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Alkenyliodonium salts

N Sh Pirkuliev, V K Brel, N S Zefirov

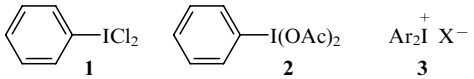
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Abstract. New data on the synthesis and chemical transformations of alkenyliodonium salts are summarised and analysed. The bibliography includes 146 references.

I. Introduction

The first synthesis of a three-coordinated iodine with at least one C–I bond was reported by Willgerodt in 1886.[1] Following preparation of (dichloro-λ^3-iodanyl)benzene † (**1**) by chlorination of iodobenzene, Willgerodt soon synthesised (diacetoxy-λ^3-iodanyl)benzene (**2**) and other organic derivatives of three- and polycoordinated iodine. By the time of the publication by Willgerodt in 1914 of his comprehensive treatise [2] on the chemistry of hypervalent iodine that summarised the data on the synthesis of tri- and pentavalent iodine-containing organic compounds, about 500 such compounds were already known. Among them, diaryliodonium salts **3** were examined most thoroughly.



1 **2** **3**

The chemistry of organic compounds of polyvalent iodine was the subject of several reviews (see, for example, Refs 3–5). However, because of rapid development of this chemistry, it is nearly impossible at the moment to consider all its aspects in the framework of only one publication.

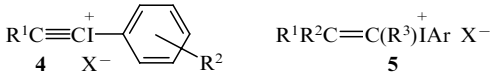
A brief review [6] has been published on iodonium salts; they were also considered in a chapter of a monograph [7] devoted to organic compounds of polyvalent iodine. The chemistry of diacyloxyiodanylarenes was treated in a special review [8] and the application of these compounds as oxidising reagents is described in a monograph.[9] A review [10] devoted to the use of compounds of polyvalent iodine, mostly organic compounds, has also been published. Interesting data on the chemistry of iodonium salts can be found in the book 'The Problems of Organic Chemistry' [11, 12] and those on the chemistry of diacyloxyiodanylarenes in two other books;[13, 14] derivatives of iodosylarenes are discussed in a separate review.[15]

Organic compounds of three- and poly-coordinated iodine are widely used as reagents in modern organic chemistry. Particular areas of synthetic application of these compounds vary depending on their structures, *viz*., on the number of organic ligands at the iodine atom [4, 7] and on the electronegativity and nucleofugality of their heteroatomic ligands.

All compounds of polyvalent iodine can be conventionally divided into several groups. The first one comprises compounds with one carbon ligand (RIX_2 and RIX_4), *viz*., hydroxy(sulfonyloxy)-λ^3-iodanylarenes, periodinanes, substituted benzoiodoxols and azides of trivalent iodine.[8, 10, 16–30] Compounds of this group are employed for selective oxidation of various organic substrates. The second group of polyvalent iodine compounds includes iodonium salts $R_2I^+X^-$ with two carbon ligands.[8, 10, 16–30] Iodonium salts do not possess strong oxidising properties and are mainly employed as precursors of nucleophilic species resulting from transformations of an organic ligand.

Depending on the nature of the organic ligand R, iodonium salts, in turn, can be conventionally classified as alkyl-, polyfluoroalkyl-, alkenyl- and alkynyl-iodonium salts. Most of alkyliodonium salts $Alk_2I^+X^-$ or $Alk(Ph)I^+X^-$, with a few exceptions,[31] are unstable and therefore have not been exploited in organic synthesis. On the contrary, polyfluoroalkyliodonium salts $R_f(Ph)I^+X^-$ are stable and represent effective electrophilic polyfluoroalkylating reagents.[32] Compounds of three-coordinated iodine with three organic ligands are, as a rule, unstable at room temperature; only a few stable representatives of this class are known to date.[33–35]

Derivatives of the type **4** containing an alkynyl group as a substituent were unknown until recently. The intense development of the chemistry of alkenyliodonium salts **5** began only recently, although the first representative of this class of compounds was described back in 1914.[2]



4 **5**

At the moment, synthetic aspects of the chemistry of alkynyliodonium salts are well developed and discussed in detail, for

† This naming is given in accord with IUPAC Nomenclature of Organic Compounds (Recommendations 1993). Furthermore, symbol λ^3 can be omitted from the names of iodine-containing compounds.

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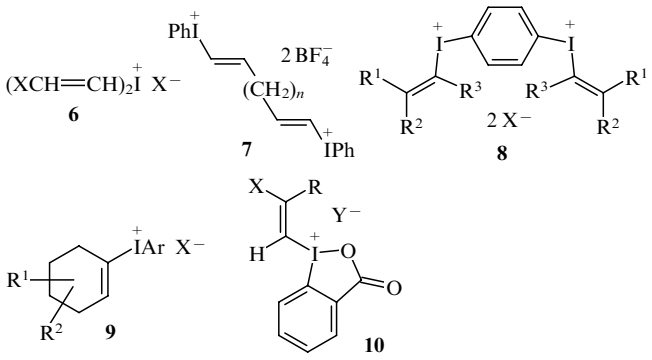
example, in monographs [36–38] and reviews [25, 39, 40] One of these reviews [25] contains a section treating the chemistry of alkenyliodonium salts. This chemistry was also briefly considered in another review [41] devoted to organic compounds of polyvalent iodine. However, new important results obtained recently in this field deserve generalisation.

It is the purpose of this review to systematise and analyse the data on the synthesis and properties of alkenyliodonium salts which were mainly published over the last 10–15 years. Earlier publications are cited only as may be necessary for the better elucidation of the issues in question.

II. Synthesis of alkenyliodonium salts

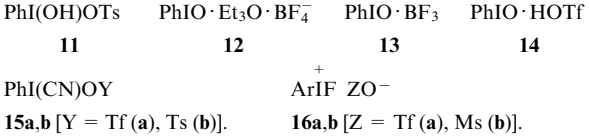
In recent decades, the interest in alkenyliodonium salts has sharply increased. Alkenyliodonium salts bearing not only alkyl, but also aryl, triflate, mesylate and other substituents at the double bond were synthesised. These compounds were demonstrated to be very promising intermediates for organic synthesis.

At present, several types of alkenyliodonium salts are known, *viz*., those with one (**5**) or two (**6**–**8**) alkenyl groups and also cyclic alkenyliodonium salts of the type **9** and **10**.



Several methods for the synthesis of alkenyliodonium salts have been described earlier.[7] However, none of them has been really convenient until recently. At present, a number of new methods have been developed, however, these did not receive much attention in relevant reviews.[25, 41] Taking this fact into account, we systematise in this Section the published data on the synthesis of alkenyliodonium salts.

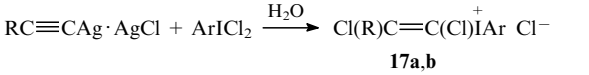
These syntheses are based on the use of electrophilic λ^3-iodanes. Among compounds of polyvalent iodine, the Koser reagent **11**, complexes of iodosylbenzene **12** and **13**, alkynyliodonium salts **4**, the iodosylbenzene trifluoromethanesulfonic acid complex **14**, cyano(hydroxy)-λ^3-iodanylbenzene triflate and tosylate (**15a**,**b**), fluoro(hydroxy)-λ^3-iodanylarene sulfonates (**16a**,**b**) are the key reagents.



15a,**b** [Y = Tf (**a**), Ts (**b**)]. **16a**,**b** [Z = Tf (**a**), Ms (**b**)].

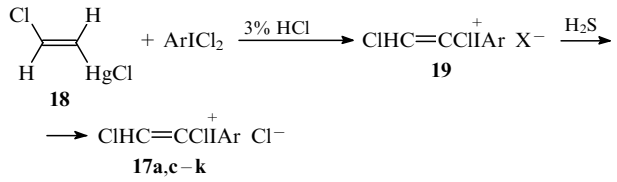
1. Syntheses starting from dichloro-λ^3-iodanylbenzene and dichloro-λ^3-iodanylalkenes

Early methods for the synthesis of alkenyliodonium salts were based on the reactions of organometallic derivatives of alkynes with dichloroiodanylarenes. Using this approach, alkenyliodonium salts **17a**,**b** have been synthesised.[2] However, on the whole, this method was rather ineffective and had a number of limitations.



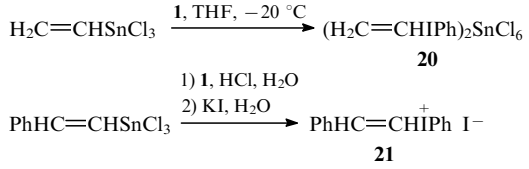
R = H, Ar = Ph (**17a**); R = Me, Ar = C_6H_4Me-2 (**17b**).

Later, the reactions of organomercuric derivatives of alkenes with dichloroiodanylarenes were proposed to synthesise alkenyliodonium salts.[42–44] Thus the treatment of *trans*-chlorovinylmercuric chloride with various dichloroiodanylarenes in dilute hydrochloric acid results in arylvinyliodonium mercurates **19** in 5%–53% yields. The latter can be converted into the corresponding arylvinyliodonium chlorides **17a**,**c**–**k** upon treatment with hydrogen sulfide.

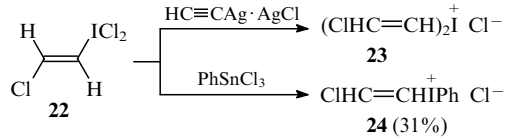


Ar = Ph (**a**), 2-MeC_6H_4 (**c**), 3-MeC_6H_4 (**d**), 4-MeC_6H_4 (**e**), 2-ClC_6H_4 (**f**), 3-ClC_6H_4 (**g**), 4-C_6H_4 (**h**), 2-$MeOC_6H_4$ (**i**), 4-$MeOC_6H_4$ (**j**), 3-$NO_2C_6H_4$ (**k**); X = $Cl \cdot HgCl_2$, $Cl \cdot 2\,HgCl_2$.

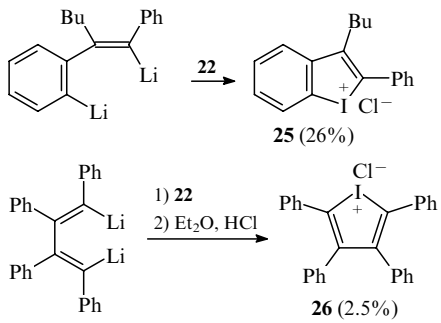
The reaction of vinyl- or styryltrichlorostannane with dichloroiodanylbenzene (**1**) leads to alkenyliodonium salts **20** or **21**.[45, 46]



1-Chloro-2-dichloroiodanylethylene **22** has been synthesised for the first time by the reaction of *trans*-chloroiodoethylene with chlorine.[47] Later, compound **22** was obtained in high yield by the reaction of acetylene with iodine trichloride.[48] Compound **22** is unstable at room temperature, but can be stored below −20 °C for two months without noticeable changes. This reagent is employed for the synthesis of alkenyliodonium salts. Thus its reactions with silver acetylenide or phenyltrichlorostannane afford compounds **23** and **24**.[46]



Diphenyliodonium chloride rather than a vinyliodonium salt of the type **24** is formed from 1-dichloroiodanyl-2-iodoethylene in 50% yield.[43] Organolithium derivatives react with compound **22** to give cyclic iodonium salts **25** and **26**.[49]

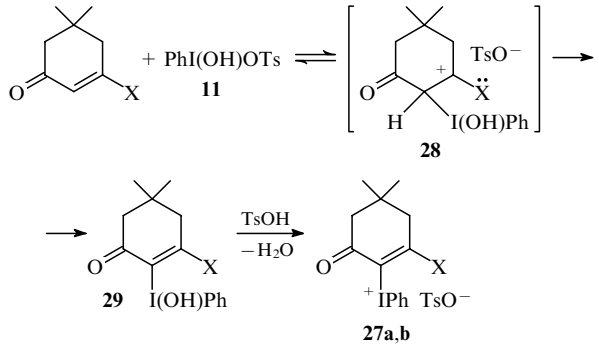


It should be noted that the reaction of dichloroiodanylbenzene with an equivalent amount of vinyllithium in THF at −70 °C affords diphenyliodonium chloride in low yield (5%).[49]

2. Syntheses starting from dihydroxy-λ^3-iodanylbenzene tosylate

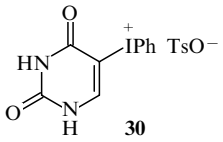
The availability of iodanylbenzene derivatives, their reasonable stabilities on storage and fair solubilities enable the use of these compounds in the synthesis of alkenyliodonium salts. The reac-

tions of dihydroxy-λ^3-iodanylbenzene tosylate (**11**) with 3-amino- and 3-ethoxy-5,5-dimethylcyclohex-2-enone in chloroform result in the formation of vinyliodonium salts **27a**,**b** in 87% and 40% yields, respectively.[50] The reaction mechanism presumably involves the initial attack by the hydroxy(phenyl)iodonium ion on the double bond followed by the deprotonation of the intermediate **28** and the exchange reaction of aryl(vinyl)iodonium hydroxide **29** with *p*-toluenesulfonic acid.



