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Alkynyliodonium Salts in Organic Synthesis

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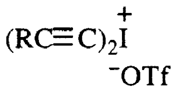
A. INTRODUCTION

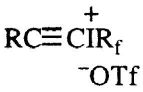
In the last two decades interest in hypervalent iodine compounds has surged.[1-5] Several new, important reagents based on organic derivatives of iodine(III) and iodine(V) have been developed and widely applied in organic synthesis. Specific areas of synthetic application of hypervalent iodine reagents are determined by their structural features such as the number of carbon ligands attached to the iodine atom and the electronegativity and leaving group ability of the non-carbon ligands. Recent examples of synthetically important hypervalent organoiodine reagents with one carbon ligand (RIX_2 or RIX_4) include numerous [hydroxy(organosulfonyloxy)iodo]arenes, Dess-Martin periodane, various substituted benziodoxoles, and hypervalent iodine azides.[1,2] All these compounds are widely used as powerful and selective oxidizing reagents. The second large group of hypervalent iodine reagents is represented by iodonium salts, $R_2I^+X^-$, which have two carbon ligands at iodine. In general, iodonium salts are not strong oxidizers and their most typical reaction is the transfer of the carbon ligand to the nucleophilic substrate. Depending on the nature of the organic ligand R, iodonium salts can be further classified as alkyliodonium, polyfluoroalkyliodonium, alkenyliodonium, aryliodonium, and alkynyliodonium salts. Alkyliodonium salts, $Alk_2I^+X^-$ or $Alk(Ph)I^+X^-$, generally lack stability and, with a few exceptions,[6] have not been exploited in synthesis. Polyfluoroalkyliodonium salts, $R_f(Ph)I^+X^-$, are stable, powerful electrophilic polyfluoroalkylating reagents,[5] while alkenyliodonium and aryliodonium salts can be used as alkenylating and arylating reagents, respectively.[1,2]

Alkynyliodonium salts represent the newest class of polyvalent iodine compounds. At present, three major structural types of alkynyliodonium salts are known, bis(alkynyl)iodonium triflates **1**,[7] alkynyl(polyfluoroalkyl)iodonium triflates **2**,[8] and alkynyl(aryl)iodonium salts **3**. Compounds **1** and **2** lack stability and have not yet demonstrated utility in synthesis, while alkynyl(aryl)iodonium salts **3** are generally stable, crystalline compounds. The anionic part of the molecule **3**, X^-, generally requires the incorporation of non-nucleophilic anions, such as triflate or tetrafluoroborate. Important additional subclasses of stable alkynyl(aryl)iodonium salts **3** are represented by bis(iodonium)acetylene **4** and the heterocyclic derivatives **5** and **6**.



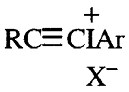
$$(RC{\equiv}C)_2\overset{+}{I}\ \ {}^{-}OTf$$

1



$$RC{\equiv}C\overset{+}{I}R_f\ \ {}^{-}OTf$$

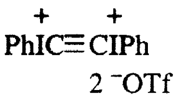
2



$$RC{\equiv}C\overset{+}{I}Ar\ \ X^-$$

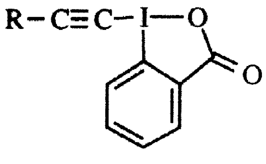
3

$X = OTs, OTf, BF_4$



$\overset{+}{\text{PhI}}\text{C}{\equiv}\text{C}\overset{+}{\text{I}}\text{Ph}$ $2\ {}^{-}\text{OTf}$

4



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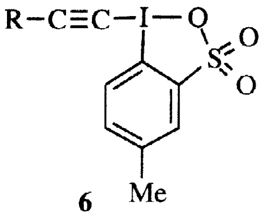


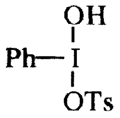
6

The first stable alkynyliodonium salts **3** were reported by Koser and coworkers in 1981;[9] however, only in the late 1980's - early 1990's were convenient, general methods of preparation developed. At present, over a hundred different alkynyliodonium salts are known.[3,4] During the last half dozen years, these compounds have found increasing application in organic synthesis due to their unique and highly useful reactivity patterns. Specifically, due to the excellent leaving group ability of the aryliodonium moiety, compounds **3** can be used as powerful electrophilic alkynylating reagents toward various organic nucleophiles. At the same time, alkynyliodonium salts are highly reactive in Michael-type conjugate addition reactions as well as Diels-Alder and 1,3-dipolar cycloadditions because of the strong electron-withdrawing properties of the iodonium group. The chemistry of alkynyliodonium salts was previously summarized in a 1992 review[3] and several book chapters published in 1994-95.[4] Some aspects of the chemistry of alkynyliodonium salts were covered in other general reviews and books on the chemistry of polyvalent iodine.[1,2] In the present review, emphasis is placed on the literature published in the last half dozen years.

B. PREPARATION AND PROPERTIES OF ALKYNYLIODONIUM SALTS

From a historical perspective, the first preparation of an alkynyliodonium salt was attempted in the mid 1960's by Beringer and Galton[10] via interaction of $PhICl_2$ with lithium phenylacetylide. However, the initial product in this reaction, alkynyliodonium chloride, was unstable due to the relatively high nucleophilicity of the chloride counter ion, and therefore it decomposed in a few hours at room temperature into a 1:1 mixture of iodobenzene and phenyl chloroacetylene. In 1979, Merkushev and coworkers[11] reported the formation of the crystalline, relatively stable, albeit hygroscopic, alkynyliodonium trifluoroacetates but characterized them only by IR spectroscopy. The first fully characterized, stable alkynyliodonium salts were tosylates **15** (Section B.1, eq. 1) prepared by Koser and coworkers *via* the interaction of [hydroxy(tosyloxy)iodo]benzene **7** with terminal alkynes.[9,12] From then on it has been recognized that the stability of alkynyliodonium salts depends on the nature of the counterion. In general, non-nucleophilic anions such as sulfonate and tetrafluoroborate, are required to stabilize the iodonium salt. Alternatively, another type of alkynyliodonium salt, derived from benziodoxole, is stabilized due to the incorporation of hypervalent iodine in a five-membered heterocycle.

The most general synthetic approach to alkynyliodonium salts involves the reaction of an electrophilic λ^3-iodane[2a] (RIX_2) with a terminal alkyne or its silylated, stannylated or lithiated derivative. The most useful, key reagents used for the preparation of alkynyliodonium salts are tosylate **7**, complexes of iodosylbenzene with Lewis acids (**8-10**), cyano(phenyl)iodonium triflate **11**, and hypervalent iodine heterocycles **12**, **13**.



$$\mathrm{Ph{-}I(OH)(OTs)}$$

7

$PhIO{\bullet}Et_3O^+BF_4^-$

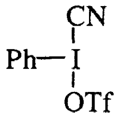
8

$PhIO{\bullet}BF_3$

9

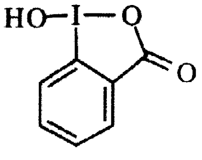
$2PhIO{\bullet}Tf_2O$

10



$$\mathrm{Ph{-}I(CN)(OTf)}$$

11



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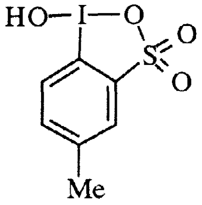


13

1. *Preparation of Alkynyl(aryl)iodonium Salts from [Hydroxy(tosyloxy)iodo]benzene*

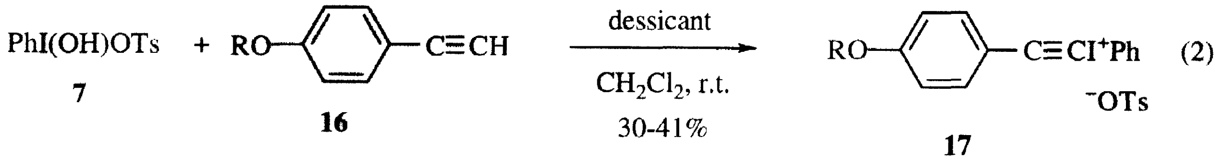
[Hydroxy(tosyloxy)iodo]benzene (HTIB) **7** is commercially available and easily accessed from (diacetoxyiodo)benzene and *p*-toluenesulfonic acid monohydrate as a colorless, stable microcrystalline solid. In the early 1980's, Koser and coworkers discovered that HTIB is an efficient reagent both for the synthesis of various iodonium salts and also for alkene oxytosylations, so in the present literature HTIB is often referred to as "Koser's reagent". HTIB **7** reacts with terminal alkynes **14** upon gentle heating in chloroform or dichloromethane to form alkynyliodonium tosylates **15** in moderate to low yield (eq. 1).[9,12]

$$\underset{\mathbf{7}}{\mathrm{PhI(OH)OTs}} + \underset{\mathbf{14}}{\mathrm{RC{\equiv}CH}} \xrightarrow[15\text{-}74\%]{\mathrm{CHCl_3}} \underset{\mathbf{15}}{\mathrm{RC{\equiv}CI^+Ph\ ^-OTs}} \qquad (1)$$

R = *i*-Pr, *i*-Bu, *s*-Bu, *t*-Bu, cyclopentyl, cyclohexyl, Ph, *p*-Tol

This reaction (eq. 1) works well only with alkynes **14** which have a bulky alkyl group or an aryl group as the substituent R. The addition of a dessicant to the reaction mixture results in broader applicability of this procedure with a greater variety of alkynes **14**.[13,14] This method is also applicable to the preparation of alkynyliodonium mesylates and *p*-nitrobenzenesulfonates by the reaction of the appropriate [hydroxy(organosulfonyloxy)iodo]benzenes with terminal alkynes **14** under similar conditions.[13,14] The tosylate anion in the molecule of **15** can be substituted with triflate by treatment of **15** with a triflate loaded anion exchange resin.[14]

In general, this method (eq. 1) has relatively low practical value because of the low chemoselectivity and low yields of alkynyliodonium salts. However, considering the commercial availability of reagent **7** and the simplicity of the experimental procedure, it is the method of choice for the synthesis of alkynyl(phenyl)iodonium tosylates **15** from arylacetylenes and terminal alkynes with bulky alkyl substituents. Recent examples of this procedure can be found in the preparation of arylethynyl(phenyl)iodonium tosylates **17** bearing long alkoxy chains and chiral alkynyl ligands from Koser' reagent **7** and the appropriate alkynes **16** (eq. 2).[15,16]



R = n-C_8H_{17}, n-$C_{10}H_{21}$, n-$C_{12}H_{25}$, n-$C_{14}H_{29}$, (S)-$C_2H_5CH(CH_3)CH_2$

2. *Preparation of Alkynyl(phenyl)iodonium Salts from Complexes of PhIO with Lewis Acids*

All other important experimental procedures for the preparation of alkynyl(phenyl)iodonium salts involve iodosylbenzene (PhIO) as the principal precursor. Iodosylbenzene is not commercially available; however, it can be easily prepared by hydrolysis of $PhI(OAc)_2$ with aqueous NaOH.[17] Iodosylbenzene is a yellowish, amorphous powder which can not be recrystallized due to its polymeric nature. Heating or extended storage at room temperature results in disproportionation of iodosylbenzene to PhI and colorless, explosive iodylbenzene, $PhIO_2$. However, handling of even large amounts of PhIO at room temperature is relatively safe.

Iodosylbenzene by itself is unreactive with alkynes or alkynylsilanes. However, in the presence of triethyloxonium tetrafluoroborate or boron trifluoride etherate it forms relatively unstable complexes (**8** and **9**) of unknown structure that are highly reactive toward alkynylsilanes. Complex **8** reacts with alkynylsilanes **18** in dichloromethane at room temperature to afford alkynyl(phenyl)iodonium tetrafluoroborates **19** in good yield (eq. 3).[18] A variation of this procedure employs the complex of PhIO with boron trifluoride etherate (**9**) followed by treatment with aqueous $NaBF_4$ (eq. 4)[18,19a] or sodium arylsulfonates (eq. 5).[20]

$$\underset{\mathbf{8}}{PhIO{\bullet}Et_3O^+BF_4^-} + \underset{\mathbf{18}}{RC{\equiv}CSiMe_3} \xrightarrow[56\text{-}75\%]{CH_2Cl_2,\ r.t.} \underset{\mathbf{19}\ \ BF_4^-}{RC{\equiv}CI^+Ph} \qquad (3)$$

R = Ph, $PhCH_2$, $PhCH_2CH_2$, n-C_8H_{17}, *cyclo*-C_6H_{11}

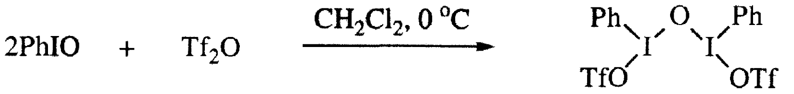
$$\underset{\mathbf{9}}{PhIO{\bullet}BF_3} + \underset{\mathbf{18}}{RC{\equiv}CSiMe_3} \xrightarrow[54\text{-}85\%]{1)\ CH_2Cl_2,\ r.t.;\ 2)\ NaBF_4,\ H_2O} \underset{\mathbf{19}\ \ BF_4^-}{RC{\equiv}CI^+Ph} \qquad (4)$$

R = Ph, $PhCH_2$, n-C_8H_{17}, Me_3Si

$$\underset{\mathbf{9}}{PhIO{\bullet}BF_3} + \underset{\mathbf{18}}{RC{\equiv}CSiMe_3} \xrightarrow[62\text{-}89\%]{1)\ CHCl_3,\ r.t.;\ 2)\ NaOSO_2Ar,\ H_2O} \underset{\underset{\mathbf{20}}{ArSO_3^-}}{RC{\equiv}CI^+Ph} \qquad (5)$$

R = Me, Et, n-Pr, n-Bu, Me_3Si; Ar = 4-MeC_6H_4 or 4-$NO_2C_6H_4$

Iodosylbenzene reacts with trifluoromethanesulfonic anhydride at 0 °C to form a yellow complex **21** (eq. 6), which is also known as Zefirov's reagent. Reagent **21** has a marginal stability at room temperature; however, it can be conveniently used *in situ* at 0 °C in dichloromethane. A freshly prepared yellow solution of **21** in dichloromethane selectively reacts with alkynylsilanes **18** (eq. 7) or alkynylstannanes **23** (eq. 8) to afford alkynyliodonium triflates **22** in moderate to high yield.[21] This method is also applicable to the synthesis of the parent ethynyl(phenyl)iodonium triflate (eq. 8).[21a]



21 (6)

$$\underset{\textbf{18}}{RC{\equiv}CSiMe_3} + \textbf{21}\ (\textit{in situ}) \xrightarrow[67\text{-}88\%]{CH_2Cl_2,\ 0\ ^\circ C} \underset{\textbf{22}}{RC{\equiv}CI^{+}Ph}\ ^{-}OTf \qquad (7)$$

$R = Ph, t\text{-}Bu, Me_3Si$

$$\underset{\textbf{23}}{RC{\equiv}CSnBu_3} + \textbf{21}\ (\textit{in situ}) \xrightarrow[45\text{-}56\%]{CH_2Cl_2,\ 0\ ^\circ C} \underset{\textbf{22}}{RC{\equiv}CI^{+}Ph}\ ^{-}OTf \qquad (8)$$

$R = H, n\text{-}Bu$

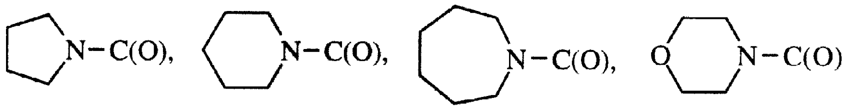
Procedures involving complexes of PhIO with Lewis acids (**8**, **9**, **21**) generally afford alkynyliodonium salts in greater yields compared to the reactions of Koser's reagent **7**. A major disadvantage of methods based on reagents **7-9** and **21** is the lack of generality since only a very limited number of functional groups R can survive these reaction conditions.

