Reactivity of Arylethynyl(phenyl)iodonium Salts Towards some 1,3-Dipoles. X-Ray Molecular Structure of 3-Mesityl-5-phenylisoxazol-4-yl(phenyl)iodonium Toluene-p-sulphonate

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Three arylethynyl(phenyl)iodonium salts reacted as 1,3-dipolarophiles with two nitrile oxides to afford phenyl(substituted isoxazolyl)iodonium salts; these gave iodoisoxazoles on reaction with nucleophiles. Phenyl(phenylethynyl)iodonium toluene-p-sulphonate reacted in the same way with nitrones but the resulting phenyl(substituted isoxazolinyl)iodonium salts, with one exception, were difficult to isolate because of ready hydrolysis. The crystal structure of 3-mesityl-5-phenylisoxazol-4-yl(phenyl)iodonium toluene-p-sulphonate has been determined.

Although known[1] since 1965, alkynyl(phenyl)iodonium salts (1) have only recently become readily accessible[2-4] and an impressive array of synthetically useful and mechanistically interesting reactions have already been discovered. These compounds are powerful electrophiles surpassing the 'triphilic' character of 1-halogenoalkynes,[5] as they offer four sites of potential attack by a nucleophile: α- and β-carbon of the triple bond, iodine, and C-1 of the phenyl ring attached to it. Examples for all four modes or reactivity have been reported, most of which involve very mild conditions with reagents such as lithiated furans and thiophenes,[6] carbanions from 1,3-diketones,[7] benzoates,[8] sulphonates,[9] and phosphates,[10,11] vinylcopper compounds,[12] and triphenylphosphine.[13]

$$RC \equiv C - \overset{\bullet}{I} - Ph \quad X^-$$

(1)
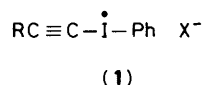
Alkynylphenyl salts with TsO^- and BF_4^- as counter anions are generally stable, but with a more nucleophilic anion they are not, e.g. $Ph \equiv CI^+Ph\ Cl^-$ on being kept at room temperature decomposes to $PhC \equiv CCl$, whereas on treatment with $NaBF_4$, instead of the expected tetrafluoroborate salt (by anion metathesis), another alkenyliodonium salt is obtained,[1] i.e. $PhC(Cl) = CHI^+Ph\ BF_4^-$.

The versatility and reactivity of compounds (1) in conjunction with our long-standing interest in the chemistry of hypervalent iodine has led us to examine the possibility of 1,3-dipolar cycloadditions to the triple bond of compounds (1). Such reactions would lead to a new route for the synthesis of iodonium salts possessing novel structural features and possibly of some interest as potential biocides and photo-initiators in polymerisations of various types.[14]

Results and Discussion

A solution of phenyl(phenylethynyl)iodonium toluene-p-sulphonate, (1a) in methylene dichloride reacted at room temperature with a slight excess of mesitonitrile oxide (2a), to afford in good yield a single product shown to be 3-mesityl-5-phenylisoxazol-4-yl(phenyl)iodonium toluene-p-sulphonate (3a).

The structure of compound (3a) was established from its elemental analysis and spectral data. Especially helpful was its mass spectrum in which the benzoyl fragment was present at m/z 105 (20%); this group comes by necessity from the product

(3a) rather than the regioisomer (4). In order to confirm its chemical identification, a crystal-structure determination was performed, which revealed a 'dimeric' form for compound (3a), shown in Figure 1. 2,6-Dichlorobenzonitrile oxide (2b) also gave, with (1a), a sole product (3d), of the same substitution pattern as compound (3a). When mesitonitrile oxide reacted with the salt (1b), it gave again one product, which on account of its mass spectrum (presence of p-ClC_6H_4CO fragment ion) was characterised as adduct (3b), by analogy with (3a). The regiospecificity of these two reactions did not occur in the reaction of salt (1c) with mesitonitrile oxide. In this case an inseparable mixture (by column chromatography and fractional crystallisation) of the two regioisomers (3c) and (4c) was obtained, in ~1:1 ratio as estimated by the two distinct peaks for the OMe protons in the ${}^1H$ n.m.r. spectrum.

Alkynes have generally a reduced dipolarophilic activity in comparison with alkenes but they may be very reactive when they bear electron-attracting groups, as is the case with dimethyl acetylenedicarboxylate.[15] The phenyliodonio group (PhI^+) is known to be powerfully electron-attracting, so that the good reactivity of salts (1) was not unexpected. A reaction performed between iodo(phenyl)acetylene (5) and mesitonitrile oxide gave also, as sole product, although more sluggishly, the adduct of similar substitution pattern as (3a), i.e. 4-iodo-3-mesityl-5-phenylisoxazole (9a), which has also been obtained by other routes and is discussed separately.