X = NH_2 (**a**), OEt (**b**).

The condensation of uracil with diacetoxyiodanylbenzene in DMF in the presence of $TsOH \cdot H_2O$ leads to compound **30** in 78% yield.[51] The reaction apparently involves the intermediate formation of the tosylate **11**.



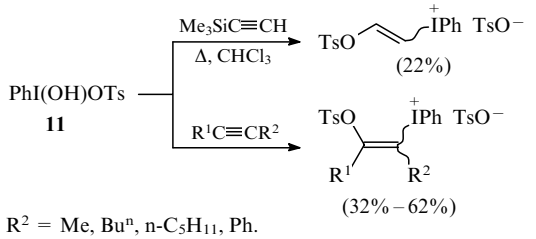
More general and simple procedure for the synthesis of (β-tosyloxyvinyl)iodonium tosylate **31** includes the reactions of dihydroxyiodanylbenzene tosylate (**11**) with terminal alkynes.[52–56]

$$RC{\equiv}CH + \mathbf{11} \xrightarrow{\Delta,\ CHCl_3} \underset{\mathbf{31a-i}\ (40\%-60\%)}{R(TsO)C{=}\overset{+}{C}HIPhTsO^-} + \underset{\mathbf{32a-i}}{RC{\equiv}\overset{+}{C}IPhTsO^-}$$

R = Pr^n (**a**), Bu^n (**b**), n-C_5H_{11} (**c**), Pr^i (**d**), sec-C_4H_9 (**e**), Bu^i (**f**), cyclo-C_6H_{11} (**g**), Bu^t (**h**), Ph (**i**).

Depending on the nature of the substituent in terminal alkynes, either alkenyl- or alkynyliodonium salts or their mixture are formed.[54] Thus pent-1-yne yields the alkenyliodonium salt **31a** exclusively (58%), 3,3-dimethylbut-1-yne gives alkynyliodonium tosylate **32h** (74%), while 3-methylbut-1-yne affords a mixture of alkenyl- (**31d**) (11%) and alkynyl-iodonium salts **32d** (15%). A correlation was found between the degree of branching in the substituent and the direction of the reactions. Thus alkynyliodonium salts are formed if the substituent is more branched than the isopropyl group (*e.g.*, Bu^t and cyclo-C_6H_{11}). Mixtures of both salts are obtained from 3-methylbut-1-yne and 4-methylpent-1-yne, which are branched in the β-position.

Trimethylsilylacetylene reacts with compound **11** with the elimination of the trimethylsilyl group to give phenyl(2-tosyloxyvinyl)iodonium tosylate.[54] Disubstituted acetylenes react with compound **11** producing vinyliodonium salts in up to 62% yield.[53]

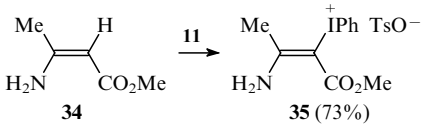


R^1, R^2 = Me, Bu^n, n-C_5H_{11}, Ph.

The reactions of compound **11** with alkenes were also studied.[53] Alkenyliodonium salt **33** (5%) was found to be a product of the reaction with 1,1-diphenylethylene.

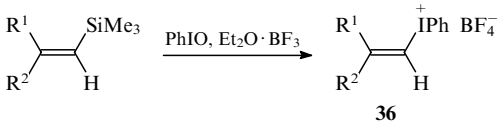
$$\mathbf{11} + Ph_2C{=}CH_2 \longrightarrow PhC(O)CH_2Ph + \underset{\mathbf{33}}{Ph_2C{=}\overset{+}{C}HIPhTsO^-} + TsOH$$

Methyl 3-aminocrotonate **34** reacts with the tosylate **11** at 20 °C to give [2-amino-1-methoxycarbonyl-(*E*)-prop-1-enyl]phenyliodonium tosylate (**35**) as the major product.[57]



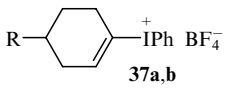
3. Syntheses starting from iodosylbenzene in the presence of Lewis acids

The first general method for the synthesis of alkenyliodonium salts was suggested in the mid-1980s.[58, 59] It was based on the reactions of silylated alkenes with iodosylbenzene in the presence of Lewis acids. These reactions proceed stereoselectively in the presence of boron trifluoride diethyl etherate to afford alkenyliodonium tetrafluoroborates **36** in high yields. The preparation of a wide range of diverse alkenyliodonium salts has demonstrated the versatility of this procedure. The yields of the reaction products reached 89%.



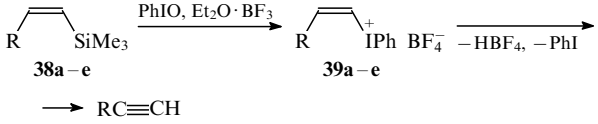
R^1 = H, Me, n-C_8H_{17}, $Ph(CH_2)_2$; R^2 = H, Me, n-C_8H_{17}, Ph, $PhCH_2$, $Ph(CH_2)_2$, *p*-$BrC_6H_4OCH_2$, *p*-$ClC_6H_4(CH_2)_2$.

Using this approach, cyclic alkenyliodonium salts, *viz.*, 4-R-cyclohex-1-enyl(phenyl)iodonium tetrafluoroborates **37a**,**b**, were synthesised.[58, 59]



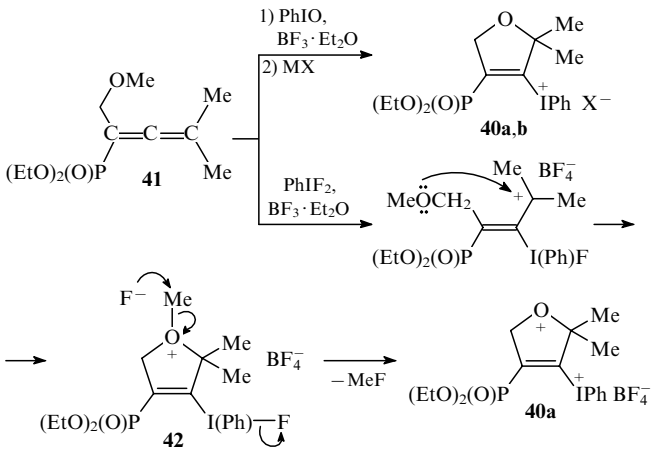
R = H (**a**), Bu^t (**b**).

The reaction of 1-trimethylsilyldec-1-ene with iodosylbenzene in the presence of boron trifluoride diethyl etherate yields dec-1-yne.[60, 61] Using NMR spectroscopy, it was shown that the reaction with the alkene **38a** occurs *via* unstable alkenyl(phenyl)iodonium salt **39a**.[58] Treatment of salts **39a**–**e** with an aqueous solution of $KClO_4$ allowed the synthesis and characterisation of stable (*Z*)-alkenyliodonium perchlorates **39a**–**e**.[61]



R = n-C_8H_{17} (**a**), $Me_2CH(CH_2)_4$ (**b**), cyclo-$C_5H_9CH_2$ (**c**), Ph (**d**), $Ph(CH_2)_3$ (**e**).

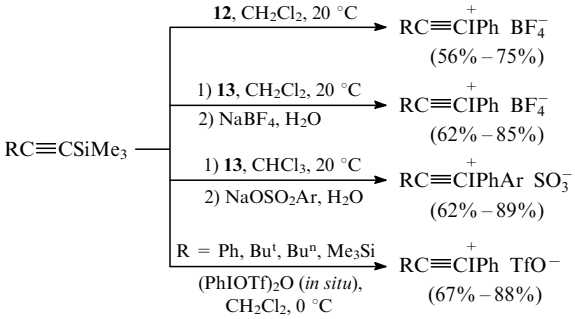
Electrophilic addition of the complex of PhIO with $BF_3 \cdot Et_2O$ to allenes was used to synthesise alkenyliodonium salts. Thus salt **40a** was obtained by the reaction of diethyl 1-methoxy-4-methylpenta-2,3-dien-2-ylphosphonate (**41**) with 2 equivs of iodosylbenzene in the presence of boron trifluoride diethyl etherate.[62] The respective perchlorate **40b** was obtained in 48% yield upon treatment of the reaction mixture with a saturated aqueous solution of $LiClO_4$. The salt **40** is also formed in the reaction of the allene **41** with a system $PhIF_2 - BF_3 \cdot Et_2O$.[62]



X = BF_4 (**a**), ClO_4 (**b**).

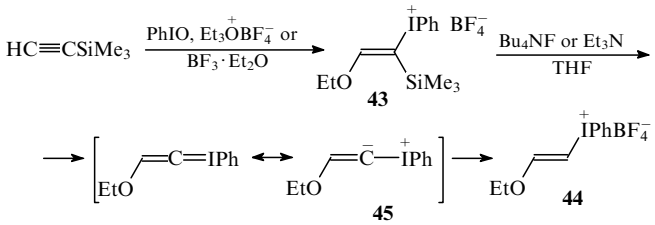
The unusual reaction course is explained by a *Z*-orientation of the electrophilic fragment I(Ph)F relative to the phosphoryl group in the intermediate **42**. In all the structures examined so far,[63–71] resulting from electrophilic additions to allenylphosphonates, *E*-orientation of the substituents at the double bond was mainly observed, which favoured the formation of oxaphospholenes.

The reactions of alkynyltrimethylsilanes with iodosylbenzene in the presence of BF_3 or $Et_3O^+ \cdot BF_4$ lead to alkynyliodonium compounds.[72–77]



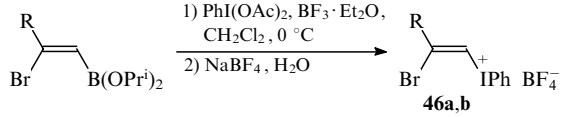
R = Ph, $PhCH_2$, $PhCH_2CH_2$, n-C_8H_{17}, cyclo-C_6H_{11};
Ar = 4-MeC_6H_4, 4-$NO_2C_6H_4$.

The addition of PhIO to trimethylsilylacetylene in the presence of triethyloxonium tetrafluoroborate or boron trifluoride diethyl etherate results in the formation of (*E*)-(2-ethoxyvinyl-1-trimethylsilyl)phenyliodonium tetrafluoroborate in 68% yield.[78] Treatment of compound **43** with tetra-n-butylammonium fluoride or triethylamine leads to vinyliodonium salt **44**. The reaction presumably occurs *via* an intermediate ylide **45**.[78]



A method allowing the stereoselective synthesis of alkenyliodonium salts from boronic acids or their esters has been described.[79] The reactions of (*Z*)-2-bromovinyl(diisopropoxy)-boranes with diacetoxyiodanylbenzene in dichloromethane at 0 °C under nitrogen followed by the anion exchange led to (*Z*)-phenyl(vinyl)iodonium tetrafluoroborates. In addition to the iodonium salt **46b**, (*Z*)-2-bromodec-2-enal (9%), 2,2-dibromodecenal (3%) and (*Z*)-1,2-dibromodec-1-ene (5%) were also formed.

