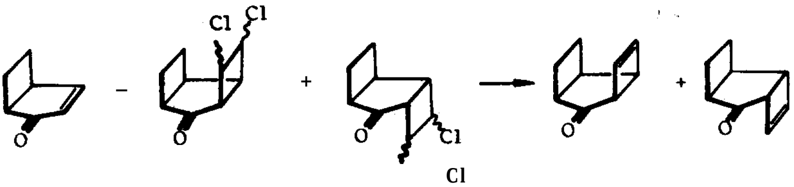


(eq. 113)

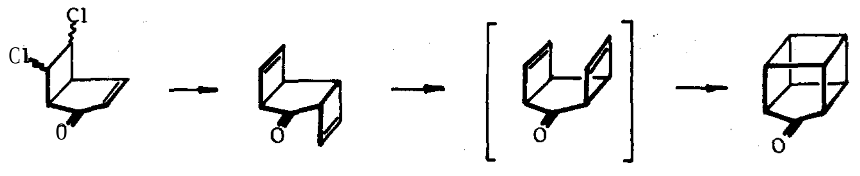


(eq.114)

This methodology provides a simple route for the synthesis of cyclobutenes as illustrated in **eqns** (115, 1 **16)**.[222,223]

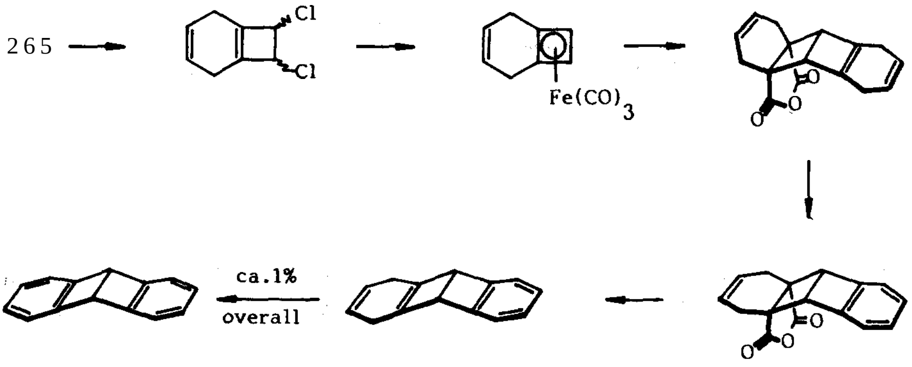


(eq. 1 1 5)



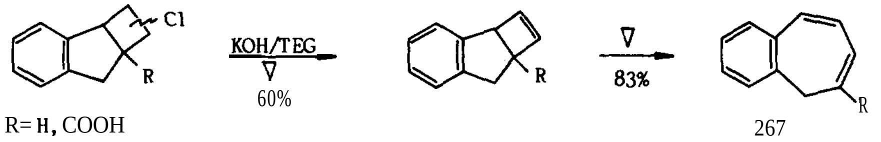
(eq. 116)

Very recently the synthesis of Dewar-anthracene through the elegant sequence of eqn (117) has been reported by **Grimme.**[224] Chloroethylene too, can be used in this type of reaction as shown



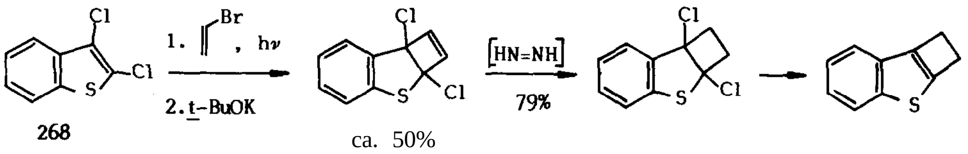
(eq. 117)

by the preparation of 267.[225] In this specific example **KOH/triethyleneglycol** has been used in the dehydrohalogenating step (eqn 118). A similar synthesis has been reported for R = **CO_2H.**[226]



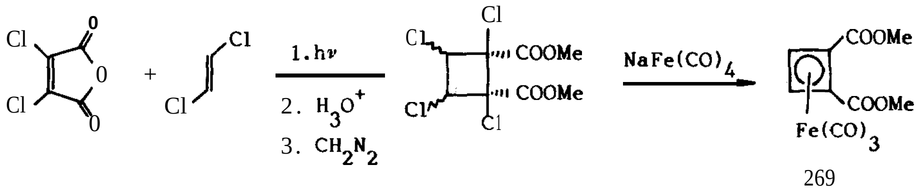
(eq. 118)

The presence of the **enone** moiety is not necessary as shown by the next example (eqn 119) in which vinyl bromide was added to 260.[227] This synthetic sequence is also an useful tool for the



(eq.119)

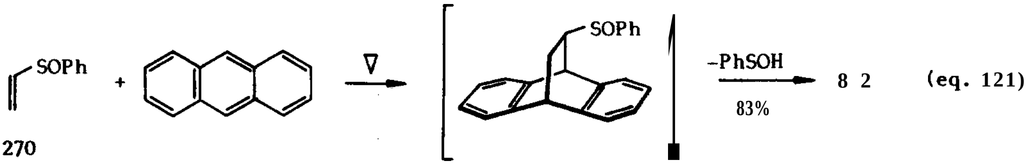
preparation of cyclobutadienes. In the sequence illustrated in eqn (119) **$NaFe(CO)_4$** functions both as dehalogenating and as **complexing** agent of the unstable product **269**[228] (eqn 120).



(eq. 120)

SULFUR-CONTAINING OLEFINS

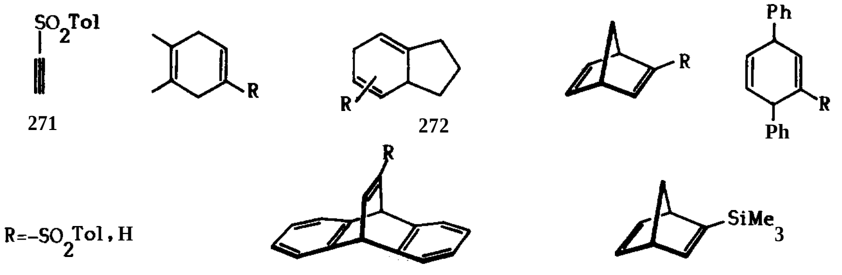
A modern and most promising method for the generation of the acetylene synthon in a cycloaddition reaction is the one that employs a sulfur substituted olefin with different oxidation state at sulfur. Obviously a sulfone presents a higher electron withdrawing ability than a sulfoxide but as usually happens for any acetylene synthon, the easier the cycloaddition the more difficult is the elimination. This is **indeed** the case of vinyl sulfoxides and sulfones. For example phenyl vinyl sulfoxide 270 would be a very useful reagent since it usually loses **PhSOH** very readily. Hence it would be possible to heat the reagent at a certain temperature in which 270 cycloadds and at the same time undergoes elimination. In this way vinyl sulfoxide is actually an acetylene equivalent since it does in one step what acetylene itself would do. **Paquette**[229] first realized its potential and demonstrated it in a number of cases. A typical example is the preparation of dibenzobarrelene 82 (eqn 121).



(eq. 121)

However, the scope of the method was limited because only **the more reactive dienes can be** used and many others are often too unreactive, including for example **1,3-cyclohexadiene** which does not react under the conditions reported.[230] The higher reactivity of the related vinyl **sulfone**[231] is of little help since the transformation of the **adduct** to the corresponding **olefin** is very **difficult.**[232] Partial or total reduction to the more useful sulfoxide or sulfide are also very **difficult.**[233] Nonetheless vinyl sulfone has been used as ethylene synthon, since the reductive transformation of the sulfone to the corresponding hydrocarbon is feasible.[231] Conceptually, however, multistep routes to convert the saturated sulfones to olefins are possible since ways have been published to convert them into ketones and hence following the already seen procedures (see preceding sections) it is possible to use vinyl sulfone as an acetylene synthon. For example Little reported a method based on the use of molybdenum peroxide.” The procedure cannot, however, be used in the presence of sensitive functional groups.

An acetylene synthon that could obviate these difficulties is tolylethynylsulfone 271 proposed by **Whitham.**[235] In fact the higher reactivity in Diels-Alder reactions associated with the sulfone moiety could be used because the derived unsaturated **adducts** are amenable to reductive **elimination.**[236] Unfortunately the reactivity is not very high, because what is gained by the higher electron withdrawing ability of the sulfone is lost by the scarce dienophilic reactivity of the triple bond. The dienes synthesized in this way are reported below including the dihydroindane 272.

