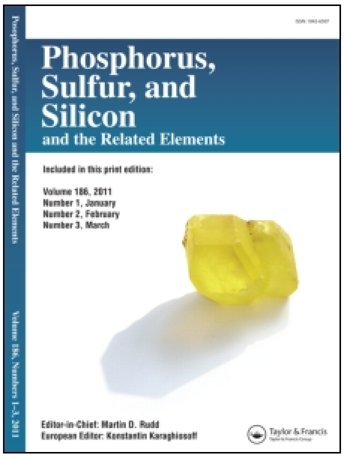

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Kurt Schank[a]; Friedrich Schroeder[a]
[a] Organische Chemie der Universitaet des Saarlandes, Saarbruecken, W. Germany

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UNUSUAL REACTION OF α,α-DIHALOGEN ETHERS WITH SULFINATE ANIONS

by

Kurt Schank and Friedrich Schroeder

Organische Chemie der Universitaet des Saarlandes,
D-66 Saarbruecken, W. Germany

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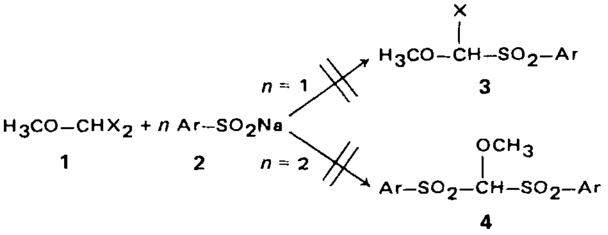
ABSTRACT

Unsymmetrical dihalogen ethers halogenate arene sulfinate anions yielding the corresponding arene sulfonyl halides in addition to other products. A reaction mechanism is proposed.

In a previous paper,[1] the synthesis of α-sulfonyl ethers by conversion of α-halogen ethers with sodium arene sulfinates under appropriate conditions has been described. In the course of our investigations on α-sulfonyl ethers we have found the surprising formation of α,α-diarenesulfonyl ethers **4** by treatment of α-halogen α-arenesulfonyl ethers **3** with potassium *t*-butanolate.[2] In order to synthesize these compounds in a larger scale by an independent method α,α-dihalogen ethers **1** were treated with sodium *p*-toluenesulfinate under same conditions which had been found successful in the series of α-monohalogen ethers:

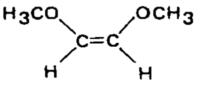


Ar = (*p*)$CH_3C_6H_4$
a: X = Cl
b: X = Br

But neither **3** nor **4** could be found in essential amounts, only traces (2–3%) of these compounds were detected by nmr, tlc, and lc. Instead of **3** and **4** wholly unexpected the tosyl halides **5** showed to be main products of the reaction. Searching for the fragment bearing the methoxy grouping small amounts of (Z)-1,2-dimethoxy ethylene **6** could be identified by ^{1}H-nmr and gc, established by adding an authentic sample (from Dynamit Nobel AG) to the solution and comparing the enhancement of the characteristic signals resp. band. As further products of the conversions the disulfide **7** and the corresponding thiosulfinate **8** were isolated. As to the reaction mechanism, the formation of the tosyl halides must result from an initial attack of sulfinate sulfur on halogen, followed by a subsequent self-condensation of the carbanionic part possibly over the methoxy carbene step:

$Ar{-}SO_2X$

5



6

$Ar{-}S{-}S{-}Ar$

7

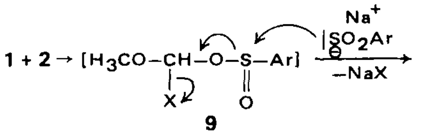
$Ar{-}SO_2{-}S{-}Ar$

8

$$1 + 2 \rightarrow Ar{-}SO_2X + [H_3CO{-}\overset{Na^+}{\overset{\ominus}{\bar{C}H}}{-}X] \rightarrow NaX + 6 \qquad (1)$$

Nucleophilic substitutions on halogen at several types of carbon halogen compounds are well known[3] and are in addition subject of recent investigations.[4] Particularly nucleophilic attack at halogen by sulfinate sulfur has been discussed at conversions of α-halogenated β-dicarbonyl compounds[5] and also in the second step of the reaction of methylene halides with sodium arene sulfinates[6] resulting in dehalogenation to methyl aryl sulfones instead of disubstitution.