The high stereoselectivity observed in the reactions of compounds (1a), (1b), and (5) with the nitrile oxide may be attributed to favourable electronic effects; the phenyliodonio and iodo groups do not exert serious steric inhibition, whereas they do act as electron acceptors. In the reaction of a series of arylacetylenes, $ArC \equiv CH$, with a nitrile oxide[16] it has been shown that whatever the substituent in the phenyl ring of the arylacetylene, the isoxazole formed was always of the same type, resulting from the attachment of the oxygen atom of the CNO group of the nitrile oxide to the substituted sp carbon atom of the arylacetylene. This regiospecificity has been attributed to unfavourable steric requirements for the opposite approach of the two partners, which is of overriding importance over electronic effects. Our compounds (1a), (1b), and (5) reacted in the same manner. The replacement of a hydrogen atom by either iodine or the phenyliodonio group, despite their bulkiness, does not appear to influence the approach of ArCNO from the same site. The bond between the sp carbon and iodine is quite long,[10] 1.969 Å in (1a), so that the iodine is far enough away and does not deter the approach of the aryl group of the nitrile oxide; the phenyl group attached to iodine in compound (1a) is at an angle
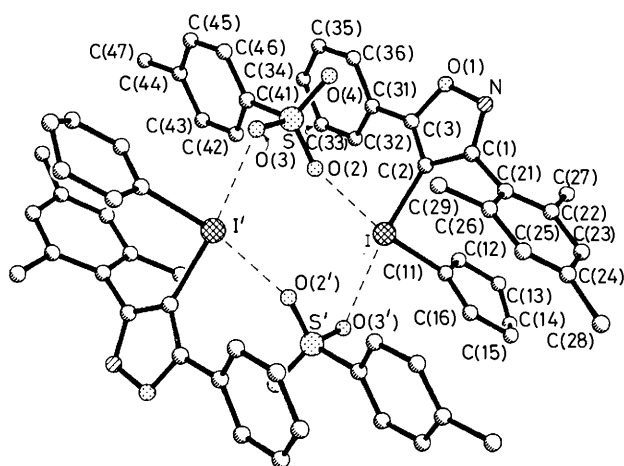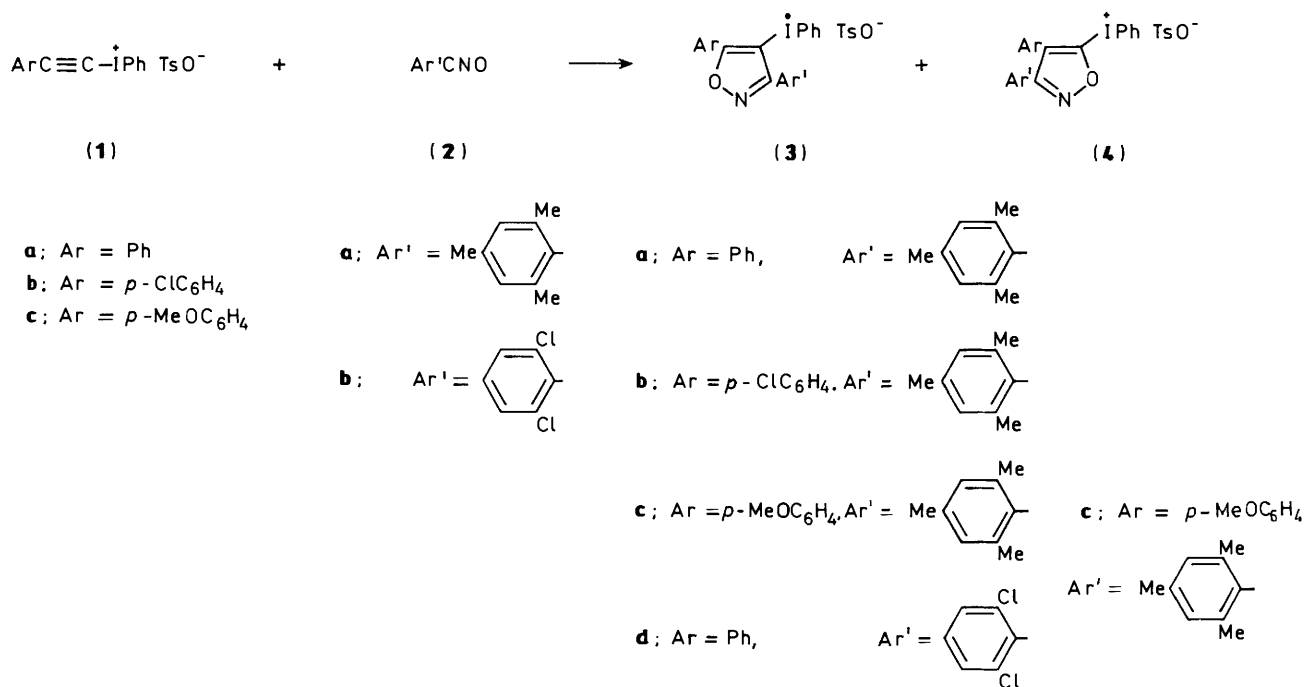
ArC≡C–IPh TsO⁻   +   Ar'CNO   ⟶

(1)   (2)   (3)   (4)

a; Ar = Ph
b; Ar = p-ClC₆H₄
c; Ar = p-MeOC₆H₄

a; Ar' = Me (Me, Me)

b; Ar' = (Cl, Cl)

a; Ar = Ph,   Ar' = Me (Me, Me)

b; Ar = p-ClC₆H₄. Ar' = Me (Me, Me)

c; Ar = p-MeOC₆H₄. Ar' = Me (Me, Me)

d; Ar = Ph,   Ar' = (Cl, Cl)

c; Ar = p-MeOC₆H₄

Ar' = Me (Me, Me)