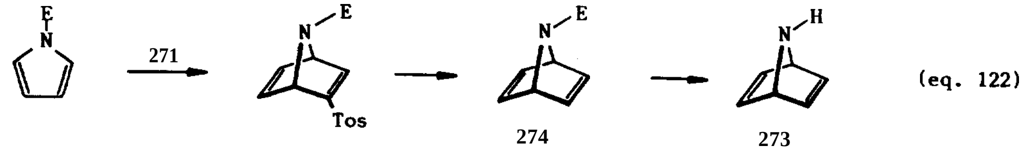


271

272

$R = -SO_2Tol, H$

An example that well illustrates the potential of this method is the achievement **by Vogel**[237] of the synthesis of **7-azanorbornadiene,** via the sequence of eqn (122).



274

273

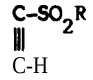
(eq. 122)

$E = -COOMe$

$Tos = -SO_2Tol$

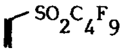
This particular molecule **could not be prepared** using **other acetylene equivalents so this represents an excellent example in which sulfonylated olefins are superior. The only previously** reported example of azanorbornadiene was by Prinzbach.[110] Although not yet reported, this reagent may also be used for the synthesis of substituted polycyclic systems because vinylsulfones in the presence of nickel salts couple with Grignard reagents in a stereospecific way.[238]

The dienophilic properties of vinylic and acetylenic sulfones have been extensively studied.[239] In particular it was observed that fluorinated sulfonyl analogues are more reactive dienophiles than aryl derivatives.[240] It is also worth mentioning the very high reactivity of trifluoromethylvinylsulfones 275 and 276.[241-243] Several groups have studied in this area in view of the wide importance in organic synthesis of the sulfonyl group[244] but none of the obtained cycloadducts has yet been manipulated in the context of the present article.



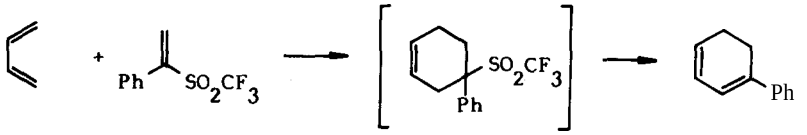
$$\begin{array}{l} C\text{-}SO_2R \\ \| \! | \\ C\text{-}H \end{array}$$

275 $R{=}CF_3, C_4F_9$



276

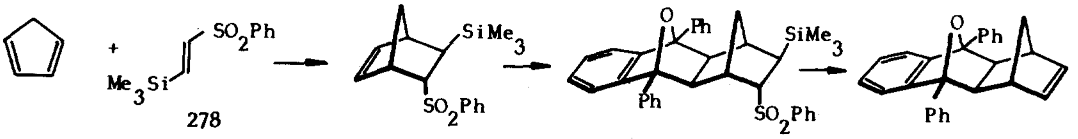
The potentiality of this class of reagents is apparent from the following equation (eqn 123) in which it is shown that triflones eliminate spontaneously from the adduct 277.



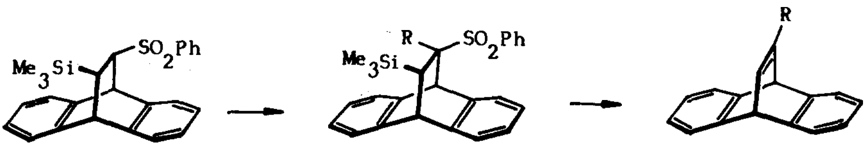
277

(eq. 123)

Another method following this line has been recently reported by Paquette[246] who proposed the silyl sulfone 278. Although its synthetic utility is greater than that of the previously reported synthons, the reactivity is still rather low and its use is limited to reactive dienes such as those shown in eqns (124-125).



(eq.124)

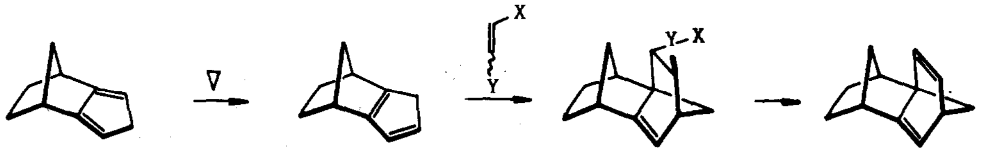


(eq. 125)

R= H, D

However this acetylene synthon is adaptable to the synthesis of the mono and di-deutero acetylene cycloadducts and for higher homologues. Lately the same author reported a number of cycloadditions to an isomer of isodicyclopentadiene 279.[247] This isomer can be captured only by poorly reactive dienophiles since the more reactive dienophiles cycloadd to the thermodynamically more stable isomer. On these bases the tested dienophiles are considered weak.

A considerable advantage over the aforementioned sulfur containing olefins is provided by the use of cisdiphenylsulfonylethylene **281**. In this molecule the olefin is doubly activated. Although its dienophilic reactivity was reported by several authors,[248] 281 has never been used as an acetylene synthon because of the lack of an easy route to form olefins from its adducts. Recently we reported[249] that sodium amalgam in methanol buffered with sodium dihydrogenphosphate is an



(eq. 126)

279 280

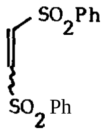
X=–SO$_2$Ph Y=–SiMe$_3$

X=Y = Cl

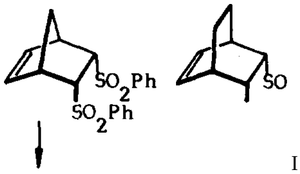
X,Y=–SOPh;, H

X,Y=–SO$_2$Ph, H

efficient method for transforming *β*-**disulfonyl** compounds into olefins in high yields. Through this route we have synthesized the following dienes in two steps.



281

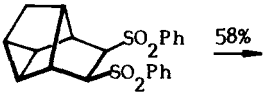


1 **(65%)**

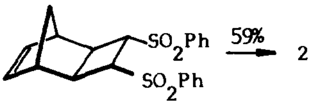
Ph I --2 SO$_2$Ph I 25 (69%)

&SO Ph I --2 SO$_2$Ph I 9 (60%)

Recently we have also succeeded in the preparation of the **adducts** of norbornadiene and quadricyclane and hence of the corresponding olefins **11** and 238. The present procedure is particularly effective for the synthesis of 238 which, by the other reported routes, is obtained only in low yields and as a mixture of **isomeric hydrocarbons.**[199]

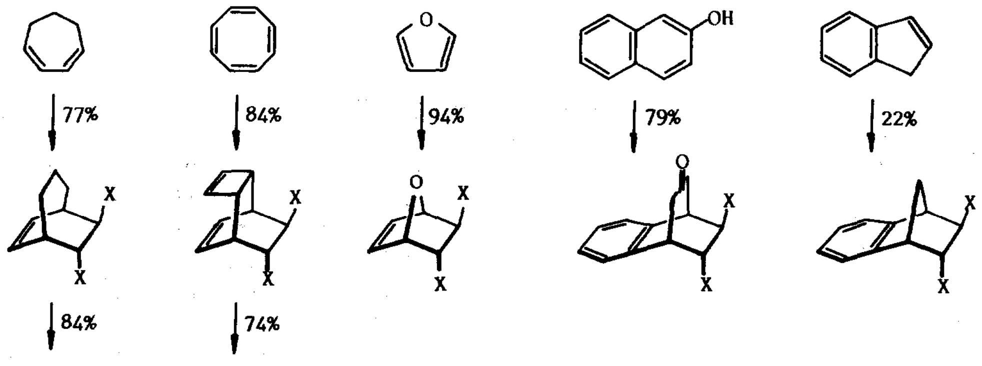


11



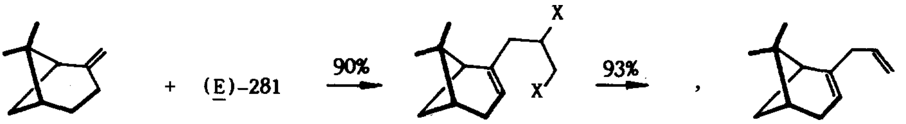
238

The **isomeric (*E*)-diphenylsulfonylethylene,**[250] as is frequently observed in Diels-Alder **reactions,**[251] is even more reactive; it adds efficiently to the rather inert dienes listed below. No reaction was observed with (Z)-diphenylsulphonylethylene. Disulphonyl ethylenes have dienophilic reactivity as high as that of **maleic** anhydride, one of the best acetylene synthon so far available, and they also provide the further advantage of requiring a reductive step rather than an oxidative step for the generation of the olefins. An example in which the advantages of these dienophiles is demonstrated is in the ene-addition of 281 to *β*-**pinene** and the subsequent transformation of the **adduct**. This sequence corresponds to the formal ene-reaction of acetylene with the substrate.