If the reactions are carried out in the presence of boron trifluoride etherate, the yields of alkenyliodonium salts are increased to 85%.

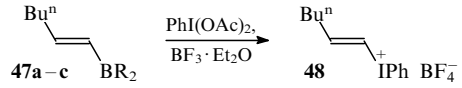


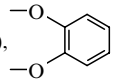
R = Bun (**a**), n-C_8H_{17} (**b**).

The yields of the salts **46** also depend on the nature of the solvent; in dichloromethane, benzene, ethyl acetate and methanol, they are higher (> 80%) than in acetonitrile and diethyl ether.

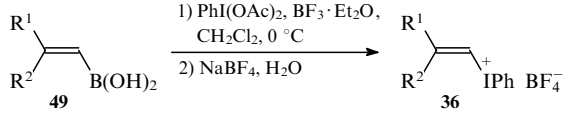
Alkoxyboranes also produce alkenyliodonium salts in reactions with other derivatives of I(III), *viz*., with PhIO in the presence of boron trifluoride etherate, dihydroxyiodanylbenzene tosylate (**11**) or $PhI(OCOCF_3)_2$.[79] When (*Z*)-2-bromohex-1-enyl(diisopropoxy)borane reacted with bis(trifluoroacetoxy)iodanylbenzene, [(*Z*)-2-bromohex-1-enyl]phenyliodonium trifluoroacetate was isolated from the reaction mixture together with the respective tetrafluoroborate as the major product.

The reaction of (*E*)-(diisopropoxy)hex-1-enylborane (**47a**) with $PhI(OAc)_2 - BF_3 \cdot Et_2O$ results in the stereoselective formation of (*E*)-vinyliodonium salt **48** (47%) and hexenal as a side-product (12%).

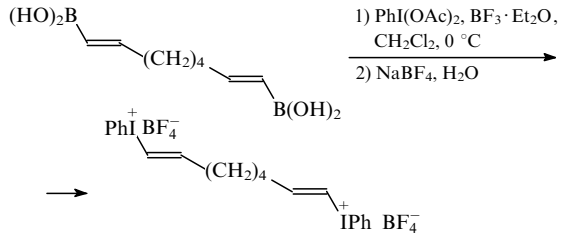


R_2 = $(OPr^i)_2$ (**a**), $-OCMe_2CMe_2O-$ (**b**),  (**c**).

Vinylboronic acids **49** react with $PhI(OAc)_2 - BF_3 \cdot Et_2O$ in dichloromethane at 0 °C under nitrogen to form vinyliodonium salts **36**.[79] This procedure allows the synthesis of not only mono-, but also bis(vinyliodonium) salts from the corresponding vinylboronic acids.[79]

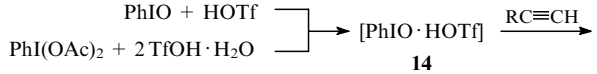


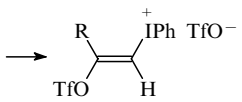
R^1 = n-C_4H_9, n-C_8H_{17}, $Ph(CH_2)_3$, $Cl(CH_2)_3$, $NC(CH_2)_3$, cyclo-$C_5H_9CH_2$, $Me_2CH(CH_2)_2$, But, Ph; R^2 = H, Me, Ph.



4. Syntheses based on the activation of iodosylbenzene with trifluoromethanesulfonic acid or its derivatives

Yet another method for the synthesis of alkenyliodonium salts is based on the reactions of alkynes with PhIO – HOTf (**14**), PhIO – Tf_2O or PhIO – Me_3SiOTf systems.[80–82] These reactions occur stereoselectively yielding (*E*)-alkenyliodonium salts **50**. Complex **14** is generated *in situ* either from a 1 : 1 mixture of iodosylbenzene and trifluoromethanesulfonic acid or from a 1 : 2 mixture of diacetoxyiodanylbenzene and $TfOH \cdot H_2O$.

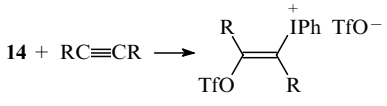




50 (62% – 100%)

R = H, Pr^n, Bu^n, n-C_6H_{13}, Ph.

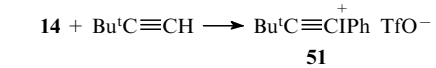
Disubstituted acetylenes also react with the complex **14** stereoselectively to form (*E*)-alkenyliodonium salts.[82]



(67% – 80%)

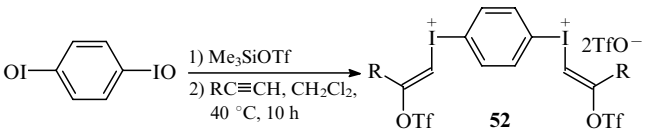
R = Me, Et.

However, only alkynyliodonim triflate **51** is formed in 42% yield in the reaction of sterically hindered 3,3-dimethylbut-1-yne with PhIO – HOTf.[82]



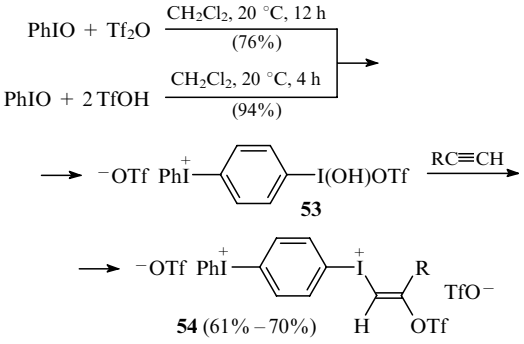
51

Activation of bis(iodosyl)benzene with trimethylsilyl triflate followed by treatment with appropriate terminal alkynes afford bis(alkenyliodonium) salts **52** in 50% – 66% yields.[83]



R = H, Me, Et, Ph.

The reaction of iodosylbenzene with 2 equivs of trifluoromethanesulfonic acid or with an equimolar amount of Tf_2O produces the iodanyl-iodonium derivative **53**. The latter readily reacts with terminal alkynes to give the corresponding *E*-alkenyliodonium salts **54**.[84, 85]

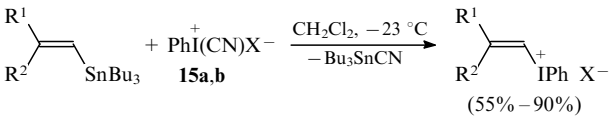


R = Pr^n, Bu^n, n-C_6H_{13} .

It should be noted that 1-trimethylsilylalkynes react with the reagent **53** with the elimination of the trimethylsilyl group to form the corresponding mono(alkynyl)iodonium salts.[85]

5. Syntheses starting from cyano(hydroxy)-λ³-iodanylbenzene triflate

A more versatile method for the synthesis of alkenyliodonium salts that allows the introduction of a wide range of different substituents at the double bond is based on the reactions of cyano(hydroxy)-λ³-iodanylbenzene sulfonates **15a**,**b** with tin-substituted alkenes.[86 – 88]



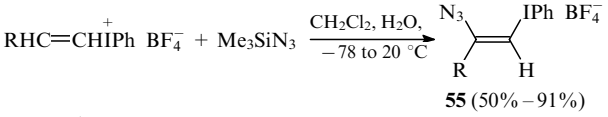
R¹, R² = Me, Bu^n, Et, Ph; X = OTf (**a**), OTs (**b**).

The reactions proceed under mild conditions and stereoselectively afford alkenyliodonium salts in high yields. Using this approach, phenyl(vinyl)iodonium triflate was synthesised starting from tributyl(vinyl)stannane.[88]

(75%)

6. Syntheses starting from alkynyliodonium salts

The reactions of alkynyliodonium salts with nucleophiles in protic solvents represent a convenient approach to stereoselective synthesis of (*Z*)-β-functionalised alkenyliodonuim salts. The ratio between the substitution and addition products depends on the nature of the counterion and nucleophile. When trimethylsilyl azide is used as a source of nucleophilic species (in the presence of water), the addition products are formed in high yields, and it is employed for the preparation of (*Z*)-(β-azidoalkenyl)iodonium salts **55**.[89]

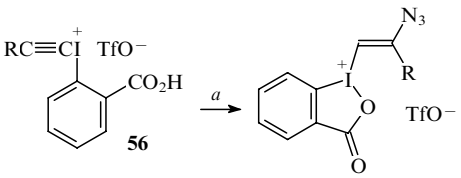


55 (50% – 91%)

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

However, the reactions of alkynyliodonium tosylates with sodium azide in the presence of methanol result in the corresponding (*Z*)-(β-azidoalkenyl)iodonium tosylates in relatively low yields.[90]

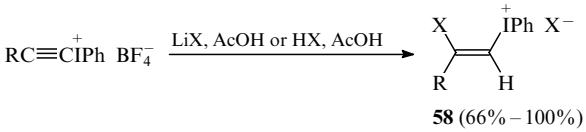
1-(*Z*)-(β-Azidovinyl)-3*H*-2,1λ³-benzooxaiodol-3-one triflates **57** have been obtained by the reactions of alkynyliodonium salts **56** with sodium azide in the presence of 18-crown-6.[91] The initial intramolecular hydrogen transfer followed by cyclisation involving the *ortho*-carboxy group may account for such unusual *syn*-stereochemistry of the azide addition.



57 (57% – 63%)

R = Bu^n, n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$;
(*a*) NaN_3, 18-C-6, CH_2Cl_2, −80 to 20 °C.

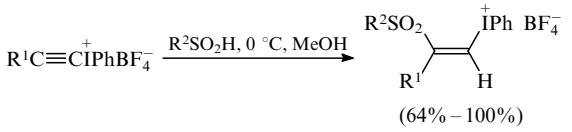
Stereoselective synthesis of (*Z*)-(β-halogenovinyl)iodonium salts **58** by the reactions of alkynyliodonium tetrafluoroborates with halide anions in an acid medium has been effected.[92, 93] Fluoride anion does not react under these conditions, while the addition of iodide anion results in a complex mixture of products probably due to the low stability of the primary addition products.[92] (*Z*)-(β-Halogenovinyl)iodonium salts **58** are useful precursors for halogenoalkylidene carbenes.[93]



58 (66% – 100%)

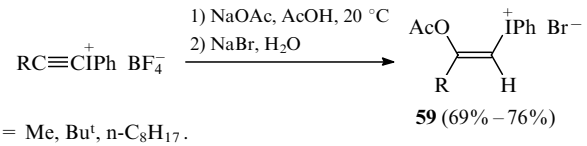
R = $PhCH_2$, $PhCH_2CH_2$, Bu^t, n-C_8H_{17}, cyclo-$C_5H_9CH_2$; X = Cl, Br.

The conjugate addition of sulfinic acids in methanol affords stereoselectively (*Z*)-(β-sulfonylvinyl)iodonium salts.[94, 95]



R^1 = Me, $Ph(CH_2)_3$, n-C_8H_{17}, cyclo-$C_5H_9CH_2$, $HO(CH_2)_2$, cyclo-$C_6H_{11}(CH_2)_2$; R^2 = Ph, 4-$NO_2C_6H_4$, 4-$MeOC_6H_4$, Bu^n.

