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REACTIONS OF CARBENES WITH BICYCLOBUTANES AND QUADRICYCLANE

CYCLOADDITIONS WITH TWO σ BONDS[1,2]

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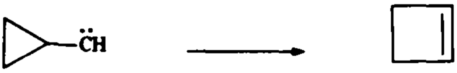
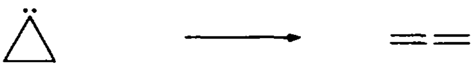
Abstract—Dicarbomethoxycarbene and dichlorocarbene add to 1,2,2-trimethylbicyclo[1.1.0]butane in such a fashion as to suggest a concerted addition in which the central and side bonds are cleaved simultaneously. MNDO calculations support such a pathway and suggest that *endo* attack on the bicyclobutane is preferred to *exo*. Reaction of the same two carbenes with quadricyclane gives substituted derivatives of the *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene system. Although these products rearrange further under the conditions of reaction and/or analysis, they can be shown to be primary products. It is suggested that quadricyclane reacts with carbenes in a concerted fashion.

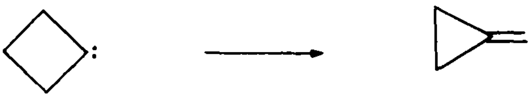
Reaction of carbenes with the C—C *single bond*

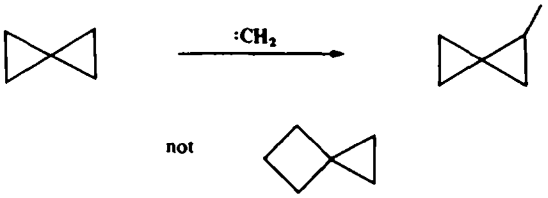
Although it is the reaction with the C═C bond that one immediately thinks of when carbenes are mentioned,[3] the reaction with single bonds has a long and honorable history as well. Indeed, the resurgence of carbene chemistry that began with the papers coming from the groups of Doering and Skell in the early and mid-1950s had as one of its major themes an investigation of the reaction of various carbenes with the C—H bond. The inspiration for this work is clearly traceable to the paper published in 1942 by Meerwein *et al.* on the photochemically induced reaction of methylene with diethyl ether and tetrahydrofuran.[4] Although aspects of this reaction are still unclear today (why, for instance, does tetrahydrofuran give substantial—*ca* 12%—amounts of tetrahydropyran in the gas phase,[5] but not in solution?[6]), it is fair to say that the broad outlines of the mechanism of reaction of both singlet and triplet carbenes with a C—H bond are worked out.

The same cannot be said for the reaction with the C—C single bond, which has received little apparent attention.[7] Presumably this is because it became clear quite early on that the reaction was going to be extraordinarily uncommon. Indeed, the only widespread examples are intramolecular in nature and include *inter alia* such well known examples as the ring expansion of cyclopropylcarbenes,[8] the conversion of cyclopropylidenes to allenes,[9] and the ring contraction of cyclobutylidenes.[10] There are other examples of "simple" C—C insertions in intramolecular chemistry, especially when competing reactions are disfavored. For instance, ring expansion of cyclobutylcarbene yields 37% cyclopentene.[11] t-Butylcarbene gives 10–60% 2-methyl-2-butene; the exact amount depending upon the mode of generation of the carbene.[12] Despite these examples, an intermolecular version of this reaction has eluded discovery. Even such promising substrates as spiropentane fail to undergo the reaction. In this case not only is substantial strain present, but both possible C—C insertions lead to the same compound, spirohexane. Methyl spiropentane is the only product observed.[13] Although there is evident reluctance for a lone C—C single bond to react, there are cases in which C—C single bonds, acting in pairs, do give products. It is our work on these reactions that we wish to report here.



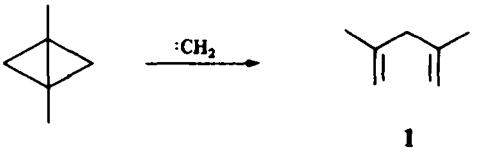






Reactions of carbenes with bicyclo[1.1.0]*butanes*

It was only shortly after the first carbene-based synthesis of a bicyclobutane[14,15] that the further reaction with carbenes was described.[15,16] The 1,3-dimethyl derivative was found to give, in addition to unexceptional products of C—H insertion, the 2,4-



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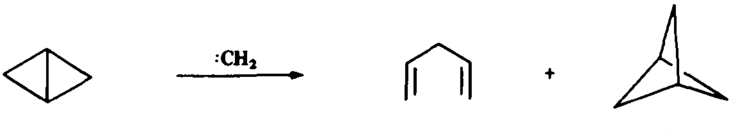
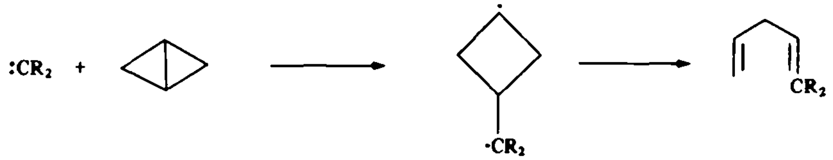
dimethyl-1,4-pentadiene, **1**.[15] The parent bicyclobutane,[16] **2**, gave a 21% yield of 1,4-pentadiene, **3** and 1% of bicyclo[1.1.1]pentane, **4**. It was remarked at the time[15] that formation of the pentadienes represented "... a pathway without parallel in the chemistry of ... carbenes."



2 **3** **4**

Wiberg[16] and, more recently, Applequist and Wheeler[17] noted the reaction of substituted bicyclobutanes with dichlorocarbene to give mixtures of bicyclo[1.1.1]pentanes and 1,4-pentadienes.

Compounding the remarkable nature of this reaction, both the Doering and Wiberg groups postulated a stepwise mechanism in which a 1,4-diradical was created only to suffer cleavage to the diene. We have earlier questioned this mechanism,[18] as both the dichlorocarbene of Wiberg *et al.*[16] and Applequist and Wheeler,[17] and the methylene of Doering and Coburn[15] are surely reacting in the singlet state, and it is most surprising to see a stepwise mechanism. Stepwise reactions of singlets with hydrocarbons are rare if not quite unknown[19] and there is no reason to suppose that these reactions involve triplet carbenes.