63 9

(E)-281 appears to be the only acetylene equivalent able to perform such a synthetic sequence (eqn 127).



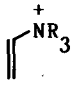
(eq. 127)

MISCELLANEOUS AND SPECULATIVE REAGENTS

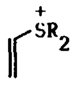
A number of other dienophiles, which could be considered as possible acetylene synthons, are available from the literature. Some of them are worth a mention, although they have not yet been used for reactions within the scope of this review.

For example aldehydes have been used to activate dienophiles.[252] Speculative but not unreasonable is the possible decarbonylation of the adducts mediated by metals.[253]

Olefins of type **282–284** should also show some dienophilic reactivity, due to the electron-withdrawing substituent and the extremely easy Hofmann elimination. Depending on the solubility of the reagent this type of compounds might also be employed in two-phase Diels-Alder processes with the dual function of reagent and of phase transfer catalyst.[254]



282



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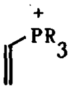
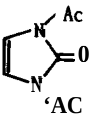


284

Furthermore a number of reagents, whose cycloadditive properties has already been tested, are amenable to speculative but not unreasonable chemical transformations with ultimate formation of a double bond. As an example 1,3-diacetyl-4-imidazolin-2-one (285) has been reacted thermally in (4 + 2)-[255] and photochemically in (2 + 2)-cycloadditions[256] to yield (among others) **286–288**.



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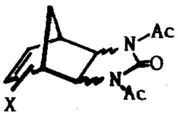
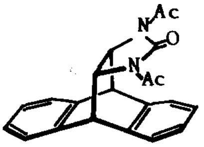
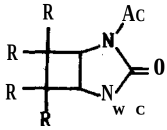


286 x= Cl



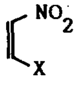
287

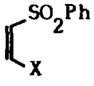


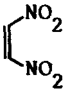
288

These compounds have been degraded with ease to the corresponding diamino derivatives,[256] which on WO_4^{2-} oxidation[257] might afford diazetidines whose denitrogenation is a well established process.[258]

A number of other possible acetylene synthons for which it is legitimate to propose a future application on the basis of recently discovered elimination routes from saturated analogues may be:[259]







Another interesting possibility that has been little studied is the need to discover synthons for alkynes additional to the parent acetylene. In view of the steric factors that may arise, the starting point will always be an acetylene synthon where it might be possible to attach appendages and functional groups. Furthermore the discovery of a chiral acetylene synthon would be of interest and the synthetic utility of this approach could be an important. future development.

REFERENCES

[1] **J.** Sauer, Angew. Chem. **78,** 233 (1966); Angew. ***Chem., Int.*** Ed. ***Engl.* 5,** 211 (1966).

[2] **J. Bastide** and *0.* **Henri** Rousseau, In The *Chemistry of* **Carbon-Carbon** *Triple Bond* **(Edited** by S. **Patal),** Part I, p. 447. Wiley, New York (1978).

[3] **T.** F. Rutledge, In *Acetylenes and **Allenes**; Addition, **Cyclization** and Polymerization Reactions.* Reinhold, New York (1969).

[4] **R.** Fuks and H. G. **Viehe,** In ***Chemistry of Acetylenes*** **(Edited** by H. G. **Viehe),** pp. 425-596. Dekker, New York (1969).

[5] **V.** Jaeger and H. G. **Viehe,** In ***Houben- Weyl: Methoden der*** *Organischen Chemie,* **Vol 5/2a,** pp. 809-912. Thieme, Stuttgart (1977).

[6] **D. Seebach,** In ***Houben-Weyl*: *Methoden der*** *Organischen Chemie,* Vol. **4/4,** pp. 371-381. Thieme, Stuttgart (1971).

[7] **H.** L. Holmes, Org. *Reactions 4,* **60** (1948).

[8] **R.** R. Hautala, R. B. King and C. Kutal, In ***Solar Energy,*** *Chemical **Conversion** and **Storage**.* **Humana** Press, Clifton, New Jersey (1979).

[9] **S. S.** Hixon, P. S. **Mariano** and H. E. Zimmerman, ***Chem. Rev.*** 73, 531 (1973).

[10] **See** Ref. 4, **p.** 482.

[11] **J.** Hyman, E. Freireich and R. E. Lidov, U.S. *Pat.* 2,875, 256; *CA 53,* **13082d** (1959).

[12] **D.** R. Fahey, ***J.*** *Org. **Chem.** 37,* 4471 (1972).

[13] **J.** E. Lyons, H. K. Myers, and A. Schneider, ***J. Chem. Soc., Chem. Commun.*** *636* (1978).

[14] **G.** N. **Schrauzer** and P. Glockner, ***Chem.*** Ber. 97, 2451 (1964).

[15] **M.** F. Mirbach, M. J. Mirbach and A. Saus, ***Z. Naturforsch*** *B, 32, 47* (1977); ***Ibid.*** *32, 281* (1977).

[16] **Y.** Sugihara, N. **Morokoshi** and I. Murata, *Tetrahedron Letters 3887* (1977).

[17] **G.** Maier, T. **Sayraç** and H. P. Reisenauer, ***Chem.*** *Ber.* **115, 2202** (1982).

[18] **F.-G.** Klaemer, E. K. G. **Schmidt** and M. A. A. Rahman, *Angew. **Chem.** 94,* 136, 137 (1982); Angew. Ckem., ***Int.*** *Ed. **Engl.** 21, 138,* 139 (1982).

[19] **H.-D.** Martin, B. Mayer, M. Puetter and H. Hoechstetter, *Angew.* ***Chem.*** *93, 695* (1981); *Angew. **Chem.**, Znt. Ed. **Engl.*** **20,** *677* (1981).

[20] **C.** Hoornaert, A. M. **Hesbain-Frisque** and L. Ghosez, *Angew. **Chem.** 87, 552 (1975); Angew. **Chem.**, **Int.*** Ed. ***Engl.*** 14, 569 (1975).

[21] **W.** P. Weber, *Silicon **Reagents** for Organic Synthesis,* Chap. 9. Springer Verlag, Berlin (1983).

[22a] **H.** G. Kuivila and C. R. Warner, *J. Org. **Chem.** 29, 2845* (1964); [b]**R.** F. **Cunico,** *J. Org. **Chem.** 36, 929* (1971); ‘A. Laporterie, J. Dubac, P. Mazerolles and M. **Lesbre,** *Tetrahedron Letters* 4653 (1971).

[23] **R.** L. Funk and K. P. C. Vollhardt, *J. Am. **Chem. Soc.** 99,* 5483 (1977); R. L. Hillard III and K. P. C. **Vollhardt,** ***Ibidem*** *99,* 4058 (1977); R. **Crigg,** R. **Scott** and P. Stevenson, *Tetrahedron **Lett.** 23, 2691 (1982);* B. *C.* **Berris,** *Y.-H.* Lai and K. P. C. Vollhardt, *J. **Chem. Soc.**,* Chem. Commun. 953 **(1982),** and cited references.

[24] **A.** Naiman and K. P. C. Vollhardt, *Angew. **Chem.** 89, 758* (1977); Angew. ***Chem.**, Znt. Ed. Engl.* 16, 708 (1977); D. J. **Brien,** A. Naiman and K. P. C. Vollhardt, *J. **Chem. Soc.**,* Chem. Commun. 133 (1982).

[25] **L.** Birkofer and D. Eichstaedt, *J.* ***Organomet. Chem.* 145,** C29 (1978).

[26] **G.** Maier, H. W. Lage, and H. P. Reisenauer, *Angew. **Chem.** 93,* 1010 (1981); *Angew **Chem., Int.** Ed. **Engl.** 20,976* (1981).

[27] **H.** W. **Lage,** H. P. Reisenauer, and G. Maier, *Tetrahedron Letters 23, 3893 (1982).*

[28] **M.** C. **Kloetzel,** *Org. React.* **4,** 1 (1948).

[29] **E.** Clar, *Tetrahedron Letters 3471 (1973);* **see** *also: S.* Tokita, K. Hiruta, K. Kitahara and H. Nishi, *Bull. **Chem. Soc.** Japan* **55,** *3933* (1982).