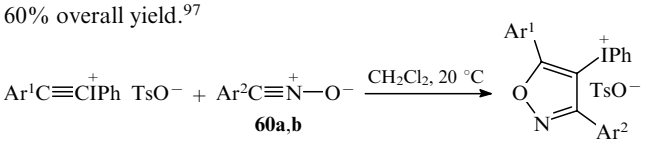
Recently, a similar approach was used to synthesise (*Z*)-(β-acetoxyvinyl)phenyliodonium bromides **59**.[96] The reaction sequence includes the conjugate addition of sodium acetate to alkynyliodonium salts in acetic acid and anion exchange in an aqueous solution of sodium bromide. The yields of the products **59** depend on the amount of sodium acetate added. The use of 0.1 equiv. of sodium acetate is optimum; the addition of a greater amount of sodium acetate decreases the yields of the targeted products considerably.[96]



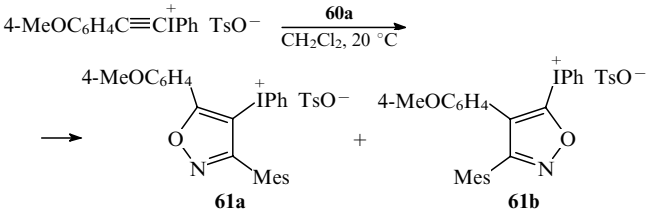
R = Me, Bu^t, n-C_8H_{17}.

Alkynyliodonium salts represent activated electron-deficient alkynes with a highly polarised triple bond. Owing to their dipolar structures, these compounds can be used as dipolarophiles in a variety of cycloaddition reactions. This provides a way to the synthesis of diverse alkenyliodonium salts.

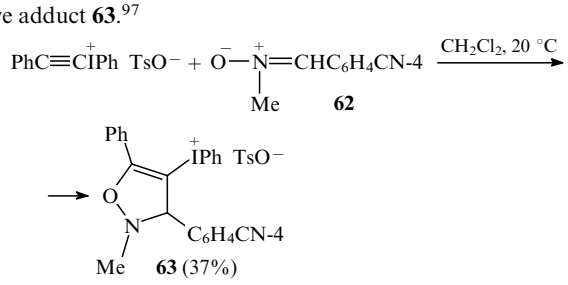
Thus (arylethynyl)iodonium tosylates react with nitrile oxides **60a**,**b** to form cycloadducts in high yields.[97] The reaction of [(4-methoxyphenyl)ethynyl]iodonium tosylate under similar conditions leads to a 1 : 1 mixture of two isomeric adducts **61a** and **61b** in 60% overall yield.[97]



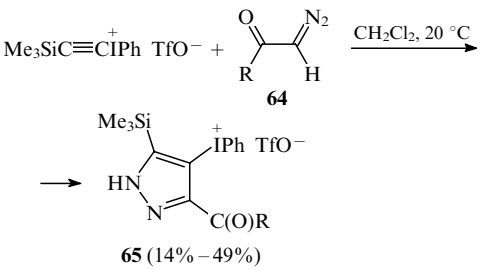
Ar^1 = Ph, 2-ClC_6H_4; Ar^2 = Mes (**a**), 2,6-$Cl_2C_6H_3$ (**b**).



Nitrone **62** reacts with (phenylethynyl)iodonium tosylate to give adduct **63**.[97]

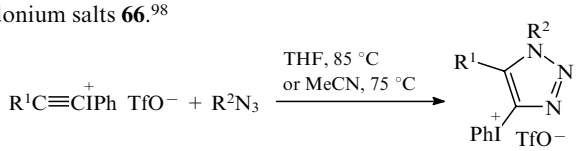


Diazocarbonyl compounds **64** form the corresponding cycloadducts **65** in the reactions with phenyl(2-trimethylsilylethynyl)-iodonium triflate.[98]



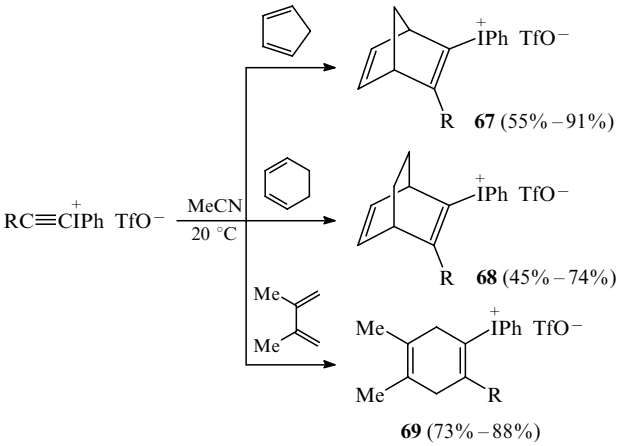
R = OMe, OEt, Ph, Bu^t.

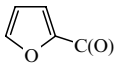
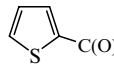
Methyl and phenyl azides react with alkynyliodonium triflates on heating in tetrahydrofuran or acetonitrile to give triazolyl-iodonium salts **66**.[98]



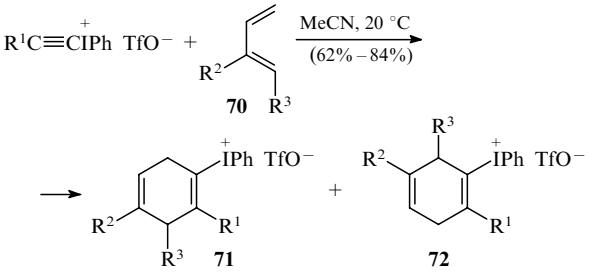
R^1 = H, Bu^t; R^2 = Me, Ph.

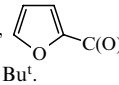
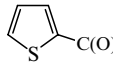
Alkynyliodonium salts can add not only to 1,3-dipolarophiles, but also to 1,3-dienes.[99] Adducts **67**–**69** are obtained as stable, crystalline compounds. Owing to the presence of two functional groups, these adducts can then be used in further reactions.

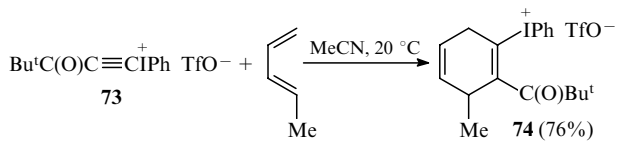


R = CN, Ts, PhCO, , .

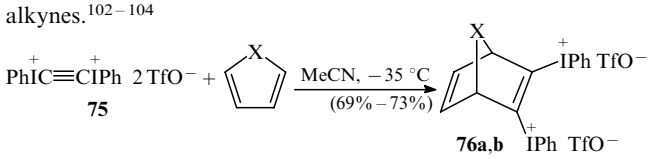
The reactions of alkynyliodonium salts with unsymmetrically substituted dienes **70** lead to mixtures of two regioisomeric cyclohexadienes **71** and **72** in 62%–84% overall yields.[100] Usually, the regioselectivity of the reactions with 2-substituted dienes is low, whereas 1-substituted dienes react more regioselectively. Thus the reaction of penta-1,3-diene with the alkynyliodonium salt **73** leads exclusively to the regioisomer **74**, the structure of which was unequivocally established by X-diffraction analysis.[100]



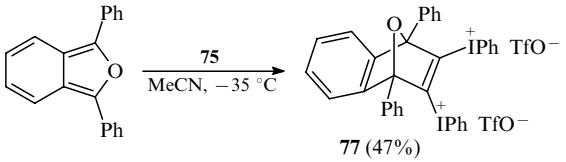
R^1 = CN, Ts, PhCO, , , $Me_2NC(O)$;
R^2, R^3 = H, Me, Et, Bu^t.



Acetylene bisiodonium salt **75** is more reactive and readily enters into reactions with cyclopentadiene, furan and 1,3-diphenylisobenzofuran in acetonitrile under mild conditions.[101] The adducts **76a**,**b** and **77** are stable and can be used in further reactions with various nucleophiles or in cross-couplings with alkynes.[102–104]



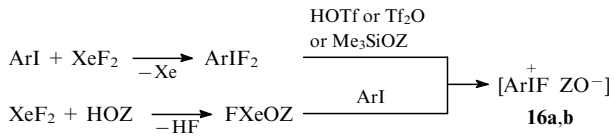
X = CH_2 (**a**), O (**b**).



7. Synthesis starting from fluoro(hydroxy)-λ³-iodanylarene sulfonates

Most of trivalent iodine organic derivatives employed in the synthesis of stable vinyliodonium salts are insufficiently reactive. Their electrophilicity can be enhanced if these compounds are converted into derivatives of strong acids containing highly nucleofugal groups as ligands. In this approach, reactive iodonium compounds are obtained in two steps, and the first step is the synthesis of readily available I(III)-derivatives from aryl iodides.

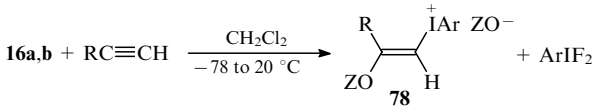
A new one-step procedure for the generation of iodanylarenes directly from aryl iodides has been proposed recently.[105–108] It was found that oxidation of aryl iodides with fluoroxenon sulfonate results in the formation of iodonium salts **16a**,**b**. The latter represent convenient starting compounds for the synthesis of diverse diaryl- and alkenyl-iodonium sulfonates. Compounds **16a**,**b** can also be obtained by the reactions of difluoroiodanylarenes with the respective sulfonic acid, its anhydride or trimethylsilyl ester.[105]



Z = Tf (**a**), Ms (**b**).

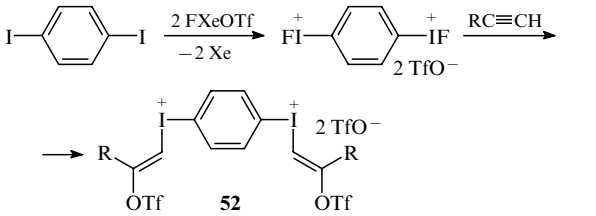
The fact that the reagents **16a**,**b** contain the highly nucleofugal sulfonate group makes them important. These compounds probably have an ionic structure. It is worth noting that the reagents **16** represent only a specific example of compounds of the general formula [$ArI^+X\ Z^-$] where X and Z denote a heteroatomic substituent and a nucleofugal group, respectively. For example, derivatives with X = OH, Z = OTf;[82] X = OH, Z = FSO_3;[41] X = OH, Z = HSO_4;[7] X = OH, Z = BF_4;[41] X = F, Z = BF_4 (Refs 41, 62) are also known. In most instances, the structures of these compounds have not been strictly established. Several of them were deduced on the grounds of chemical transformations of these intermediates in reactions with various organic substrates. For example, the reactions with alkynes, aromatic compounds and enol silyl ethers gave rise to iodonium salts[41, 58, 59, 62, 82] and β-diketones.[41]

Fluoro(hydroxy)iodanylarene sulfonates **16** react stereoselectively with terminal alkynes to form (*E*)-[β-(sulfonyloxy)alk-1-enyl](aryl)iodonium sulfonates **78**;[105, 109] the structure of one of these compounds was proved by X-diffraction analysis.[108]



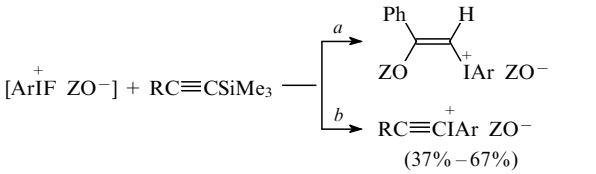
Z = Tf, Ms; Ar = Ph, 4-MeC_6H_4, 2-MeC_6H_4, 4-$NO_2C_6H_4$;
R = H, Pr^n, Bu^n, n-C_8H_{17}, CH_2OH, CH_2OMe, CH_2Cl,CH_2CH_2OH.