Figure 1. Clinographic projection of the unit cell, showing the atom numbering scheme

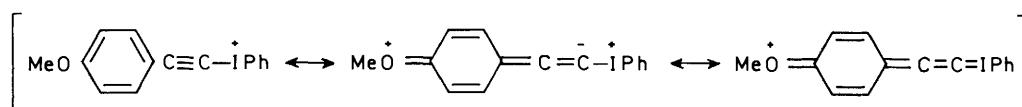of 95° to the linear C≡C–I group[10] and does not exert stereochemical inhibition.

The lack of theoretical calculations makes difficult an assessment of the electrophilicity of sp carbon atoms in these compounds and their reactivity is not at all helpful. The only useful information which may be used for a qualitative assessment of the reactivity of our compounds comes from [13]C n.m.r. spectroscopy. Data are available[17] for phenylacetylene and its iodide (5) but not for the salt (1a). However, approximate values for its sp carbon atoms may be estimated by analogy from measured values[10] of some aliphatic RC≡CI and RC≡CI⁺Ph TsO⁻ pairs, as shown below.
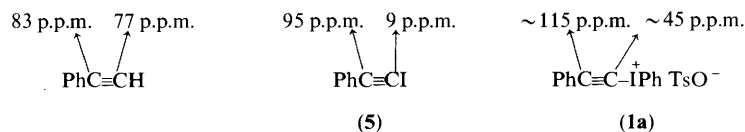
The heavy-atom effect of iodine does not permit a direct comparison between both sp C atoms in compounds (5) and (1a); however, since C-1 in phenylacetylene appears to be a little more electron deficient than C-2, and since the corresponding C atom in (5) resonates at still lower field, it may be concluded that C-2 is even more electron deficient in (1a) and that therefore these C atoms are better sites for attachment of O of the nitrile oxides, in comparison with phenylacetylene. Both iodine and to a higher degree the phenyliodonio group reduce π-electron density at the β-carbon by combination of −I and especially −M effects.[17] The presence of a para-methoxy group in compound (1c) cation increases π-electron density of the β-carbon and it now becomes feasible for the O end of the nitrile oxide to be attached to the other carbon atom. In p-MeOC₆H₄C≡CH this mode is not observed since there is no resonance stabilisation, as is the case in the cation of (1c).

The regioselectivity of our cycloadditions with nitrile oxides may be considered using Houk's approximation.[18] The energy levels and coefficients for the frontier orbitals of nitrile oxides are known but no theoretical calculations are available for alkynyliodonium salts, for which only qualitative assessments can be made. We suggest that since the PhI⁺ group is strongly electron-withdrawing, it is likely that stabilisation of the transition state leading to the 5-arylisoxazoles may be effected with either HOMO- or LUMO-dipole control. As a result it is expected that both these transition states will be of comparable energy, as shown schematically in Figure 2.

In order to explain the formation of both regioisomers when the para-methoxy alkynyliodonium salt (1c) was used, it is assumed that the MeO group causes a substantial increase of the LUMO coefficient for the α-C atom of (1c). Thus a HOMO-dipole-controlled transition state of low energy becomes possible leading to the formation of a 4-arylisoxazole. A similar interpretation has been proposed for the cycloaddition of mesitonitrile oxide with methyl propiolate.[18]

83 p.p.m.   77 p.p.m.   95 p.p.m.   9 p.p.m.   ~115 p.p.m. ~45 p.p.m.

PhC≡CH   PhC≡CI   PhC≡C–IPh TsO⁻

(5)   (1a)

$$MeO \bigotimes C\equiv C-IPh \longleftrightarrow MeO=\bigotimes=C=C-IPh \longleftrightarrow MeO=\bigotimes=C=C=IPh$$
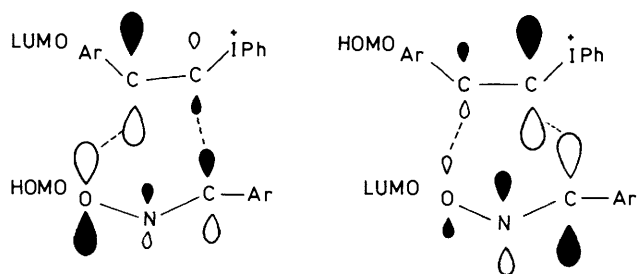
(1c)

Figure 2. Possible orbital interactions in the transition state for the cycloaddition of iodonium compounds (1) and nitrile oxide (2) leading to isoxazoles (3)