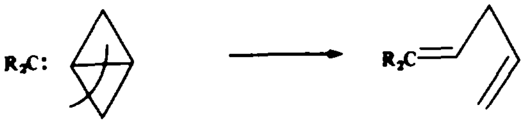


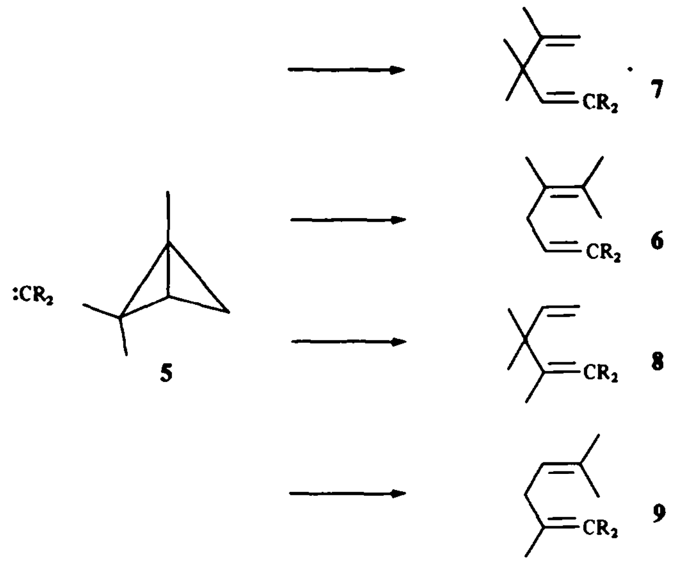
Although no intermolecular C—C insertion is known, there does exist an intramolecular version of the reaction of carbenes with bicyclobutanes, which involves a *double* C—C insertion. This appears in the fragmentation reactions of cyclopropylcarbenes. Stereochemical experiments have shown that both the ring expansion and fragmentation reactions are concerted in the usual context of this word. At least no intermediates sufficiently long lived as to permit rotation about C—C bonds may be involved.[8] In particular, the carbene attached to the 3-membered ring undergoes cleavage by simultaneous[20] breaking of both adjacent C—C bonds. It seemed possible—even probable—to us that the reaction of carbenes with bicyclobutanes was the intermolecular complement to this known intramolecular reaction.

Because its stepwise reactions seemed predictable to us, 1,2,2-trimethylbicyclo[1.1.0]butane, **5**, suggested itself as a substrate for study. The four possible products, **6**–**9**, are shown below. Were addition of a carbene to be stepwise, the tertiary radical should be favored. Moreover, opening of this diradical should produce the compound containing a tetra-substituted rather than a di-substituted double bond (bond "a" should break more easily than bond "b"). So **6** is the predicted product of this reaction rather than **7**, **8** or **9**. We investigated the reaction of **5** with two singlet carbenes, dicarbomethoxycarbene and dichlorocarbene. Diazomalonic ester[21] and chloroform served as the sources of the reactive intermediates, and thus two very different modes of generation could be investigated.

Irradiation of dimethyldiazomalonic ester in **5** led to a single major product (15% yield, 72% of products). The 250 MHz ^{1}H-NMR spectrum showed signals for two terminal methylene protons ($\delta = 4.85$), and the lone "acrylate-like" proton ($\delta = 6.93$) β to two ester groups (methylacrylate itself has a signal at $\delta = 6.35$). In addition, singlet signals appeared at δ 1.28 (6H) and δ 1.73 (3H) for the methyl groups, and at δ 3.75 and 3.78 ppm for the two methoxy groups. This spectrum serves to eliminate **6a**, **8a** and **9a**, but is as expected for **7a**.

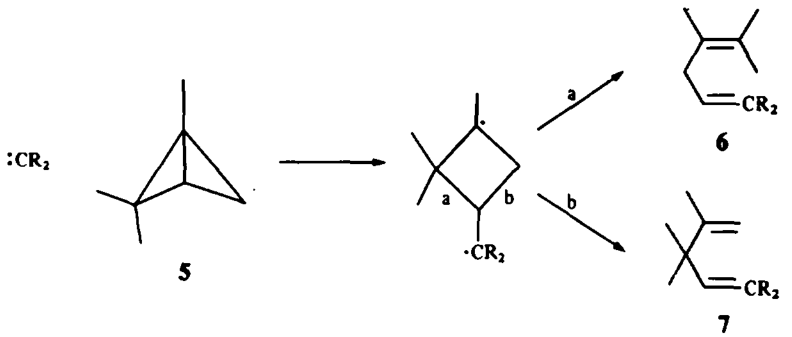
Similarly, reaction of **5** with CHCl$_3$/t-butoxide led to a single major product (69% of products) whose 90 MHz ^{1}H-NMR spectrum showed it to have the structure **7b** [δ 1.30 (s, 6H), 1.75 (br s, 3H), 4.80 (br s, 2H), 5.90 (s, 1H)]. These products (**7a**, **7b**) are most difficult to explain using the traditional stepwise mechanism which we think is now best abandoned. In its place we offer the two bond "pluck" mechanism in which no



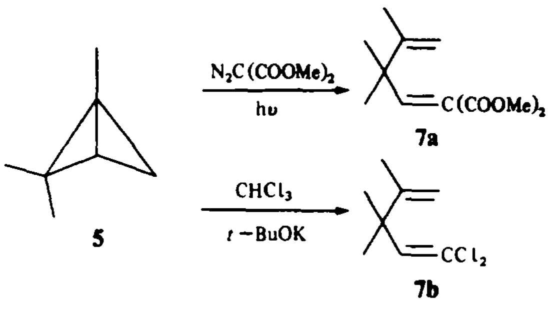


a R = $COOCH_3$
b R = Cl

The four possible penta-1,4-dienes from **5**



intermediate appears along the reaction coordinate. The central and side bonds of the bicyclobutane are cleaved simultaneously by the carbene.[20]



Theoretical investigations

Results from semiempirical calculations in the MNDO approximation[22,23] on the reaction between singlet methylene and bicyclobutane **2** provide support for a concerted two-bond cleavage mechanism. The significant findings may be summarized as follows:

(a) Despite extensive searching in the area of the C_5H_8 potential surface which might be expected to encompass the proposed singlet diradical intermediate, no energetic minimum could be located at either the MNDO or the MNDO+CI[24] levels. Although it is difficult to eliminate completely the possibility of such a minimum at this level of theory, there is little likelihood that a potential well of any substantial depth could lie in this region. All "reasonable" starting geometries quickly collapsed to the 1,4-pentadiene structure **3** during geometry optimization.

(b) Three transition states were located for singlet carbene attack on bicyclobutane. These are shown in Fig. 1 and their energies at the MNDO and MNDO-CI levels are listed in Table 1, along with relevant values for comparison.

The mode of approach giving rise to transition states A and B (Fig. 1) corresponds to that calculated by Lehn and Wipff[25] as the most energetically favorable site for protonation on the bicyclobutane ring system. The HOMO in bicyclobutane is essentially the strongly bent C_1—C_3 bond, and is composed of nearly pure 2p orbitals, which distribute considerable electron density outside the two bridgeheads.[26] The empty 2p orbital of the incoming carbene fragment is oriented to interact well with these exposed lobes of the bicyclobutane HOMO.[27] Thus A and B result from electrophilic attack by $:CH_2$ on the bridgehead of the bicyclobutane.