Earlier, (*E*)-(2-trifluoromethylsulfonyloxyvinyl)(aryl)iodonium sulfonates **78** were obtained by the electrophilic addition of the [PhIO – HOTf] reagent to alkynes.[82] However, the synthesis of β-functionalised vinyliodonium salts by this method required an additional step including the conversion of iodobenzene into iodosobenzene followed by the activation of the latter with methanesulfonic acid. Compared with this procedure, the use of a novel oxidant, *viz*., fluoroxenon sulfonate, which already contains the sulfonate group, allows a one-step preparation of β-functionalised vinyliodonium salts directly from iodobenzene and terminal alkynes. In addition, the reagents **16** are more reactive towards alkynes than the system [PhIO – HOTf], and readily enter into reactions even at −70 °C. This method was shown to be suitable for the synthesis of bis(alkenyl)-*p*-phenyleneiodonium salts **52**.[110]



R = H, Me, Et, Ph, Pr^n, n-C_8H_{17}, CH_2Cl.

It is important to note that exclusively *Z*-alkenyliodonium salts are formed in the reactions with phenyl(trimethylsilyl)acetylene.[106, 109] The structure of one of such salts has definitively been established by means of X-diffraction analysis.[106] This stereochemical result differs in principle from other cases where adducts of iodosobenzene with fluorosulfonic or trifluoromethanesulfonic acid[81, 82] reacted with alkynes to give *E*-β-substituted iodonium salts. It should also be noted that the reactions of other alkynyltrimethylsilanes with the reagents **16a**,**b** give rise to the corresponding alkynyliodonium salts.

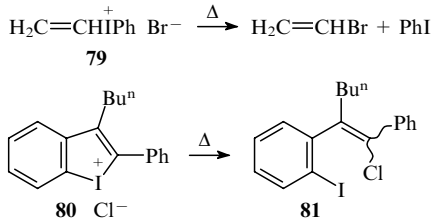


Z = Tf: Ar = Ph (58%), *p*-MeC_6H_4 (53%); Z = Ms, Ar = Ph (56%);
(*a*) R = Ph, HOZ, CH_2Cl_2, −78 to 20 °C;
(*b*) R = H, Bu^n, Bu^t, $MeOCH_2$, CH_2Cl; CH_2Cl_2, −78 to 20 °C.

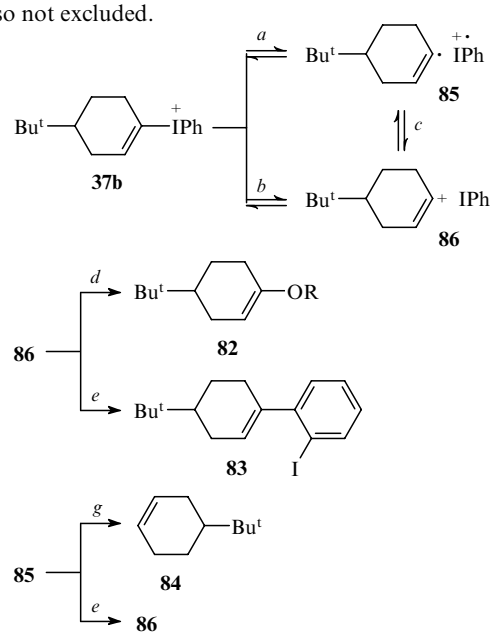
III. Reactions of alkenyliodonium salts

Exploration of chemical properties of alkenyliodonium salts was begun only in the mid-1980s. Although the majority of alkenyliodonium salts are rather stable compounds and can be stored for a relatively long time without any noticeable changes, most of them undergo thermal destruction on heating. As a rule, the thermal decomposition of alkenyliodonium salts involves the cleavage of a bond between I^+ and the carbon atom of the alkenyl fragment. Thermolysis of *trans*-chlorovinyliodonium salts is accompanied by the formation of acetylene.[42, 43, 46] Iodobenzene and vinyl bromide in the ratio of 1 : 1 are formed upon thermal decom-

position of solid phenyl(vinyl)iodonium bromide **79**; no other products have been detected.[46] Thermal decomposition of a cyclic iodonium salt **80**, which occurs at a melting temperature, leads to a mixture of substituted *cis*- and *trans*-stilbenes **81**.[49]

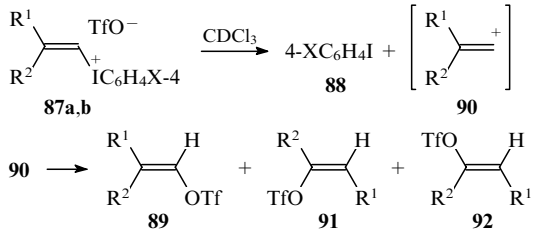


Alkenyliodonium salts undergo solvolysis and fragmentation. The mechanism of solvolysis of (4-*tert*-butylcyclohex-1-enyl)phenyliodonium tetrafluoroborate (**37b**) in ethanol and aqueous solutions was examined.[111] It was shown that the phenyliodonio group is about 10^6 times as good a leaving group as the triflate. In addition to the expected products, *viz*., **82** and iodobenzene, the solvolysis also yielded the internal return product **83** and a small amount of 4-*tert*-butylcyclohexene (**84**) resulting from a single-electron transfer. A mechanism involving initial heterolysis to form a contact ion pair **85** followed by a single-electron transfer to lead to an intermediate **86** was suggested. However, a possibility that the species **86** is formed upon homolysis of the $C-I^+$ bond is also not excluded.



(*a*) $C-I^+$ bond heterolysis; (*b*) $C-I^+$ bond homolysis; (*c*) single-electron transfer; (*d*) ROH (solvolysis); (*e*) internal return; (*g*) $-$PhI.

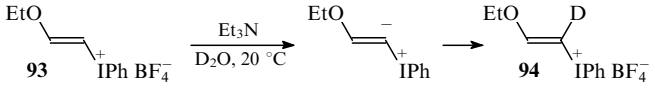
Fragmentations of 2,2-disubstituted alkenyliodonium salts **87a**,**b** in $CDCl_3$ follow a similar mechanism. However, in this case, triflates **91** and **92** are formed as the products of a cationic rearrangement of an intermediate **90** together with the solvolysis products **88** and **89**.[112]



$R^1 = R^2 = Me$, $X = CF_3$ (**87a**); $R^1 = Ph$, $R^2 = Et$, $X = H$ (**87b**).

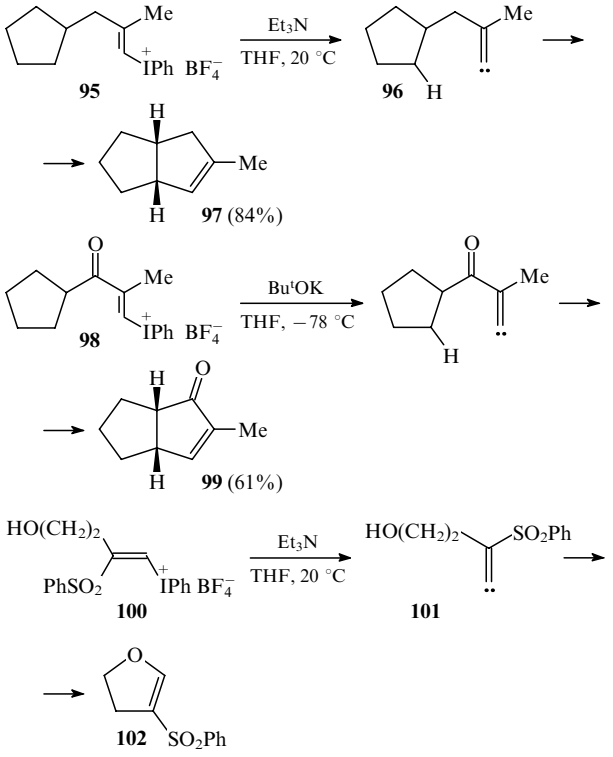
Obviously, the presence of the I^+ArX^- fragment significantly affects the electron density distribution not only in the groups vicinal to this fragment, but also in the molecule as a whole. Thus according to the ^1H NMR spectra of *E*- and *Z*-alkenyliodonium salts, the α-proton of the alkenyl group (with respect to the I^+Ar fragment) is rather acidic.[58, 61] The I^+ArX^- group is also responsible for the substantially enhanced $C-H$ acidity of some other compounds.[113]

Being highly acidic, the α-hydrogen atom can readily be removed from alkenyliodonium salts even by such weak bases as amines.[78, 114] An exchange of deuterium for the α-vinylic proton and to form deuterio-derivative **94** takes place upon treatment of (*E*)-(2-ethoxyvinyl)phenyliodonium salt **93** with triethylamine and D_2O in THF. The reaction presumably involves the intermediate formation of a vinyliodonium ylide **45**.[114]



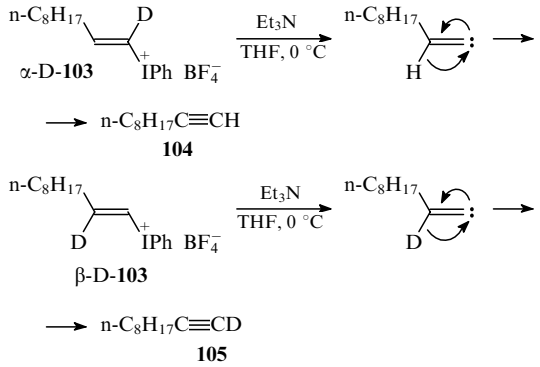
1. Generation of alkylidenecarbenes from vinyliodonium salts

Owing to the high nucleofugality of the I^+ArX^- group, vinyliodonium salts readily undergo reductive elimination of iodobenzene generating thereby highly reactive alkylidenecarbenes. The latter can further transform into cyclopentenes through an intramolecular regioselective insertion into the $C-H$ bond (1,5-insertion). Thus α-elimination in the iodonium salt **95** followed by the 1,5-insertion in the species **96** proceed under mild conditions (Et_3N, 25 °C) yielding 2-methylbicyclo[3.3.0]oct-1-ene (**97**). Similarly, the ketone **99** is obtained from the iodonium salt **98**.[115] This procedure can also be applied to alkenyliodonium salts bearing the OH group. Thus compound **100** eliminates iodobenzene to produce carbene **101**, which then inserts into the $O-H$ bond to form 2,3-dihydrofuran derivative **102**.[95]

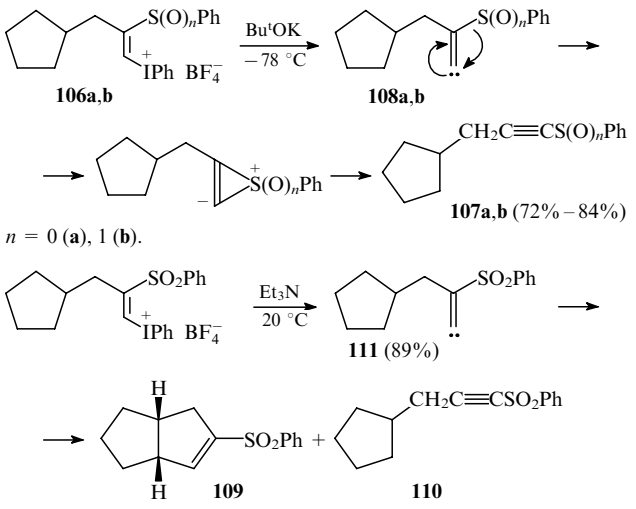


Reactions of deuterated alkenyliodonium salts **103** with triethylamine at 0 °C lead to terminal alkynes **104** (10% deuterium) and **105** (89% deuterium) in quantitative yields. The compositions of the reaction products indicate that alkylidenecarbenes predominantly arise through α-elimination and subsequent 1,2-hydrogen shift rather than through a *syn*-β-elimination process.[115] The absence, in the reaction mixture, of cyclopentene

derivatives suggests that the 1,2-α-hydrogen shift following 1,5-insertion of alkylidenecarbenes into the C—H bond is very unfavourable.[116]

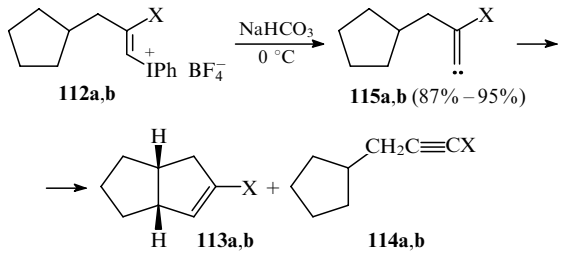


Elimination of iodobenzene from iodonium salts **106a**,**b** under the action of potassium *tert*-butoxide leads to alkynes **107a**,**b** as the main products. The α-phenylthio and α-phenylsulfinyl groups in alkylidenecarbenes **108a**,**b** are good leaving groups. Their migration apparently occurs *via* sulfonium ylides.[95] In contrast to compounds **106a**,**b**, an iodonium salt with the α-phenylsulfonyl group gives predominantly 2-phenylsulfonylbicyclo[3.3.0]oct-1-ene (**109**) (the ratio **109** : **110** = 4 : 1). This shows that the carbene **111** preferentially inserts into the C—H bond rather than undergoes migration of the sulfur-containing substituent despite the very good migrating ability of this group.[116]



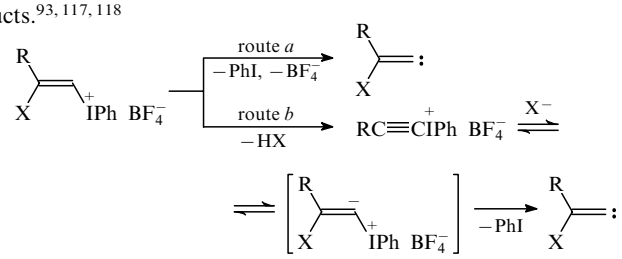
n = 0 (**a**), 1 (**b**).