[30] **K.** Alder, ***Neurere Methoden der Praeparative Organische*** Chemie, Vol. 1, p. 251. Verlag Chemie, Weinheim (1944).

[31] **K.** Alder, *Preparative **Organische** Chemie,* Vol. II", **p.** 125. Verlag Chemie, **Weinheim** (1953).

[32] **T.** Matsuo and S. Mihara. *Bull. **Chem. Soc. Japan*** *48,* 3660 (1975).

[33] **G.** Maier and B. Hoppe, ***Tetrahedron*** *Letters 861* (1973).

[34] **G.** Maier, *Angew **Chem.** 86,* 491 (1974); *Angew. **Chem. Int.** Ed. **Engl.** 13, 425* (1974).

[35] **W.** von E. **Doering,** M. Farber and A. Sayigh, *J. Am. **Chem. Soc.** 74, 4370 (1952).*

[36] **R.** Kuhn and I. Hammer, ***Chem.*** *Ber. 83,413* (1950); W. von E. **Doering** and M. Finkelstein, *J. Org. **Chem.*** **23, 141 (1958).**

[37] **S. Beckmann** and R. **Schaber,** ***Liebigs*** *Ann. **Chem.** 585,* 154 (1954).

[38] **J.** Hine, J. A. Brown, L. H. **Zalkow,** W. E. Gardner and M. Hine, *J. Am. **Chem. Soc.*** **77,** *594* (1955).

[39] **E.** E. van **Tamelen** and D. Carty, ***J. Am. Chem. Soc.*** 93, 6102 (1971).

[40] **R.** Criegee, H. Kristinsson, D. **Seebach** and F. **Zanker,** Chem. ***Ber.*** *98,* 2331 (1965).

[41] **E.** Grovenstein, Jr., D. V. Rao and J. W. Taylor, ***J.*** *Am. **Chem. Soc.** 83, 1705* (1961).

[42] **B.** M. **Trost** and F. Chen, *Tetrahedron Letters 2603* (1971).

[43] **P.**Ho, S. Oida and K. **Wiesner,** ***J. Chem. Soc.,*** Chem. Commun. 883 (1972); K. Wiesner, P. Ho, R. C. Jain, S. F. Lee, **S.** Oida and A. Philipp, ***Can. J. Chem.*** 51, 1448 (1973).

[44] **G.** L. **Grunewald** and D. P. Davis, *J. Org. **Chem.*** **43,** *3074,* (1978).

[45] **W.** G. **Dauben,** G. T. Rivers, R. J. Twieg and W. T. Zimmerman, *J. Org. **Chem.*** 41, 887 (1976).

[46] **W.** Spielmann, H.-H. **Fick,** L.-U. Meyer and A. de Meijere, *Tetrahedron Letters 4057* (1976).

[47] **D.** Kaufmann, H.-H. **Fick,** 0. Schallner, W. Spielmann, L.-U. Meyer, P. Goelitz and A. de Meijere, Chem. *Ber.* 116, 587 (1983).

[48] **Y.** Sugihara, K. Hasbimoto, M. Yoshikawa and I. Murata, *Tetrahedron Letters 23,* 1925 (1982).

[49] **J.** E. L. **McDoland** and J. S. Roberts, *Tetrahedron Letters* 4521 (1976).

[50] **J.** R. Peyser and T. W. **Flechtner,** *J. Org. **Chem.*** 41, 2028 (1976).

[51] **S.** Masamune, N. Nakamura, M. Suda and H. **Ona,** *J. Am. Chem.* ***Soc.* 95, 8481** *(1973).*

[52] **A.** J. Baker, A. M. Chalmers, W. W. Flood, D. D. **MacNicol,** A. B. Penrose and R. A. Raphael, *J. **Chem. Soc.***, **Chem.** Commun. 166 (1970).

[53] **I.** M. Takakis and W. C. Agosta, ***J. Org. Chem.*** ***43,*** 1952 (1978).

[54] **R.** Joesel and G. Schroeder, ***Liebigs*** *Ann. **Chem.*** 1428 (1980).

[55] **T.** Tsuji, H. Ishitobi and H. **Tanida,** *Bull. **Chem. Soc. Japan** 44, 2447* (1971).

[56] **R.** T. Luibrand and **E.** M. Fujinari, *J. Org. **Chem.*** **45,** *958* (1980).

[57] **R.** T. Luibrand, B. M. Broline, K. A. Charles and R. W. **Drues,** *J. Org. **Chem.** 46,* 1874 (1981).

[58] **L.** F. Fieser and M. J. Haddadin, ***J.*** *Am. **Chem. Soc.*** **86,** *2392* (1964).