1,3-Dipoles other than nitrile oxides are also reactive towards the salt (1a). Several nitrones derived from substituted benzaldehydes reacted with (1a) but only in one case was the expected adduct obtained. This was with nitrone (6) which gave, as sole adduct, the dihydroisoxazolyl(phenyl)iodonium toluene-p-sulphonate (7), having the same substitution pattern with the adducts from (1a) and nitrile oxides, in 37% yield; a by-product was the parent aldehyde (8).
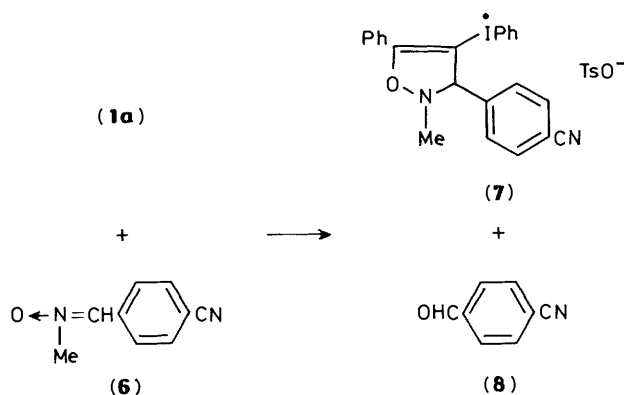

The structural assignment of compound (7) was again based mainly on the benzoyl fragment in its mass spectrum, of high relative intensity (87%). It is important to mention that compound (7) was isolated without chromatographic separation; when the rest of the reaction mixture was subjected to column chromatography a 15% yield of p-cyanobenzaldehyde as the sole product was obtained, along with some by-products mentioned below. All other nitrones tested also reacted with compound (1a) and the reagents were consumed completely over a period of 1—4 days on being stirred at room temperature; the reaction time indicates for nitrones a reactivity broadly similar to that of nitrile oxides. However, no adducts could be isolated and the main products obtained were the aldehydes coming formally from hydrolysis of the nitrones: p-ClC₆H₄CH= N(O)Me gave 54% of p-ClC₆H₄CHO, p-MeOC₆H₄CH= N(O)Me gave 70% of p-MeOC₆H₄CHO, and PhCH=N(O)Ph gave 67% of PhCHO. A multitude of minor products was also produced in all reactions with nitrones; these proved difficult to purify and identify and the only positively identified

compounds were phenyl iodide and iodo(phenyl)acetylene. Another product obtained from all reactions in small amounts contaminated with a nitrogen-containing impurity was apparently the vinylic iodonium salt PhC(OTs)=CHI⁺Ph TsO⁻. This tentatively proposed structure is based on an m/z fragment at 400, corresponding to PhC(OTs)=CHI, and the characteristic yellow colour given when mixed with a solution of sodium diethyldithiocarbamate. This test is of general applicability for iodonium salts[19] and the colour is due to formation of an iodane, ArI(R')SSCNEt₂, where R' may be an aryl, an alkynyl, or an alkenyl group.

The formation of aldehydes must be a secondary reaction, since the reaction mixture before work-up contained only a trace of aldehyde, as shown by its ¹H n.m.r. spectrum. We suggest that in all cases an adduct such as (7) is initially formed but when chromatographic separation is attempted it is hydrolysed inside the column. This ease of hydrolysis has been confirmed for compound (7), which when passed through a silica gel column afforded only the aldehyde (8). It is noted that the reaction of C,N-diphenylnitrone with (phenylsulphonyl)-alkynes gives acylindoles, believed to result from initially unstable 2,3-dihydroisoxazoles.[20]

The reaction of compound (1a) with diphenylnitrilimine [formed in situ from PhC(Cl)=NNHPh and triethylamine] did not give any adduct and the only isolated product was iodo-(phenyl)acetylene in 44% yield. The presence of triethylamine apparently catalysed the thermal decomposition of compound (1a). A complex mixture of products was obtained from the reaction of (1a) with PhSO₂N₃ and also with NaN₃. Compound (1a) did not show dienophilic character with furan and 3,6-dipyridyl-1,2,4,5-tetrazine at room temperature; upon heating, only decomposition products of (1a) were produced.

The most interesting property of diaryliodonium salts is their reaction with nucleophiles of various types, in which arylation of the nucleophile may occur by several mechanisms. Diaryl-iodonium salts with two different aryl groups give normally two sets of products, in ratios depending on electronic and steric factors according to equation (1).

$$ArI^+Ar' + Nu^- \longrightarrow ArNu + Ar'I$$

$$\text{and } ArI + Ar'Nu \quad (1)$$
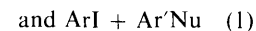
Some reactions of the iodonium salt (3a) with nucleophiles have been briefly examined. Initially a metathetical reaction of (3a) with NaI resulted in the formation of the iodide (3e);
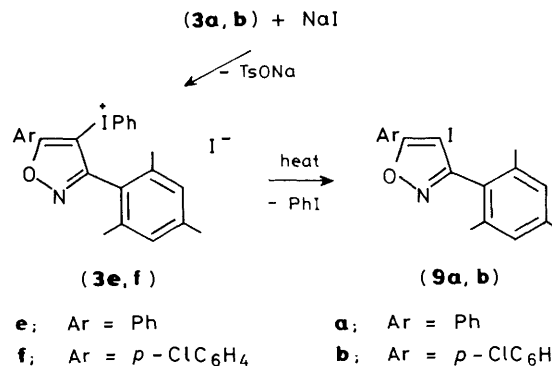
similarly, (3b) gave the iodide (3f). These salts upon heating in the absence of solvents were converted into phenyl iodide and the corresponding iodoisoxazoles (9a and b). Compound (9a) was identical with the adduct from the reaction between iodo(phenyl)acetylene and mesitonitrile oxide.

