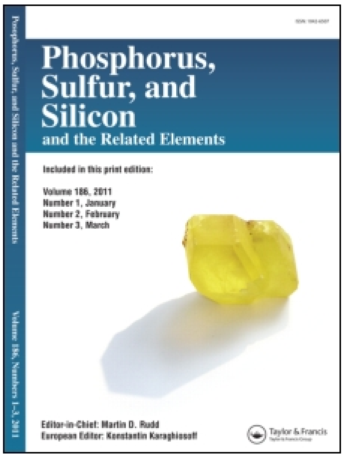

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A REDOX REACTION OF (DICHLOROIODO)METHYL PHENYL SULFONE

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Communication

A REDOX REACTION OF (DICHLOROIODO)METHYL PHENYL SULFONE

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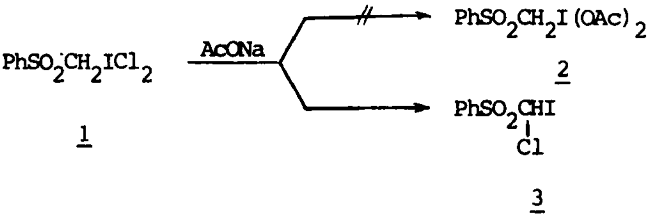
The title compound, $PhSO_2CH_2ICl_2$, is converted by metal acetates into either (chloro-iodo)methyl phenyl sulfone, $PhSO_2CHClI$, or esters $PhSO_2CH(OCOR)I$.

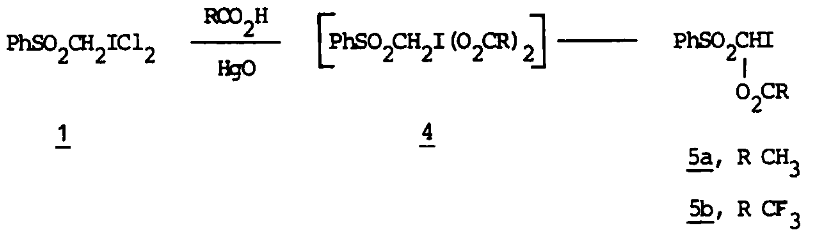
Key words: (Dichloroiodo)methyl phenyl sulfone; (chloro-iodo)methyl phenyl sulfone; (phenylsulfonyliodo)methyl acetate.

The chemistry of α-halogenated sulfones in general[1,2] and α-iodosulfones in particular has attracted considerable attention over the years. Several approaches are available for the preparation of α-iodosulfones of various types.[3–6] These may be alkylated to form C-alkyl-α-iodosulfones[7] or arylated to form phenyl aryl sulfones[8]; further, they may give alkenes upon oxidation[9,10] or base treatment,[11] whereas they have been the subject of mechanistic studies in relation to their reduction[12] and their capacity to act as good electron acceptors.[13] In addition, iodomethyl alkyl (or aryl) sulfones rank among the few aliphatic iodides which form stable derivatives of iodine (III), of the general formula $RSO_2CH_2ICl_2$ (R=alkyl or aryl), the chemistry of which is not well investigated. These compounds dissociate thermally into the organic iodide and chlorine; their kinetics have been studied in various solvents.[3] Upon basic hydrolysis they afford not the expected iodosyl derivatives (RSO_2CH_2IO) but are reduced to the iodides, inorganic chloride and probably hypochlorite rather than elemental oxygen, as originally suggested.[14] Aliphatic iodides, RCH_2I, generally give unstable I,I-dichlorides[14,15] decomposing into RCH_2Cl and ICl. This reactivity mode is unfavorable, when there is an adjacent sulfonyl group. The stability of (dichloroiodo)methyl sulfones is apparently of steric rather than electronic origine.[3]



Since (dichloroiodo)arenes, $ArICl_2$, are converted by metal carboxylates into (diacyloxyiodo)arenes,[16] $ArI(OOCR)_2$, an attempt was made to obtain (diacetoxyiodo)methyl p-tolyl sulfone from the corresponding dichloride and sodium acetate, without success.[17] On a closer examination of the analogous reaction of (dichloroiodo)methyl phenyl sulfone 1 with sodium acetate we find that indeed no 2 results but instead a redox reaction occurs under formation of the hitherto unreported (chloro-iodo)methyl sulfone 3.