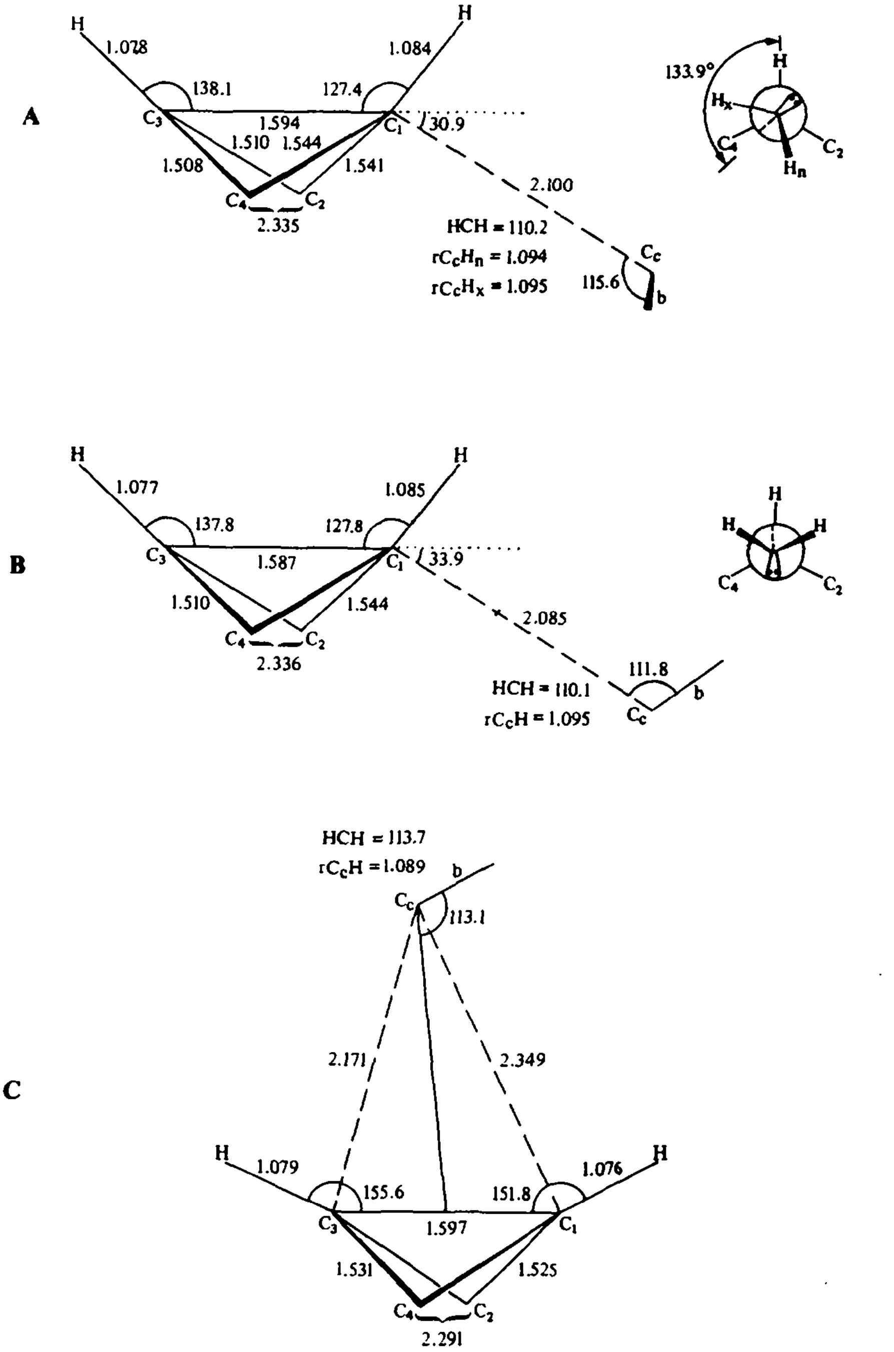


Fig. 1. Structure of transition states A, B and C. Distances are in Å, angles in degrees. Newman projections represent a view down the C_c—C_1 axis. For comparison, the bicyclobutane and $^1CH_2$ geometries at the same theoretical level are:

Bicyclobutane:

$rC_1C_2 = 1.527$
$rC_1C_3 = 1.536$
$rC_2C_4 = 2.315$
$rC_1H = 1.074$
$\angle C_3C_1H = 141.2$

$^1CH_2$:

$rC_cH = 1.091$
$\angle HCH = 111.1$

A has C_1 symmetry, while both B and C are C_s. The orientation of the carbene fragment is shown by the $\angle HC_cH$ bisector line marked "b" (dotted line in the Newman projections). Despite the formal C_1 symmetry of A, *if the carbene hydrogens are ignored*, this structure very nearly has C_s symmetry, as demonstrated by the near equality of the C_c—C_2 and C_c—C_4 distances (2.927 and 2.918 Å respectively; compare 2.930 Å in B). The carbene in A is not appreciably "cocked", i.e. for the *endo* and *exo* carbene hydrogens H_n and H_x, $\angle C_1C_cH_n = 105.2° \simeq \angle C_1C_cH_x = 103.4°$ (compare $\angle C_1C_cH = 102.3°$ in B).

Table 1. Calculated energies (kcal/mol) of selected stationary points in the ^{1}:CH$_2$ + bicyclobutane (BCB) reaction surface

	C_1—C_c Distance	MNDO		MNDO-CI[b]		
		ΔH_f	$\Delta\Delta H_f$[a]	ΔH_f	$\Delta\Delta H_f$[a]	$\Delta\Delta H_{CI}$
2 + :CH$_2$[c]	∞	171.4	0	166.2	0	−5.2
TS "A"	2.100 Å	182.5	+11.1	180.0	+13.8	−2.5
TS "B"	2.085 Å	182.6	+11.2	180.4	+14.2	−2.1
TS "C"	2.171 Å[d]	189.3	+17.9	185.0	+18.8	−4.3
 **4**	1.573 Å	58.3	−113.1	58.1	−108.1	−0.2
 **3**	1.340 Å	24.5	−46.9	22.3	−143.9	−2.2

[a] Energies relative to ^{1}CH$_2$ + BCB.

[b] CI energies calculated at MNDO geometries. Note that further optimization at the MNDO + CI level did not change the final geometries or energies significantly in the cases tested.

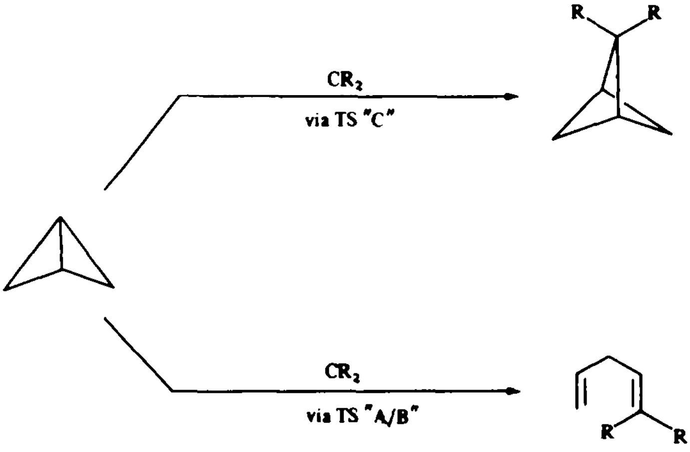
[c] The separate fragment energies are: MNDO: ^{1}CH$_2$ = 107.4, BCB = 64.0; MNDO-CI: ^{1}CH$_2$ = 101.4, BCB = 61.6. However, in performing the limited CI used here, it is necessary to perform the CI calculation consistently on the entire C_5H_8 system.