3. *Preparation of Alkynyl(phenyl)iodonium Triflates from Cyano(phenyl)iodonium Triflate and Alkynylstannanes*

The most versatile contemporary method of preparation of alkynyl(phenyl)iodonium triflates employs cyano(phenyl)iodonium triflate **11** as the iodine transfer reagent. Compound **11** can be conveniently prepared from iodosylbenzene, cyanotrimethylsilane and trimethylsilyl triflate.[22,23] An alternative procedure for the preparation of reagent **11** and several other cyano(aryl)iodonium triflates, ArI(CN)OTf, involves [bis(trifluoroacetoxy)iodo]arenes, $ArI(OCOCF_3)_2$, cyanotrimethylsilane and trimethylsilyl triflate.[24] The interaction of a large variety of readily available β-functionalized alkynylstannanes **23**[25,26] with reagent **11** under very mild conditions provides ready access to diverse β-functionalized alkynyliodonium salts **22** (eq. 9) in good isolated yields.[27,28]

$$\underset{\mathbf{23}}{RC\equiv CSnBu_3} + \underset{\mathbf{11}}{PhI(CN)OTf} \xrightarrow[42\text{-}89\%]{CH_2Cl_2,\ -42\,^{\circ}C} \underset{\mathbf{22}}{RC\equiv CI^{+}Ph}\ TfO^{-} \qquad (9)$$

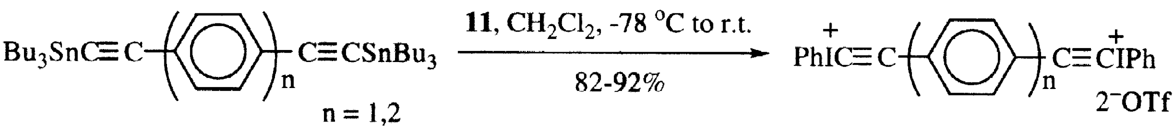
R = H, Me, *n*-Bu, 1-cyclohexenyl, MeOCH$_2$, ClCH$_2$, BrCH$_2$, CN, Cl,
MeC(OH)Ph, Ts, *t*-BuC(O), PhC(O), MeOC(O), Me$_2$NC(O),
1-adamantyl-C(O), 2-furyl-C(O), 2-thienyl-C(O), cyclopropyl-C(O),



This procedure is useful for the preparation of the bis-iodonium acetylenes **24** and **25** (eq. 10 and 11),[23] conjugated **26** (eq. 12) and unconjugated **27** (eq. 13) bis(alkynyliodonium) salts,[29,30] tris(alkynyliodonium) salts **28** (eq. 14),[30b] and diynyl(phenyl)iodonium triflates **29**[31] (eq. 15).

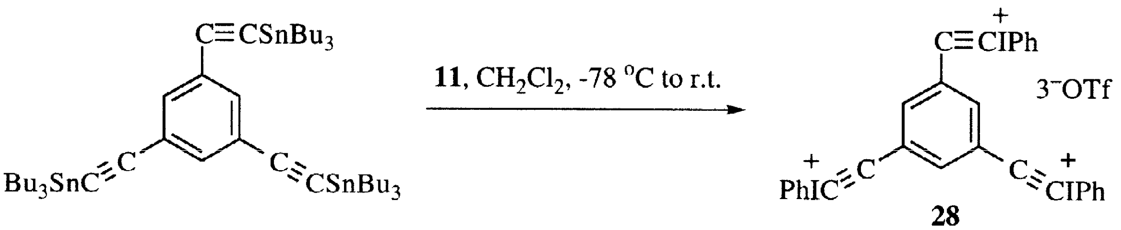
$$Bu_3SnC\equiv CSnBu_3 + \underset{\mathbf{11}}{2PhI(CN)OTf} \xrightarrow[81\%]{CH_2Cl_2,\ -30\,^{\circ}C} \underset{\mathbf{24}}{Ph\overset{+}{I}C\equiv C\overset{+}{I}Ph}\ 2^{-}OTf \qquad (10)$$

$$Me_3SnC\equiv C-C\equiv CSnMe_3 \xrightarrow[85\%]{\mathbf{11},\ CH_2Cl_2,\ -30\,^{\circ}C} \underset{\mathbf{25}}{Ph\overset{+}{I}C\equiv C-C\equiv C\overset{+}{I}Ph}\ 2^{-}OTf \qquad (11)$$



26 (12)

$$\underset{n\,=\,2,\,4,\,5}{Bu_3SnC\equiv C\left(CH_2\right)_n C\equiv CSnBu_3} \xrightarrow[90\text{-}93\%]{\mathbf{11},\ CH_2Cl_2,\ -78\,^{\circ}C\ \text{to r.t.}} \underset{\mathbf{27}}{Ph\overset{+}{I}C\equiv C\left(CH_2\right)_n C\equiv C\overset{+}{I}Ph}\ 2^{-}OTf \qquad (13)$$



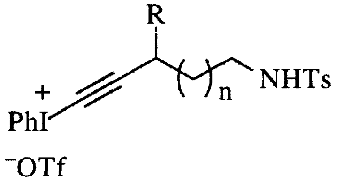
28 (14)

$$RC\equiv C-C\equiv CSnBu_3 \xrightarrow[72\text{-}96\%]{\mathbf{11},\ CH_2Cl_2,\ -40\ ^\circ C} RC\equiv C-C\equiv C\overset{+}{I}Ph\ {}^-OTf \qquad (15)$$

R = Me, *n*-Bu, *t*-Bu, Ph, Me_3Si

29

A recent elegant example of the synthetic application of this versatile procedure is the preparation of various alkynyliodonium tosylamides **30-32** from reagent **11** and the appropriate alkynylstannanes.[32,33] Compounds **30-32** are formed under these conditions in high yields (80-90%) and can be used in subsequent transformations without additional purification (see Section C4).



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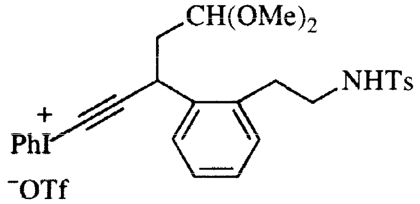

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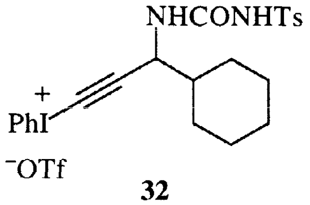
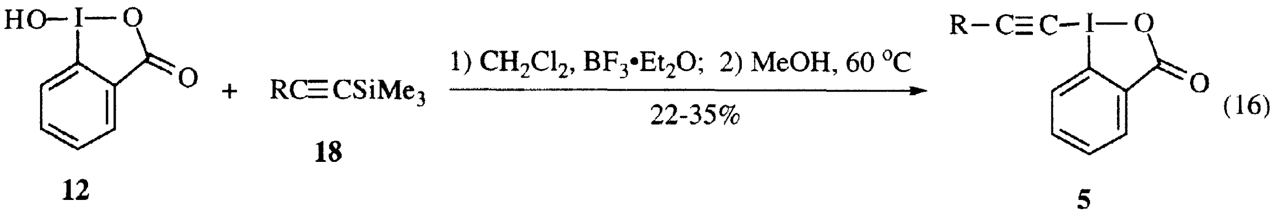


32

n = 1,2
R = $(CH_2)_2Ph$, C_6H_{11}, *i*-Pr, Ph, etc.

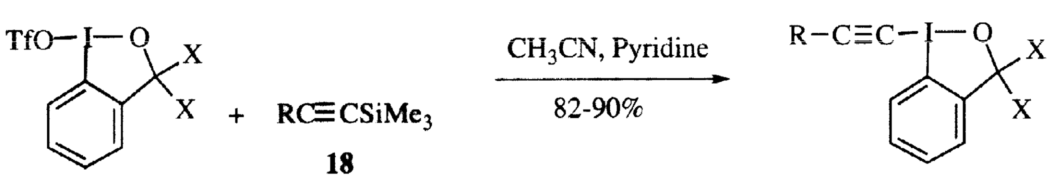
4. *Preparation of Alkynylbenziodoxolones and Alkynylbenziodoxathiolones*

Alkynylbenziodoxolones **5** were first prepared in moderate yields by the reaction of 1-hydroxy-1,2-benziodoxol-3(1*H*)-one **12** with alkynylsilanes **18** in the presence of BF_3-etherate followed by heating in methanol (eq. 16).[34]



R = *cyclo*-C_6H_{11}, *n*-C_8H_{17}, *t*-Bu

A more general procedure for the preparation of alkynylbenziodoxoles **5** and **35** employs 1-(trifluoromethanesulfonyloxy)benziodoxoles (**33**, **34**) as the reagents (eq. 17). Triflates **33** and **34** can be readily prepared from the appropriate 1-hydroxybenziodoxoles and trimethylsilyl triflate and used *in situ*.[35]



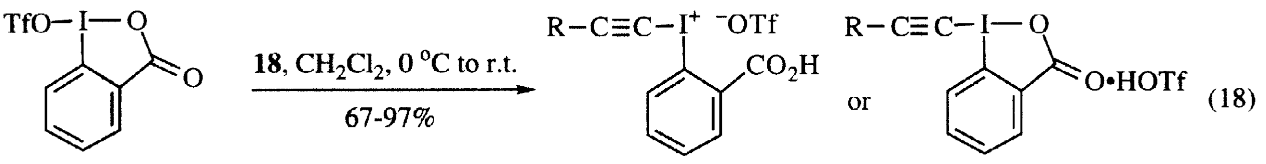
(17)

33: 2X = O
34: X = CF_3

R = *t*-Bu, $SiMe_3$, Si(*i*-Pr)$_3$, Ph, 1-cyclohexenyl

5: 2X = O
35: X = CF_3

Carrying out this reaction in the absence of pyridine results in the formation of alkynyl triflates **36** (eq. 18).[36-38] In the original papers,[36-38] the acyclic structure **36a** was assigned for these compounds. However, according to our recent unpublished X-ray data, the benziodoxolone structure **36b** with a molecule of triflic acid coordinated by the carbonyl oxygen, is more appropriate for these products.[39]

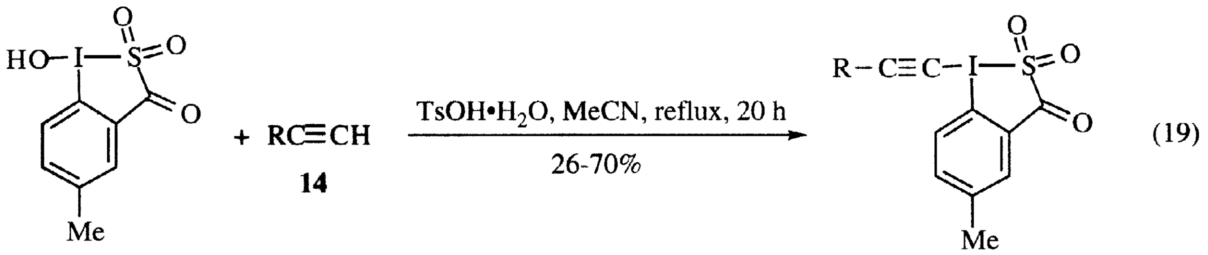


(18)

33 **36a** **36b**

R = Me_3Si, *n*-Bu, *t*-Bu, *n*-C_6H_{13}, *n*-C_8H_{17}, *n*-C_9H_{19}, Ph

Interaction of terminal alkynes **14** with benziodoxathiolone **13** in the presence of toluenesulfonic acid gives heterocyclic alkynyliodonium salts **6** in moderate yields (eq. 19).[40]



(19)

13 **6**

R = *n*-Pr, *n*-Bu, *i*-Bu, *s*-Bu, *t*-Bu, *n*-C_5H_{11}, *n*-C_6H_{13}, *cyclo*-C_6H_{11}, Ph

5. *Properties and Structure of Alkynyliodonium Salts*

Most of the known alkynyl(aryl)iodonium salts are prepared as white microcrystalline products that are insoluble in water and nonpolar organic solvents and moderately soluble in acetonitrile and other polar organic solvents. Their thermal stability varies over a broad range depending on the nature of the counterion and the substituent on the acetylenic β-carbon. The most stable species are heterocyclic alkynylbenziodoxoles **5**, **35** and alkynylbenziodoxathiolones **6**; these compounds generally decompose in the range of 160-200°C and, in our experience, can be stored for extended periods of time even at room temperature. Noncyclic alkynyl(aryl)iodonium triflates and tosylates bearing an aryl or unsubstituted alkyl group at the acetylenic β-carbon, as well as the bis-iodonium acetylene **24**, the unconjugated bis(alkynyliodonium) salts **27**, and the parent ethynyl(phenyl)iodonium triflate, in general have a decomposition point in the range of 120-140 °C and can be stored for several months in a refrigerator. Most of the functionalized iodonium alkynyliodonium triflates **22** have low thermal stability, while diynyliodonium triflates **25** and **29** are unstable and should be handled only at low temperature.

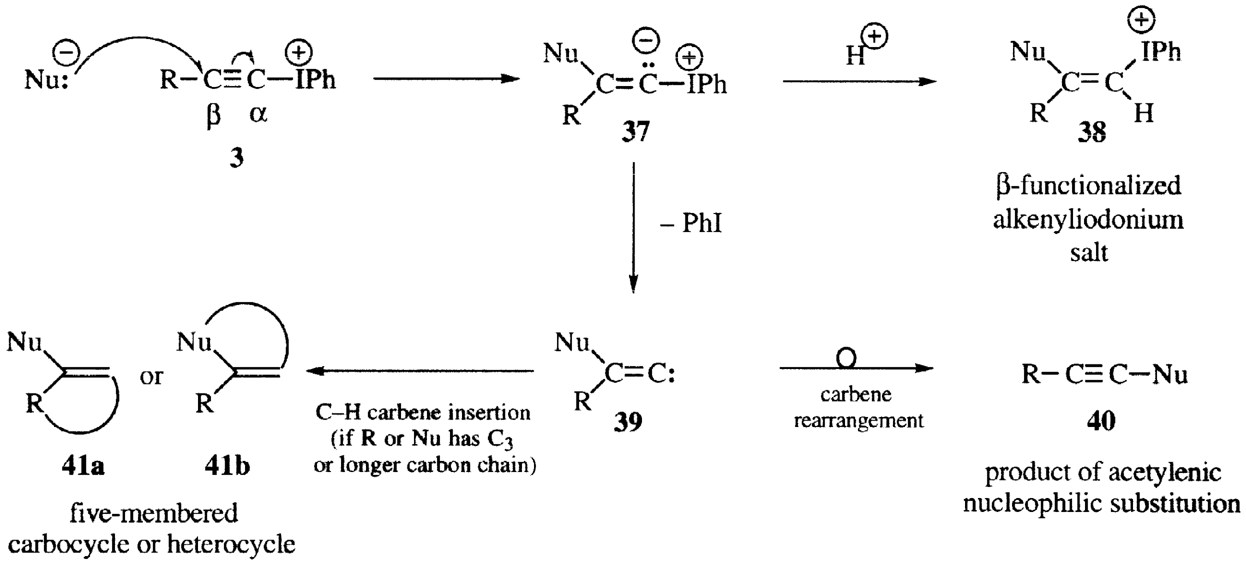
Alkynyliodonium salts can be conveniently identified by IR and NMR spectral data. In the infrared spectrum, the most characteristic absorption is the triple bond band between 2120 and 2190 cm^{-1}. Likewise, in the ^{13}C NMR spectrum, the most distinctive signals are the acetylenic α- and β-carbons, with the former generally between 10 and 40 ppm and the latter at 110-120 ppm.

Single-crystal X-ray structural data for six alkynyliodonium compounds have been reported: four alkynyl(phenyl)iodonium salts including the parent ethynyl(phenyl)iodonium and the cyanoethynyl(phenyl)iodonium triflates,[14,21a,27a,41] bis(alkynyl)iodonium triflate **1** (R = i-Pr_3Si),[7a] and alkynylbenziodoxolone **5**[34] (R = cyclohexyl). The data are all consistent with the pseudo-trigonal bipyramidal, or T-shaped geometry, of iodonium species. In all known cases, the aryl group occupies an equatorial position whereas the alkynyl moiety and the counter ion occupy apical positions. The alkynyl-iodine bond length is 2.0 ± 0.03 Å. The I-O distances vary from 2.34 to 2.70 Å. The C_{sp}-I-O bond angles vary from 166° to 172° and the C_{sp^2}-I-C_{sp} bond angles are between 90° and 95°.