[59] C. A. **Grob,** M. Obta and A. Weiss, Angew *Chem.* 70, 343 (1958).
[60] C. A. Grob, M. Ohta, E. Renk and A. Weiss, *Helv. Chim. Acta 41,* 1191 (1958).
[61] **R.** Criegee, In *Oxidation in Organic Chemistry* Part A (Edited by K. **Wiberg)** pp. 297-301; Academic Press, New York (1965); G. M. Rubottom in Part D **(W.** S. Trahanovsky) (Ed.) 1982, pp. 81-89; R. A. Sheldon and J. K. **Kochi,** *Org. React.* **19, 279** (1972).
[62] **K.** Alder and S. Schneider, *Liebigs Ann. Chem. 524,* 189 (1936).
[63] **E.** J. **Corey** and A. W. Gross, *Tetrahedron Letters 21,* 1819 (1980).
[64] **M. Avram,** E. Sham and C. D. Nenitzescu, *Liebigs Ann. Chem. 636, 184* (1960).
[65] C. D. Nenitzescu, M. Avram, I. I. Pogany, G. D. Mateescu, and M. Farcasiu, *Acad. Rep. Populare Romine, Studii Cercetari Chim.* **11, 7 (1963);** *CA* **60,** *6764* (1964).
[66] C. W. Jefford, T. W. Wallace and M. **Acar,** *J.* Org. *Chem.* 42, 1654 (1977).
[67] C. A. Grob and A. Weiss, *Helv. Chim. Acta 43,* 1390 (1960).
[68] **G.** Weitemeyer and A. **de Meijere,** *Angew. Chem. 88,* 721 (1976); *Angew Chem., Int. Ed. Engl.* **15,** *686* (1976).
[69a] C. M. Cimarusti and J. Wolinsky, *J. Am. Chem. Soc.* 90, 113 (1968); *J. Org. Chem.* 36, 1871 (1971); [b]**S. Geribaldi,** G. Torri and M. Azzaro, *Bull. Soc. Chim. Fr.* **2521, 2836** (1973); [c]**P.** Yates and G. E. Langford, Can. *J. Chem.* 59,344 (1981).
[70] **K.** Kitahonoki and Y. Takano, *Tetrahedron Letters* 1597 (1963); *Tetrahedron 25, 2417* (1969).
[71] **R.** C. **Cookson** and N. S. Wariyar, *J. Chem. Soc. 2302* (1956).
[72] H. E. Zimmerman, R. S. Givens and R. M. **Pagni,** *J. Am. Chem. Soc. 90, 6096* (1968).
[73] **W.** H. Jones, D. **.Mangold** and H. Plieninger, *Tetrahedron 18, 267* (1962); K. Takeda, K. Kitahonoki, M. **Sugiura** and Y. Takano, *Chem. Ber. 95, 2344* (1962); M. C. Kloetzel and H. L. Herzog, *J. Am. Chem. Soc. 72,* 1991 (1950).
[74a] N. J. Hales, H. Heaney and J. H. Hollinshead, *Synthesis 707* (1975); [b]**R.** P. Johnson, A. Exarchou, C. W. Jefford and R. C. Hahn, *J.* Org. *Chem.* **42, 3758** (1977); [c]N. J. Hales, H. Heaney, J. H. Hollinshead, P. Singh; G. Crass, M. Pohmakotr and D. Seebacher, Org. *Synth. 59, 71* (1980).
[75] **L.** H. Zalkow and D. R. **Brannon,** *J. Chem. Soc. 5497* (1964).
[76] **W.** A. Ayer and C. E. McDonald, Can. J. *Chem. 43,* 1429 (1965).
[77a] W. A. Ayer, C. E. McDonald and G. G. Iverach, *Tetrahedron Lett. 1095* (1963); [b]**L.** H. Zalkow and N. N. Girotra, *J. Org. Chem. 28 2037* (1963); 29, 1299 (1964).
[78] **E.** E. van **Tamelen,** S. R. Zawacky, R. K. Russel and J. G. **Carlson,** *J. Am. Chem. Soc.* **105,** 142 (1983).
[79] **J.** K. **Kochi,** *J. Am. Chem. Soc.* **87,** 1811 (1965).
[80a] G. A. Russell, R. G. Keske, G. Holland, J. Mattox, R. S. Givens and K. Stanley, *J. Am. Chem. Soc. 97,* 1892 (1975; [b]**Y.** E. Rhodes, P. E. Schueler and V. G. **DiFate,** *Tetrahedron Letters 2073* (1970); T. E. Schueler and Y. E. Rhodes, *J. Org. Chem. 39, 2063* (1974).
[81a] N. B. Chapman, S. Sotheeswaran and K. J. Toyne, *J. Chem. Soc.,* Chem. Commun. 214 (1965); [b]**J.** Wolinsky and R. B. **Login,** *J. Org. Chem.* 37, 121 (1972); [c]**J.** D. Slee and E. **LeGoff,** *J. Org. Chem.* **35,** *3897* (1970).
[82] **M.** J. Goldstein, S. Natowsky, E. Heilbronner and V. **Hornung,** *Helv. Chim. Acta 56, 294* (1973).
[83] **P.** von R. Schleyer and R. E. Leone, *J. Am. Chem. Soc.* 90, 4164 (1968).
[84] **G.** A. Russell, G. W. Holland, K.-Y. Chang, R. G. Keske, J. Mattox, C. S. C. Chung, K. Stanley, **K.** Schmitt, R. Blankespoor and Y. Kosugi, *J. Am. Chem. Soc. %, 7237* (1974).
[85] **S.** Masamune, H. Cuts and M. G. **Hogben,** *Tetrahedron Letters 1017* (1966).
[86] **L.** A. Paquette and L. C. Stowell, *J. Am. Chem. Soc. 92, 2584* (1970); 93, 2459 (1971).
[87] **W.** G. **Dauben,** M. G. Buzzolini, C. H. Schallhom, D. L. Whalen and K. J. **Palmer,** *Tetrahedron Letters 787* (1970); W. G. **Dauben,** C. H. Schallhom and D. L. Whalen, *J. Am. Chem. Soc.* **93, 1446** (1971).
[88] **R. Furstoss** and J.-M. Lehn, *Bull. Soc. Chim. Fr. 2497* (1966).
[89] **A.** de Meijere, D. Kaufmann and 0. Schallner, *Angew. Chem. 83,404* (1971); *Angew. Chem., Int. Ed. Engl.* **10,417** (1971).
[90] **E. LeGoff** and S. **Oka,** *J. Am. Chem. Soc.* **91,** *5665* (1969).
[91] **K.** T. Mak, K. Srinivasachar and N.-C. C. Yang, *J. Chem. Soc.,* Chem. Commun. 1038 (1979).
[92] **E.** J. Corey and J. Casanova, Jr., *J. Am. Chem. Soc.* **85,** *165* (1963).
[93] **S.** Wolfe and J. R. Campbell, *Synthesis* 117 (1979).
“I. G. Dinulescu, M. Pop, F. Chiraleu, M. Avram and C. D. Nenitzescu, *Rev. Roum. Chem.* **19,** 1197 (1974).
[95a] J. Meinwald, G. E. Samuelson and M. Ikeda, *J. Am. Chem. Soc.* **92, 7604** (1970); [b]**W. Hartmann** and H.-G. Heine, Angew. *Chem. 83,* 291 (1971); *Angew. Chem., Int. Ed. Engl.* **10,** *272* (1971).
[96] **J.** E. Shields, D. Gavrilovic, J. Kopecky, W. **Hartmann** and H.-G. Heine, *J. Org.* Chem. 39, 515 (1974).
[97] I. Willner and M. Rabinovitz, *J. Org. Chem. 45, 1628* (1980); *Tetrahedron Letters 1223* (1976); *Tetrahedron* **35,** *2359* (1979).
[98] **G. Popp,** *Eastman Org. Chemicals Bull.* **45(3), 1** (1973).
[99] **H.** Plieninger and W. Lehnert, *Chem. Ber.* **100,** 2427 (1967).
[100] **P.** Radlick, R. Klem, S. Spurlock, J. J. Sims, E. E. van **Tamelen** and T. Whitesides, *Tetrahedron Letters 5117* (1968).
[101] **H.** H. **Westberg** and H. J. **Dauben,** Jr., *Tetrahedron Letters 5123* (1968).
[102] **C.** B. Warren, J. J. Bloomfield, J. S. **Chickos** and R. A. Rouse, *J. Org. Chem.* **38,** 4011 (1973).
[103] **L.** A. Paquette and M. J. Wyvratt, *J. Am. Chem. Soc.* %, 4671 (1974); H. Park and L. A. Paquette, *J. Org. Chem.* **45,** *5378 (1980).*
[104] **D.** McNeil, B. R. Vogt, J. J. Sudol, S. Theodoropulos and E. Hedaya, *J. Am. Chem. Soc.* **96,** *4673* (1974).
[105] **R.** J. Temansky, D. W. Balogh and L. A. Paquette, *J. Am. Chem. Soc.* **104,** *4503* (1982).
[106] **R.** Gompper and A. Schmidt, *Angew. Chem. 92, 468* (1980); *Angew. Chem., Int. Ed. Engl.* **19,** *463* (1980).
[107] **S.** Kikkawa, R. L. Bartosiewicz and **S.** I. **Miller,** *J. Org. Chem. 27, 320* (1962).
[108] **E.** Pfaff and H. Plieninger, *Chem. Ber.* **115,** 1967 (1982).
[109] **A.** P. **Marchand** and R. W. Allen, *J. Org. Chem.* **40,** 2551 (1975).
[110] H. Prinzbach and H. **Babsch,** *Heterocycles* **11,** 113 (1978).
[111] **P.** Bruckmann and M. Klessinger, *Angew. Chem. 84, 543* (1972); *Angew Chem.,* Znt. *Ed.* **Engl. 11, 524** (1972).
[112] **Y.** E. Rhodes, P. E. Schueler and V. G. **DiFate,** *Tetrahedron Letters 2073* (1970).
[113] **E.** Vogel, W. Frass and J. Wolpers, *Angew Chem. 75, 979* (1963).
[114] **R.** Breslow, J. Napierski and A. H. Schmidt, *J. Am. Chem. Soc. 94, 5906* (1972).
[115] **L.** Chardonnens and H. Chardonnens, *Helv. Chim. Acta 49,* 1931 (1966).
[116] **A.** Krebs, E. **Franken** and **S.** Mueller, *Tetrahedron Letters 22, 1675* (1981).

[117] L. A. Paquette, W. P. Melega and J. D. Kramer, *Tetrahedron Letters* 4033 (1976).

[118] [a] A. Galbraith, T. Small and V. Boekelheide, *J. Org. Chem.* 24, 582 (1959); [b] A. Galbraith, T. Small, R. A. Barnes and V. Boekelheide, *J. Am. Chem. Soc.* 83, 453 (1961); [c] V. Boekelheide and A. Miller, *J. Org. Chem.* 26, 431 (1961).

[119] H. P. Figeys and A. Dralants, *Tetrahedron* **28**, 3031 (1972).

[120] N. Z. Huang, J. H. Jia, L. L. Wang, T.-L. Chan and T. C. W. Mak, *Tetrahedron Letters* 23, 4797 (1982).

[121] R. A. Snow, C. R. Degenhardt and L. A. Paquette, *Tetruhedron Letters* 4447 (1976).

[122] E. N. Cain, R. Vukov and S. Masamune, *J. Chem. Soc.*, Chem. Commun. 98 (1969).

[123] H. Prinzbach and D. Hunkler, *Angew. Chem.* 79, 232 (1967); *Angew. Chem., Znt. Ed. Engl.* 6, 247 (1967).

[124] D. H. R. Barton, H. A. Dowlatshahi, W. B. Motherwell and D. Villemin, *J. Chem. Soc.*, Chem. Commun. 732 (1980) and cited references.

[125] H. Plieninger, W. Lehnert and D. Mangold, *Chem. Ber.* **100**, 2421 (1967).

[126] M. V. Lakshmikantham and M. P. Cava, *J. Org. Chem.* 41, 882 (1976).

[127] T. L. Gilchrist, C. W. Rees, D. Tuddenham and D. J. Williams, *J. Chem. Soc.*, Chem. Commun. 691 (1980); T. L. Gilchrist, D. Tuddenham, R. McCague, C. J. Moody and C. W. Rees, *Ibid.* 657 (1981).