Compound (9a) has also been obtained from its sulphonate analogue (3a) and two other nucleophiles. The first was sodium diethyldithiocarbamate, $Et_2NCSS^-Na^+$, which we have found[19] to give, with diaryliodonium salts, stable iodanes $Ar_2ISSCNEt_2$. In the present case the corresponding iodane was formed (yellow colouration) but it was not stable enough to be isolated and upon work-up the iodoisoxazole (9a) and phenyl diethyldithiocarbamate ($Et_2NCSSPh$) were isolated. The second nucleophile was sodium nitrite, the reaction of which with various iodonium salts is catalysed by Cu^{++} and does not involve formation of an iodane.[21] Compound (9a) was again formed, along with nitrobenzene, making it clear that nucleophiles do not attack the heterocyclic ring of compound (3a) under various conditions. The reason for this regiospecificity must be the stereochemical inhibition experienced at C-4 of the isoxazole ring by the adjacent phenyl and mesityl groups. There is plenty of evidence that steric factors may be often more important than electronic ones in analogous reactions.[19]

X-*Ray Structure Determination of Compound* (3a).—The determination confirms the chemical identification of compound (3a) (Figure 1). The geometry about the iodine involves a square-planar arrangement of two primary I–C bonds and two secondary I ··· O bonds. The primary bonds of iodine to the phenyl and isoxazolyl rings have lengths of 2.100(3) and 2.078(4) Å, respectively, whereas the C–I–C angle is 92.3(1)°, *i.e.* values normally expected for iodonium salts.[22] These rings are almost perpendicular with an angle between their least-square mean planes of 83.6(2)°. The secondary I ··· O bonds with lengths I ··· O_2 2.735(2) and I ··· O_3^i 2.691(3) Å are almost aligned with the primary bonds [angles 169.5(1)° and 172.12(8)°] to form a nearly planar tetragonal co-ordination arrangement around iodine. It is noted that these secondary bonds are among the shortest measured bonds of this kind of hypervalent iodine compounds.[22] There is no way to distinguish between intramolecular and intermolecular bonds and one may speak of a dimer forming a chair-shaped eight-membered ring, in which I, O(2), O(3), and S and their centrosymmetric equivalents participate around an inversion centre. Such pseudo-rings have also been observed in two other dimeric iodine(III) compounds: dibenziodolyl pyrrolidinedithiocarbamate[23] and an unusual 1,6-dipole.[11]

Experimental

I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer. [1]H N.m.r. spectra were recorded on a Varian A-60A spectrometer. Mass spectra were obtained from a Hitachi–Perkin-Elmer RMU-6L single-focusing spectrometer at 70 eV. Light petroleum refers to that fraction boiling in the range 40—60 °C.

Phenyl(phenylethynyl)iodonium toluene-*p*-sulphonate (1a) was prepared from phenylacetylene and [hydroxy(tosyloxy)-iodo]benzene.[3,10] The same method with slight adaptations (ratio of reactants 2:1 and time of stirring 20 h) was applied for the synthesis of iodonium salts (1b) and (1c) with starting materials *p*-chlorophenylacetylene and *p*-methoxyphenylacetylene, respectively.

p-*Chlorophenylethynyl*(*phenyl*)*iodonium toluene*-p-*sulphonate* (1b) was obtained in 32% yield, m.p. 131—133 °C (decomp.) (from methylene dichloride–light petroleum); $v_{max.}$(Nujol) 2 160 cm^{-1}; δ(CDCl$_3$) 2.33 (3 H, s) and 7.00—8.32 (13 H, m); *m/z*

341/339, 264/262, 248, and 204 (Found: C, 49.3; H, 3.0. $C_{21}H_{16}ClIO_3S$ requires C, 49.38; H, 3.16%).

p-*Methoxyphenylethynyl*(*phenyl*)*iodonium toluene*-p-*sulphonate* (1c) was obtained in 35% yield, m.p. 135—139 °C (decomp.) (from methylene dichloride–light petroleum); $v_{max.}$(Nujol) 2 140 cm^{-1}; δ(CDCl$_3$) 2.32 (3 H, s), 3.83 (3 H, s), and 6.72—8.30 (13 H, m); *m/z* 302, 248, and 204 (Found: C, 52.3; H, 3.8. $C_{22}H_{19}IO_4S$ requires C, 52.18; H, 3.78%).

Phenyl(*substituted isoxazolyl*)*iodonium Toluene*-p-*sulphonates* (3a—d) *and* (4c). *General Procedure.*—A solution of iodonium salt (1a—c) (1 mmol) and nitrile oxide (2a—b) (1.2 mmol) in methylene dichloride (15 ml) was stirred at room temperature under nitrogen with protection from daylight for ~48 h. The solvent was evaporated off and diethyl ether was added which caused precipitation of the iodonium salt.