C. APPLICATION OF ALKYNYLIODONIUM SALTS IN ORGANIC SYNTHESIS

1. *General Patterns of Reactivity*

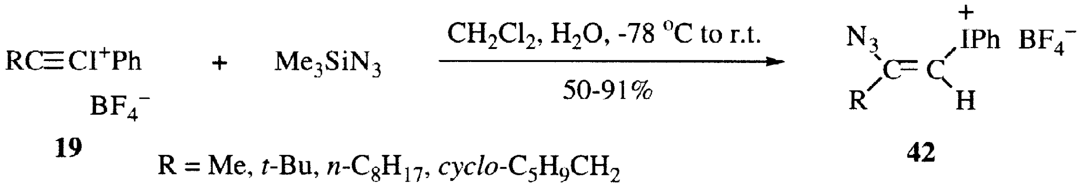
Alkynyliodonium salts are highly reactive in Michael-type conjugate addition reactions as well as Diels-Alder and other cycloadditions because of the strong electron-withdrawing properties of the iodonium group. The inductive electron withdrawing ability of the phenyliodonium group PhI^+, as measured by the Taft inductive parameter, is σ_I=1.24 (σ_I=0.39 for iodine).[42] Alkynyliodonium salts serve as electrophilic acetylene equivalents in reactions with a wide variety of nucleophiles, as well as excellent cycloaddition partners in Diels-Alder and 1,3-dipolar cycloaddition processes. General pathways of reactivity of alkynyl(phenyl)iodonium salts with nucleophilic reagents are summarized in Scheme 1. All available evidence indicates that the initial step in this reaction is a conjugate addition of the nucleophile to the electron-deficient β-acetylenic carbon of **3** to form the iodonium ylide **37**. In the presence of a proton source, this ylide intermediate can be protonated to afford a stable alkenyliodonium salt **38** as the final product. An alternative pathway includes the loss of iodobenzene, which was shown to be an excellent leaving group, 10^6 better than triflate according to recent kinetic data.[43] The loss of iodobenzene leads to the alkylidene carbene **39** as the next intermediate.[44] If either of the substituents R or Nu in **39** is a group or atom with a high migratory aptitude, the carbene undergoes rearrangement to the alkyne **40**. The final result of this process is a nucleophilic acetylenic substitution of iodobenzene *via* an addition-elimination-rearrangement pathway, as outlined in Scheme 1. Alternatively, if both of the substituents R or Nu in **39** have poor migratory aptitude, the carbene inserts into any available C-H bond at C5 to form a cyclic product **41**. The exact distribution of products **40** and **41** (Scheme 1) depends both on the specific reaction conditions and the nucleophile employed. In general, only "soft" nucleophiles react well with alkynyliodonium salts **3**; "hard" nucleophiles such as simple enolates, alkoxides, alkyllithiums, etc., give only decomposition products.



Scheme 1. Mechanism of Reaction of Alkynyliodonium Salts with Nucleophiles

2. *Preparation of Alkenyliodonium Salts by Conjugate Addition to Alkynyliodonium Salts*

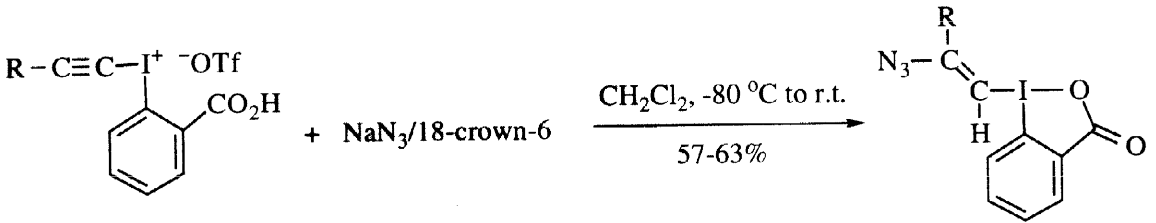
The reaction of alkynyliodonium salts **3** with nucleophilic species in protic solvents provides a convenient and selective approach to various β-functionalized alkenyliodonium salts **38** as shown in Scheme 1. The reaction of alkynyliodonium tetrafluoroborates **19** with trimethylsilyl azide in the presence of water leads to the stereoselective formation of (Z)-(β-azidovinyl)iodonium salts **42** (eq. 20).[45] Likewise, the treatment of alkynyliodonium tosylates with sodium azide in the presence of methanol affords the appropriate (Z)-β-azido alkenyliodonium tosylates in a relatively low yield.[46]



$$\mathrm{RC{\equiv}CI^+Ph\ BF_4^-}\ (\mathbf{19}) + \mathrm{Me_3SiN_3} \xrightarrow[50\text{-}91\%]{\mathrm{CH_2Cl_2,\ H_2O,\ -78\ ^{\circ}C\ to\ r.t.}} (Z)\text{-}\mathrm{N_3(R)C{=}CH\,I^+Ph\ BF_4^-}\ (\mathbf{42}) \qquad (20)$$

R = Me, t-Bu, n-C_8H_{17}, $cyclo$-$C_5H_9CH_2$

A similar procedure was employed in a recent synthesis of (E)-(β-azidovinyl)benziodoxolones **43** (eq. 21).[38] The unusual *syn*-stereochemistry of the addition in this case was explained by intramolecular proton transfer and the successive cyclization controlled by the *ortho*-carboxy group.

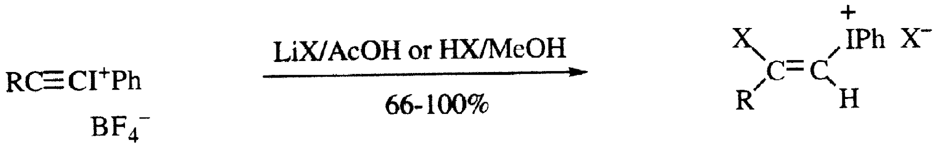


(21)

36 **43**

R = n-C_4H_9, n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$

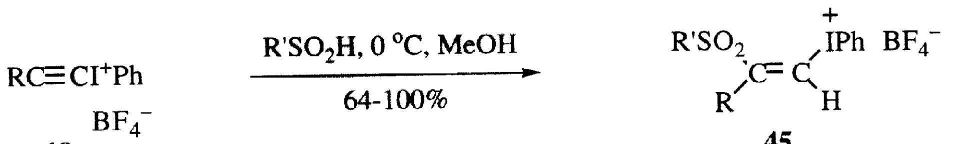
Various (Z)-(β-halovinyl)iodonium salts **44** are produced stereoselectively in the reaction of alkynyliodonium tetrafluoroborates **19** with halide anions under acidic conditions (eq. 22).[47,48] Fluoride ion does not react with **19** under these conditions, while addition of iodide anion results in a complex mixture of products presumably due to the facile decomposition of the initial addition product.[47] (Z)-(β-Halovinyl)iodonium salts **44** are useful precursors to α-haloalkylidenecarbenes.[48] A similar conjugate addition of sulfinic acids to **19** in methanol results in a stereoselective formation (Z)-(β-sulfonylvinyl)iodonium salts **45** (eq. 23).[49,50]



(22)

19 **44**

R = $PhCH_2$, $PhCH_2CH_2$, t-Bu, n-C_8H_{17}, *cyclo*-$C_5H_9CH_2$
X = Cl, Br

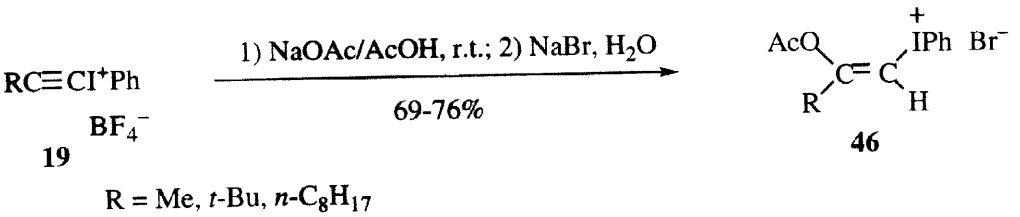


(23)

19 **45**

R = Me, $Ph(CH_2)_3$, n-C_8H_{17}, $HO(CH_2)_2$, *cyclo*-$C_5H_9CH_2$, *cyclo*-$C_6H_{11}(CH_2)_2$
R' = Ph, p-$NO_2C_6H_4$, p-$MeOC_6H_4$, n-Bu

Recently, a similar approach was employed in the synthesis of (Z)-(β-acetoxyvinyl)phenyliodonium bromides **46** (eq. 24).[51] In this reaction, sodium acetate in acetic acid was used as the nucleophilic reagent in the conjugate addition step and the final product **46** was isolated after anion exchange with sodium bromide. The yield of product **46** in this reaction is highly sensitive to the amounts of sodium acetate; the best yields are observed in the presence of 0.1 equivalent of sodium acetate, while larger amounts of the additive lead to a significant decrease in the yields of product **46**.[51]

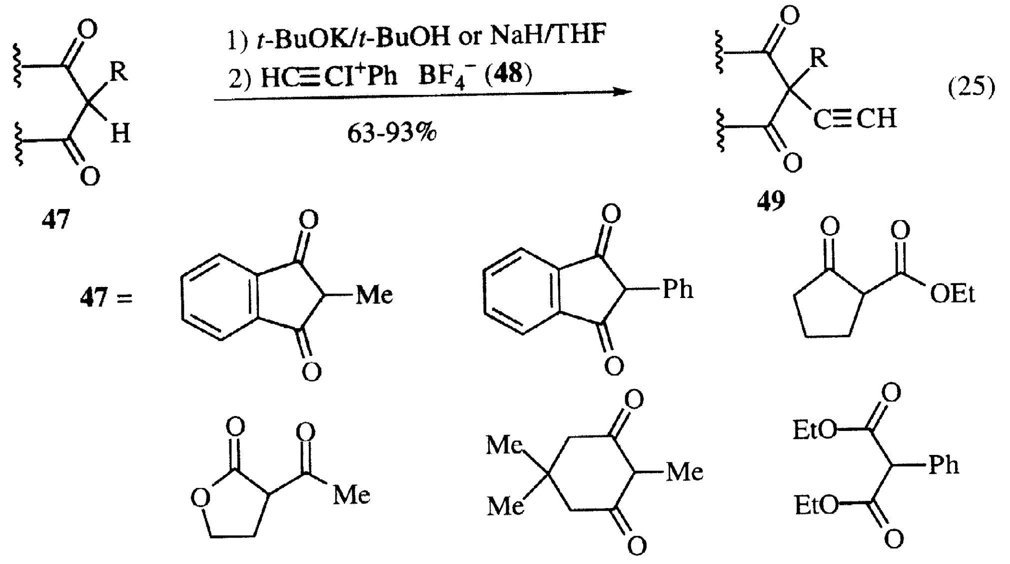


(24)

3. *Preparation of Functionalized Acetylenes by Acetylenic Nucleophilic Substitution of Alkynyliodonium Salts*

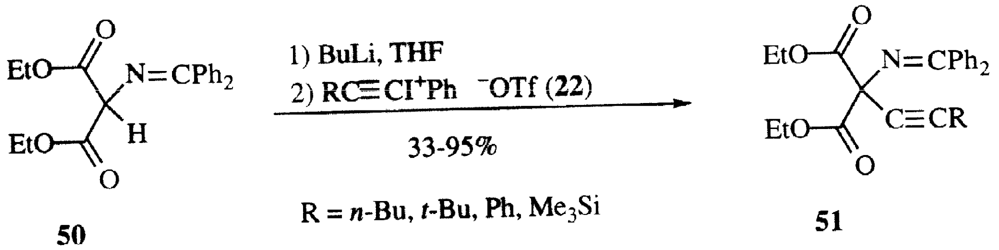
The reaction of alkynyliodonium salts **3** with nucleophilic species under aprotic conditions can afford a product of nucleophilic substitution **40** or a cyclic product **41** (Scheme 1) depending on the β-substituent (R) in the iodonium salt, specific reaction conditions, and the nucleophile employed. In general, the predominant, high yield formation of functionalized acetylenes **40** is observed in the reactions of iodonium salts **3** (R = H, Me, Et, TMS, or any other group in which 1,5-carbene insertion is impossible) with various "soft" nucleophiles.

Reaction of Alkynyliodonium Salts with Carbon Nucleophiles. The parent ethynyliodonium tetrafluoroborate **48** reacts with diverse enolates of β-dicarbonyl compounds to give the respective alkynylated products **49** in a high yield (eq. 25).[19a] The anion of nitrocyclohexane can also be ethynylated under these conditions.[19a] A similar alkynylation of 2-methyl-1,3-cyclopentanedione by ethynyliodonium salt **48** was applied in the key step of the synthesis of chiral methylene lactones.[19b]



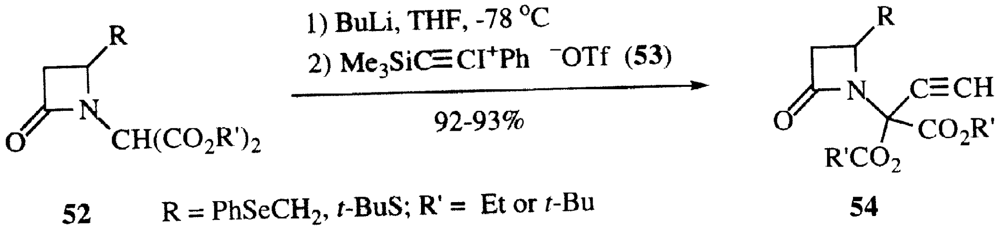
(25)

Likewise, the reaction of the lithium enolate of aminomalonate **50** with several alkynyliodonium triflates **22** affords alkynylmalonates **51** in good yields (eq. 26).[21b] The best yields in this reaction are observed when a freshly prepared solution of the lithium enolate in THF is added to a stirred cold solution of the iodonium salt. The use of potassium enolate instead of lithium, or addition of the reagents in a different order, results in lower yields of products **51**.



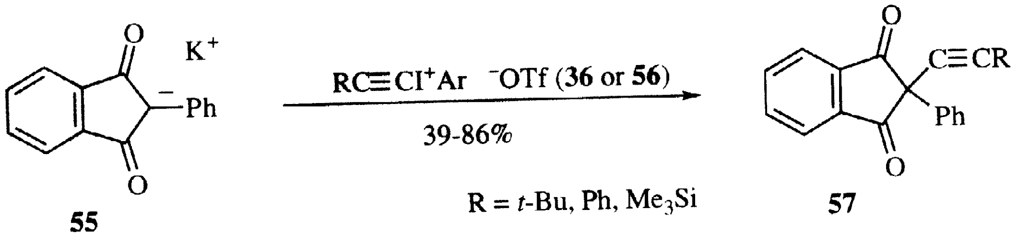
(26)

Under similar conditions, (2-oxoazetidinyl)malonates **52** can be alkylnylated by (trimethylsilyl)ethynyl iodonium triflate **53** (eq. 27). In contrast to the previous reaction (eq. 26), this alkynylation directly affords the desilylated terminal alkynes **54** as the final isolated products.[52]



(27)

The reaction of the enolate anion of 2-phenyl-1,3-indandione **55** with alkynyl(aryl)iodonium triflates **36** or **56** gives the appropriate 2-alkynyl indandione **57** (eq. 28).[37,53a] Likewise, alkynyliodonium tosylate **15** can be used for the alkynylation of the cyclic malonate **58** (eq. 29).[53b]



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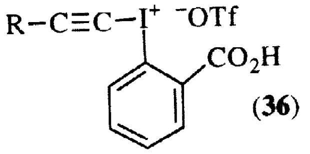
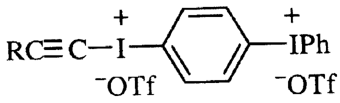
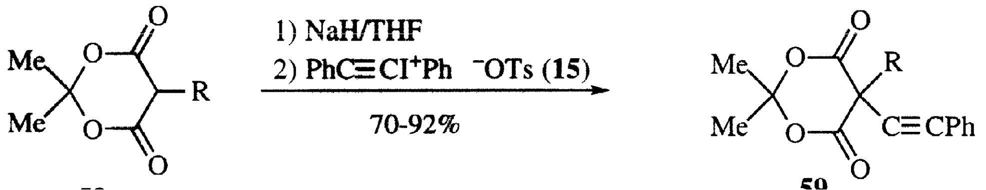


(**36**)



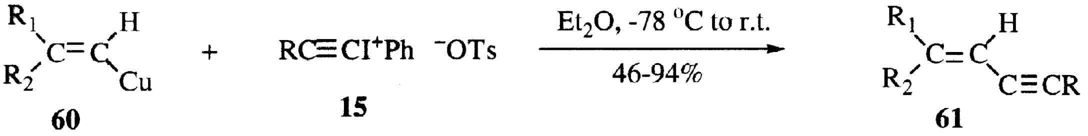
(**56**)



58 **59** (29)