[128] Z. Lidert and C. W. Rees, *J. Chem. Soc.*, Chem. Commun. 317 (1983).

[129] T. Inukai and M. Kasai, *J. Org. Chem.* 30, 3567 (1965).

[130] C. A. Grob, H. Kny and A. Gagneux, *Helv. Chim. Acta* 40, 130 (1957).

[131] C. W. Bird, R. C. Cookson, J. Hudec and R. 0. Williams, *J. Chem. Soc.* 410 (1963).

[132] W. C. Wildman and D. R. Saunders, *J. Org. Chem.* 19, 381 (1954); *J. Am. Chem. Soc.* 76, 946 (1954).

[133] H. E. Zimmerman, G. L. Gmnewald, R. M. Paufler and M. A. Sherwin, *J. Am. Chem. Soc.* 91, 2330 (1969).

[134] R. K. Russell, R. E. Wingard, Jr. and L. A. Paquette, *J. Am. Chem. Soc.* **96**, 7483 (1974).

[135] O. Diels and K. Alder, *Liebigs Ann. Chem.* 490, 257 (1931).

[136] J. Daub and P. von R. Schleyer, *Angew. Chem.* **80**, 446 (1968); *Angew Chem., Znt. Ed. Engl.* 7, 468 (1968).

[137] E. Wiskott and P. von R. Schleyer, *Angew. Chem.* 79, 680 (1967); *Angew Chem., Znt. Ed. Engl.* 6, 694 (1967).

[138] G. W. Klumpp and J. Stapersma, *Tetrahedron Letters* 747 (1977).

[139] A. C. Cope, E. Ciganek and N. A. LeBel, *J. Am. Chem. Soc.* **81**, 2799 (1959).

[140] C. F. Wilcox, Jr. and G. C. Whitney, *J. Org. Chem.* 32, 3348 (1967).

[141] G. N. Fickes and T. E. Metz, *J. Org. Chem.* 43, 4057 (1978).

[142] T. W. Wickersham, L. P. Li and E. J. Warawa, *Synthesis* 399 (1975).

[143] K. Alder, R. Hartmann and W. Roth, *Liebigs Ann. Chem.* 613, 6 (1958).

[144] W. R. Vaughan and A. C. Schoenthaler, *J. Am. Chem. Soc.* **80**, 1956 (1958).

[145] D. P. Stack, PhD thesis, University of Illinois at Urbana Champaign, 1981.

[146] W. P. Norris, *J. Org. Chem.* 33, 4540 (1968).

[147] J. Sauer, A. Mielert, D. Lang and D. Peter, *Chem. Ber.* 98, 1435 (1965).

[148] T. R. Kelly and R. W. McNutt, *Tetrahedron Letters* 285 (1975).

[149] J. Y. Vanderhoek, *J. Org. Chem.* 34, 4184 (1969).

[150] J.H. Rigby, J.-M. Sage and J. Raggon, *J. Org. Chem.* **47**, **4815** (1982); J. H. Rigby and J.-M. Sage, *Ibid.* **48**, **3591** (1983).

[151] S. Ranganathan, D. Ranganathan and A. K. Mehrotra, *Synthesis* 289 (1977); L. Stella and J.-L. Boucher, *Tetruhedron Letters* **23**, 953 (1982); H. Kotsuki and H. Nishizawa, *Heterocycles* 16, 1287 (1981).

[152] K. Alder and H. F. Rickert, *Liebigs Ann. Chem.* 543, 1 (1940).

[153] C. Weitemeyer and A. de Meijere, *Angew. Chem.* **88**, 721 (1976); *Angew. Chem., Znt. Ed. Engl.* **15**, 686 (1976).

[154] C. W. Jefford, T. W. Wallace and M. Acar, *J. Org. Chem.* 42, 1654 (1977).

[155] R. Gompper and K.-H. Etzbach, *Angew. Chem.* 90, 630 (1978); *Angew. Chem., Znt. Ed. Engl.* 17, 603 (1978).

[156] R. Gompper and K.-H. Etzbach, *Angew. Chem.* 91, 500 (1979); *Angew. Chem., Znt. Ed. Engl.* **18**, 470 (1979).

[157] H.-D. Martin and D. Forster, *Angew. Chem.* 84, 65 (1972); *Angew. Chem., Znt. Ed. Engl.* 11, 54 (1972).

[158] [a] R. W. Hoffmann, R. Schuettler, W. Schaefer and A. Schweig, *Angew. Chem.* 84,533 (1972); *Angew Chem., Znt. Ed. Engl.* **11**, 512 (1972); [b] L. A. Paquette and M. J. Broadhurst, *J. Org.* Chem. **38**, 1893 (1973); [c] R. W. Hoffmann, H. Kurz, M. T. Reetz and R. Schuettler, *Chem. Ber.* **108**, 109 (1975); [d] R. W. Hoffmann and J. Becherer, *Tetrahedron* 34, 1187 (1978); [e] P. R. Story, *J. Org. Chem.* 26, 287 (1961).

[159] D. N. Butler and I. Gupta, *Can. J. Chem.* 60, 415 (1982).

[160] R. H. Shapiro, Org. React. 23, 405 (1976).

[161] [a] C. A. Grob and J. Hostynek, *Helv. Chim. Actu* 46, 1676 (1963); [b] E. Mueller, *Chem. Ber.* **109**, 3793 (1976).

[162] C. W. Jefford, T. W. Wallace, N.-T. H. Cau and C. G. Rimbault, *J. Org. Chem.* 44, 689 (1979).

[163] A. de Meijere and L.-U. Meyer, *Tetrahedron Letters* 2051 (1974).

[164] A. de Meijere, 0. Schallner and C. Weitemeyer, *Tetrahedron Letters* 3483 (1973); A. de Meijere, C. Weitemeyer and 0. Schallner, Chem. *Ber.* 110, 1504 (1977).

[165] H. K. Hall, Jr., *J. Org. Chem.* 25, 42 (1960).

[166] P. K. Freeman and D. M. Balls, *J. Org. Chem.* 32, 2354 (1967); *Tetrahedron Letters* 437 (1967); P. K. Freeman, D. M. Balls and D. J. Brown, *J. Org.* Chem. 33, 2211 (1968).

[167] D. A. Lightner, J. K. Gawronski and T. D. Bouman, *J. Am. Chem. Soc.* 102, 5749 (1980).

[168] W. T. Brady, *Tetrahedron* 37, 2949 (1981); *Synthesis* 415 (1971).

[169] L. R. Smith, G. E. Gream and J. Meinwald, *J. Org. Chem.* 42, 927 (1977); G. E. Gream, L. R. Smith and J. Meinwald, *Ibid.* **39**, 3461 (1974).

[170] M. Christl and R. Lang, *J. Am. Chem. Soc.* **104**, 4494 (1982).

[171] W. Grimme and E. Schneider, *Angew. Chem.* **89**, 754 (1977); *Angew. Chem., Znt. Ed. Engl.* 16, 717 (1977).

[172] W. Grimme and H. G. Koeser, *Angew. Chem.* **92, 307 (1980)**; *Angew. Chem., Znt. Ed. Engl.* 19, 307 (1980).

[173] W. Adam and 0. De Lucchi, unpublished results.

[174] M Oda R. Breslow and J. Pecoraro, *Tetrahedron Letters* 4419 (1972); R. Breslow and M. Oda, *J. Am. Chem. Soc.* 94, 4787 (1972).

[175] [a] E. J. Corey, F. A. Carey and R. A. E. Winter, *J. Am. Chem. Soc.* **87**, 934 (1965); [b] E. J. Corey and R. A. E. Winter, *Ibid.* **85**, 2677 (1963); [c] E. J. Corey, *Pure Appl. Chem.* **14**, **19** (1967).