Concerning the by-products **7** and **8**, their formation is not explained by scheme A. Especially in the case of X = Cl, equation 1 should not be the main reaction path because of the considerable formation of **8** (56%). Since the halogen ethers of type **3** in absence of strong bases are rather stable compounds, no nucleophilic substitution of halide in **1** by sulfinate sulfur—but by sulfinate oxygen—is expected, introducing the formation of **7** and **8**:



$$1 + 2 \rightarrow [H_3CO{-}CH(X){-}O{-}S(=O){-}Ar] \xrightarrow[-NaX]{Na^+\ |\overset{\ominus}{S}O_2Ar}$$

9

$$HCO_2CH_3 + [Ar{-}SO_2{-}SO{-}Ar] \qquad (2)$$

10 **11**

The presence of **10**, observed by nmr and gc, was not characteristic because of its possibly independent formation by hydrolysis of **1**. The decay of **11** the formation of which was supposed following the fragmentation as in equation 2, yielding **7** and **8**, has been studied thoroughly by Kice and Pawlowski.[7] An inverse fragmentation with primary attack of **2** at the halogen of **9** also could be discussed to explain the formation of **5**, but thereafter the formation of **6** would be unexplained. Furthermore, sodium salts of sulfinic acids are weak bases. In order to establish that nucleophilic attack at halogen and no deprotonation took place in the initial step, equal experiments have been carried out in presence of equimolar amounts of potassium *t*-butanolate in abs. DMF as solvent. In these cases no tosyl halide could be detected, thiosulfonate **8** was main product besides small amounts of disulfide **7** and the sulfonyl ethers **3** and **4** which both are supposed to be products of S-addition of sulfinate to methoxy-chloro-carbene; **7** and **8** should be products of a preceding O-addition.

Experimental Section

Tosyl halides 5 by Reaction of Dihalomethyl methyl Ethers 1 with Sodium *p*-Toluenesulfinate 2 in Benzene

9.8 g (0.055 mol) of finely powdered anhydrous sodium *p*-toluenesulfinate **2** were suspended in 60 ml of abs. benzene by stirring and a solution of dihalogen ether **2** (0.05 mol in 10 ml of abs. benzene) was added dropwise (in the case of **2b** a weak increase of temperature was observed). After refluxing the mixture for 3 hr and cooling, the inorganic residue (5.1 g, 6.1 g, respectively), consisting of sodium chloride or bromide, unconverted sodium *p*-toluenesulfinate and *p*-toluenesulfonate, was separated by filtration and the solvent was removed i.vac.; the remaining crystalline mixture (9.95 g and 10.95 g) was investigated by ^{1}H-nmr spectroscopy (δ [ppm], s, $CDCl_3$, TMS int.stand.) and the following products were recognized by their characteristic signals (verified by addition of small amounts of the corresponding authentic samples and observing the enhancement of the concerning characteristic signals):

5a: CH_3 2.49
3a: CH_3 2.49; OCH_3 3.62; CH 6.06
5b: CH_3 2.49
3b: CH_3 2.49; OCH_3 3.58; CH 6.36
7: CH_3 2.30
8: CH_3 2.38; CH_3 2.41

Furthermore, these products were identified by tlc. From the reaction mixtures the tosyl halides **5** were isolated by extraction with boiling ether and cooling. From the resulting residue (including the residue of the mother liquor after evaporating the solvent) *p*-methylthiophenyl tosylate **8** was obtained by recrystallization from methanol; yields, calculated for a 0.05 molar scale, using $X = Cl$: 3.25 g (34.2%) **5a**, mp 68°; 3.9 g (56.1%) **8**, mp 75°; **3a** (*ca.* 2%) and **7** (*ca.* 2–3%) were determined from the nmr spectrum. For $X = Br$: 6.9 g (58.8%) **5b**, mp 93°; 1.45 g (20.9%) **8**, mp >70°; **3b** (*ca.* 3.5%) and **7** (*ca.* 10%) were determined from the nmr spectrum. All isolated substances have been compared with authentic samples.

In a separate experiment, the volatile components have been determined as follows: Instead of evaporating the solvent *i.vac.*, it had been distilled off from the reaction mixture. The presence of methyl formiate (**10**) and of (Z)-dimethoxy ethylene (**6**) has been investigated by gc and ^{1}H-nmr spectroscopy at first without and then in the presence of a small amount of the corresponding authentic compound.

Reaction of 1a with 2 and Potassium *t*-Butanolate in abs. DMF

2.3 g (0.2 mol) dichloromethyl methyl ether were added dropwise to a solution of 3.56 g (0.02 mol) **2** and 2.24 g (0.02 mol) potassium *tert*-butanolate in 50 ml abs. DMF. After the exothermal reaction had subsided the mixture was stirred for 3 hr at 100°, then cooled and poured onto ice water. From the mixture crystalline **8** separated (1.9 g (68.3%) after recrystallization from ether). After extracting the aqueous layer twice with methylene chloride, the organic phase was dried with calcium chloride and the solvent evaporated. The oily residue consisted of further **8** as well as of small amounts of **7**, **3** and **4**, verified by tlc and ^{1}H-nmr. No **5a** could be detected in this case.

Acknowledgment

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