R = $PhCH_2$, $PhC{=}CHCH_2$, 4-$ClC_6H_4CH_2$, 4-$MeC_6H_4CH_2$, 3-furylmethyl, Me_2CH, $Me_2CHCH_2CH_2$

Direct coupling of alkynyliodonium tosylates **15** with vinylcopper reagents **60** affords 1,3-enynes **61** (eq. 30) in good isolated yields.[54,55] This reaction is highly stereoselective and proceeds with retention of the alkene geometry. It is assumed that this reaction proceeds through an oxidative addition of the alkynyl species to give a Cu(III) intermediate, followed by reductive elimination and coupling.[54,55]



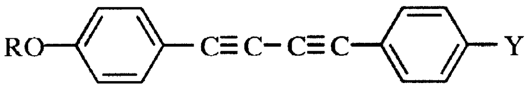
60 **15** **61** (30)

R = *t*-Bu, *n*-Bu, Ph; R_1 and R_2 = Me, Et, *n*-Pr, *n*-Bu, Ph

A similar coupling of alkynyliodonium tosylates **15** with dialkynylcuprates **62** leads to conjugated diynes **63** (eq. 31).[56] This method can be used for the preparation of unsymmetrical diynes in moderate yield. Recently, this coupling was employed in the synthesis of various liquid-crystalline diaryldiacetylenes **64**.[15,16]

$$\underset{\mathbf{62}}{(R'C{\equiv}C)_2Cu(CN)Li_2} + \underset{\mathbf{15}}{RC{\equiv}CI^+Ph\ ^-OTs} \xrightarrow[65\text{-}75\%]{THF,\ -70\ ^\circ C\ to\ r.t.} \underset{\mathbf{63}}{R'C{\equiv}C{-}C{\equiv}CR} \qquad (31)$$

R = *t*-Bu, *n*-Bu, *n*-C_6H_{13}, Ph, *p*-$MeOC_6H_4$; R' = *n*-Pr, *n*-Bu, Ph, *p*-$MeOC_6H_4$



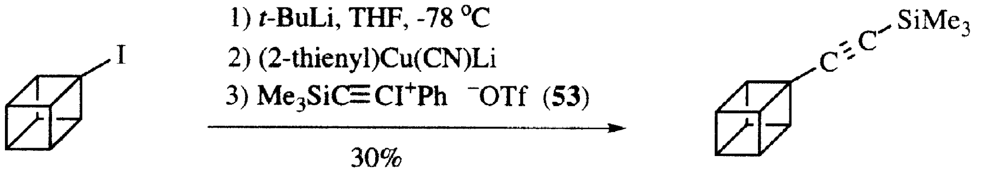
64

R = *n*-C_8H_{17}, *n*-$C_{10}H_{21}$, *n*-$C_{12}H_{25}$, *n*-$C_{14}H_{29}$, (S)-$C_2H_5CH(CH_3)CH_2$
Y = NO_2, CF_3, CN, CH_3, etc.

Likewise, alkynyliodonium tosylates can be coupled with dialkyl- and diphenyl cuprates **65** to afford the appropriate alkyl- and phenyl-substituted alkynes **66** (eq. 32).[56a] An interesting recent example of this reaction involves the coupling of alkynyliodonium salt **53** with cubyl cuprate generated *in situ* from iodocubane **67** (eq. 33).[56b]

$$\underset{\mathbf{65}}{R'_2CuLi} + \underset{\mathbf{15}}{RC{\equiv}CI^+Ph\ ^-OTs} \xrightarrow[52\text{-}90\%]{\text{THF, -70 °C to r.t.}} \underset{\mathbf{66}}{R'C{\equiv}CR} \qquad (32)$$

R = t-Bu, n-C_6H_{13}, Ph; R' = Me, n-Bu, Ph



67 **68** (33)

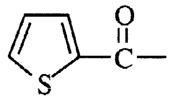
The palladium catalyzed alkoxycarbonylation of alkynyliodonium tosylates **15** in methanol or ethanol in the presence of trialkylamine proceeds under mild conditions to give alkyne carboxylates **69** in good yield (eq. 34).[57]

$$\underset{\mathbf{15}}{RC{\equiv}CI^+Ph\ ^-OTs} + CO\ (1\ atm) + R'OH \xrightarrow[59\text{-}80\%]{\substack{Pd(OAc)_2\ (0.2\ mol.\text{-}equiv.)\\ Bu_3N\ or\ Et_3N,\ r.t.}} \underset{\mathbf{69}}{R'C{\equiv}CCO_2R'} \qquad (34)$$

R = n-Bu, Ph, p-$MeOC_6H_4$; R' = Me, Et

Reaction of Alkynyliodonium Salts with Nitrogen Nucleophiles. The only example of nucleophilic acetylenic substitution in alkynyliodonium salts with a nitrogen nucleophile is represented by the reaction with lithium diphenylamine **70** (eq. 35).[58] Various push-pull ynamine products **71** can be prepared by this method from β-functionalized alkynyliodonium triflates **22** in reasonable isolated yields.

$$\underset{\mathbf{22}}{RC{\equiv}CI^+Ph\ ^-OTf} + \underset{\mathbf{70}}{LiNPh_2} \xrightarrow[43\text{-}66\%]{Et_2O,\ -78\ °C\ to\ r.t.} \underset{\mathbf{71}}{RC{\equiv}CNPh_2} \qquad (35)$$

R = Me_3Si, Ts, t-BuC(O), PhC(O), 

Reaction of Alkynyliodonium Salts with Oxygen Nucleophiles. Reactions of a wide range of oxygen nucleophiles with alkynyliodonium salts have been reported. In general, both alkoxides RO^- and siloxides R_3SiO^- give only decomposition products rather than the desired alkoxy- and siloxyacetylenes. Bisiodonium ethyne **24** reacts with two equivalents of lithium phenoxide to give diphenoxyethyne **72** in moderate yield (eq. 36).[23b]

$$\underset{\mathbf{24}}{\overset{+}{Ph}\overset{}{I}C{\equiv}C\overset{+}{I}Ph\ 2\overset{-}{O}Tf} + 2PhOLi \xrightarrow[57\%]{MeCN,\ -35\ ^{\circ}C\ to\ r.t.} \underset{\mathbf{72}}{PhOC{\equiv}COPh} \qquad (36)$$

The softer sulfonate, carboxylate, and phosphate anions all readily react with alkynyliodonium tosylates to give hitherto unknown alkynyl sulfonate, carboxylate and phosphate esters. Reaction of alkynyliodonium salts **73** in dry acetonitrile with catalytic amounts of CuOTf or AgOTs leads to the formation of alkynyl sulfonate esters **74** (eq. 37).[14] A similar reaction of bisalkynyl tosylates **75** results in modest yields of bis-tosylates **76** along with some monotosylates (eq. 38).[59]

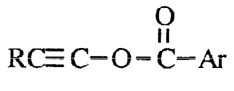
$$\underset{\mathbf{73}}{R'C{\equiv}CI^{+}Ph\ ^{-}OSO_2R} \xrightarrow[37\text{-}88\%]{CuOTf\ (0.1\ mol.\text{-}equiv.),\ MeCN,\ r.t.} \underset{\mathbf{74}}{R'C{\equiv}COSO_2R} \qquad (37)$$

R = Me, Ts; R' = Me, *n*-Bu, *s*-Bu, *t*-Bu, Ph, *p*-Tol

$$\underset{\mathbf{75}}{Ph\overset{+}{I}C{\equiv}C\left(CH_2\right)_nC{\equiv}C\overset{+}{I}Ph\ \ 2^{-}OTs} \xrightarrow[18\text{-}26\%]{5\%\ AgOTf,\ CH_2Cl_2,\ r.t.} \underset{\mathbf{76}}{TsOC{\equiv}C\left(CH_2\right)_nC{\equiv}COTs} \qquad (38)$$

n = 4, 5, 6, 8

Alkynyl carboxylate esters **77** can be obtained in a low yield by passing alkynyl(phenyl)iodonium tosylates **15** through a benzoate-loaded ion exchange column (eq. 39).[60] A more general and efficient approach to alkynyl carboxylates **77** employs direct interaction of bis(acyloxyiodo)benzene with lithium acetylides.[61] Bisalkynyl benzoates **78** can be isolated in 6-15% yields from the reaction of bisalkynyl triflates **27** with sodium benzoates (eq. 40).[59] All alkynyl esters are sensitive to moisture and readily undergo hydration, which explains the low isolated yields.



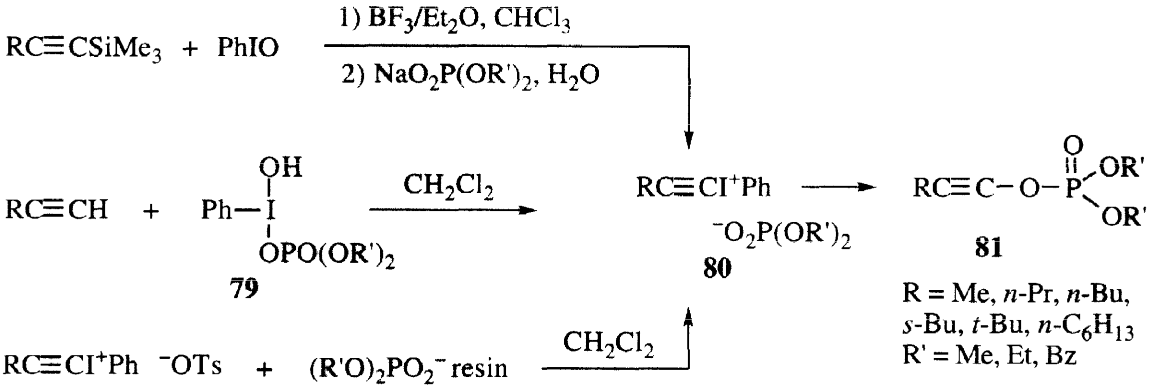
$$\underset{\mathbf{15}}{RC{\equiv}CI^{+}Ph\ ^{-}OTs} + ArCO_2^{-}\ resin \xrightarrow[10\text{-}40\%]{CH_2Cl_2,\ r.t.} \underset{\mathbf{77}}{RC{\equiv}C{-}O{-}\overset{O}{\overset{\|}{C}}{-}Ar} \qquad (39)$$

Ar = Ph, *p*-$MeOC_6H_4$; R = *s*-Bu, *t*-Bu

$$\underset{\mathbf{27}}{Ph\overset{+}{I}C{\equiv}C\left(CH_2\right)_nC{\equiv}C\overset{+}{I}Ph\ \ 2^{-}OTf} \xrightarrow[6\text{-}18\%]{ArCO_2Na,\ CH_2Cl_2,\ -78\ ^{\circ}C\ to\ r.t.} \underset{\mathbf{78}}{ArOCOC{\equiv}C\left(CH_2\right)_nC{\equiv}COCOAr} \qquad (40)$$

n = 6, 8; Ar = Ph, *p*-$NO_2C_6H_4$

Alkynyl phosphate esters **81** are prepared in reasonable isolated yields (20-60%) by either treatment of alkynyl(phenyl)iodonium salts with dialkyl phosphate anion or the reaction of terminal alkynes with [hydroxy(phosphoryloxy)iodo]benzene **79** (Scheme 2).[62] All these methods involve alkynyl(phenyl)iodonium phosphate **80** as an isolable intermediate. Alkynyl esters have potent biological activity: the alkynyl benzoates **77** are protease inhibitors,[63] whereas alkynyl phosphate esters **81** are excellent inhibitors of bacterial phosphotriesterase.[64]



Scheme 2. Preparation of Alkynyl Phosphate Esters

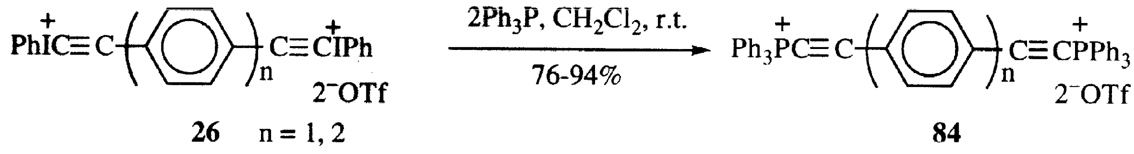
Reaction of Alkynyliodonium Salts with Phosphorus Nucleophiles. Alkynyliodonium triflates **22** react with triphenylphosphine under mild conditions in the dark with the formation of alkynylphosphonium triflates **82** in excellent yields (eq. 41).[65] A similar substitution in alkynyliodonium tetrafluoroborates with triphenylphosphine in tetrahydrofuran requires photochemical activation.[66]

$$\underset{\mathbf{22}}{RC{\equiv}CI^+Ph\ \ ^-OTf} + Ph_3P \xrightarrow[85\text{-}98\%]{CH_2Cl_2,\ -78\ ^\circ C\ \text{to r.t.}} \underset{\mathbf{82}}{RC{\equiv}CP^+Ph_3\ \ ^-OTf} \qquad (41)$$

R = Me, n-Bu, t-Bu, Ph, Me_3Si

Likewise, reaction of bisalkynyl triflates **24**, **26**, and **27** give bisphosphonium diynes **83**, **84**, and **85**, respectively (eqs 42-44).[23,29] Phosphacubane **86** may be alkynylated with alkynyliodonium triflates **22** to give alkynylphosphacubanes **87** (eq. 45).[67]

$$\underset{\mathbf{24}}{Ph\overset{+}{I}C{\equiv}C\overset{+}{I}Ph\ \ 2\overset{-}{O}Tf} \xrightarrow[59\%]{2Ph_3P,\ CCl_4,\ \text{r.t.}} \underset{\mathbf{83}}{Ph_3\overset{+}{P}C{\equiv}C\overset{+}{P}Ph_3\ \ 2^-OTf} \qquad (42)$$



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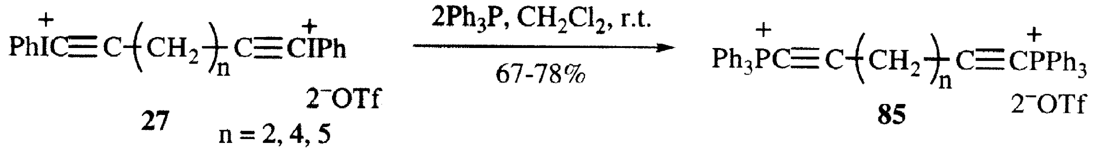

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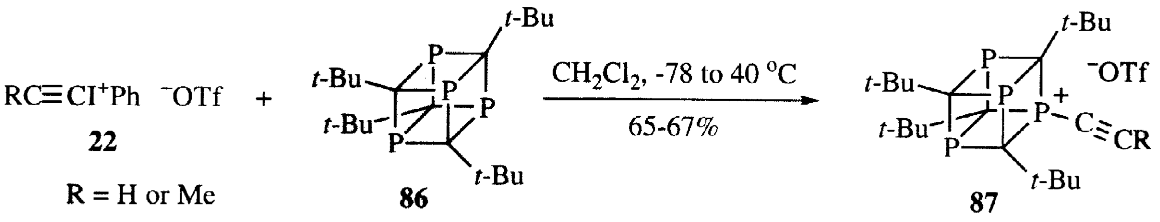
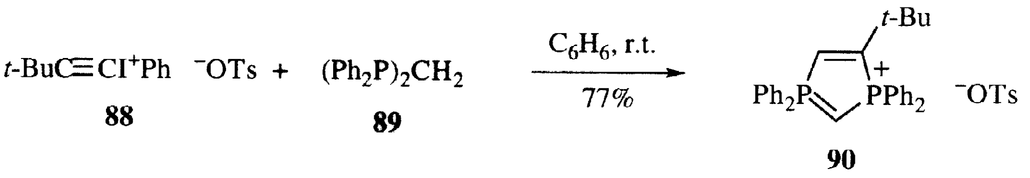


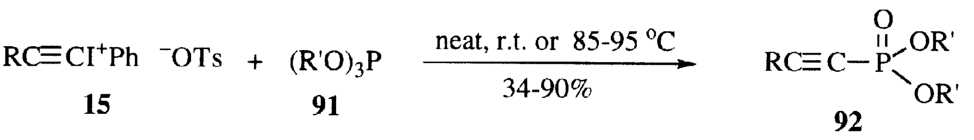
(45)

Reaction of *t*-butylethynyl(phenyl)iodonium tosylate **88** with bis(diphenylphosphino)methane **89** gives the previously unknown diphospholium ion **90** (eq. 46).[68]