[176] [a] E. Vedejs and E. S. C. Wu, *J. Org. Chem.* 39, 3641 (1974); [b] M. Tichy and J. Sicher, *Tetrahedron Letters* 4609 (1969); [c] T. L. Nagabhushan, *Can. J. Chem.* 48, 383 (1970); [d] D. Horton and C. G. Tindall, Jr., *J. Org. Chem.* 35, 3558 (1970); [e] L. A. Paquette, J. C. Philips and R. E. Wingard, Jr., *J. Am. Chem. Soc.* **93**, **4516** (1971); [f] J. N. Hines, M. J. Peagram, G. H. Whitham and M. Wright, *J. Chem. Soc., Chem.* Commun. 1593 (1968); [g] G. H. Whitham and M. Wright, *J. Chem.*

Soc. C 883, 886, 891 (1971); [h]T. Aratani, Y. Nakanisi and H. Nozaki, *Tetrahedron* **26, 4339** (1970); [j]M. F. Semmelhack and R. D. Stauffer, *Tetrahedron Letters 2667* (1973); [y]J. Daub, V. Erhardt, J. Kappler, and V. Trautz, *J. Organom. Chem.* 69, 423 (1974); [l]E. J. Corey and P. B. Hopkins, *Tetrahedron Letters 23,* 1979 (1982).

[177]M. S. Newman and R. W. Addor, *J.* Am. *Chem. Soc.* 77, 3789 (1955).

[178]J. Daub, V. Trautz and U. Erhardt, *Tetrahedron Letters 4435* (1972); J. Daub, G. Endress, U. Erhardt, K. H. Jogun, J. Kappler, A. Lamner, R. Pfiz and J. J. Stezowski, *Chem. Ber.* **115,** 1787 (1982).

[179]J. Daub, J. Kappler, K.-P. Krenkler, S. Schreiner and V. Trautz, *Liebigs Ann. Chem.* 1730 (1977).

[180]J. Daub and U. Erhardt, *Tetrahedron 28, 181* (1972); J. Daub and V. Trautz, *Tetrahedron Letters 3265* (1970); J. Daub. U. Erhardt and V. Trautz, *Chem. Ber.* **109, 2197 (1976).**

[181]U. Erhardt and J. Daub, *J. Chem. Soc.*, Chem. Commun 83 (1974).

[182]W. K. Anderson and R. H. Dewey, *J.* Am. *Chem. Soc.* 95, 7161 (1973).

[183]An other method to prepare 222 is anyway practicable: H.-M. Fischler and W. Hartmann, *Chem. Ber.* **105, 2769** (1972).

[184]N. D. Field, *J. Am. Chem. Soc.* **83,** *3504* (1961).

[185]H. Prinzbach and H. Babsch, *Angew. Chem. 87, 772* (1975).

[186]D. N. Reinhoudt, *Real Trav. Chim. Pays-Bas* **101, 277** (1982).

[187]W. Hartmann, L. Schrader and D. Wendisch, *Chem. Ber.* **106,** 1076 (1973).

[188]W. Hartmann, H.-M. Fischler and H.-G. Heine, *Tetrahedron Letters 853* (1972); H.-M. Fischler, H.-G. Heine and W. Hartmann, *Ibid. 857* (1972).

[189]W. Hartmann, Chem. *Ber.* **101, 1643 (1968).**

[190]H.-D. Scharf and J. Mattay, *Tetrahedron Letters* 401 (1977).

[191]R. H. Grubbs, *J. Am. Chem. Soc. 93, 6693* (1970); *Synthesis* 219 (1971).

[192]D. W. Whitman and B. K. Carpenter. *J. Am. Chem. Soc.* **102.** *4272* (1980).

[193]H.-D. Scharf, *Angew. Chem.* **86,** *567* (1974); *Angew. Chem., Int. Ed. Engl.* **13,** *520* (1974); R. L. Blankesp-oor and D. Gollehon, *J.* Org. *Chem. 42, 63* (1977).

[194]N. C. Barua and R. P. Sharma, *Tetrahedron Letters 23, 1365* (1982).

[195]A. G. M. Barrett and D. H. R. Barton and R. Bielski, *J. Chem. Soc. Perkin Z 2378* (1979); F. W. Eastwood, K. J. Harrington, J. S. Josan and J. L. Pura, *Tetrahedron Letters 5223* (1970); W. T. Borden, P. W. Concannon and D. I. Phillips, *Ibid 3161* (1973); J. C. Camahan, Jr. and W. D. Closson, *Ibid. 3447* **(1972),** and references cited on these papers.

[196]K. MacKenzie, *J. Chem. Soc. 473* (1960).

[197]H.-D. Martin, S. Kagabu and H. J. Schiwek, *Tetrahedron Letters 3311* (1975).

‘“H.-D. Martin, A. Oftring, R. Iden, E. Schwichtenberg and H.-J. Schiwek, *Tetrahedron Letters 23,* 841 (1982).

[199]L. G. Cannell, *Tetrahedron Letters* **5967** (1966); Shell International Research Maatschappij N. V. Neth. Appl. **6,503,999;** *CA 64,* **P11103h** (1966); L. G. Cannell, *French Put.* **1,435,268;** *CA 66,* **10659v** (1967).

[200]T. J. Katz, J. C. Camahan, Jr. and R. Boecke, *J.* Org. Chem. 32, 1301 (1967).

[201]R. M. Coates and J. L. Kirkpatrick, *J. Am. Chem. Soc. 92, 4883* (1970).

[202]L. Lombardo, D Wege and S. P. Wilkinson, *Austral. J. Chem. 27, 143* (1974); L. Lombardo and D. Wege, *Tetrahedron* **30,** 3945 (1974).

[203]D. N. Butler, A. Barrette and R. A. Snow, *Synth. Commun. 5,* 101 (1975).

[204]T. Sasaki, K. Kanematsu, I. Ando and 0. Yamashita, *J. Am. Chem. Soc. 98, 2686* (1976).

[205]R. Huisgen, M. Seidel, G. Wallbillich and H. Knupfer, *Tetrahedron 17, 3* (1962).

[206]R. Huisgen and M. Christl, *Angew. Chem. 79, 471* (1967); *Angew. Chem., Znt. Ed. Engl. 6, 456* (1967).

[207]R. Huisgen, *Angew. Chem. 75,604* (1963); H. Kwart and K. King, *Chem. Reu. 68,415* (1968); J. L. Ripoll, A. Rouessac and F. Rouessac, *Tetrahedron 34,* 19 (1978).

[208]K. Alder and H. F. Rickert, *Liebigs Ann. Chem. 543,* 1 (1940).

[209]J. K. Stille and D. A. Frey, *J. Am.* Chem. *Soc.* 81, 4273 (1959).

[210]S. J. Cristol and N. L. Hause, *J. Am. Chem. Soc. 74,* 2193 (1952); S. J. Cristol and R. K. Bly, *Ibid. 82, 6155* (1960).

[211]S. J. Cristol and W. Y. Lim, *J. Org. Chem. 34,* 1 (1969).

[212]L. Fuchsbauer, Dissertation, Würzburg University 1982.

[213]K. Alder, H.-J. Ache and F. H. Flock, *Chem. Ber. 93, 1888* (1960).

[214]73% yield in the dehalogenating step are reported by: C. F. Wilcox, Jr. and R. R. Craig, *J. Am. Chem. Soc. 83, 4258* (1961).

[215]M. Hanack, H. Eggensperger and R. Haehnle, *Liebigs Ann. Chem. 652, 96* (1962).

[216]See Ref. 6, p. **209ff.**

[217]For a general review: P. G. Bauslaugh, *Synthesis 287* (1970).

[218a]S. Sugihara, T. Sugimura and I. Murata, *J. Am. Chem. Soc.* **103, 6738** (1981); [b]*Ibid.* **104, 4295 (1982).** [c]*Chem. Lett.* 1103 (1980).

[219]R. L. Cargill and J. W. Crawford, *Tetrahedron Letters* 169 (1967); R. L. Cargill, D. M. Pond and S. 0. LeGrand, *J.* Org. *Chem. 35, 359* (1970); A. B. Smith III and P. J. Jerris, *Ibid. 47, 1845* (1982).

[220]T. Tsuji, Z. Komiya and S. Nishida, *Tetrahedron Letters* **21, 3583** (1980); T. Tsuji and S. Nishida, *Ibid. 24, 3361* (1983).

[221]Y. Tobe, K. Kakiuchi, Y. Odaira, T. Hosaki, Y. Kai and N. Kasai, *J. Am. Chem. Soc.* **105,** 1376 (1983).

[222]R. L. Cargill, T. J. King, A. B. Sears and M. R. Willcott, *J.* Org. *Chem.* 36, 1423 (1971).

[223]K. Yano, *J.* Org. Chem. 42, 1728 (1977).

[224]W. Pritschins and W. Grimme, *Tetrahedron Letters 23,* 1151 (1982).

[225]W. Metzner and K. Morgenstem, *Angew. Chem. 80,366* (1968); Angew. Chem., *Znt. Ed. Engl. 7, 379* (1968); W. Metzner and W. Hartmann, *Chem. Ber.* **101, 4099, 4106** (1968).