[d] Note that the C_3—C_c distance is 2.349 Å.

Although A appears better disposed than B for concerted cleavage of both the central and a side bond of bicyclobutane, at the C_1—C_c distance (*ca* 2.1 Å) in A and B, these two structures are nearly degenerate in energy, and are separated by a rotational barrier (around the C_1—C_c axis) of less than 1 kcal/mol. However, as carbene approach progresses the symmetrical B-like geometry quickly becomes destabilized relative to an A-like structure, the symmetry breaks, and a smooth progression toward **3** ensues. The side bond which breaks is that *anti* to the carbene lone pair, i.e. the C_1—C_4 bond in A (Fig. 1). At all C_1—C_c distances between the transition points A and B and the final 1.34 Å distance in **3**, there is a strong attractive gradient between C_1 and C_c, showing no hint of the suggested diradical intermediate.

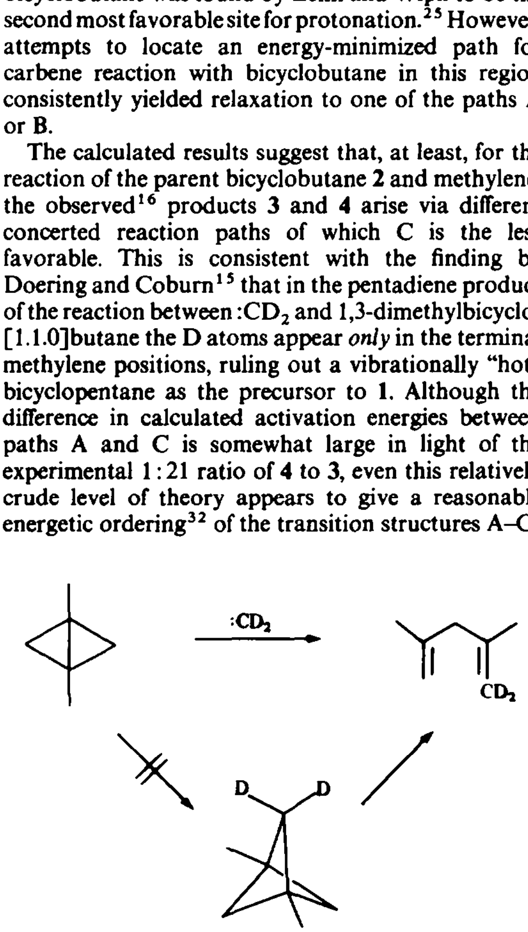
Transition state C was the only stationary point found for approach of methylene toward the top (C_1—C_3 bond) of the bicyclobutane molecule. This structure bears some similarities to those calculated for the reaction of :CH$_2$ with ethylene using a variety of methods.[20,28,29] The unsymmetrical approach (C_s but not C_{2v}) orients the empty carbene 2p orbital to overlap with the central electron density maximum of the C_1—C_3 bond, simultaneously minimizing steric bumping of the carbene and the bridgehead hydrogens. At a closer approach, the carbene fragment tilts upward, giving a more symmetrical geometry which progresses smoothly toward the final bicyclo[1.1.1]pentane geometry. As with the side approach, no sign of an intermediate appears in this mode of reaction.

Within the MNDO approximation, the side approach of path A is preferred by 5 kcal/mol (6.8 without C.I.) over the top approach of path C. The calculated activation energies are 13.8 (11.1) and 18.8 (17.9) kcal/mol respectively at the MNDO-CI (MNDO) level. These values are roughly three times as large as that calculated by Schoeller and Aktekin[28a] for the reaction of methylene with ethylene. More important, the two pathways give rise to different products. The side approach produces the observed 1,4-pentadiene but the top approach gives bicyclo[1.1.1]pentane. The calculated activation barrier for ring opening of bicyclo[1.1.1]pentane to 1,4-pentadiene is 60.0 kcal/mol at the MNDO level, in reasonable agreement with the experimental value of 49 kcal/mol.[30a] It appears that approach of the carbene from the top of **2** cannot avoid the bicyclo[1.1.1]pentane potential energy well and therefore cannot yield 1,4-pentadiene **3** directly.



A variety of other approach directions has been considered, including those examined by previous investigators for approach of a proton to bicyclobutane.[25,31] However, many of these hypothetical trajectories do not represent true minimum energy pathways (i.e. only one non-zero gradient) and collapse to one of those already discussed. In particular, approach to the center of a C_1—C_2 bond in bicyclobutane was found by Lehn and Wipff to be the second most favorable site for protonation.[25] However, attempts to locate an energy-minimized path for carbene reaction with bicyclobutane in this region consistently yielded relaxation to one of the paths A or B.

The calculated results suggest that, at least, for the reaction of the parent bicyclobutane **2** and methylene, the observed[16] products **3** and **4** arise via different concerted reaction paths of which C is the less favorable. This is consistent with the finding by Doering and Coburn[15] that in the pentadiene product of the reaction between :CD_2 and 1,3-dimethylbicyclo[1.1.0]butane the D atoms appear *only* in the terminal methylene positions, ruling out a vibrationally "hot" bicyclopentane as the precursor to **1**. Although the difference in calculated activation energies between paths A and C is somewhat large in light of the experimental 1 : 21 ratio of **4** to **3**, even this relatively crude level of theory appears to give a reasonable energetic ordering[32] of the transition structures A–C.



It is possible that a diradical mechanism may still be appropriate for systems which have radical stabilizing substituents on the carbene and at the bridgehead positions of the bicyclobutane. For example, the production of significant quantities of bicyclo[1.1.1]pentane products in the reaction of methyl 3-methyl bicyclobutane-1-carboxylate[17] with :CCl_2 may conceivably occur via side attack, as in transition state A, giving a stabilized singlet diradical. In this case, ring flipping and closure to the bicyclo[1.1.1]pentane would be competing successfully with the bond cleavage leading to 1,4-pentadienes.

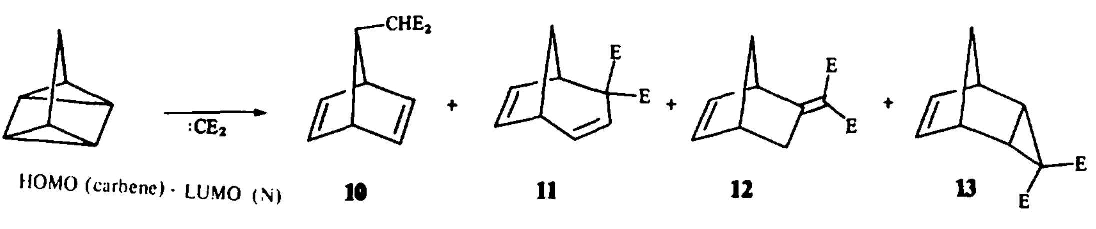
Reaction of carbenes with quadricyclane

Naturally one would like to know the bounds of this reaction. Would it, for instance, occur in the reaction of methylene with simple cyclopropanes? There is no indication of such a reaction, although it does not seem to have been sought specifically. Ethylene is a product of the photolysis of diazomethane or ketene in cyclopropane, but there are many possible mechanisms not involving the two-bond cleavage reaction for its formation.[33] No cleavage was noted when carbomethoxycarbene was allowed to react with nortricyclene—the main products were those of C—H insertion.[34] At the very least the reaction with simple cyclopropanes cannot be a major one. What about compounds more closely related to bicyclobutanes? How much can the three-membered rings of bicyclo[1.1.0]butane be expanded and still preserve the reaction? This question remains unanswered as we decided not to investigate the parent bicyclo[2.1.0] system but instead to take a shortcut and use the then commercially available quadricyclane. Naturally we paid the price of all shortcutters and we must now go back to the parent system to answer the previous question.[35] However, we received an undeserved dividend in the discovery of still another reaction of divalent carbon with two σ bonds. Once again we investigated both dicarbomethoxycarbene and dichlorocarbene.