(46)

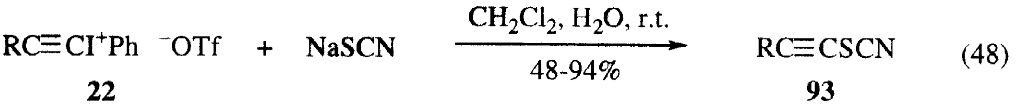
Various alkynyliodonium tosylates react with excess trialkyl phosphites **91** in the absence of solvent to give dialkyl alkynylphosphonates **92** via an Arbuzov type process (eq. 47).[69]



(47)

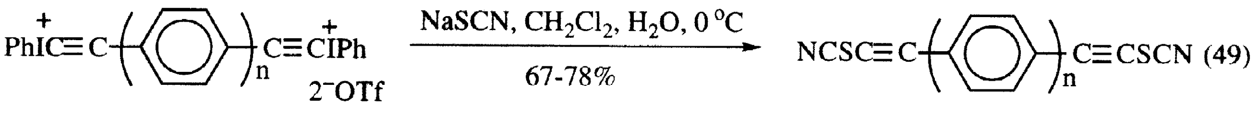
R = *i*-Pr, *s*-Bu, *t*-Bu, cyclopentyl, Ph; R' = Me, Et, *i*-Pr

Reaction of Alkynyliodonium Salts with Sulfur Nucleophiles. Reactions of alkynyliodonium salts with a wide variety of sulfur nucleophiles have been reported in the literature. Alkynyliodonium triflates **22** and bisalkynyl triflates **26** and **27** react with sodium thiocyanate under mild conditions with the formation of alkynyl thiocyanates **93** or bisalkynyl dithiocyanates **94** and **95**, respectively (eqs 48-50).[59,70] Likewise, alkynyl thiocyanates **93** are obtained in high yield upon treatment of alkynyliodonium triflates **56** or **36** with potassium thiocyanate in dimethylformamide (eqs 51 and 52).[37,53a]



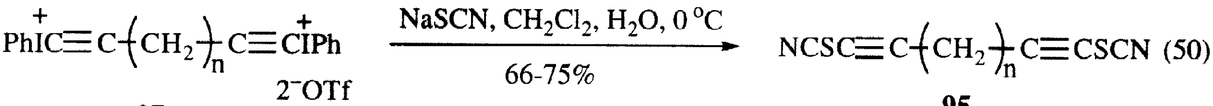
$$\underset{\mathbf{22}}{RC\equiv CI^+Ph\ ^-OTf} + NaSCN \xrightarrow[48\text{-}94\%]{CH_2Cl_2,\ H_2O,\ r.t.} \underset{\mathbf{93}}{RC\equiv CSCN} \quad (48)$$

R = Me, *n*-Bu, *t*-Bu, Ph, Me_3Si, $MeOCH_2$, *t*-BuC(O)



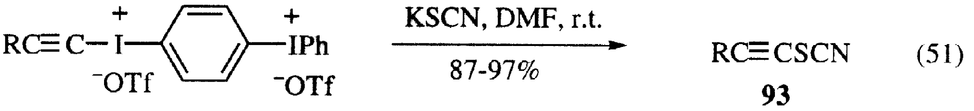
26 n = 1, 2

94

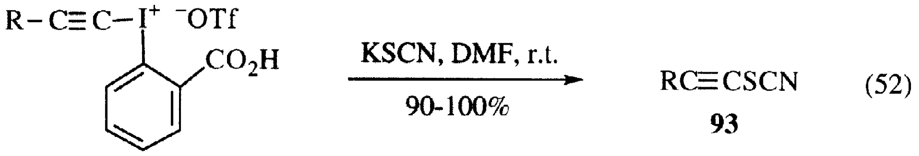


$$\underset{\mathbf{27}}{Ph\overset{+}{I}C\equiv C\!\left(CH_2\right)_n\!C\equiv C\overset{+}{I}Ph\ \ 2^-OTf} \xrightarrow[66\text{-}75\%]{NaSCN,\ CH_2Cl_2,\ H_2O,\ 0\ ^\circ C} \underset{\mathbf{95}}{NCSC\equiv C\!\left(CH_2\right)_n\!C\equiv CSCN} \quad (50)$$

n = 2, 4, 6, 8

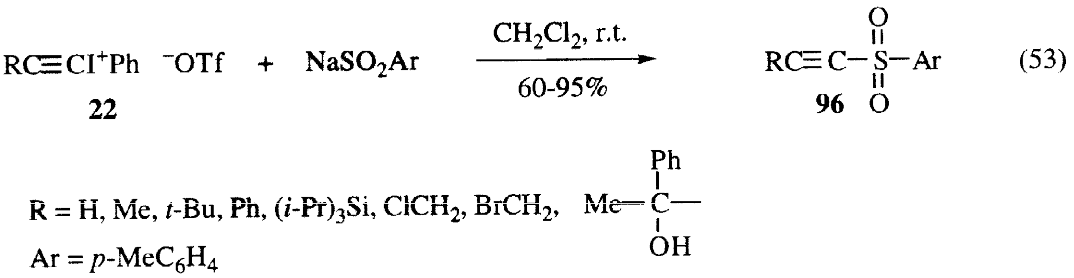


56 R = *n*-Bu, *t*-Bu, *n*-C_6H_{13}, Ph



36 R = *n*-Bu, Ph

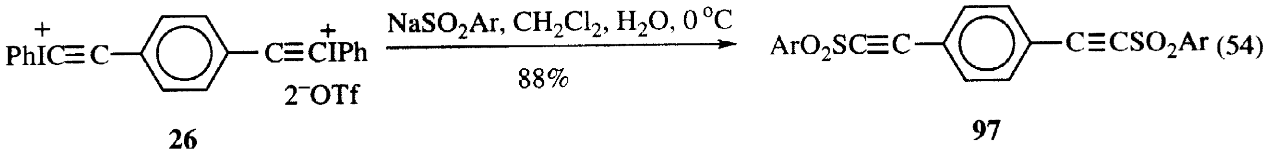
The interaction of mono- or bis(alkynyliodonium) triflates **22** and **26** with sodium arylsulfinate under mild conditions in dichloromethane affords alkynylsulfones **96** and **97**, respectively (eqs 53 and 54).[71] Similarly, alkynyliodonium tosylates **15** react with sodium arylsulfinates in the presence of a phase-transfer catalyst (TEBA) to give alkynyl sulfones **96** in high yield (eq. 55).[72]



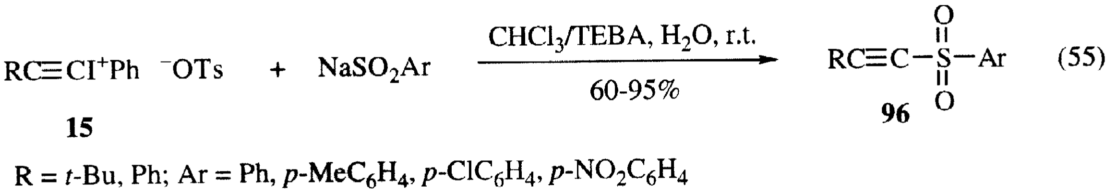
$$\underset{\mathbf{22}}{RC{\equiv}CI^+Ph\ {}^-OTf} + NaSO_2Ar \xrightarrow[60\text{-}95\%]{CH_2Cl_2,\ r.t.} \underset{\mathbf{96}}{RC{\equiv}C{-}S(=O)_2{-}Ar} \quad (53)$$

R = H, Me, *t*-Bu, Ph, (*i*-Pr)$_3$Si, ClCH$_2$, BrCH$_2$, $Me{-}C(Ph)(OH){-}$

Ar = *p*-MeC$_6$H$_4$



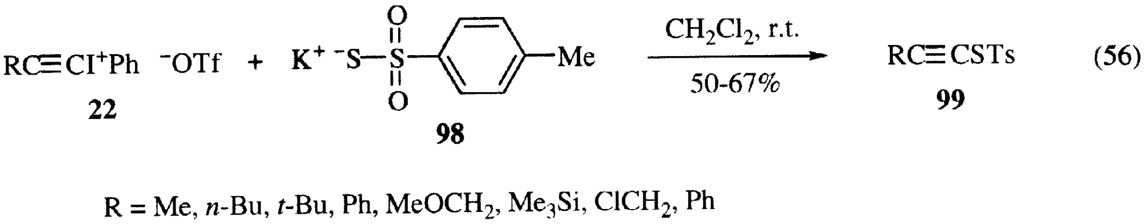
$$\underset{\mathbf{26}}{PhI^+C{\equiv}C{-}C_6H_4{-}C{\equiv}CI^+Ph\ \ 2\,{}^-OTf} \xrightarrow[88\%]{NaSO_2Ar,\ CH_2Cl_2,\ H_2O,\ 0\,^\circ C} \underset{\mathbf{97}}{ArO_2SC{\equiv}C{-}C_6H_4{-}C{\equiv}CSO_2Ar} \quad (54)$$



$$\underset{\mathbf{15}}{RC{\equiv}CI^+Ph\ {}^-OTs} + NaSO_2Ar \xrightarrow[60\text{-}95\%]{CHCl_3/TEBA,\ H_2O,\ r.t.} \underset{\mathbf{96}}{RC{\equiv}C{-}S(=O)_2{-}Ar} \quad (55)$$

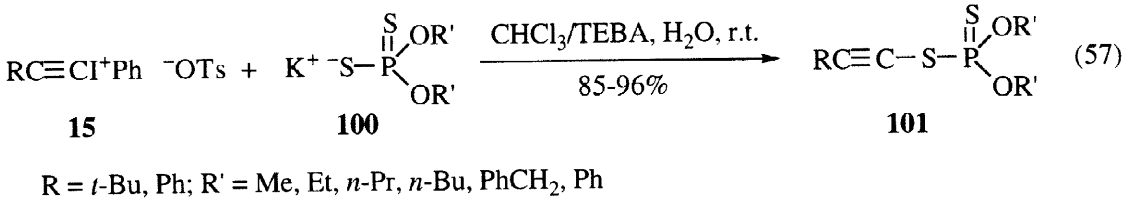
R = *t*-Bu, Ph; Ar = Ph, *p*-MeC$_6$H$_4$, *p*-ClC$_6$H$_4$, *p*-NO$_2$C$_6$H$_4$

The reaction of alkynyliodonium triflates **22** with potassium *p*-toluenethiosulfonate **98** gives the hitherto unknown alkynyl thiotosylate **99** (eq. 56).[73] Likewise, alkynyl phosphorodithioates **101** can be prepared by the interaction of alkynyliodonium tosylates **15** with potassium salts **100** (eq. 57).[74]



$$\underset{\mathbf{22}}{RC{\equiv}CI^+Ph\ {}^-OTf} + \underset{\mathbf{98}}{K^+\,{}^-S{-}S(=O)_2{-}C_6H_4{-}Me} \xrightarrow[50\text{-}67\%]{CH_2Cl_2,\ r.t.} \underset{\mathbf{99}}{RC{\equiv}CSTs} \quad (56)$$

R = Me, *n*-Bu, *t*-Bu, Ph, MeOCH$_2$, Me$_3$Si, ClCH$_2$, Ph



$$\underset{\mathbf{15}}{RC{\equiv}CI^+Ph\ {}^-OTs} + \underset{\mathbf{100}}{K^+\,{}^-S{-}P(=S)(OR')_2} \xrightarrow[85\text{-}96\%]{CHCl_3/TEBA,\ H_2O,\ r.t.} \underset{\mathbf{101}}{RC{\equiv}C{-}S{-}P(=S)(OR')_2} \quad (57)$$

R = *t*-Bu, Ph; R' = Me, Et, *n*-Pr, *n*-Bu, PhCH$_2$, Ph

Reaction of Alkynyliodonium Salts with Selenium and Tellurium Nucleophiles. Acetylenic selenides **102** and tellurides **103** are conveniently prepared by interaction of alkynyliodonium tosylates **15** with sodium selenides or tellurides in DMF (eqs 58 and 59).[75,76]

$$\underset{\mathbf{15}}{\mathrm{RC{\equiv}CI^{+}Ph\ \ ^{-}OTs}} + \mathrm{ArSeNa} \xrightarrow[55\text{-}71\%]{\mathrm{DMF,\ 70\text{-}80\ ^{\circ}C}} \underset{\mathbf{102}}{\mathrm{RC{\equiv}CSeAr}} \tag{58}$$

R = t-Bu, Ph; Ar = Ph, o-MeC_6H_4, p-MeC_6H_4, p-ClC_6H_4

$$\underset{\mathbf{15}}{\mathrm{RC{\equiv}CI^{+}Ph\ \ ^{-}OTs}} + \mathrm{ArTeNa} \xrightarrow[48\text{-}70\%]{\mathrm{DMF,\ 70\text{-}80\ ^{\circ}C}} \underset{\mathbf{103}}{\mathrm{RC{\equiv}CTeAr}} \tag{59}$$

R = t-Bu, Ph; Ar = Ph, p-MeC_6H_4, p-BrC_6H_4, $C_{10}H_8$

Similarly, reactions of β-functionalized alkynyliodonium triflates **22** with PhSeK or PhTeLi (generated *in situ* from black tellurium powder and phenyllithium) afford novel, push-pull alkynyl phenyl selenides **104** and tellurides **105** in good yields (eqs 60 and 61).[77]

$$\underset{\mathbf{22}}{\mathrm{RC{\equiv}CI^{+}Ph\ \ ^{-}OTf}} + \mathrm{PhSeK} \xrightarrow[63\text{-}84\%]{\mathrm{MeCN,\ -42\ ^{\circ}C\ to\ r.t.}} \underset{\mathbf{104}}{\mathrm{RC{\equiv}CSePh}} \tag{60}$$

R = Me_3Si, CN, CO_2Me, COPh, CO(t-Bu)

$$\underset{\mathbf{22}}{\mathrm{RC{\equiv}CI^{+}Ph\ \ ^{-}OTf}} + \mathrm{PhTeLi} \xrightarrow[54\text{-}84\%]{\mathrm{Et_2O/cyclohexane,\ -78\ to\ 0\ ^{\circ}C}} \underset{\mathbf{105}}{\mathrm{RC{\equiv}CTePh}} \tag{61}$$

R = Me_3Si, CN, CO_2Me, COPh, CO(t-Bu)

Reaction of Alkynyliodonium Salts with Triphenylarsine. The reaction of alkynyliodonium tetrafluoroborates **19** with triphenylarsine provides a useful tool for the synthesis of hitherto unknown alkynyl(triphenyl)arsonium tetrafluoroborates **106** in high yields (eq. 62).[78]

$$\underset{\mathbf{19}}{\mathrm{RC{\equiv}CI^{+}Ph\ \ BF_4^{-}}} + \mathrm{Ph_3As} \xrightarrow[77\text{-}97\%]{\mathrm{CH_2Cl_2,\ r.t.}} \underset{\mathbf{106}}{\mathrm{RC{\equiv}CAs^{+}Ph_3\ \ BF_4^{-}}} \tag{62}$$

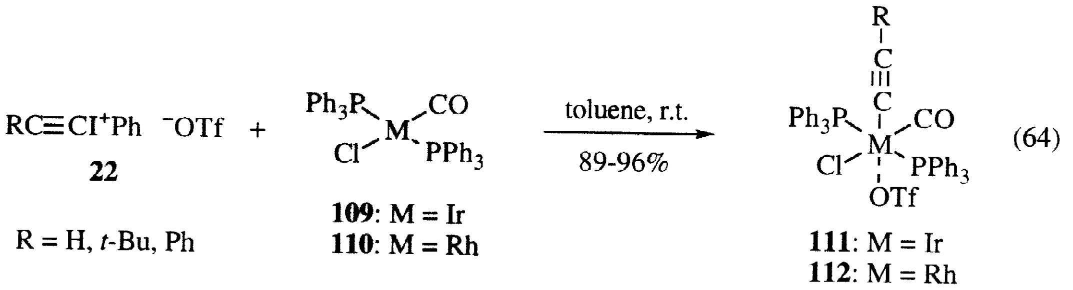
R = H, Me, n-C_8H_{17}, $MeCH_2CH(Me)CH_2$, *cyclo*-$C_5H_9CH_2$, *cyclo*-C_6H_{11}, t-Bu, Me_3Si, Ph