3-*Mesityl*-5-*phenylisoxazol*-4-*yl*(*phenyl*)*iodonium toluene*-p-*sulphonate* (3a) was obtained in 76% yield, m.p. 173—176 °C (from methylene dichloride–light petroleum); $v_{max.}$(Nujol) 1 605 and 1 555 cm^{-1}; δ(CDCl$_3$) 1.73 (6 H, s), 2.28 (3 H, s), 2.38 (3 H, s), 6.80—7.68 (14 H, m), and 7.99—8.34 (2 H, m); *m/z* 389, 262, 248, 204, and 105 (Found: C, 58.4; H, 4.4; N, 1.9. $C_{31}H_{28}INO_4S$ requires C, 58.39; H, 4.42; N, 2.20%).

5-(p-*Chlorophenyl*)-3-*mesitylisoxazol*-4-*yl*(*phenyl*)*iodonium toluene*-p-*sulphonate* (3b) was obtained in 82% yield, m.p. 209—212 °C (from methylene dichloride–light petroleum); $v_{max.}$(Nujol 1 605 and 1 570 cm^{-1}; δ(CDCl$_3$) 1.73 (6 H, s), 2.32 (3 H, s), 2.40 (3 H, s), 6.92—7.62 (13 H, m), and 8.10—8.32 (2 H, m); *m/z* 425/423, 298/296, 270/268, 248, 204, and 141/139 (Found: C, 55.3; H, 4.0; N, 2.2. $C_{31}H_{27}ClINO_4S$ requires C, 55.40; H, 4.05; N, 2.08%).

3-*Mesityl*-5-(p-*methoxyphenyl*)*isoxazol*-4-*yl*(*phenyl*)-*iodonium toluene*-p-*sulphonate* (3c) *and* 3-*mesityl*-4-(p-*methoxyphenyl*)*isoxazol*-5-*yl*(*phenyl*)*iodonium toluene*-p-*sulphonate* (4c) were obtained in 60% yield as a mixture which could not be separated by recrystallisation or column chromatography. The mixture had a broad m.p., 139—161 °C, which remained the same after recrystallisation (from methylene dichloride–light petroleum); $v_{max.}$(Nujol) 1 630, 1 590, and 1 580 cm^{-1}; δ(CDCl$_3$) 1.77 (6 H, s), 2.32 (3 H, s), 2.38 (3 H, s), 3.83 and 3.93 (taken together 3 H, 2 s, integration showed a ratio 42:58), and 6.72—8.33 (15 H, m); *m/z* 419, 292, 264, 204, and 135 (Found: C, 57.65; H, 4.5; N, 2.0. $C_{32}H_{30}INO_5S$ requires C, 57.57; H, 4.53; N, 2.10%).

3-(2,6-*Dichlorophenyl*)-5-*phenylisoxazol*-4-*yl*(*phenyl*)-*iodonium toluene*-p-*sulphonate* (3d) was obtained in 71% yield, m.p. 180—186 °C (from methylene dichloride–light petroleum); $v_{max.}$(Nujol) 1 590 and 1 550 cm^{-1}; δ(CDCl$_3$) 2.30 (3 H, s), 6.92—7.75 (15 H, m), and 8.06—8.27 (2 H, m); *m/z* 417/416/415, 290/289/288, and 105 (Found: C, 50.8; H, 3.2; N, 1.9. $C_{28}H_{20}Cl_2INO_4S$ requires C, 50.62; H, 3.03; N, 2.10%).

3-*Mesityl*-5-*phenylisoxazol*-4-*yl*(*phenyl*)*iodonium iodide* (3e) was obtained from tosyl derivative (3a) (0.5 mmol) and NaI (1 mmol) which were stirred in acetonitrile (10 ml) for 90 min at 0 °C. The reaction mixture was concentrated to a small volume and upon addition of methylene dichloride sodium toluene-*p*-sulphonate was precipitated and removed by filtration. The filtrate was concentrated and upon addition of light petroleum compound (3e) crystallised out (0.219 g, 74%), m.p. 141—142 °C (Found: C, 48.65; H, 3.45; N, 2.3. $C_{24}H_{21}I_2NO$ requires C, 48.59; H, 3.57; N, 2.36%).

4-*Iodo*-3-*mesityl*-5-*phenylisoxazole* (9a) was obtained by two methods: (a) compound (3e) was heated in an oil-bath until it melted with decomposition. Chromatography on a silica gel column with light petroleum and light petroleum–ethyl acetate (50:1) as eluants gave phenyl iodide and compound (9a) in 78% yield, m.p. 132—134 °C (from ethanol); $v_{max.}$(Nujol) 1 610 and 1 570 cm^{-1}; δ(CDCl$_3$) 2.10 (6 H, s), 2.35 (3 H, s), 6.92

(2 H, s), 7.33—7.65 (3 H, m), and 8.00—8.28 (2 H, m); m/z 389 (M^+), 262, 234, and 105 (Found: C, 55.6; H, 4.2; N, 3.5. $C_{18}H_{16}INO$ requires C, 55.54; H, 4.14; N, 3.60%). (b) Equimolecular amounts of iodophenylacetylene and mesitonitrile oxide were stirred in methylene dichloride for 11 days at room temperature. The reaction was completed by refluxing for 7 h. Chromatography as in (a) afforded some unchanged iodophenylacetylene and compound (9a) in 83% yield.