[226]J. S. Swenton, K. A. Burdett, D. M. Madigan, T. Johnson and P. D. Rosso, *J. Am. Chem. Soc. 97, 3428* (1975).

[227]D. C. Neckers and F. L. Wagenaar, *J.* Org. *Chem.* **46, 3939** (1981); M. Sindler-Kulyk and D. C. Neckers, *Ibid. 48, 1275* (1983).

[228]G. Berens, F. Kaplan, R. Rimerman, B. W. Roberts and A. Wissner, *J. Am. Chem. Soc. 97, 7076* **(1975),** and cited references.

[229]L. A. Paquette, R. E. Moerck, B. Harirchian and P. D. Magnus, *J. Am. Chem. Soc.* **100, 1597 (1978).**

[230]O. De Lucchi and G. Modena, unpublished results.

[231]R. V. C. Carr and L. A. Paquette, *J. Am. Chem. Soc. 102,853* (1980); L. A. Paquette and R. V. C. Carr, *Ibid.* **102, 7553** (1980): R. D. Little and L. Brown. *Tetrahedron Letters 21. 2203* (1980).

[232]A. K. Colter and R. E. Miller, Jr.; *J.* Org. *Chem. 36,* 1898 (1971).

[233] J. N. Gardner, S. Kaiser, A. Krubiner and H. Lucas, Can. *J.* Chem. **51,** 1419 (1973).

“R. D. Little and S. 0. Myong, Tetrahedron *Letters* 21, 3339 (1980); see also: J. R. Hwu, *J.* Org. ***Chem.* 48, 4432** (1983).

[235] **A.** P. Davis and G. H. **Whitham,** ***J. Chem. Soc.,*** Chem. Commun. 639 (1980).

[236] **V. Pascali** and A. **Umani-Ronchi,** ***J. Chem. Soc.,*** Chem. Commun. 351 (1973); B. M. Trost, H. C. Amdt, P. E. Strege and T. R. Verhoeven, *Tetrahedron **Letters*** 3477 (1976); B. M. Trost and P. L. Omstein, Ibid. 22, 3463 (1981).

[237] **H.-J.** Altenbach, B. **Blech,** J. A. Marco and E. Vogel, Angew. ***Chem.*** 94, 789 (1982); *Angew. Chem., Znt. Ed.* Engl. 21, 778 (1982).

[238] **G.-L.** Fabre, M. Julia and J.-N. Verpeaux, *Tetrahedron Letters 23, 2469 (1982).*

[239] **K.** Alder, H. F. Rickert and E. Windemuth, Chem. *Ber.* **71, 2451** (1938); J. C. Philips and M. Oku, ***J.*** *Am.* ***Chem. Soc.* 95, 6495** (1973); *Ibid.* ***94,*** *1012 (1972);* J. A. Hirsch, R. W. Kosley, Jr., R. P. **Morin,** G. **Schwartzkopf** and R. D. Brown, ***J.*** *Heterocycl.* ***Chem.*** *12, 785 (1975);* A. Hassner and W. Chau, *Tetrahedron Letters 23, 1989 (1982);* E. A. Fehnel and M. Carmack, ***J.*** *Am.* Chem. ***Soc.*** 70, 18 13 (1948); J. C. Philips and M. Oku, ***J.*** Org. Chem. **37, 4479** (1972); T. **Graafland,** W. C. Nieuwpoort and J. B. N. Engberts, *J. Am.* Chem. ***Soc.*** 103, 4490 (1981).

[240] **H.** R. Snyder, H. V. Anderson and D. P. **Hallada,** *J. Am. Chem.* ***Soc.*** *73, 3258 (1951); C. S.* Rondestvedt, Jr. and J. C. Wygant, *Ibid. 73, 5785 (1951).*

[241] **R.** S. Glass and D. L. Smith, ***J.*** *Org. Chem. 39, 3712 (1974).*

[242] **M.** Hanack and F. Mama, *Tetrahedron Letters 661 (1977).*

[243] **K.** Laping and M. Hanack, *Tetrahedron Letters 1309 (1979).*

“P. D. **Magnus,** ***Tetrahedron*** *33, 2019 (1977).*

[245] **J.** B. Hendrickson, A. **Giga** and J. Wareing, *J. Am. Chem.* ***Soc. 96,*** *2275 (1974);* J. B. Hendrickson and P. L. Skipper, *Tetrahedron 32. 1627* **(1976):** J. B. Hendrickson. D. D. **Sternbach** and K. W. Bair. ***Acc.*** Chem. Res. 10. 306 (1977).

[246] **L.** A. Paquette and R. **V. Williams,** *Tetrahedron* ***Letters* 22, 4643** *(1981);* R. V. C. **Carr, R.** V. Williams and **L. A. Paquette,** *J. Org. Chem. 48, 4976 (1983).*

[247] **L.** A. Paquette, R. V. Williams, R. V. C. **Carr,** P. Charumilind and J. F. Blount, ·***J.*** *Org. Chem. 47, 4566 (1982).*

[248] **H.** R. Snyder and D. P. **Hallada, *J.*** *Am. Chem.* ***Soc.*** *74, 5595 (1952);* W. E. Truce and R. J. **McManimie,** *Ibid.* **75,** *1672 (1953);* W. E. **Parham** and J. Heberling, ***Ibid.*** *77,* 1175 (1955); M. Cinquini, S. Colonna, and F. **Montanari,** *J. Chem.* ***Soc.*** *C 572 (1970);* W. E. Truce, M. G. Rossmann, F. M. Perry, R. M. Burnett and D. J. Abraham, *Tetrahedron 21, 2899 (1965).*

[249] **O.** De Lucchi and G. Modena, *J.* Chem. ***Soc.,*** Chem. Commun. 914 (1982); *Phosphorus* ***and Sulfur*** *14, 229 (1983).*

[250] **O.** *De* Lucchi and G. Modena, *Tetrahedron Letters 24, 1653 (1983).*

[251] **J.** Sauer, H. Wiest and A. Mielert, Chem. *Ber. 97,* 3183 (1964); J. Sauer, D. Lang and H. Wiest, *Zbid. 97, 3208 (1964).*

[252] **A.** Gorgues, P. **Batail** and A. Le **Coq,** *J. Chem.* ***Soc.,*** Chem. Commun. 405 (1983); A. Gorgues, A. Simon, A. **Le Coq** and F. **Corre,** *Tetrahedron Letters 22, 625* (1981); R. **Gelin** and A. Debard, *Compt. Rend. 257, 2995* (1963).

[253] **F.** Merger, In *Houben- Weil:* ***Methoden der Organischen*** *Chemie* Vol. **5/1b,** pp. 364-368. Thieme Stuttgart (1972).

[254] **D.** C. **Rideout** and R. Breslow, *J.* Am. ***Chem. Soc.*** 102, 7816 (1980).

[255] **R.** A. Whitney, *Tetrahedron Letters 22, 2063* (1981).

[256] **K.** H. **Scholz,** J. **Hinz,** H.-G. Heine and W. Hartmann, *Liebigs Ann. Chem. 248 (1981).*

[257] **F.** D. Greene and K. E. Gilbert, *J. Org. Chem. 40,* 1413 (1975); S. F. Nelsen and P. D. Bartlett, *J. Am.* Chem. ***Soc.* 88,** 137 (1966).

[258] **W.** Adam and 0. De Lucchi, *Angew.* Chem. 92, 815 (1980); *Angew.* ***Chem.,*** *Znt. Ed.* ***Engl.*** 19, 762 (1980).

[259] **M.** Julia and J.-M. Paris, *Tetrahedron Letters 4833 (1973);* M. Julia, M. Launay, J.-P. Stacino and J.-N. Verpeaux, ***Ibid.*** *23, 2465 (1982);* B. Lythgoe and I. Waterhouse, ***Ibid.*** *4223 (1977); N.* **Ono,** R. Tamura, J. Hayami and A. Kaji, ***Ibid.*** 763 (1978); N. **Ono,** R. Tamura, T. Nakatsuka, J. Hayami and A. Kaji, *Bull. Chem.* ***Soc.*** *Japan* **53, 3295** *(1980); N.* Ono, H. Miyake, R. Tamura, I. Hamamoto and A. Kaji, ***Chem.*** *Lett.* 1139 *(1981);* P. J. Kocienski, *Chem. Znd.* **(*London*)** *548 (1981).*