Reaction of Alkynyliodonium Salts with Organometallic Nucleophiles. Reactions of transition metal complexes with alkynyliodonium salts can result in the alkynylation of either a ligand or the metal center. A recent example of ligand alkynylation is represented by the synthesis of novel chromium alkynyl isocyanide complexes **108** from alkynyliodonium salts and cyanide **107** (eq. 63).[79]

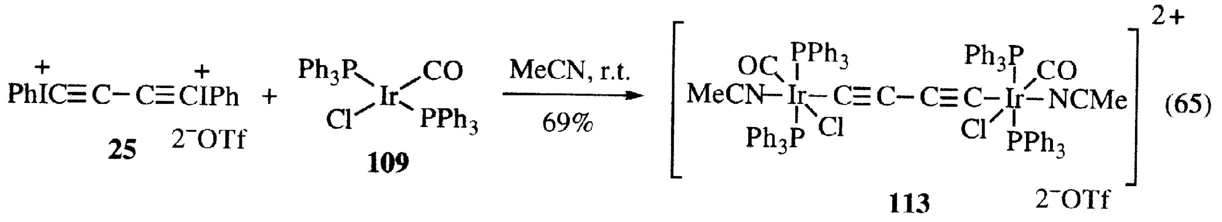
$$\underset{\mathbf{107}}{[\mathrm{Cr(C{\equiv}N)(CO)_5}]^- \ \mathrm{Et_4N^+}} + \underset{\mathbf{3}}{\mathrm{RC{\equiv}CI^+Ph\ X^-}} \xrightarrow[17\text{-}29\%]{\mathrm{CH_2Cl_2},\ \text{reflux}} \underset{\mathbf{108}}{\mathrm{(CO)_5CrC{\equiv}N{-}C{\equiv}CR}} \qquad (63)$$

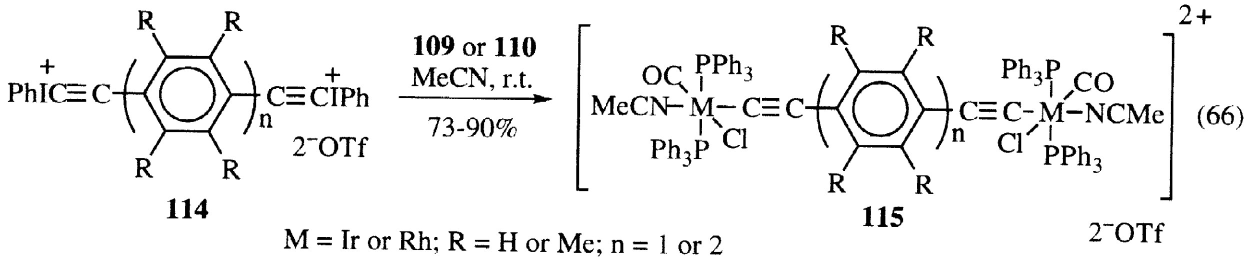
R = H (X = OTf), Me_3Si (X = BF_4), Ph (X = OTs)

Reaction of the square planar Vaska's complex **109** or its rhodium analog **110** with alkynyliodonium triflates **22** results in the hexacoordinate σ-acetylide complexes **111** or **112**, respectively (eq. 64).[80] This alkynylation occurs with retention of configuration at the metal center.

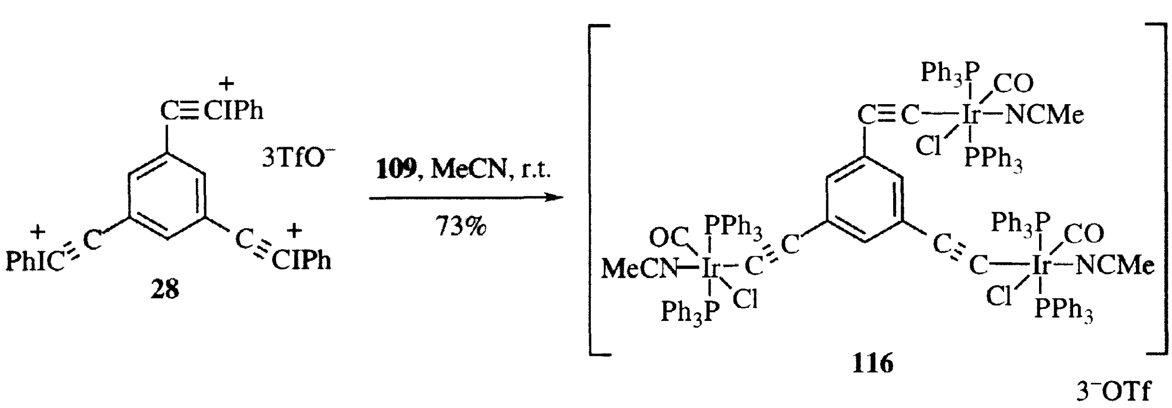


A similar reaction of bis(alkynyliodonium) triflates **25** and **114** and tris(alkynyliodonium) salt **28** leads to the preparation of rigid-rod, di- and trimetallic σ-acetylide complexes **113**, **115**, and **116**, respectively (eqs 65-67).[30] These novel complexes are particularly interesting due to their potential application as advanced materials in the areas of non-linear optics, organic conductors, and liquid crystals.



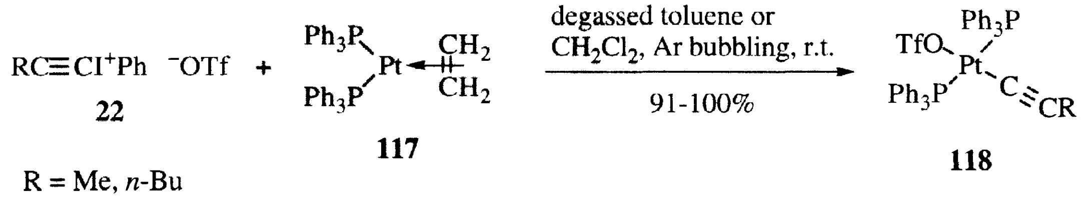


M = Ir or Rh; R = H or Me; n = 1 or 2

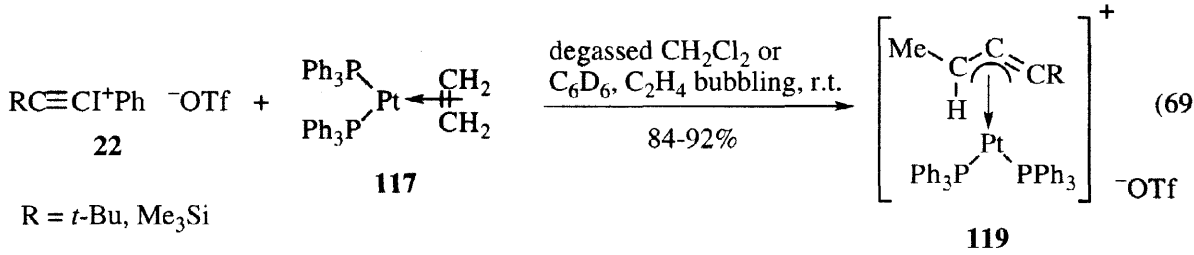


(67)

The interaction of alkynyliodonium triflates **22** with platinum(0) complex **117** may lead to either σ-acetylide platinum(II) complex **118** (eq. 68) or the novel η^3-propargyl/allenyl platinum complex **119** (eq. 69), depending upon both the group R and the exact reaction conditions.[81] Bulky substituents such as *t*-butyl and trimethylsilyl favor formation of complex **119**, whereas smaller substituents such as methyl favor σ-complex **118**.



(68)

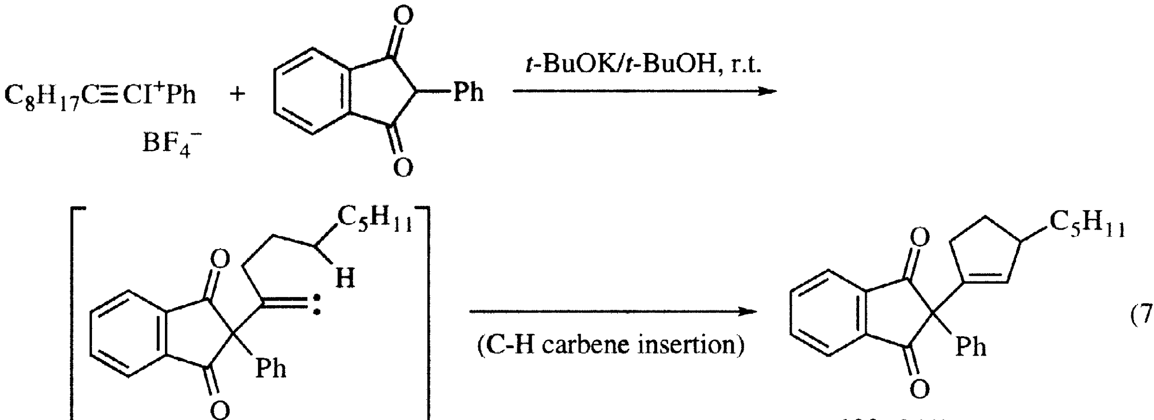


(69)

4. *Preparation of Five-Membered Carbocycles and Heterocycles via 1,5-Carbene Insertion*

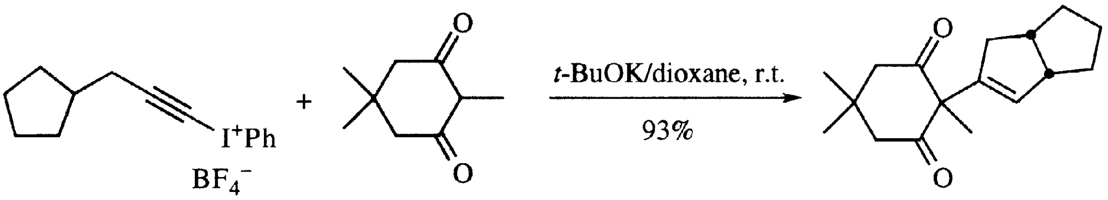
The predominant formation of five-membered carbocycles or heterocycles (**41**, Scheme 1) *via* a sequential conjugate addition-carbene insertion pathway is generally observed in the reactions of the appropriate alkynyliodonium salts **3** (R = long alkyl chain or other group with C-H bond available at C5) with various relatively "hard" nucleophiles. Typical nucleophiles used to initiate these selective cyclizations are enolate, azide, sulfinate, tosylamide, thioamide and some other anions.

Synthesis of Cyclopentenes. Cyclopentenes are commonly formed in the reaction of the appropriate alkynyliodonium salts with enolate anions. Various alkynyliodonium tetrafluoroborates interact with β-dicarbonyl enolates to give products of cyclopentene annulation in 50-90% yield.[44] Several examples of such annulations are shown in eqs 70-72. The carbene cyclization can also occur when the long alkyl chain is part of the enolate nucleophile, as illustrated by the reaction of propynyliodonium salt **122** with β-diketone **123** (eq. 72).[44]



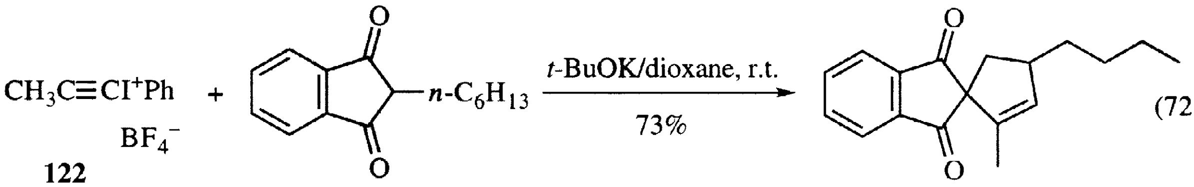
120 (84%)

(70)



121

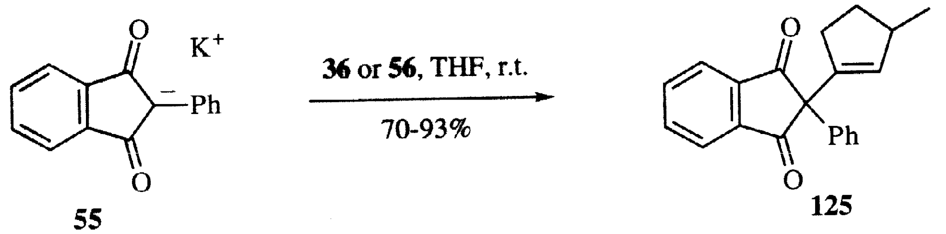
(71)



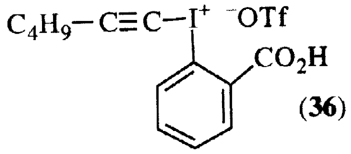
122 **123** **124**

(72)

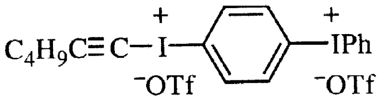
Alkynyliodonium triflates **36** and **56** react with the enolate anion of 2-phenylindan-1,3-dione **55** to afford the cyclopentenyl derivative **125** (eq. 73).[37,53a]



(73)

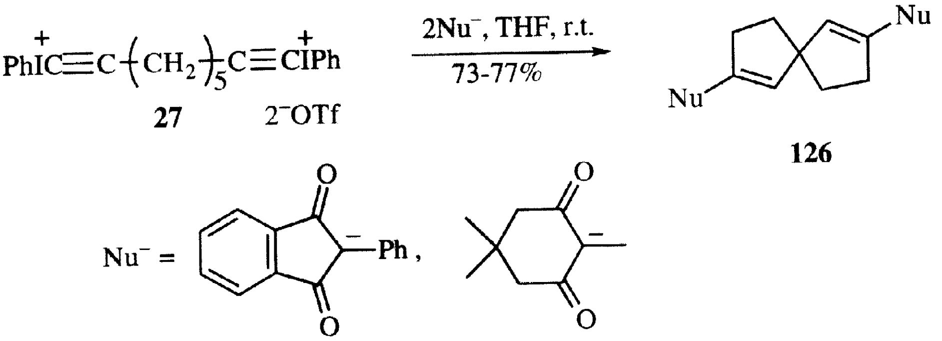


(36)



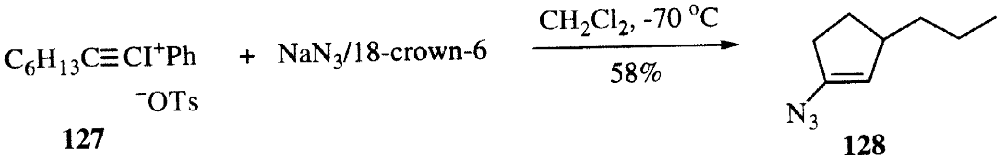
(56)

A similar reaction of bis(alkynyliodonium) triflate **27** gives the corresponding bis-insertion products **126** (eq. 74).[82]



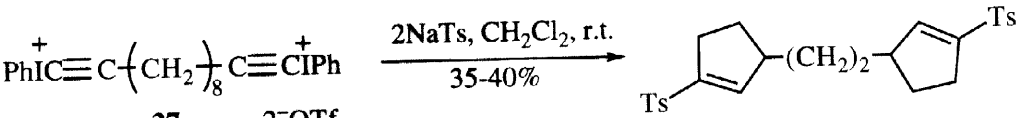
(74)

The cyclopentene annulations can also occur in reactions of alkynyliodonium salts with nitrogen- and sulfur nucleophiles. Specifically, azidocyclopentene **128** is formed upon treatment of octynyliodonium tosylate **127** with sodium azide in dichloromethane (eq. 75).[46]



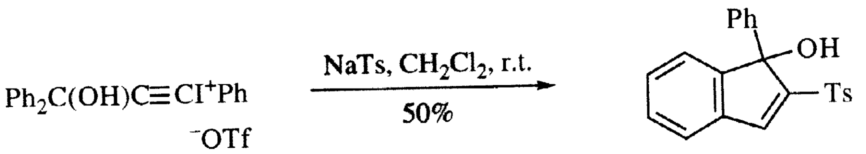
(75)

Sodium toluenesulfinate reacts with bis(alkynyliodonium) triflates **27** to afford the respective products of bis-insertion, for example **129** (eq. 76).[82] The reaction of sodium toluenesulfinate with alkynyliodonium salt **130** results in substituted indene **131** *via* alkylidene carbene aromatic C-H bond insertion (eq. 77).[83]