Reactions of halogen-containing alkenyliodonium salts of similar structures yield different products depending on the nature of the halogen atom in these salts. Thus chlorine-substituted salt **112a** gives a 38 : 62 mixture of the product of 1,5-insertion of a carbene into the C—H bond (**113a**) and the rearrangement product (**114a**). Only bromoalkyne **114b** is formed from the bromine-substituted salt **112b** due to the more preferable migration of the bromine atom in the carbene **115b**.[93]

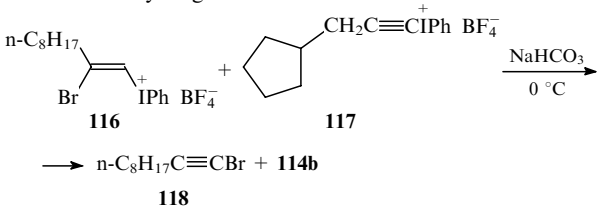


X = Cl (**a**), Br (**b**).

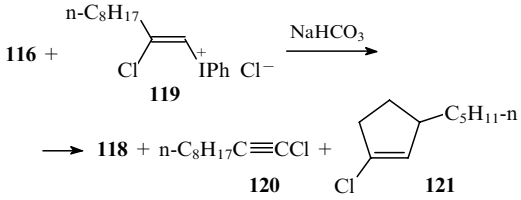
α-Halogenoalkylidenecarbenes are generated in the α-elimination of iodobenzene from (*Z*)-(2-halogenoalkenyl)iodonium salts (route *a*). However, in this case the reaction apparently also involves the more stereoelectronically favourable base-induced *anti*-β-elimination of HX giving rise to alkynyliodonium salts (route *b*). The Michael addition of a halide ion and subsequent reductive elimination of iodobenzene lead to the final products.[93, 117, 118]



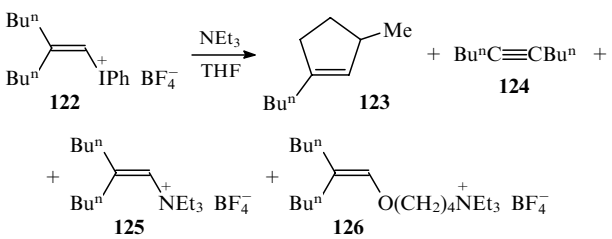
Possible transformations of the carbene formed were elucidated in a cross-reaction of (*Z*)-(2-bromoalkenyl)iodonium **116** and alkynyliodonium tetrafluoroborates **117** with sodium hydrogencarbonate. Alkynes **118** and **114b** were formed in the ratio 7 : 3, thus indicating that α-bromoalkylidenecarbene is generated through both α-elimination of the phenyliodonio group and *anti*-β-elimination of hydrogen bromide.[93]

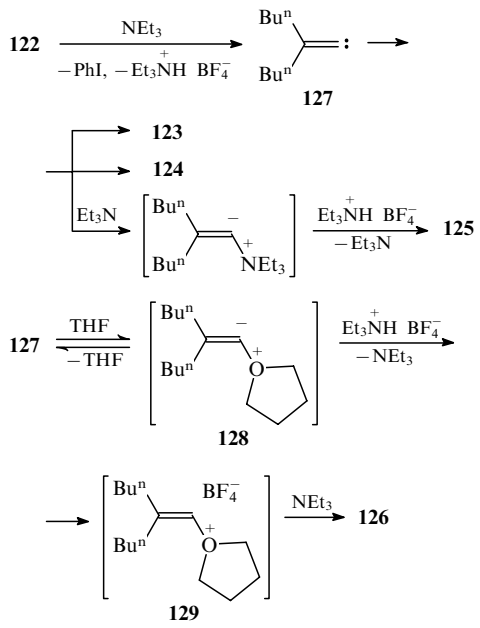


2-Bromovinyliodonium salt **116** more readily undergoes *anti*-β-elimination than the 2-chlorovinyliodonium salt **119**. This follows from the fact that a 78 : 13 : 9 mixture of compounds **118**, **120** and **121** is formed in the cross-reaction of both salts with $NaHCO_3$.[93]



The direction of reactions involving the intermediacy of alkylidenecarbenes was found[119–121] to be also dependent on the nature of solvent employed. In diethyl ether or THF, the complexation of alkylidenecarbenes with these solvents, *viz*., the formation of oxonium ylides, was observed. Thus treatment of alkenyliodonium salt **122** with triethylamine in THF yields a mixture of products **123**–**125** formed as the result of 1,5-insertion of the carbene **127** into the C—H bond, 1,2-migration of the butyl group and also the reaction of salt **122** with triethylamine. In addition, a nucleophilic attack of the intermediate carbene **127** on tetrahydrofuran to form oxonium ylide **128** and further transformation of the latter into compound **126** *via* oxonium salt **129** also occur.[122]





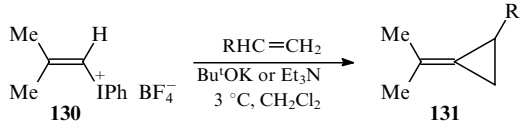
The course of the reactions is also controlled by the temperature (Table 1). On lowering the reaction temperature, the yields of the products **123**–**125** derived from alkylidenecarbene **127** are decreased, and the yield of the ether **126** derived from vinyloxonium ylide **128** is increased. These effects were explained as the reversibility of the process of oxonium ylide **128** formation, although no solid proof for the existence of an equilibrium between free alkylidenecarbenes and oxonium ylides was obtained.

Table 1. The ratio of the reaction products of compound **122** with Et_3N in THF.

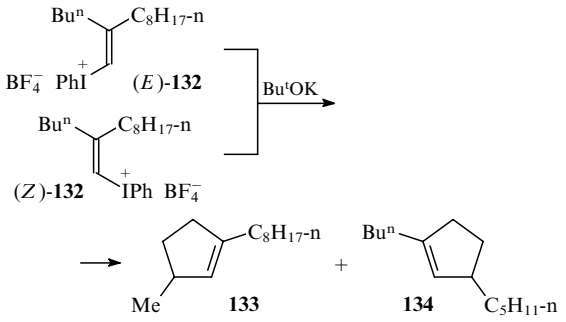
Temperature /°C	Time /h	Overall yield (%)	Yields of reaction products (%)				Ratio (**123** + **124** + **125**) : : **126**
			123	**124**	**125**	**126**	
60	10	90	74	14	< 1	2	98 : 2
40	10	95	75	11	< 1	9	90 : 10
20	10	99	75	8	1	15	85 : 15
0	10	98	71	3	1	23	77 : 23
0 [a]	10	78	48	2	1	27	65 : 35
0 [b]	10	87	44	2	1	40	54 : 46
0 [c]	10	92	44	3	3	42	54 : 46

Note. The reaction mixture was preliminarily kept for 2 days at: [a] −20 °C; [b] −40 °C; [c] −60 °C.

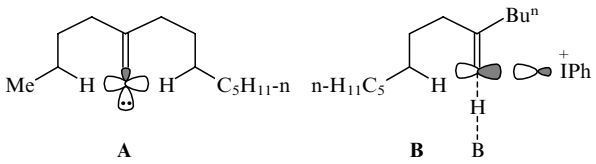
An alkylidenecarbene generated from the alkenyliodonium salt **130** adds to alkenes to give alkylidenecyclopropanes **131**.[123] Its addition to *cis*- and *trans*-4-methylpent-2-enes occurs stereospesifically.



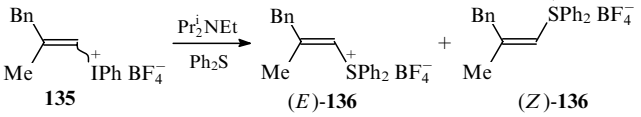
The ratio of isomeric cyclopentenes **133** and **134** formed upon treatment of both *Z*- and *E*-isomers of the iodonium salt **132** with Bu^tOK is 1 : 1 and is independent of the geometry of the starting compounds or the reaction conditions. This suggests the participation of the alkylidenecarbene as an intermediate species in this reaction.[115]



Complete loss of regioselectivity testifies that this intermediate species represents a 'true' carbene (structure **A**) rather than a carbenoid (structure **B**) in which the 'memory effect' would be preserved to some extent.



In the presence of sulfides, alkylidenecarbenes give vinylsulfonium salts as the products of onium species transformations. An assumption that these reactions occur *via* free alkylidenecarbenes was put forward on the grounds of stereochemical studies.[122] Thus (*E*)-vinylsulfonium salt (*E*)-**136** was the major product [the ratio (*E*)-**136** : (*Z*)-**136** is 69 : 31] in the reactions of both *E*- and *Z*-iodonium salts **135** with diisopropylamine in the presence of diphenyl sulfide. Such stereoselectivity most likely results from different bulkiness of two α-substituents in the alkylidenecarbenes formed.

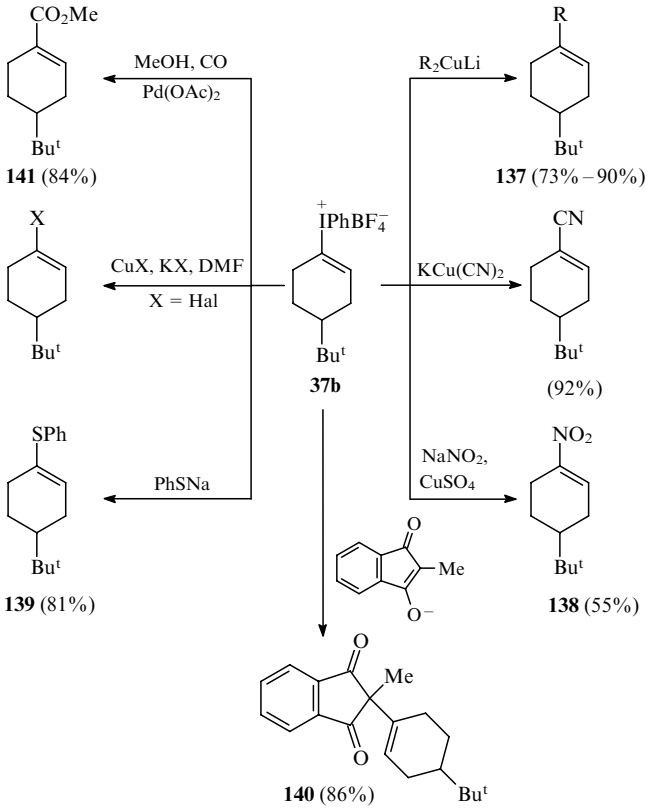


The ρ constants for the reactions of 2-methyl-1-propylidene, generated from the salt **130**, with different styrene derivatives in the presence of Et_3N and Bu^tOK have been determined (−0.56 and −0.55, respectively) by measuring relative rates for these reaction.[123] Since free alkylidenecarbenes are relatively 'soft' nucleophiles, their reactions usually have small negative ρ values. In contrast, carbenoids generated from other precursors possess much more pronounced electrophilic properties and therefore their reactions have high negative ρ values.