Irradiation of dimethyldiazomalonate in quadricyclane led to four products, **10–13**. Compounds **11** and **13** are known as products of the reaction of dicarbomethoxycarbene with norbornadiene.[21] We have found that the other two products, **10** and **12**, are also produced in small amounts from the reaction with norbornadiene. The structure of **12** was verified by an independent synthesis from dehydronorcamphor and dimethylmalonate. The structure of **10** rests upon an examination of its 250 MHz ^{1}H-NMR spectrum. As quadricyclane and norbornadiene are obviously related and as both give **10–13**, it must be shown that **10–13** are indeed products of reaction of quadricyclane and not formed from norbornadiene. Table 2 shows the amounts of **10–13** formed from the two precursors, as determined by gas chromatography. Clearly the ratios are very different. Nor is there any evidence of isomerization of quadricyclane to norbornadiene in the reaction; thus we can say with confidence that

Table 2. Reaction of dicarbomethoxycarbene with quadricyclane (Q) and norbornadiene (N)

Substrate	Relative per cent			
	10	**11**	**12**	**13**
Q	15	70	11	4
N	tr	57	8	35



HOMO (carbene) · LUMO (N)

isomerization of quadricyclane to norbornadiene does not precede product formation.

Although **11** would be the product of two-bond cleavage analogous to that found in bicyclobutanes, we have shown that this is not the mechanism of its formation. Rather, **11** is a secondary product, formed along with **12** by the thermal reaction of the real primary product, **14**. Pure **13** and **14** can be obtained by column chromatography of the products of the reaction of norbornadiene with dicarbomethoxycarbene. Pyrolysis of **14** in the injector port (248°) of a gas chromatograph yielded both **11** and **12**. The *endo* adduct **13** was stable under these conditions. Examination of the 250 MHz ^{1}H-NMR spectrum of the crude reaction mixture of quadricyclane and dicarbomethoxy carbene showed peaks due to **13** and **14**, but nothing attributable to **11** or **12**. Although we have no proof of the mechanism of rearrangement of **14** to **11** and **12**, an economical version involves the cleavage of a cyclopropane bond followed either by hydrogen shift or a second bond cleavage to give diradical **15** and finally closure. Alternatively, equilibration of the homoallyl-cyclopropylcarbinyl pair followed by cleavage could give **16**, just a rapid Cope rearrangement away from **11**.[30b] In any event, the primary product in this reaction is the *exo*-cyclopropane **14**.

In our hands[36] the reaction of quadricyclane with dichlorocarbene, generated four different ways, presents a similar picture. The products are **17**–**20**. Once more the question of the intervention of norbornadiene in this reaction was settled by a comparison of the relative ratios of **17**–**20** formed from each precursor (Table 3). As before, the product ratios from norbornadiene and quadricyclane are very different. Thus we are observing a direct reaction with quadricyclane and not an isomerization to norbornadiene followed by reaction with the carbene. The reaction of dichlorocarbene with norbornadiene has been studied in detail by the groups of Klumpp[37] and Jefford.[41] Although compound **20** is unreported by the

