Phenyliodonium Bis(Perfluoroalkane sulphonyl) Methide; Synthesis and Reactions as a Precursor of Bis(Perfluoroalkanesulphonyl) Carbene

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Photoreaction of the title compound $PhI^+{}^-C(R_FSO_2)_2$ which was synthesised by the reaction of bis(perfluoroalkanesulphonyl) methane with diacetoxyiodobenzene, with alkene, methanol, bromine and benzene gave corresponding addition or insertion products, *via* the bis(perfluoroalkanesulphonyl) carbene, $(R_FSO_2)_2C$: intermediate.

Following previous studies on difluorocarbene[1,2] we have extended our studies to work on bisperfluoroalkanesulphonyl carbenes. This note describes a simple method for preparing precursors to these species that involves oxidation of the disubstituted alkanes with diacetoxyiodobenzene.[3,4]

The reaction in Scheme 1 was conveniently carried out in CH_2Cl_2 at room temperature under atmospheric pressure. Warming to 40 °C was required for the reaction of **3c** (see Table 1).

Comparing two similar compounds $PhI^+{}^-C(RCO)_2$, and $PhI^+{}^-C(PhSO_2)_2$,[5,6] the derivatives **3** were stable at room temperature for several months. Recrystallization of **3a** from CH_3CN and CH_2Cl_2 gave fine colourless crystals. The X-ray structure analysis showed that the crystal contains two independent molecules (Fig. 1); the I, C, S, S four atoms are planar, and the C–I bond distance (1.89 Å) of **3a** is shorter than that of a normal C–I single bond (sp^3C-I, 2.14; sp^2C-I, 2.03; spC-I, 1.99 Å).[7] All these data indicated a double-bond character for the C–I in compound **3a**, Scheme 2.

$$\underset{\mathbf{1}}{CH_2Y^1Y^2} + \underset{\mathbf{2}}{C_6H_5I(OAc)_2} \xrightarrow{CH_2Cl_2} \underset{\mathbf{3a\text{–}c}}{C_6H_5I^+{}^-CY^1Y^2} + 2\,AcOH$$

	Y^1	Y^2
3a;	CF_3SO_2	CF_3SO_2
b;	$C_4F_9SO_2$	$C_4F_9SO_2$
c;	$-SO_2(CF_2)_3SO_2-$	

Scheme 1

Compound **3a** can be heated to melting without decomposition, when irradiated with a 400 W low-pressure mercury

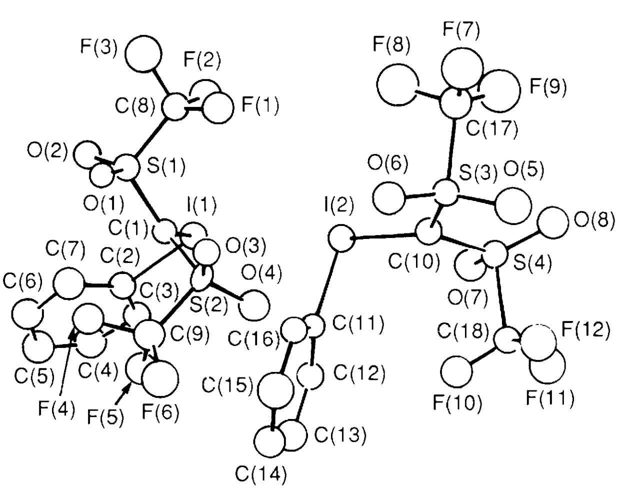


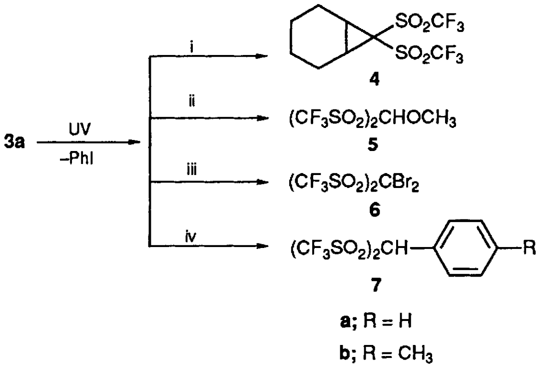
Fig. 1

Table 1 Preparation of **3**

T/°C	*t*/h	Products	M.p./°C	Yields (%)
room temp.	24	**3a**	140	71
room temp.	24	**3b**	165 (dec.)	59
room temp.	24	**3c**	193	40
40	12	**3c**	193	75

$$C_6H_5I^{+}{}^{-}C(CF_3SO_2)_2 \longleftrightarrow C_6H_5I{=}C(CF_3SO_2)_2$$

Scheme 2



Scheme 3 *Reagents, conditions and yields*: i, cyclohexene, 40%; ii, CH_3OH, 49%; iii, Br_2/CH_2Cl_2, 69%; iv, C_6H_6, 61, $C_6H_5CH_3$, 70%

lamp, however, it decomposed readily and gave a bis(trifluoromethanesulphonyl) carbene intermediate. Several reactions studied are shown in Scheme 3.

Thus cycloaddition occurred with cyclohexane to yield 7,7-bis(trifluoromethanesulphonyl)bicyclo[4.1.0]heptane **4**. When irradiated in methanol, the O-H bond insertion product **5** was obtained. Dibromo bis(trifluoromethanesulphonyl) methane **6** was easily prepared from the reaction of **3a** with Br_2 in CH_2Cl_2. Carbon–hydrogen bond insertion was observed during the photolysis of **3a** in benzene or toluene. The latter has two different types of C–H bonds, however, the insertion only occurred on the sp^2C–H bond giving arylated disulphone **7b**.

The structures of the new compounds **3**, **4**, **5** and **7** were fully supported by spectral data and microanalyses.†

In conclusion, the convenience of preparation of phenyliodonium bis(perfluoromethanesulphonyl) methane together with its ready reaction with many organic molecules make these compounds an attractive di(perfluoromethanesulphonyl) carbene precursor.

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† *Crystal data*: **3a**, $C_9H_5F_6IO_4S_2$, $M = 482$, crystal dimensions 0.2 × 0.2 × 0.2 mm; space group $P2_1/n$; $a = 10.132(4)$, $b = 13.486(3)$, $c = 21.60(8)$ Å, $\beta = 94.50(1)$; $U = 2943.3$ Å^3; $D_c = 2.177$ g cm^{-3}; $T = 293$ K; $Z = 4$; $F(000) = 1840$; $\mu = 25.1$ cm^{-1}; Mo-Kα radiation ($\lambda = 0.7107$ Å), $0 < 2\theta < 50°$; 6771 reflections measured, 2414 with $F^2 > 3\sigma(F^2)$ used in the refinement. Data were corrected for Lorentz–polarisation, but not for absorption. Anisotropic refinment for non-hydrogen atoms (except for Ph carbon atoms) led to $R = 0.085$. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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