Another approach, using 1, trifluoroacetic acid and mercuric oxide also did not afford the expected $PhSO_2CH_2I(O_2CCF_3)_2$, 4, but its transformation product 5b.



Despite their similarity, 3 and 5 are not formed in the same way. Sodium acetate acts as a base abstracting a proton from 1 which must be fairly acidic, since the dichloroiodo group is strongly electron-withdrawing,[18] with a σ_I value of 1.17. The resulting carbanion has two possibilities: either chlorine migrates from iodine to carbon, under formation of an iodate intermediate, $PhSO_2CH(Cl)I^-Cl$, which expels chloride; or chloride elimination occurs first and an iodonium ylide is formed, $PhSO_2CH^-I^+Cl$, followed by chlorine migration. The first pathway appears more likely, since the iodate is better stabilized than the ylide. When the reaction was run in the presence of pyridine, a considerable increase in yield was noted. Mercuric trifluoroacetate is not basic enough, so that it acts primarily as a nucleophile, i.e., substitution at I(III) occurs, with formation of 4; this is so unstable that when equimolecular quantities of reagents are used, it is converted into 5b by the same routes available to 1, a considerable part of 1 remaining unreacted. The acetoxylated 5a rather than 3 was obtained, when trifluoroacetic acid was replaced by acetic acid. It appears that in this case mercuric acetate is less basic than sodium acetate and acts preferentially as a nucleophile, like mercuric trifluoroacetate. With a 1:2 ratio of 1: $Hg(OAc)_2$, 5a was formed in high yield.

Preliminary experiments suggest that (dichloroiodo)methane sulfonamide, $H_2NSO_2CH_2ICl_2$, can also undergo analogous transformations.

EXPERIMENTAL

(Chloro-iodo)methyl phenyl sulfone, 3. (Dichloroiodo)methyl phenyl sulfone (3.53 g, 10 mmol) in 50 ml of dry acetonitrile and 2 ml of pyridine was stirred with anhydrous sodium acetate (1.64 g, 20 mmol) at 40°C for 72 h. The residue after removal of volatiles was chromatographed on a silica gel column using petroleum ether (bp 40–60 °C) and dichloromethane (1:1) as eluant. After some unreacted 1, 3 was eluted (3.14 g, 89% yield), mp 82–84 °C (from dichloromethane-hexane); ν_{max} 3045, 2890, 1580, 1340, 1160, 750 cm^{-1}; $\delta(CDCl_3)$ 4.43 (s, 1H), 7.21–7.51 (m, 5H); m/z 316/8 (M^+, 11), 281 (43), 189/91 (25), 141 (100).

Anal. Calcd for $C_7H_6ClIO_2S$: C, 26.54; H, 1.89. Found: C, 26.68; H, 1.88

(Phenylsulfonyl-iodo)methyl acetate, 5a. (Dichloroiodo)methyl phenyl sulfone (3.53 g, 10 mmol) in 60 ml of dry acetonitrile and 2.4 g (40 mmol) acetic acid was stirred with red mercuric oxide (4.34 g, 20 mmol) at room temperature for 48 h. The residue after removal of mercury salts and volatiles was chromatographed as above (eluant dichloromethane:ethyl acetate 4:1) to give 5a (2.92 g, 86% yield), mp 127–129 °C (from dichloromethane-hexane); ν_{max} 3030, 2900, 1695, 1540, 1305 cm^{-1}; $\delta(CDCl_3)$ 1.82 (s, 3H), 4.45 (s, 1H), 7.32–7.60 (m, 5H); m/z 340 (M^+, 11), 325 (8), 281 (56), 141 (100). *Anal.* Calcd for $C_8H_9IO_4S$: C, 31.76; H, 2.65. Found: C, 31.38; H, 2.69.

(Phenylsulfonyl-iodo)methyl trifluoroacetate, 5b. The same procedure as above with a 1:1 ratio of 1 and HgO gave 5b (42% yield), mp 140–142 °C (from dichloromethane-hexane); ν_{max} 1680, 1550, 1310 cm^{-1}; $\delta(CDCl_3)$ 4.53 (s, 1H), 7.27–7.52 (m, 5H); m/z 349 (M^+, 19), 325 (37), 281 (48), 141 (100). *Anal.* Calcd for $C_8H_6F_3IO_4S$: C, 27.41; H, 1.52. Found: C, 27.46; H, 1.56.

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