27 **129**

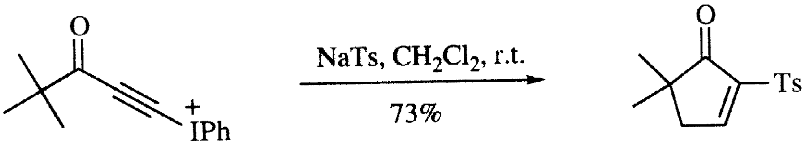
(76)



130 **131**

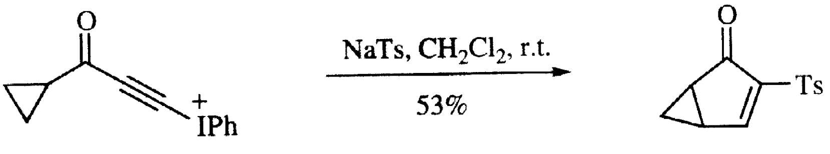
(77)

Synthesis of Cyclopentenones. A variety of substituted 2-cyclopentenones are obtained in good yields by the reaction of sodium toluenesulfinate with β-ketoethynyl(phenyl)iodonium triflates.[28] Several specific examples of this reaction are shown in eqs 78-81. This methodology readily affords not only simple cyclopentenones but also fused bicyclic systems (eqs 79 and 81) and γ-lactams (eqs 80 and 81).[28]



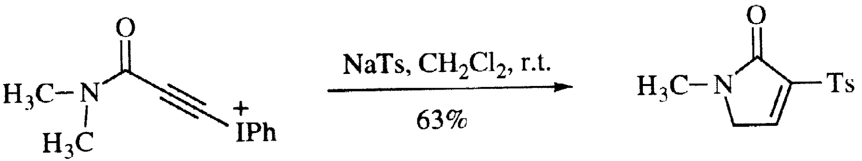
132 **133**

(78)



134 **135**

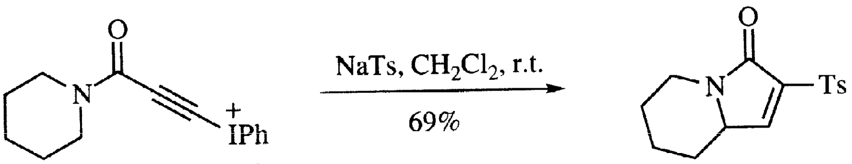
(79)



⁻OTf

136 **137**

(80)

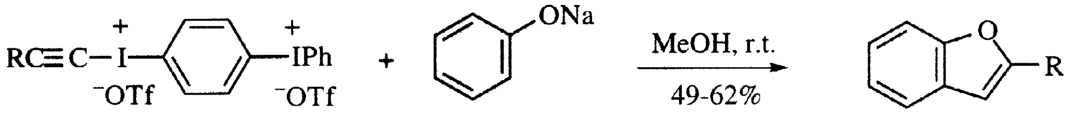


⁻OTf

138 **139**

(81)

Synthesis of Benzofurans. Benzofurans **140** are obtained by the interaction of iodonium salts **56** with sodium phenoxide in methanol (eq. 82).[84] This reaction proceeds *via* a formal intramolecular alkylidene carbene insertion into the *ortho*-CH bond of the phenoxy ring.

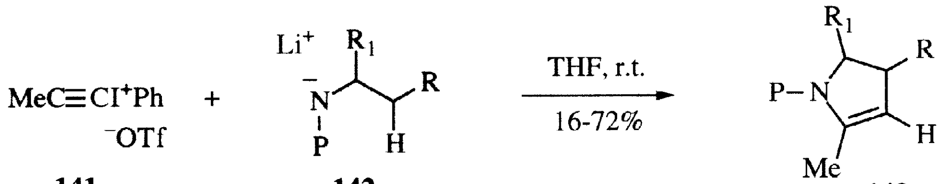


(82)

56 **140**

R = n-Bu, t-Bu, n-C_6H_{13}, n-$C_{10}H_{21}$

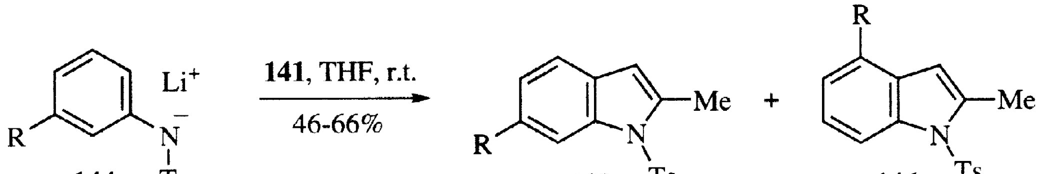
Synthesis of Dihydropyrroles and Indoles. A variety of five-membered nitrogen heterocycles can be prepared efficiently by inter- or intramolecular addition/cyclizations of sulfonamide anions with alkynyliodonium salts. The intermolecular variant employs the combination of the amides **142** (eq. 83) or anilides **144** (eq. 84) with propynyl(phenyl)iodonium triflate **141**.[33,85] The yield of dihydropyrroles **143** is extremely sensitive to the nature of the protective group P (eq. 83); the tosyl group in **142** proved superior to the other carbonyl- or sulfonyl-based species examined in this study.[33] The reaction of propynyl(phenyl)iodonium triflate **141** with anilides **144** results in a non-regioselective formation of indoles **145** and **146** (eq. 84) due to intramolecular alkylidene carbene insertion into the *ortho*-CH bonds.[85]



(83)

141 **142** **143**

P = PhCO, F_3CCO, F_3CSO_2, Ts; R = Ph, Me, OMe; R + R_1 = $(CH_2)_4$

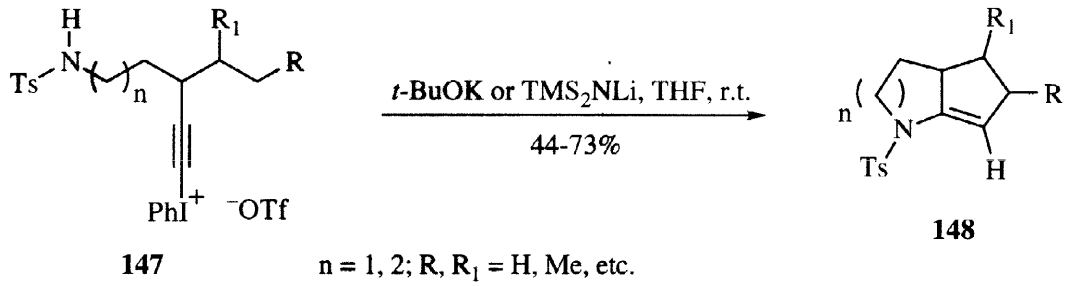


(84)

144 **145** **146**

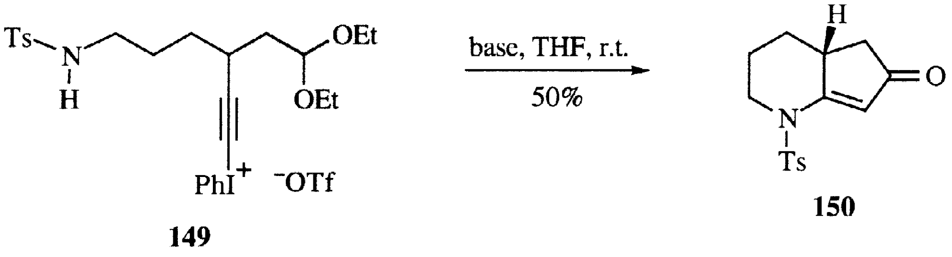
R = H, Me, OMe, CO_2Me, CO_2-t-Bu

The intramolecular variant of this cyclization is achieved by treatment of iodonium salts **147** with a base in THF (eq. 85).[85]

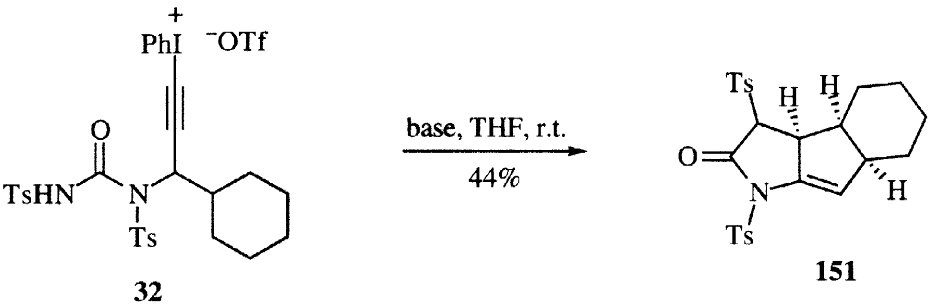


n = 1, 2; R, R$_1$ = H, Me, etc. (85)

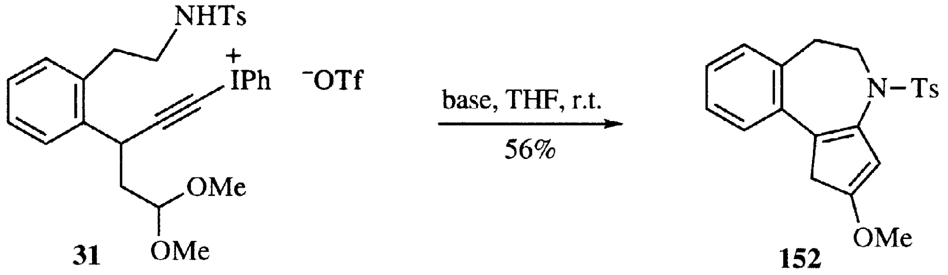
These intramolecular bicyclizations can provide an efficient entry into polycyclic alkaloid skeleta; several specific examples of bicyclizations are shown in eqs 86-88.[32] Alkynyliodonium salts **147**, **149**, **31**, and **32**, key precursors in these reactions, are conveniently prepared from the appropriate alkynylstannanes (see Section B3) and can be used without additional purification.[32,85]



(86)

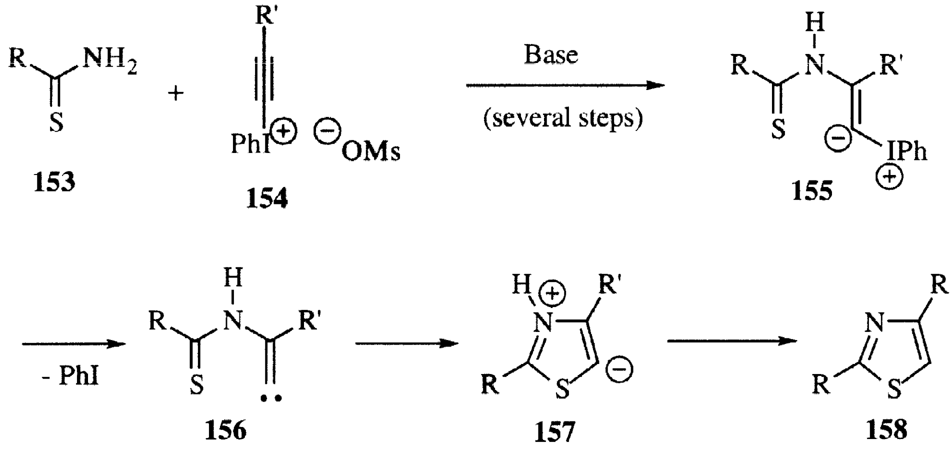


(87)



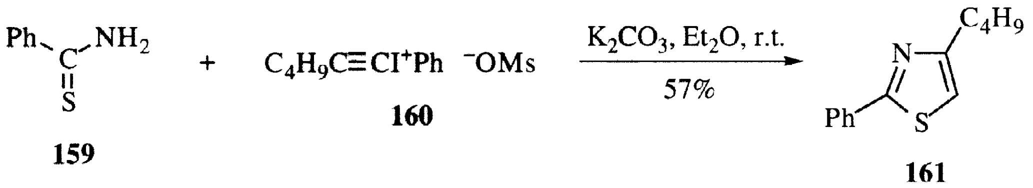
(88)

Synthesis of Thiazoles. Recently, a new synthesis of thiazoles **158** by cyclocondensation of thioamides **153** and alkynyl(aryl)iodonium mesylates **154** was reported.[86] It was postulated that this reaction proceeds *via* the alkylidene carbene **156** as a key intermediate. Cycloaromatization of carbene **156** leads to the observed heterocycles **158** (Scheme 3).



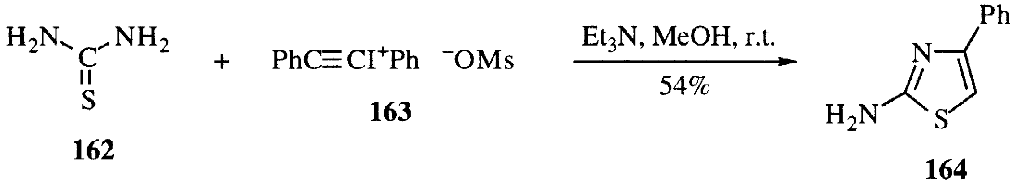
Scheme 3. Preparation of Thiazoles by Cyclocondensation of Thioamides and Alkynyliodonium Mesylates

Several examples of the synthetic application of this cyclization for the preparation of thiazoles are shown in eqs 89-92.[86] In general, a range of solvents and bases can be used in this reaction. Thiazole **161** is formed cleanly after mixing mesylate **160** and thioamide **159** in ether in the presence of solid potassium carbonate for 3 hours as the only significant component in the reaction mixture besides starting materials and iodobenzene (eq. 89).[86]



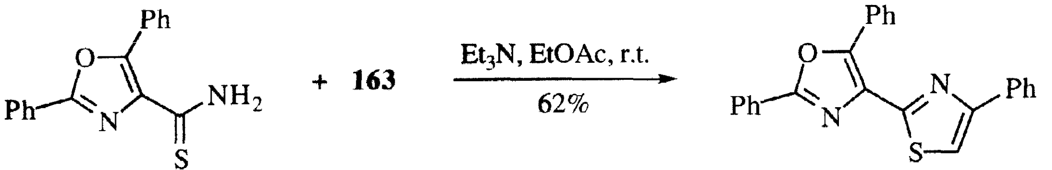
(89)

For the preparation of 2-aminothiazole **164**, thiourea **162** and (phenylethynyl)(phenyl)iodonium mesylates **163** are allowed to react in methanol in the presence of equimolecular amount of triethylamine (eq. 90).[86]



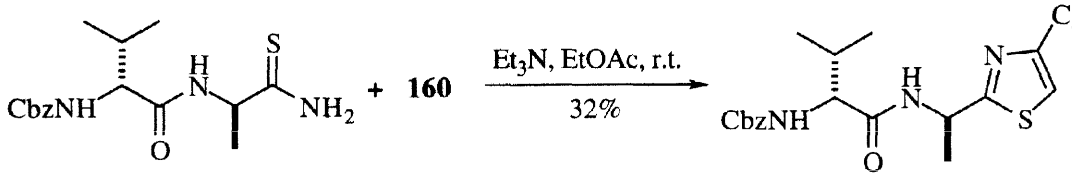
(90)

Synthesis of the biazole **166** is readily accomplished in good yield from thioamide **165** and mesylate **163** in ethyl acetate in the presence of triethylamine (eq. 91).[86] Likewise, the peptidyl thiazole **168** is obtained from *N*-protected valine-alanine thioamide **167** (eq. 92).[86]



165 **166**

(91)

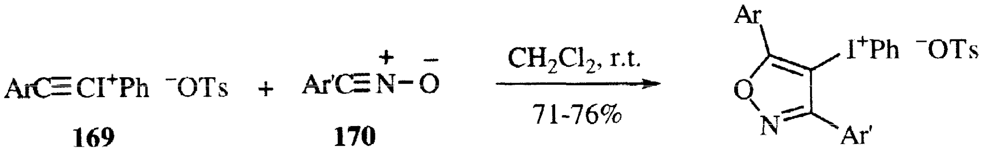


167 Cbz = $-C(O)OCH_2Ph$ **168**

(92)