5-(p-*Chlorophenyl*)-4-*iodo*-3-*mesitylisoxazole* (9b) was produced by thermolysis of the iodide (3f), obtained in 88% yield by a procedure similar to that for the salt (3e), under similar conditions as for compound (9a), in 95% yield; m.p. 140—142 °C (from ethanol); $\nu_{max.}$(Nujol) 1 600 cm⁻¹; δ(CCl₄) 2.12 (6 H, s), 2.35 (3 H, s), 6.97 (2 H, s), 7.53 (2 H, d), 8.19 (2 H, d); m/z 425/423 (M^+) and 141/139 (Found: C, 51.0; H, 3.4; N, 3.3. $C_{18}H_{15}ClINO$ requires C, 51.02; H, 3.57; N, 3.30%).

3-(p-*Cyanophenyl*)-5-*phenyl*-2,3-*dihydroisoxazol*-4-*yl*-(*phenyl*)*iodonium Toluene*-p-*sulphonate* (7).—A solution of C-(p-cyanophenyl)-N-methylnitrone (6) (0.16 g, 1 mmol) and compound (1a) (0.476 g, 1 mmol) in methylene dichloride (20 ml) was stirred under nitrogen in the dark for 6 days at room temperature. The reaction mixture was concentrated to a small volume and diethyl ether was added. After the mixture had been kept at −10 °C overnight an oil separated, which was crystallised upon intense rubbing to afford crystals (0.235 g, 37% yield), m.p. 121 °C (from methylene dichloride–light petroleum); $\nu_{max.}$(Nujol) 2 220, 1 630, and 1 590 cm⁻¹; δ(CDCl₃) 2.32 (3 H, s), 2.96 (3 H, s), and 6.83—7.90 (19 H, m); m/z 388, 248, 204, and 105 (Found: C, 56.4; H, 3.8; N, 4.3. $C_{30}H_{25}IN_2O_4S$ requires C, 56.60; H, 3.95; N, 4.40%). The mother liquor was chromatographed and afforded p-cyanobenzaldehyde (0.020 g, 15% yield). Similar conditions were employed for the reaction of compound (1a) with other nitrones but no crystalline compound could be obtained and upon chromatography the benzaldehydes were the main isolated products, along with small amounts of PhI, PhC≡CI, and probably PhC(OTs)= CHI⁺Ph TsO⁻

Reactions of Compound (3a) *with Nucleophiles*.—The reaction with Et₂NCSSNa was performed by stirring equimolecular quantities of the reagents in water at room temperature in the dark for 1 h. Work-up followed by column chromatography gave first compound (9a) (84% yield) and then Et₂NCSSPh (85% yield). The reaction with NaNO₂ was performed in aqueous dimethylformamide with catalytic amounts of CuSO₄. After the mixture had been stirred for 3 days at room temperature in the dark, work-up and column chromatography afforded first nitrobenzene (26% yield) and then compound (9a) (35% yield.). In neither reaction was PhI detected.

X-*Ray Crystallography of* 3-*Mesityl*-5-*phenylisoxazol*-4-*yl*-(*phenyl*)*iodonium Toluene*-p-*sulphonate* (3a).—Crystals of compound (3a) were grown from methylene dichloride–light petroleum. A single crystal of approximate dimensions 0.55 × 0.30 × 0.30 mm was used.

Crystal data. $C_{31}H_{28}INO_4S$, M = 637.54, triclinic, space group $P\bar{1}$, a = 13.152(3), b = 8.440(2), c = 13.951(6) Å, α = 85.83(3), β = 114.57(2), γ = 89.17(2)°, V = 1 402.90 Å³, Z = 2, D_m = 1.49 g cm⁻³, D_c = 1.51 g cm⁻³, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 12.0 cm⁻¹, $F(000)$ = 644. Data were collected with a Syntex P2₁ four-circle diffractometer. Maximum 2θ was 48° with scan range ±1.0° (2θ) around the $K\alpha_1$–$K\alpha_2$ angles, can speed 2.4—20° depending on the intensity of a 1 sec prescan; backgrounds were measured at each end of the scan for 100% of the scantime. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. Three standard reflections measured

Table 1. Atom co-ordinates (× 10⁴)