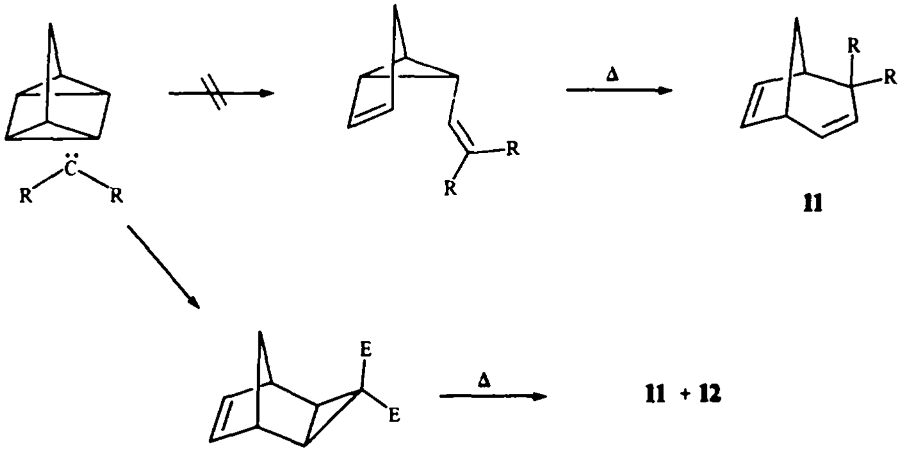


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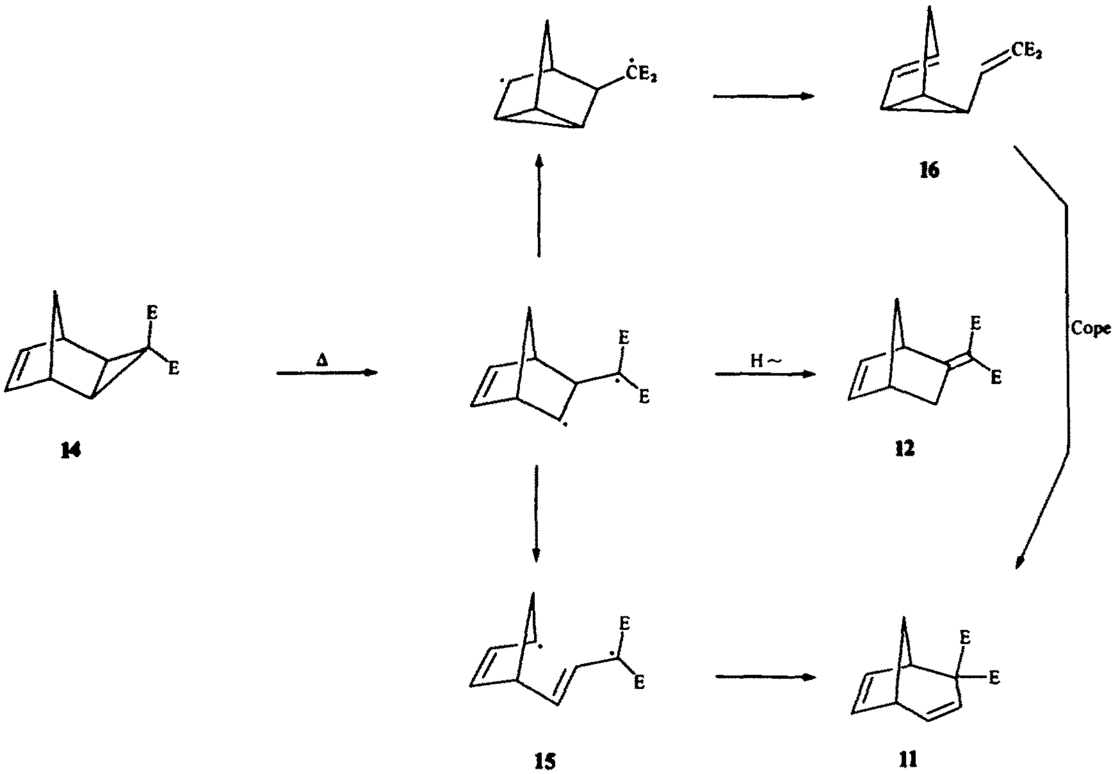
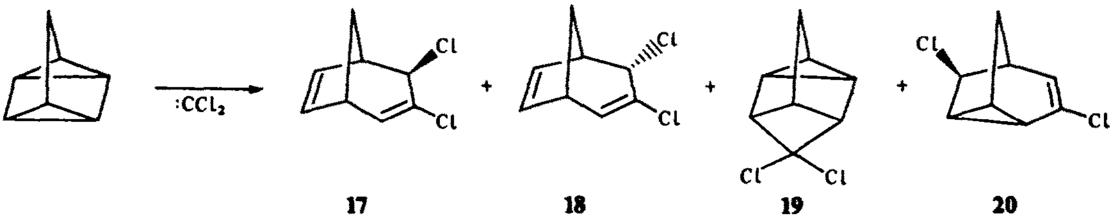
Table 3. Reaction of quadricyclane (Q) and norbornadiene (N) with dichlorocarbene

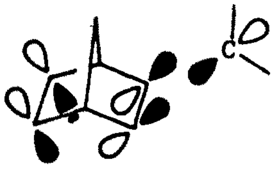
Run	Substrate	Method	Relative per cent					Reference for method
			17	**18**	**19**	**20**	**21**	
1	Q	this work phase transfer 1	57	tr	tr	43	—	37
2	Q	this work phase transfer 2	61	tr	tr	39	—	38
3	Q	this work phase transfer 3	73	tr	tr	27	—	36, 39
4	N	phase transfer 1	77	12	11	—	—	37
5	N	this work phase transfer 1	55	5	12	28	—	37
6	N	run 5, 17 + 18 + 19 = 100%	76	7	17			
7	N	this work phase transfer 2	43	5	16	36	—	38
8	N	run 7, 17 + 18 + 19 = 100%	67	8	25			
9	Q	this work $CHCl_3$/t-BuOK	—	—	tr	—	large	40
10	Q	Ref. 36 phase transfer 3	42.3	0.7	57	—	—	36, 39



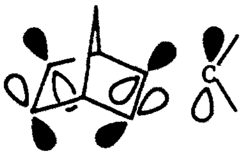


Klumpp group,[37] in our hands it is formed from norbornadiene along with **17**–**19**.[42]

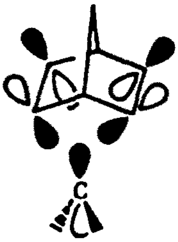
The reaction of quadricyclane with dichlorocarbene has also been reported before.[36] (Entry 10, Table 3.) In this work **19** is reported to be the major product of the reaction. We cannot explain the discrepancy with our work. Compound **19** is a stable material, surviving all manner of chemical manipulations.[37b] We analysed our crude reaction mixtures directly using 250 MHz ^{1}H-NMR spectroscopy. Although we are able to detect

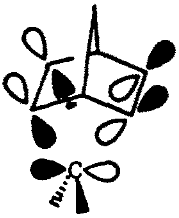


HOMO (carbene) - LUMO (Q)

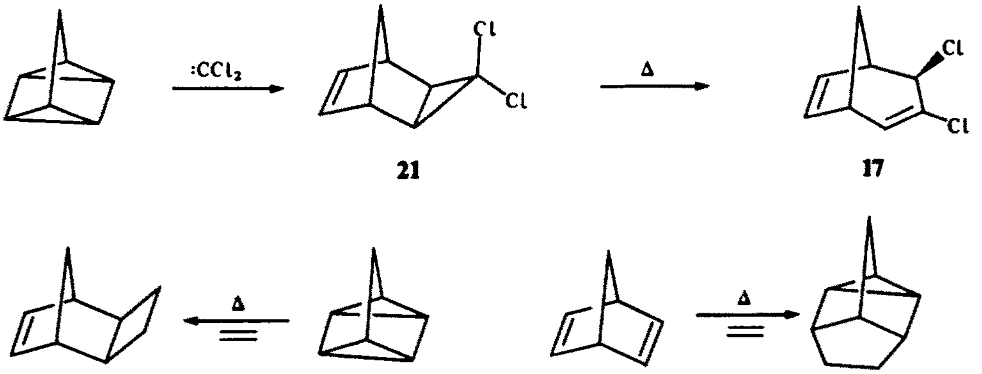


HOMO (carbene) - LUMO (Q)



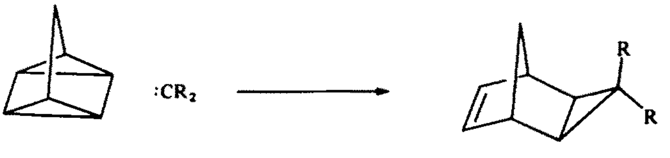


HOMO (carbene) - LUMO (N)



21 **17**

Reaction of norbornadiene and quadricyclane with alkanes



14,**21**

and isolate the appropriate 10% or so of **19** in the reaction of dichlorocarbene with norbornadiene, in our hands four different methods of generation of dichlorocarbene in quadricyclane failed to produce more than traces of **19**.

Compound **17** is known to be a product of thermal isomerization of **21**.[37] It therefore seemed likely that **21** was the real direct product of addition of dichlorocarbene to quadricyclane, as had been the case for **14**. Compound **21** can be detected in the crude reaction mixture when dichlorocarbene is generated by alcoholysis of chloroform,[40] a process leading to less rearrangement than the various phase transfer reactions. (Entry 9, Table 3.) So once again it can be shown that the initial product of reaction of quadricyclane with the carbene is the *exo*-cyclopropane **21**.

We have no calculations as yet on this point, but "back-of-the-envelope" theory supports the notion that addition of a singlet carbene to quadricyclane could give **14** or **21**. Both the HOMO (carbene)–LUMO (quadricyclane) and LUMO (carbene)–HOMO (quadricyclane) interactions are favorable. By contrast the corresponding favorable interactions for the norbornadiene/carbene combination lead to *endo*-homo-1,4-addition which is, of course, observed for norbornadiene but not (by us) for quadricyclane.