5. *Cycloaddition Reactions of Alkynyliodonium Salts*

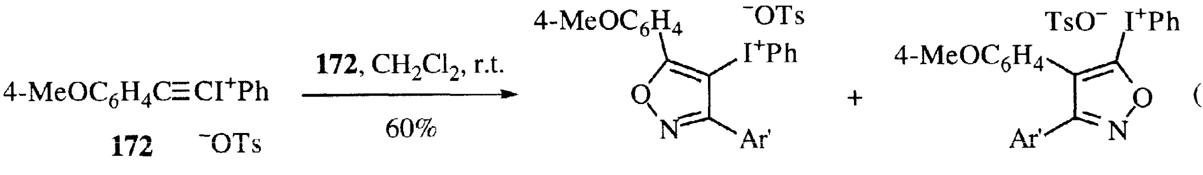
[3+2] Dipolar Cycloadditions. Alkynyliodonium salts represent highly activated, electron-deficient alkynes with a strongly polarized triple bond. Due of the dipolar structure, they can behave as good 1,3-dipolarophiles in various [3+2] cycloaddition reactions. The reaction of (arylethynyl)iodonium tosylates **169** with nitrile oxides **170** affords cycloadducts **171** as sole products in good yield (eq. 93).[87] For (*p*-anisylethynyl)iodonium tosylate **172** this cycloaddition is not regioselective; an inseparable mixture of regioisomers **173** and **174** is obtained in this case (eq. 94).[87]



169 **170** **171**

(93)

Ar = Ph, 2-ClC_6H_4; Ar' = 2,4,6-$Me_3C_6H_2$, 2,6-$Cl_2C_6H_3$

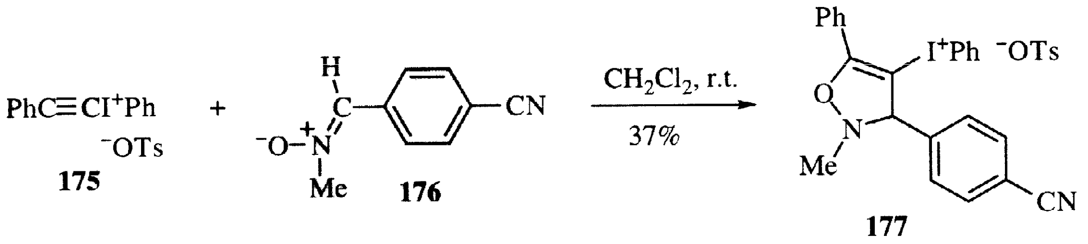


172 **173** 1 : 1 mixture **174**

(94)

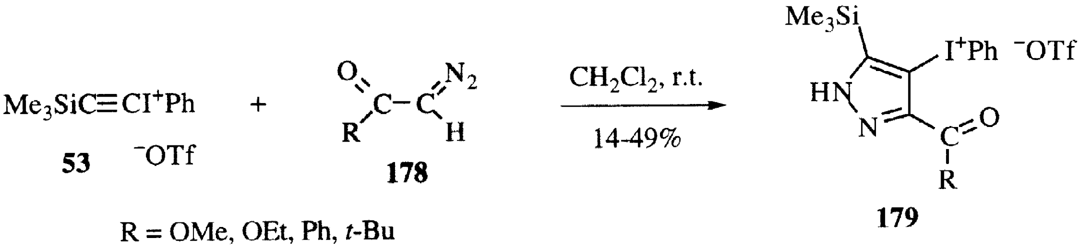
Ar' = 2,4,6-$Me_3C_6H_2$

The nitrone **176** reacts with (phenylethynyl)iodonium tosylate **175** to give cycloaddition product **177** in moderate yield (eq. 95).[87]



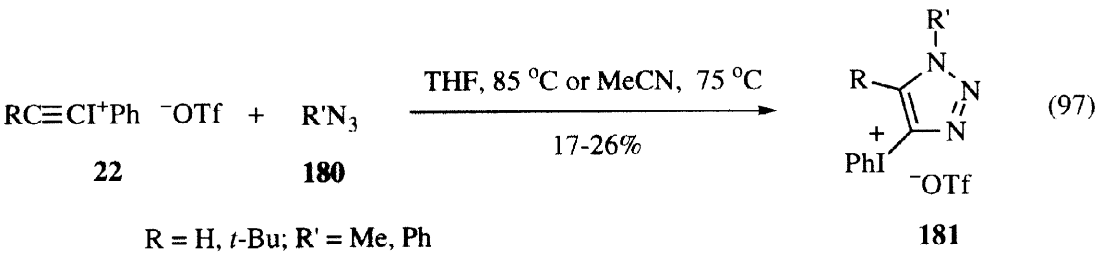
(95)

A similar cycloaddition of (trimethylethynyl)iodonium triflate **53** with diazocarbonyl compounds **178** affords pyrazolyliodonium salts **179** as sole regioisomers (eq. 96).[88] Methyl and phenyl azides (**180**) react with alkynyliodonium triflates **22** upon heating in tetrahydrofuran or acetonitrile to give low yields of triazolyliodonium salts **181** as sole regioisomers (eq. 97).[88]



(96)

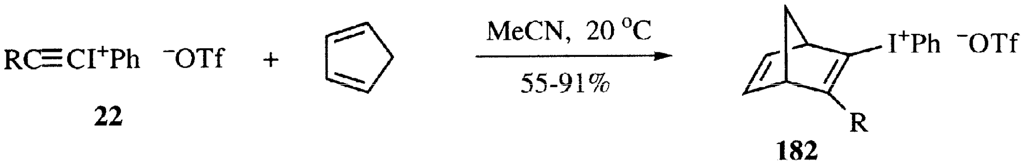
R = OMe, OEt, Ph, *t*-Bu



(97)

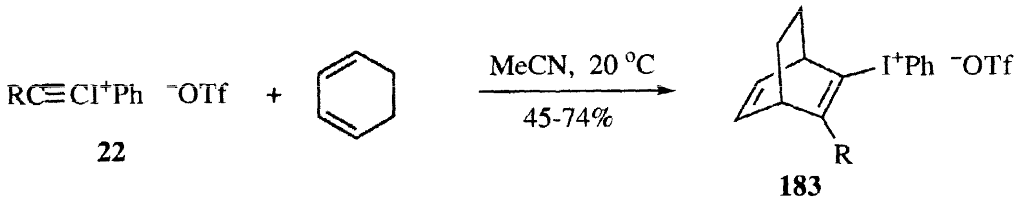
R = H, *t*-Bu; R' = Me, Ph

[4+2] Diels-Alder Cycloadditions. Alkynyliodonium salts **22** functionalized with electron-withdrawing substituents R in the β-position readily undergo [4+2] Diels-Alder cycloadditions with a wide range of dienes. Several examples of these cycloadditions are shown in eqs 98-100.[27a] All adducts **182-184** are stable microcrystalline solids with two functionalities, the iodonium moiety and R, that may be used for further synthetic elaboration.



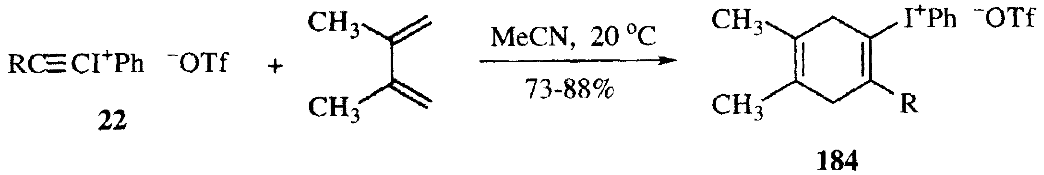
(98)

R = CN, Ts, PhC(O), 2-furyl-C(O), 2-thienyl-C(O)



(99)

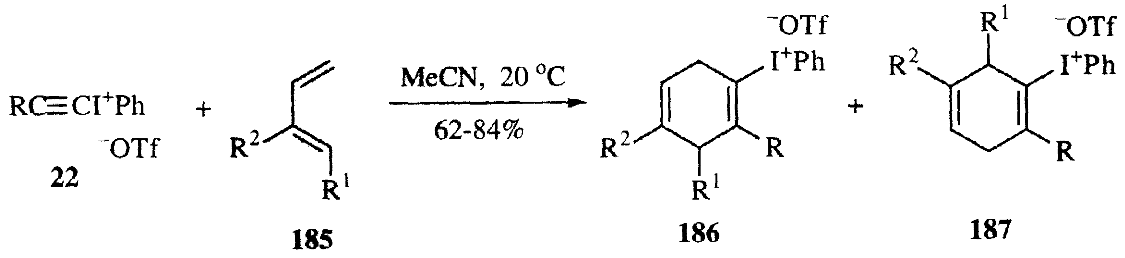
R = CN, Ts, PhC(O), 2-furyl-C(O), 2-thienyl-C(O)



(100)

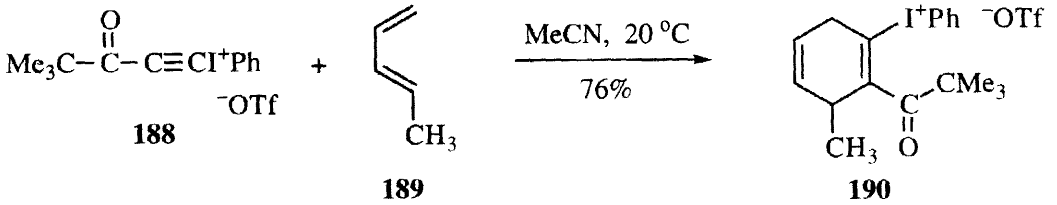
R = CN, Ts, PhC(O), 2-furyl-C(O), 2-thienyl-C(O)

The reaction of alkynyliodonium salts **22** with unsymmetrically substituted dienes **185** results in a mixture of two regioisomeric cyclohexadienes **186**, **187** (eq. 101).[89] In general, this cycloaddition (eq. 101) shows low regioselectivity in the case of 2-substituted dienes and has a better degree of regioselectivity in the case of 1-substituted dienes. Moreover, the reaction of 1-methylbutadiene **189** with alkynyliodonium salt **188** selectively affords a single regioisomer **190**, whose structure was established by X-ray analysis (eq. 102).[89]



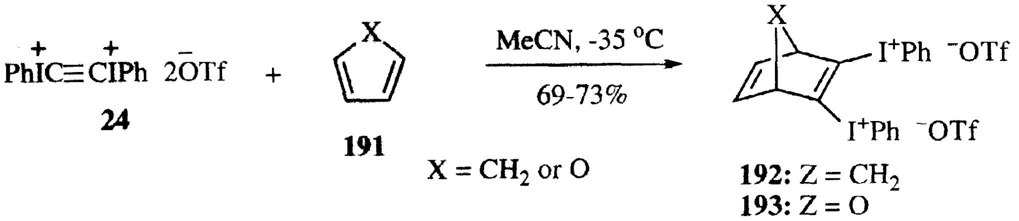
(101)

R = CN, PhC(O), 2-furyl-C(O), 2-thienyl-C(O), $Me_2NC(O)$; R^1, R^2 = H. Me, Et, *t*-Bu

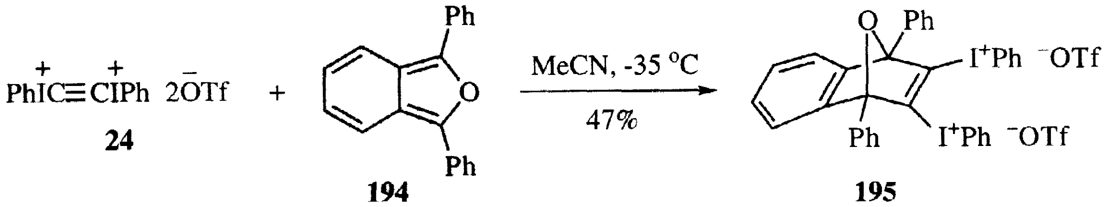


(102)

The bis-iodonium acetylene **24** is even more reactive than **22** and undergoes Diels-Alder reaction with cyclopentadiene, furan and 1,3-diphenylisobenzofuran **194** in acetonitrile under very mild conditions (eqs 103, 104).[23b] All adducts (**192**, **193**, **195**) are isolated in the form of stable microcrystalline solids; the structure of adduct **192** was established by X-ray data. Products **192** and **193** can be reacted further with nucleophiles or combined in a cross-coupling reaction with lithiated or stannylated alkynes.[90-92]



(103)



(104)

D. CONCLUSIONS

The preceding survey and review of the chemistry of alkynyliodonium salts reflects an active current interest in this highly versatile, new class of valuable, functionalized acetylenes. Due to the superb leaving group ability of the iodobenzene moiety, alkynyliodonium salts serve as efficient electrophilic alkynylating reagents in reactions with diverse nucleophiles. They are excellent precursors to five-membered carbocycles and heterocycles *via* 1,5-carbene insertion. And, finally, alkynyliodonium salts are superb cycloaddition partners in a variety of electrocyclic reactions. Their ready availability from commercial precursors, reasonable stability, ease of handling, and versatility should stimulate imaginative uses and thereby greatly enhance the continued development of acetylene chemistry.

E. ACKNOWLEDGMENTS

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Biographical sketch

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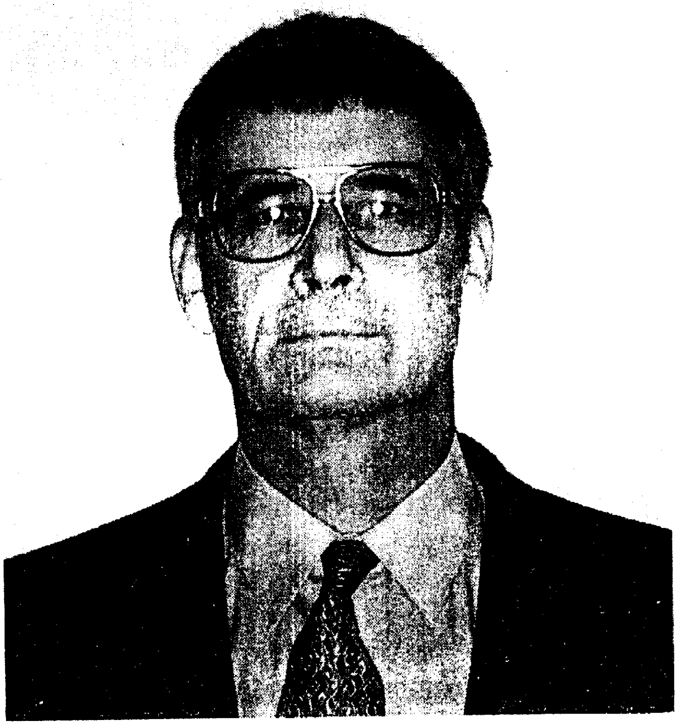

Peter J. Stang

Viktor V. Zhdankin

Viktor V. Zhdankin was born in 1956 in Sverdlovsk, Russia. His M.S. (1978), Ph.D. (1981), and Dr.Chem.Sci. (1986) degrees were earned at Moscow State University in the research laboratories of Professor N.S. Zefirov. In 1987 he was appointed as Senior Research Fellow - Head of Research Group at the Department of Chemistry, Moscow State University, Moscow. He moved to the University of Utah in 1990, where he worked as Instructor of organic chemistry and Research Associate. In 1993 he joined the faculty of the University of Minnesota, Duluth. He has published more than 140 research papers as well as eight reviews and book chapters. His main research interests are in the fields of synthetic and mechanistic organic chemistry of hypervalent main-group elements (iodine, xenon, selenium, sulfur, and phosphorus) and organofluorine chemistry.

Peter J. Stang

Peter J. Stang was born in 1941 in Nürnberg, Germany, raised in Hungary until 1956, and educated in the USA. He earned a B.S. in chemistry, magna cum laude, from DePaul University in Chicago in 1963 and a Ph.D. from U.C.-Berkeley in 1966. After NIH postdoctoral work at Princeton, he joined the faculty at Utah in 1969 where, since 1992, he holds the rank of Distinguished Professor of Chemistry, and served as Department Chair from 1989-1995. His research interests over the years involved reactive intermediates like vinyl cations and unsaturated carbenes, organometallic chemistry, strained ring systems and, most recently, polyvalent iodine and alkynyl ester chemistry. His current efforts focus on nanoscale molecular architecture and the design and self-assembly of metallacyclic polygons and polyhedra via coordination. He is the author or coauthor of over 320 scientific publications, including two dozen reviews and five monographs. From 1982 until the present he has been an Associate Editor of JACS and also serves on numerous Editorial Advisory Boards. Professor Stang has been the recipient of the A.von Humboldt Senior Scientist Award (1977, 1997); JSPS Fellow (1985, 1998); Lady Davis Fellow, Haifa, Israel (1986); Fulbright Hays Senior Scholar, Zagreb, Croatia (1988). In 1992 he was awarded honorary doctorates from the Russian Academy of Sciences and Lomonosov Moscow State University. In 1998 he was the recipient of the ACS James Flack Norris Award in Physical-Organic Chemistry.