Atom	x	y	z
I	475(<1)	−51(<1)	1 947(<1)
S	−2 293(1)	−818(1)	−766(1)
O(1)	−2 263(2)	−1 805(3)	2 452(2)
O(2)	−1 225(2)	−412(3)	17(2)
O(3)	−2 167(2)	−1 372(3)	−1 679(2)
O(4)	−2 891(2)	−1 859(3)	−362(2)
N	−1 511(3)	−3 149(4)	2 891(2)
C(1)	−587(3)	−2 747(4)	2 824(2)
C(2)	−697(2)	−1 146(4)	2 377(2)
C(3)	−1 751(3)	−624(4)	2 163(2)
C(11)	1 665(3)	−141(4)	3 526(2)
C(12)	1 456(3)	724(5)	4 228(3)
C(13)	2 224(5)	531(7)	5 264(3)
C(14)	3 173(6)	−397(8)	5 576(4)
C(15)	3 374(4)	−1 178(6)	4 858(5)
C(16)	2 645(3)	−1 070(5)	3 818(3)
C(21)	415(3)	−3 833(4)	3 222(3)
C(22)	1 091(3)	−4 028(4)	4 315(3)
C(23)	2 080(4)	−4 941(5)	4 658(3)
C(24)	2 424(4)	−5 636(5)	3 977(4)
C(25)	1 736(4)	−5 491(5)	2 932(4)
C(26)	723(4)	−4 576(4)	2 509(3)
C(27)	781(4)	−3 255(5)	5 098(3)
C(28)	3 518(5)	−6 555(6)	4 349(5)
C(29)	8(4)	−4 432(5)	1 353(3)
C(31)	−2 417(2)	857(4)	1 715(2)
C(32)	−1 939(3)	2 312(5)	1 894(3)
C(33)	−2 576(3)	3 681(5)	1 469(4)
C(34)	−3 703(3)	3 650(6)	875(4)
C(35)	−4 197(3)	2 255(6)	723(4)
C(36)	−3 571(3)	832(5)	1 125(3)
C(41)	−3 095(3)	1 001(4)	−1 251(2)
C(42)	−2 602(3)	2 434(5)	−996(3)
C(43)	−3 225(5)	3 832(5)	−1 431(4)
C(44)	−4 356(4)	3 841(6)	−2 090(4)
C(45)	−4 814(3)	2 419(7)	−2 290(4)
C(46)	−4 211(3)	1 008(5)	−1 884(3)
C(47)	−5 035(6)	5 384(8)	−2 560(5)

Table 2. Selected bond lengths (Å) and angles (°)

I–C(2)	2.078(4)	C(3)–O(1)	1.340(5)
I–C(11)	2.100(3)	O(1)–N	1.415(4)
I ⋯ O(2)	2.735(2)	N–C(1)	1.305(6)
I ⋯ O(3)ⁱ	2.691(3)	C(1)–C(21)	1.472(5)
C(1)–C(2)	1.426(5)	C(3)–C(31)	1.457(5)
C(2)–C(3)	1.351(5)		
C(2)–I–C(11)	92.3(1)	C(2)–C(1)–C(21)	127.4(4)
C(2)–I ⋯ O(2)	78.3(1)	C(1)–C(2)–C(3)	105.8(3)
C(2)–I ⋯ O(3)ⁱ	172.12(8)	I–C(2)–C(1)	124.8(3)
C(11)–I ⋯ O(2)	169.5(1)	I–C(2)–C(3)	128.7(3)
C(11)–I ⋯ O(3)ⁱ	79.9(1)	C(2)–C(3)–O(1)	108.5(3)
O(2) ⋯ I ⋯ O(3)ⁱ	109.56(8)	C(2)–C(3)–C(31)	135.5(4)
I ⋯ O(2)–S	160.2(2)	O(1)–C(3)–C(31)	115.9(3)
I ⋯ O(3)ⁱ–Sⁱ	110.5(1)	C(3)–O(1)–N	109.6(3)
N–C(1)–C(2)	110.5(3)	O(1)–N–C(1)	105.6(3)
N–C(1)–C(21)	122.0(3)		

Symmetry operation (i): $-x$, $-y$, $-z$.

every 70 reflections showed a 20% decay of intensity. Correction for intensity drop and Lorentz-polarisation but not for absorption were applied to all 4 066 reflections collected. 290 Symmetry-equivalent data were averaged (R_i 0.017) to give a final data set of 3 599 unique reflections with $|F_o| > 4\sigma|F_o|$.

The structure was solved by Patterson synthesis for iodine, and least-squares and difference Fourier methods for all

remaining atoms. Blocked full-matrix least-squares refinement, using F, minimising $\Sigma w(|F_o| - |F_c|)^2$ converted to final agreement factors $R\ 0.0295$, $R_w\ 0.0339$, $(\nabla/\sigma)_{max.}\ 0.22$, $S\ 0.8$ for all unique reflections. Weights in the final cycle of refinement were given by $w = 1.00/(\sigma^2 F + 0.0040 F^2)$. Hydrogen atoms at calculated fixed positions were included in the last cycles of the refinement. The final difference Fourier peaks of $0.88\ e\ \text{Å}^{-3}$ were found close to the iodine atom.

Computing with the SHELX76[24] on an IBM 4381/M13. Scattering factors and f' and f'' corrections were stored in the program for iodine from International Tables for X-ray Crystallography.[25] Final atomic co-ordinates are given in Table 1, and selected bond lengths and angles in Table 2; atomic numbering is shown in Figure 1.* Tables of least-squares plane and dihedral angles are available as a Supplementary Publication [SUP 56733 (4 pp.)].†

Acknowledgements

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* *Supplementary data* (see section 5.6.3 of Instructions for Authors, in the January issue). H Atom co-ordinates, bond lengths and angles, and anisotropic temperature factors for non-H atoms have been deposited at the Cambridge Crystallographic Data Centre.
† For details, see section 4.4 of the Instructions for Authors, in the January issue.

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