Quadricyclane is known to undergo similar reactions with multiple bonds.[44–46] Of particular importance is the work of Tabushi *et al.*[45] in which it was established that thermal cycloadditions with olefins proceeded with retention of stereochemistry to give *exo*-cyclobutanes. By contrast norbornadiene reacts in a different concerted fashion, to give the products of *endo*-homo-1,4-addition.[47] Carbenes seem to behave much as do double bonds in their reactions with quadricyclane and norbornadiene. Both olefins and halocarbenes react with norbornadiene to give some homo-1,4-addition. Carbenes, of course, also react in normal fashion to give the *exo* and *endo* cyclopropanated products. Thus quadricyclane reacts with both double bonds and carbenes quite differently from norbornadiene, giving *exo* cyclobutanes and *exo* cyclopropanes, respectively. Although we necessarily lack the stereochemical label required to probe the question of concert, it does not seem excessive to suggest that the formation of **14** and **21** represents a new example of the concerted reaction of divalent carbon with two σ bonds.

EXPERIMENTAL

General data. M.ps were determined by using a Thomas Hoover Unimelt apparatus and are uncorrected.

Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, GA 30366.

Routine NMR were recorded on a Varian A-60A spectrometer (60 MHz), a Perkin–Elmer R-32 spectrometer (90 MHz, continuous wave operation), a Varian XL-100 spectrometer (^{1}H, 100.083 MHz; ^{13}C, 25.196 MHz), or JEOLCO-JEOL FX 90 Q spectrometer (^{1}H-NMR, 89.55 MHz; ^{13}C, 22.50 MHz, Fourier transform mode). High-field (250 MHz) spectra were taken on a Bruker WM-250 spectrometer.

IR spectra were recorded on Perkin–Elmer 237B or 283 IR spectrophotometers.

Preparative gas chromatography was performed on a Varian A90A gas chromatograph (thermal conductivity detector) with helium as carrier gas, using 1/4 in. copper or aluminum columns.

Mass spectra were obtained on an AEI MS-9 mass spectrometer (electron impact). GC/MS runs were conducted on a Hewlett–Packard 5992B instrument.

Gas chromatography columns. Column A: 2 m × 1/4 in. packed with 12% SE-30 on Chromosorb W. *Column B*: 6′ × 1/8″ glass 3% SP2250 on Chromosorb WAW/DMCS 80/100. *Column C*: 3′ × 1/8″ glass 3% OV101 on Chromosorb W-HP 100/200.

1,1-*Dibromo*-2,2,3,3-*tetramethylcyclopropane*.[48,49] To a mixture of 45.9 ml (0.53 mol) CHBr$_3$, 35.7 ml (0.30 mol) 2,3-dimethyl-2-butene, 1.2 ml EtOH, and 0.6 g triethylbenzylammonium chloride, 150 ml 50% NaOH soln was added over

15 min at 45°. The reaction was vigorously stirred at 45° for 3.5 hr after which the product was poured over 250 ml H_2O. The organic layer was separated and the aqueous layer was washed twice with 50 ml CH_2Cl_2. The combined organic layers were washed with 50 ml H_2O, 50 ml 0.5 M HCl, and 50 ml H_2O and then dried over $MgSO_4$. The solvent was evaporated and the product (brown crystals) was recrystallized once from methanol yielding 39 g (51% yield) of white crystals. M.p. 82–83°, lit.[49] 77–78°.

1,2,2-*Trimethylbicyclo*[1.1.0]*butane*.[50] All glassware was base-washed in a KOH/EtOH bath. To a stirred soln of 39 g (0.154 mol) 1,1-bibromo-2,2,3,3-tetramethylcyclopropane in 5.0 ml diethyl ether cooled to −30° to −40° in a Dry Ice/acetone bath, 130 ml 1.4 M CH_3Li (in ether) was added dropwise over 30 min. The mixture was stirred for an additional 30 min. Then 50 ml 10% K_2CO_3 soln was added slowly. The ether layer was separated, and the aqueous layer was extracted twice with 25 ml diethyl ether. The combined ether layers were washed twice with 25 ml 10% K_2CO_3 aq and dried overnight over K_2CO_3. The residual organic layer was distilled yielding 4 ml (20% yield) of 1,1,2-trimethylbicyclo-[1.1.0]butane.

Photolysis of dimethyl diazomalonate in 1,2,2-*trimethylbicyclo* [1.1.0]*butane*

A soln of 100 μl in diazomalonate was photolysed in 4 ml 1,2,2-trimethylbicyclo[1.1.0]butane for 10 hr with a Hanovia 450 W medium pressure mercury lamp. Unreacted bicyclobutane was recovered by vacuum distillation. Analysis at 168° on Col. A showed three major products in the ratio 6 : 2 : 1. NMR analysis showed the major product to be 1,1-dicarbomethoxy-3,3,4-trimethylpenta-1,4-diene in a 14.2% yield. (Found: C, 63.54; H, 8.06. Calc for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02%.)

The second product was dimethylmalonate and the third has a 250 MHz ^{1}H-NMR spectrum consistent with 1,1-dicarbomethoxybicyclo[1.1.1]pentane. This assignment cannot be considered secure, however.

Reaction of 1,2,2-*trimethylbicyclo*[1.1.0]*butane with dichlorocarbene*

To approximately 1 g (0.01 mol) 1,2,2-trimethylbicyclo-[1.1.0]butane and 1.12 g (0.01 mol) $(CH_3)_3COK$ stirring in 3 ml pentane, 0.82 ml (0.01 mol) $CHCl_3$ was added dropwise over 20 min at −25°. The soln was initially yellow/orange and turned pale red with the addition of $CHCl_3$. After 30 min of additional stirring 10 ml of 10% K_2CO_3 aq was added slowly and the organic layer was recovered. The pale yellow product was dried over Na_2SO_4. Analysis by gas chromatography on Column A at 75° showed three products in the ratio 7.2 : 2.2 : 1.

Photolysis of dimethyl diazomalonate in quadricyclane and norbornadiene

A mixture of 1 ml (0.9 g, 1 mmol) of quadricyclane [or 1 ml (0.9 g, 1 mmol) of norbornadiene] and 50 μl (0.65 g, 4.11 mmol) of dimethyl diazomalonate was placed in a quartz photolysis tube, which was degassed by the freeze–thaw method. The mixture was irradiated for 10 hr with a 450 W medium pressure Hanovia mercury arc filtered by Pyrex. The solvent was then removed on a vacuum line and analysed by vapor phase chromatography on Column B at 189° to be sure it contained no products. The remaining orange liquid was analysed directly by NMR spectroscopy. Yields were calculated based upon NMR spectroscopy and vapor phase chromatography. The total yields for the quadricyclane and norbornadiene reactions were 3.4% and 12% respectively. The products were then isolated in one of two ways. (a) The products were collected from vapor phase chromatography on a column A at 191° and analysed by NMR spectroscopy, ^{1}H-NMR ($CDCl_3$) δ 6.82 (t, 2), 6.62 (t, 2), 3.72 (s, 6), 3.58 (d, 1), 3.42 (br s, 2), 3.00 (d, 1). Precise mass. Calculated for $C_{12}H_{14}O_4$: 222.0892. Found: 222.0890 ± 0.0025. (b) The products were separated by column chromatography (hexane/silica gel) and 20 × 25 ml collections were made. The collected products were analysed by NMR spectroscopy.

