Tetrahedron Letters, Vol.31, No.34, pp 4821-4824, 1990
Printed in Great Britain

0040-4039/90 \$3.00 + .00
Pergamon Press plc

A GENERAL APPROACH TO UNSYMMETRICAL TRICOORDINATE IODINANES: SINGLE STEP PREPARATION OF MIXED IODOSOBENZENE SULFONATES $PhI(X)OSO_2R$, VIA REACTION OF IODOSOBENZENE WITH Me_3SiX

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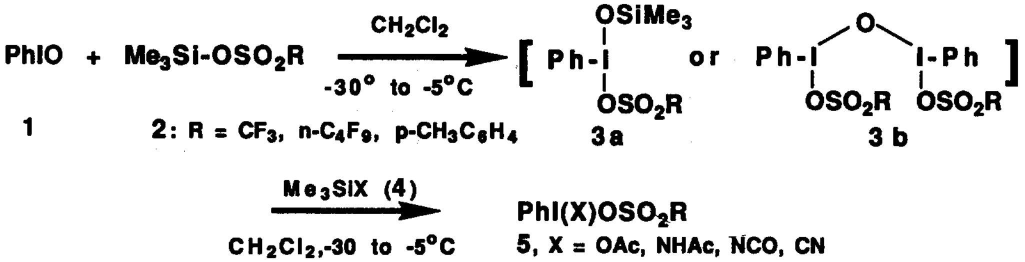
Summary. *Mixed iodonium sulfonates of the type* $PhI(X)OSO_2R$ *(X = OAc, NHAc, NCO, CN; R =* CF_3, C_4F_9, $p\text{-}CH_3C_6H_4$*) have been prepared by the reaction of PhIO with the appropriate derivatives of trimethylsilane.*

In the last decade there has been a resurgence of interest in tricoordinate iodine(III) compounds primarily because of their value as synthetic reagents[1]. The overwhelming majority of stable tricoordinate iodine(III) compounds with heteroatom groups, i.e. $ArIL_1L_2$, have identical ligands ($L_1 = L_2$ =Cl, F, RCOO). The only known unsymmetrical, mixed iodososalts, the [hydroxy(sulfonyloxy)iodo]-benzenes[2], $PhI(OH)OSO_2R$ (R = Me, p-tolyl), have been especially useful in numerous, diverse synthetic organic transformations[3]. Hence, in this paper we wish to report the ready formation, via a simple general procedure, of other unsymmetrical tricoordinate iodine species, namely mixed iodonium sulfonates, $PhI(X)OSO_2R$ **5** with X = O, N, and C-ligands. Interaction of TMS-sulfonate **2** with commercial iodosobenzene **1** in CH_2Cl_2 results in the formation of either adduct **3a** and/or the known [4] μ-oxo-bridged species **3b**. Subsequent addition of the appropriate trimethylsilyl derivative **4** affords the desired mixed iodonium sulfonate **5** in excellent yields as microcrystalline solids.



In a typical procedure 10 mmoles of **2** was added to a stirred suspension of 2.2 g (10 mmoles) of PhIO in 30 ml of CH_2Cl_2 at -30°C under nitrogen. The mixture was allowed to warm to -5°C and stirred until formation of a yellow homogenious solution. The solution was recooled to -30°C and 11 mmoles of **4** was added, via a syringe, and the mixture allowed to warm to -10 - -5°C and stirred for about one hour. The precipitate was filtered under nitrogen, washed with cold ether and dried in vacuo yielding material of >98% purity. Analytically pure material may be obtained by recrystallization from CH_3CN-Et_2O solution. The yields, physical properties, and spectral data for several representative examples of products **5** are summarized in the Table.

The products were characterized by IR, multi-nuclear NMR and microanalysis. Specifically the infrared indicated the characteristic absorbtion signals of the X-group (CN, OAc, NCO, etc). The ^1H NMR had the typical 2:1:2 aromatic signals characteristic of the phenyl group in iodonium salts and the ^{13}C NMR spectra were consistent with the proposed structures.