2. Vinylic nucleophilic substitution in alkenyliodonium salts. The aryliodonio group is known to be one of the best leaving groups in nucleophilic substitution reactions.[111, 124] Owing to the capability of aryl(vinyl)iodonium salts to generate vinylic cations under remarkably mild conditions, these salts can formally be considered as vinylic cation equivalents. The reactions of (4-*tert*-butylcyclohex-1-enyl)phenyliodonium tetrafluoroborate **37b** with various nucleophiles [58, 59] are exemplified in Scheme 1.

Alkylation of alkenyliodonium salts with organometallic compounds to give substituted cyclohexenes **137** occurs successfully only with lithium organocuprates; other organometallic compounds are oxidised by the iodonium salt **37b**. Substitutions by halide ions in the presence of the respective copper(I) halides in DMF at 20 °C result in nearly quantitative yields of products. Good product yield is also obtained in the reaction with cyanide ion. The salt **37b** reacts with sodium nitrite in the presence of copper(II) sulfate to give nitroalkene **138** without any traces of

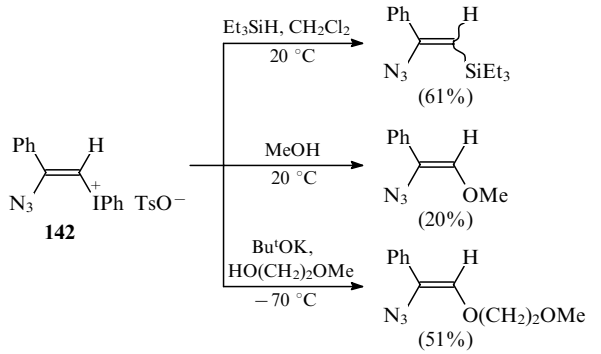
Scheme 1



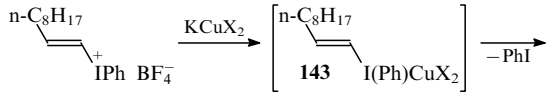
137: R = Me, Ph, Bu.

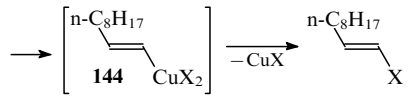
nitrite. The reaction with sodium benzenethiolate yields (4-*tert*-butylcyclohex-1-enyl) phenyl sulfide (**139**), while with indandione enolate it leads to the C-vinylation product **140** (see also Ref. 125). Vinyliodonium salt **37b** is carbonylated in methanol in the presence of palladium salts as catalysts to afford ester **141**.

Reactions of several nucleophiles with 2-azidoalkenyliodonium salts **142** prepared *in situ* by the addition of sodium azide to alkynyliodonium salts have been studied.[90] In all cases, the iodine-containing fragment was substituted by nucleophiles.



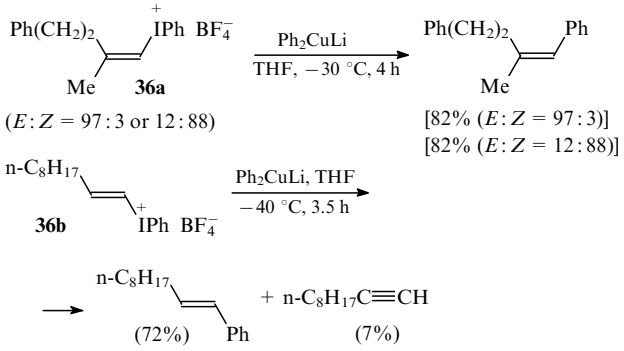
Nucleophilic substitutions of vinyliodonium salts in the presence of copper compounds occur stereospecifically with retention of the initial configuration.[126, 127] This was the reason to reject an idea of a free-radical mechanism for such reactions. Instead, a mechanism involving the intermediacy of three-coordinated iodine species **143** and three-coordinated copper **144** was suggested.[102, 126, 127]



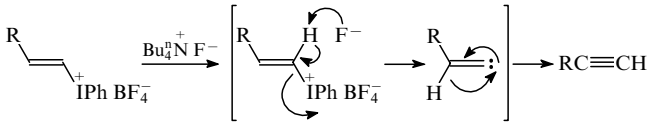


X = Cl, Br.

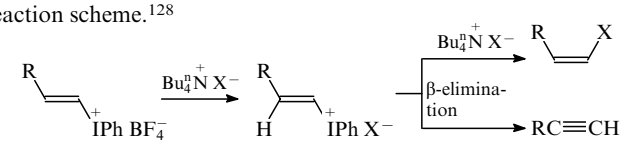
The stereochemistry of vinylic nucleophilic substitution has been studied in detail in the reactions of alkenyl(phenyl)iodonium salts **36a**,**b** with Ph_2CuLi in tetrahydrofuran. It was found that compound **36a** gives the products in high yields and with complete retention of the initial configuration. By contrast, the reactions of compound **36b** are accompanied by elimination to form the corresponding alkyne.[58]



The substitution of the iodine-containing fragment in vinyliodonium salts by halide, under the action of tetrabutylammonium halides in dichloromethane in the absence of copper(I) halides, occurs with inversion of configuration, which competes with elimination and the formation of alkynes.[128] Transformations of α- and β-deuterated substrates were examined in order to elucidate the mechanism of these reactions. Based on the results obtained [128] it was concluded that elimination in the reactions with Bu^n_4NF results from the initial attack by the fluoride ion on the α-hydrogen atom followed by rearrangement of the carbene formed.



By contrast, other halide ions react through the β-elimination mechanism. The yields of elimination products are increased in the series: $I^- < Br^- < Cl^- < F^-$; the dependence on the nature of a substituent at the C(2) atom has the order: *n*-alkyl < benzyl < phenyl. Stereoselectivity of the reactions decreases in the same order. With an increase in the excess of tetrabutylammonium halide in the reaction, a noticeable drop in the ratio alkyne : vinyl halide is observed, thus indirectly confirming the proposed reaction scheme.[128]



R = n-C_8H_{17}, $Ph(CH_2)_3$, Ph; X = Cl, Br, I.

Nucleophilic substitutions of the iodine-containing fragment in the iodonium salt **35** occur, as a rule, in good yields (Table 2); the ratio of stereoisomers depends on the nature of the nucleophile and the reaction conditions.[57]

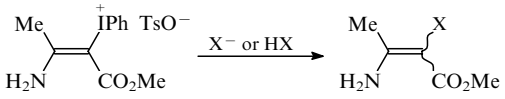
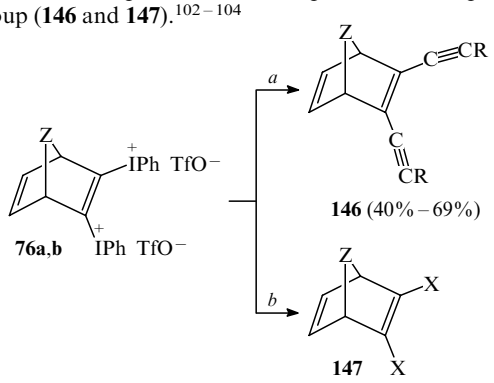


Table 2. Nucleophilic substitution of the iodine-containing fragment in compound **35**.

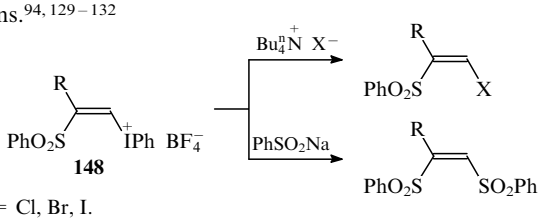
Product **145**	X	Reaction conditions			Yield (%)
		reagent	solvent	time /h	
a	Br	$Bu_4N^+Br^-$	CH_2Cl_2	12	78
b	NO_2	$NaNO_2$, $CuSO_4$	DMF, H_2O	12	20
c	TsO	TsONa	DMF	12	25
d	CN	KCN	DMF, H_2O	12	60
e	Et_2N	Et_2NH	CH_2Cl_2	4	80
f			CH_2Cl_2	4	83

Bisiodonium salts **76a**,**b** react with anionic nucleophiles to form the nucleophilic substitution products of the phenyliodonio group (**146** and **147**).[102–104]



Z = O (**a**), CH_2 (**b**); (*a*) CH≡CR, BuLi, CuCN, CH_2Cl_2, −78 to 25 °C, 12 h, R = $SiMe_3$, Bu^t, Bu^n, Ph; (*b*) NaX, CuX; X = Br, I, CN, PhCOO.

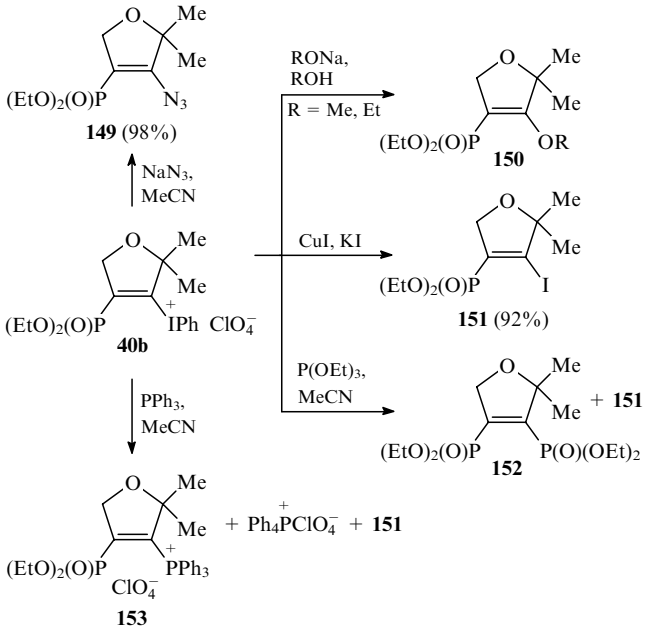
Nucleophilic substitutions in (*Z*)-(2-phenylsulfonyl)alkenyliodonium salts **148** with tetrabutylammonium halides or sodium benzenesulfinate proceed with retention of configurations.[94,129–132]



X = Cl, Br, I.

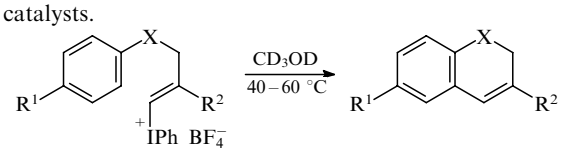
Heterocyclic iodonium salts also undergo nucleophilic substitution. Thus the reactions of compound **40b** with nucleophiles lead to the corresponding cyclic adducts through a two-step addition–elimination process and/or reductive elimination following attack by a nucleophile on the iodine atom (Scheme 2).[62] Perchlorate **40b** reacts with sodium azide in acetonitrile to give vinyl azide **149** in nearly quantitative yield. The reactions of compound **40b** with sodium methoxide and sodium ethoxide in the respective alcohol afford vinyl ethers **150** in 83% and 91% yields, respectively. Compound **40b** reacts with a mixture of equimolar amounts of potassium and copper(I) iodides to give vinylic iodide **151** in 67% yield. In the reaction with triphenylphosphine, vinylic iodide **151** and the phenylation product of triphenylphosphine, *viz*., tetraphenylphosphonium perchlorate (22% yield), are formed along with the expected vinylphosphonium salt **153** (20% yield).