Synthesis of 5-bis(methoxycarbonyl)methylenebicyclo[2.2.1] *hept-2-ene* (**12**)[51,52]

In a 25 ml 3-necked flask were placed 1.00 g (9.3 mmol) of dehydronorcamphor,[53–55] 0.77 ml (0.89 g 6.7 mmol) of dimethylmalonate, 0.74 ml (0.77 g, 13 mmol) of AcOH, and 0.21 g (2.1 mmol) of $ZnCl_2$. The mixture was heated at 100° for 42 hr. The temp was not allowed to rise above 100°. The resulting dark brown mixture was poured into 10 ml of water. The aqueous layer was extracted with 5 × 7 ml of ether. The combined organic layers were extracted with 3 × 10 ml of 10% $NaHCO_3$ aq, dried over $MgSO_4$ and filtered. The solvents were removed by rotary evaporation. The concentrated brown soln was analysed directly by vapor phase chromatography on a column A at 175°. The products were collected and analysed by gas chromatography–mass spectroscopy on column C.

^{1}H-NMR ($CDCl_3$) δ 6.33 (m, 1), 6.04 (m, 1), 3.82 (s, 3), 3.80 (br s, 1), 3.74 (s, 3), 3.08 (br s, 1), 2.63, 2.28 (AB, 2), 1.74 (m, 1), 1.54 (m, 1).

Precise mass. Calculated for **12** $C_{12}H_{14}O_4$: 222.0892. Found: 222.0890 ± 0.002.

Phase transfer dichlorocarbene reactions with quadricyclane and norbornadiene

Phase transfer method 1.[37] A mixture of 80 ml (15 mol) of 50% (w/w) NaOH aq, 0.34 g (1.5 mmol) of triethylbenzylammonium chloride, 2 ml of EtOH, and 10.0 ml (9.22 g, 0.10 mol) of quadricyclane [or 10.8 ml (9.22 g, 0.10 mol) of norbornadiene] was placed in a 500 ml 3-necked flask in a water bath at room temp. The mixture was vigorously stirred with an overhead stirrer while 81 ml (119 g, 1 mol) of $CHCl_3$ was added dropwise over a period of 30 min. The mixture was then stirred for an additional 20 hr. After 17 hr of this stirring, 100 ml of CH_2Cl_2 was added to the flask to thin the soln. Once the stirring was complete, the mixture was poured into an excess (500 ml) of water, then extracted with 3 × 100 ml of CH_2Cl_2. A brown solid, insoluble in water and CH_2Cl_2, was discarded. The combined organic extracts were washed with 1 × 100 ml of water, 1 × 100 ml of 2N HCl, and 1 × 100 ml of water, then dried over $MgSO_4$ and filtered. The solvents were removed by rotary evaporation. The dense brown liquid remaining was analysed directly by 250 MHz NMR spectroscopy.

Phase transfer method 2.[38] A mixture of 8.21 ml (7.54 g, 0.082 mol) of quadricyclane [or 8.83 ml (7.54 g, 0.82 mol) of norbornadiene], 170 ml (3.2 mol) of 50% (w/w) NaOH aq, and 20 ml of benzene was emulsified using an overhead stirrer at high speed. The catalyst, 0.32 g (1.4 mmol) of triethylbenzylammonium chloride, was added, followed by 70 ml (103 g, 0.86 mol) of $CHCl_3$ added dropwise from a pressure equalizing funnel over a period of 4 hr. A thick brown soln resulted which was stirred for an additional 2 hr. Throughout the reaction the flask was kept in a water bath at room temp. The mixture was then added to 600 ml of water and filtered overnight. The filtrate was extracted with 4 × 100 ml, 1 × 50 ml of ether. The combined ether extracts were washed with 1 × 100 ml of 2 N HCl, 1 × 100 ml of sat NaCl aq, and then dried over $MgSO_4$ and filtered. The solvents were removed by rotary evaporation. A dense brown liquid remained which was analysed directly by 250 MHz NMR spectroscopy.

The products were then collected by vapor phase chromatography on column A at 105° and analysed by 250 MHz NMR spectroscopy. The total yield of the quadricyclane reaction, determined by NMR spectroscopy, was 12%.

Phase transfer method 3.[39] Quadricyclane (0.92 g, 10 mmol), "Centrimide" (36.5 mg, 0.1 mmol) and $CHCl_3$ (5.4 ml) were stirred at 50° as NaOH aq (3.2 g in 6.4 ml H_2O) was added over 15 min. After an additional 2 hr stirring, *ca* 10 ml ice water was added and the mixture acidified with 10% H_2SO_4 and extracted with 3 × 10 ml portions of ether. The combined ether layers were washed with water and NaCl aq, then dried over $MgSO_4$ and filtered. The solvents were removed by rotary evaporation to leave a brown liquid that was analysed directly by 250 MHz NMR spectroscopy.

Dichlorocarbene reactions generating cyclopropanes from quadricyclane and norbornadiene[40]

To a mixture of 3.00 ml (2.76 g, 0.03 mol) of quadricyclane [or 3.24 ml (2.76 g, 0.03 mol) of norbornadiene], 3.36 g (0.03 mol) of potassium t-butoxide, and 20 ml of n-pentane at 0° was added 2.43 ml (3.57 g, 0.03 mol) of $CHCl_3$ in small portions. Gas was generated. The mixture was stirred with a magnetic stirrer for 1 hr at room temp. The resulting yellow soln was poured into an equal volume (approximately 30 ml) of water. The mixture was extracted with 4 × 30 ml of n-pentane. The combined organic layers were dried over $MgSO_4$, filtered, and the n-pentane removed by rotary evaporation. The soln was analysed directly by 250 MHz NMR spectroscopy.

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[1] Support for this work by the National Science Foundation through grant CHE 81-01212 is gratefully acknowledged. One of us (JEJ) thanks the NIH for support through grant GM6462 to Leland C. Allen.

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[29] It should be noted that on the *ab initio* reaction surfaces (see refs. 28*b* and *c*) the reaction of methylene and ethylene has zero activation barrier. However, MNDO gives similar results for *substituted* carbenes to those calculated at the *ab initio* (STO-3G) level, and the *geometrical* evolution of the reaction path appears to be quite similar at both levels.[28a]

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[42] Compound **20** fails to survive gas chromatography, but can be detected in the 250 MHz ^{1}H-NMR spectrum of the crude reaction mixture. Professor Klumpp graciously provided us with a 60 MHz ^{1}H-NMR spectrum of his crude reaction mixture and it appears that **20** was indeed produced in the older work. The conclusions of the Klumpp work would be unaffected by the formation of this compound, which is doubtless a product of secondary rearrangement under ionic conditions.[43]

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