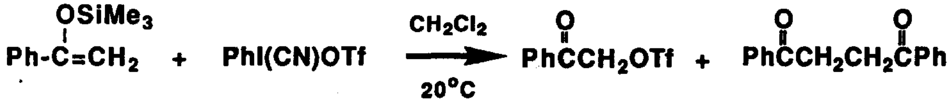
This method is clearly general for the formation of any mixed iodonium sulfonate **5**, being limited only by the stability of the final product **5**. For example, where as the acetates, nitriles and isocyanates listed in the Table are stable isolable compounds, adducts **5** with X = $N(CH_3)_2$, ONH_2, N_3 and CH_2CN are unstable and rapidly decompose between -30° and 0°C with the formation of iodobenzene and uncharacterized polymeric material. Moreover, in the preparation of the iodonium triflates **5** (R = CF_3) Me_3SiOTf may be replaced by 0.5 equivalents of triflic anhydride $(CF_3SO_2)_2O$ in the first step of the procedure resulting in products of comparable purity and yield. This observation supports the intermediacy of the known[4] μ-oxo-bridged species **3b** as the likely first step in the pathway of the reaction.

These mixed iodonium sulfonates **5** should have wide ranging applications in organic synthesis analogous to the highly useful [hydroxy(sulfonyloxy)iodo]-benzenes[3].

Table. Physical and Spectral Properties of Mixed Iodonium Sulfonates $PhI(X)OSO_2R$

Entry	X	R	Yield,%	mp,°C (dec.)	IR (in CCl_4, cm^{-1}), selected absorbtions	NMR (CD_3CN, δ, ppm) ^1H	^{13}C	^{19}F
1	OAc	CF_3	78	91	1721 (CO); 1280, 1229, 1169, 1053, 1031 (OTf and OAc)	8.3-8.2 m (2H) 7.8-7.6 m (1H) 7.6-7.5 m (2H) 2.1 s (3H)	175.0 (CO); 137.6, 135.3, 132. 9 (Ph); 120.5 d (J = 118 Hz, CF_3), 18.5 (CH_3)	-78.0 (CF_3)
2	CN	CF_3	89	118	2182 (CN); 1294, 1257, 1208, 1182, 1034 (OTf)	8.4-8.3 m (2H), 7.9-7.8 m (1H), 7.75-7.65 m (2H)	137.1, 135.6, 134.6, 119.6 (Ph); 120.8 d (J = 118 Hz, CF_3), 68.3 (CN)	-76.5 (CF_3)
3	CN	p-$CH_3C_6H_4$	91	108	2167 (CN); 1266, 1133, 1104, 989 (OTs)	8.2-7.2 m (9H), 3.1 s (3H)	146.0, 139.5, 137.9, 131.2, 129.1, 128.3, 126.3, 118.1 (Ar); 94.7 (CN); 21.3 (CH_3)	
4	CN	n-C_4F_9	84	124	2181 (CN); 1301, 1210, 1140, 1010, 985 (ONf)	8.4-8.3 m (2H), 7.9-7.8 m (1H), 7.7-7.6 m (2H)	136.5, 134.9, 133.9, 103.0 (Ph), 119 br. m (C_4F_9), 68.5 (CN)	4.8 m (2F) -2.2 m (2F) -6.6 m (2F) -81.2 t (3F)
5	NHAc	CF_3	97	167	3280 (NH); 1673 (CO); 1255,1173, 1030 (OTf)	8.5 br. s (1H) 8.3-8.2 m (2H), 7.7-7.6 m (1H), 7.4-7.2 m (2H), 2.1 s (3H)	172.6 (CO), 136.2, 134.1, 132.4, 118.3 (Ph), 120.9 d (J = 118 Hz, CF_3), 20.4 (CH_3)	-78.6 (CF_3)
6	NCO	CF_3	51	55	2506, 1622 (NCO), 1259, 1174, 1024 (OTf)	8.3-7.5 m	172.5 (CO), 136.6, 135.0,132.8,122.7(Ph) 120.8 d (J =118Hz, CF_3)	-78.6 (CF_3)

For example, preliminary results show that PhI(CN)OTf reacts with silyl enol ether **6** under mild conditions with the formation of keto-triflate **7** (30%) and the coupled 1,4-diketone **8** (50%).



$$\underset{\mathbf{6}}{Ph\text{-}\overset{OSiMe_3}{\overset{|}{C}}{=}CH_2} + PhI(CN)OTf \xrightarrow[20^{\circ}C]{CH_2Cl_2} \underset{\mathbf{7}}{Ph\overset{O}{\overset{\|}{C}}CH_2OTf} + \underset{\mathbf{8}}{Ph\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}Ph}$$

6 **7** **8**

This reaction is similar to the one with [hydroxy(sulfonyloxy)iodo]benzene resulting in α-sulfonyloxy carbonyl compounds[5].

Acknowledgement. This work was supported by the NCI of NIH (2ROCA16903) in the USA.

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(Received in USA 23 May 1990)