Scheme 2

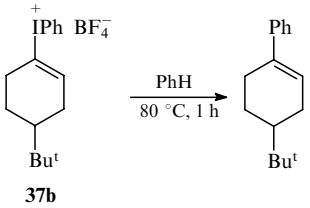


3. Vinylation of aromatic compounds with vinyliodonium salts

As is known, direct introduction of the vinylic group into aromatics by electrophilic substitution is rather inefficient because of the low reactivities of vinyl halides. Unlike vinyl halides, vinyliodonium salts do enter into the reactions of electrophilic aromatic substitution. These substitutions can proceed as an intramolecular process to lead to cyclic systems, if vinyliodonium salts have suitable structures.[133] Compared with Friedel–Crafts reactions they proceed under milder conditions and in the absence of catalysts.



X = CH_2, O; R^1, R^2 = H, Me, Cl, Br.

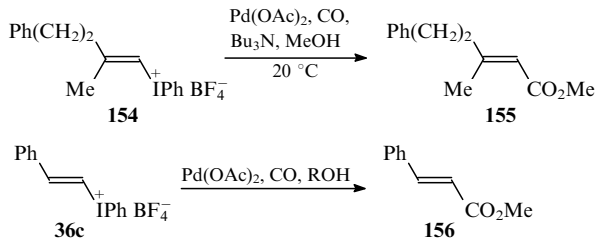


37b

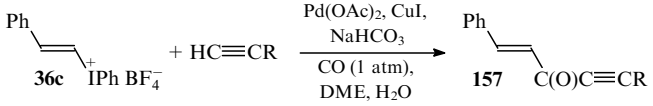
(*Z*)-Alkenyliodonium salts do not cyclise under the same conditions. An $S_E(Ar)$-substitution mechanism was suggested [133] in which iodobenzene is eliminated from the intermediate iodocyclopropane, though other mechanisms cannot be ruled out.

4. Palladium-catalysed cross-coupling

Vinyliodonium salts were found to undergo cross-couplings with activated alkenes. The reactions conditions are milder than those used in the Heck reaction. Thus salts **154** and **36c** are carbonylated in the presence of palladium at 20 °C with complete retention of configurations to form α,β-unsaturated esters **155** and **156**.[58,134]

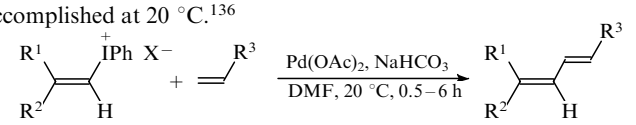


Enynones **157** were synthesised from alkenyliodonium salt **36c** and terminal alkynes under similar conditions in the presence of copper iodide.[135]



R = Bu (76%), Ph (88%).

A highly stereoselective synthesis of conjugated dienes **158** is accomplished at 20 °C.[136]

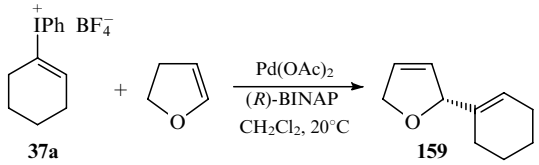


158 (60%–85%)

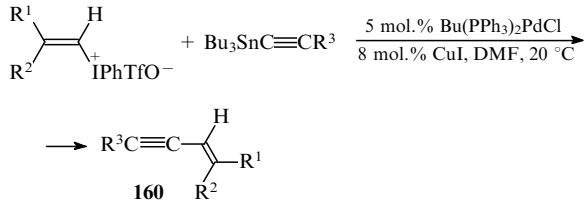
R^1 = H, Bu^n, OTs; R^2 = Bu^n, Ph, OTs, ;

R^3 = Ph, COMe, CO_2Me, CHO; X = OTs, BF_4.

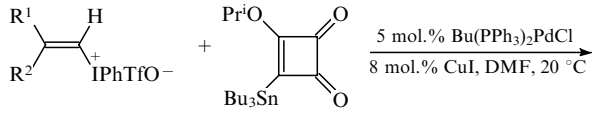
An asymmetrical version of the Heck reaction was implemented in the presence of a chiral ligand, *viz.*, (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [(*R*)-BINAP].[137]

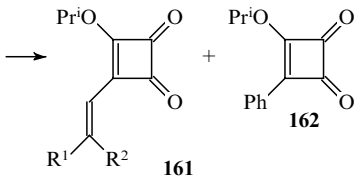


Furthermore, in the presence of palladium, alkenyliodonuim salts react under mild conditions with alkynyl-,[86] allyl-[138] and alkenyl-stannanes.[86, 138] The reactions with alkenylstannanes occur faster but less selectively to give various unidentified compounds along with the major product.



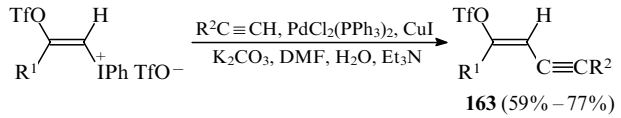
R^1	R^2	R^3	Yield of **160** (%)
Bu^n	Bu^n	Ph	77
Me	Et	Ph	64
Et	Me	Ph	66
Bu^n	Bu^n	Bu^tCO	66
Bu^n	Et	$C(O)N(CH_2)_4$	67





R^1 = R^2 = Me (70%), R^1 = Bu^n, R^2 = Et (60%);
R^1 = R^2 = Bu^n (65%); R^1 = Et; R^2 = Bu^n (76%).

Terminal alkynes readily react with alkenyl(aryl)iodonium salts bearing the TfO group in the β-position at 30–40 °C in DMF : H_2O (6 : 1) to form enynes **163** in high yields.[139]



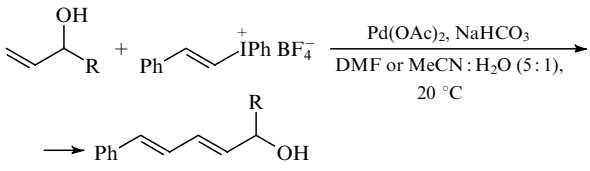
163 (59%–77%)

R^1 = Bu^n, H, CH_2OMe, Ph; R^2 = n-C_8H_{17}, Ph, CH_2OMe, $SiMe_3$, CH_2Cl, Pr^n.

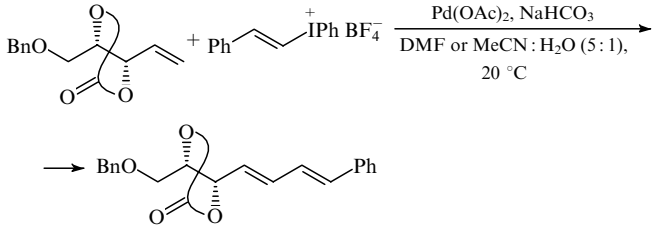
The reaction rates were found to be higher in polar solvents.[139] Small variations in the basicity of amines almost do not affect the reaction rates and the yields of the coupling products. Complexes of palladium with triphenylphosphine ligands were found to be the most efficient. The addition of CuBr instead of CuI does not affect the reaction rates. An induction period (~ 1–2 h) is observed in the CuCl-catalysed reactions, after which the reaction rates become the same as in the case of CuI. The optimum ratio of $PdCl_2(PPh_3)_2$ to CuI is 2 : 3. The reaction rates are increased on addition of water to the system DMF–Et_3N–[Pd], this effect depending on the palladium catalyst employed. Thus the maximum rate acceleration on addition of water is observed in the presence of $PdCl_2(PPh_3)_2$.

In aqueous media in the presence of ligand-free palladium catalysts, unsubstituted alkenyliodonium salts also enter into reactions with terminal alkynes.[140]

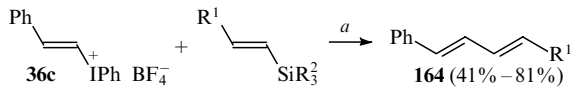
Alkenyliodonium salts react with allylic alcohols [in the presence of $Pd(OAc)_2$ (see Ref. 141) or a polymeric palladium catalyst [142]] and allylic cyclic carbonates.[143]



R = H, n-C_5H_{11}.



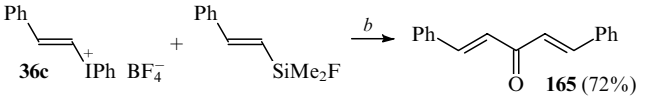
In the presence of palladium catalysts, alkenyliodonium salts also undergo the cross-coupling reactions with organoelement compounds.[144–146] Thus, in the reaction of phenyl(styryl)-iodonium tetrafluoroborate **36c** with vinylfluorosilanes, only the β-styryl group was transformed to afford the cross-coupling products, dienes **164**, in high yields.[145]



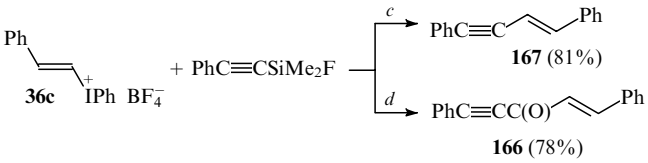
R^1 = Bu^n, Ph; R^2_3 = MeF_2, F_3, Me_2F;
(*a*) η^3-$C_3H_5PdCl_2$, KF or $Bu^n_4N^+F^-$, DMF, 20 °C, 5 min.

To account for the palladium-catalysed reactions of vinylfluorosilanes with alkenyliodonium salts, a mechanism involving the interaction of an electrophilic alkenyliodonium salt with catalytically active Pd(0), the reductive elimination of iodobenzene to form alkenylpalladium tetrafluoroborate and the transmetallation reaction with vinylfluorosilanes was proposed.[145]

Carbonylation of alkenyliodonium salts in the presence of Pd complexes[145,146] can serve as a convenient procedure for the synthesis of unsaturated ketones, *viz*., **165** and **166**. Enyne **167** is smoothly obtained on coupling of alkynylfluoromethylsilane with the iodonium salt **36c**.[145]

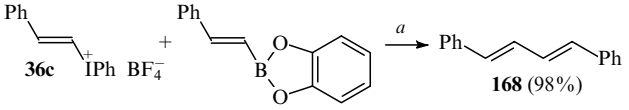


(*b*) η^3-$C_3H_5PdCl_2$, $Bu^n_4N^+F^-$, DME, CO (1 atm), 20 °C, 5 min.



(*c*) η^3-$C_3H_5PdCl_2$, KF or $Bu^n_4N^+F^-$, DMF, 20 °C, 5 min;
(*d*) η^3-$C_3H_5PdCl_2$, $Bu^n_4N^+F^-$, DME, CO (1 atm), 20 °C, 5 min.

The cross-coupling of alkenyliodonium salt **36c** with a large series of boronates in the system $Pd(PPh_3)_4$–Na_2CO_3–DMF–H_2O has been effected and in all cases the cross-coupling product **168** was obtained in virtually quantitative yield.[144]



(*a*) [$Pd(PPh_3)_4$], Na_2CO_3, DME : H_2O = 4 : 1, 20 °C, 10 min.

IV. Conclusion

From the data presented in this review one can see that alkenyliodonium salts are of interest for synthetic organic chemistry. These compounds are rather effective oxidants and can readily undergo free-radical transformations. They also possess high electrophilicities, which can be changed within a wide range by varying the ligands at the iodine atom, and are featured by the presence of the highly nucleofugal iodine-containing group.

Alkenyliodonium salts with several functional groups attract ever-growing interest. Such reagents allow the introduction into substrates of rather complex fragments under mild conditions.

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