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A SIMPLE SYNTHESIS OF DIHALOMETHYL SULFONES

W. Middelbos, J. Strating and B. Zwanenburg
Department of Organic Chemistry, The University
Zernikelaan, Groningen, The Netherlands

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The preparation of dihalomethyl sulfones as described in literature[1,2,3] is rather laborious. We wish to report a simple method for the synthesis of the title compounds.

Reaction of the sodium arenesulfinates I a,b,c with either chloroform or bromoform in the presence of aqueous base gives the dichloromethyl and dibromomethyl sulfones, respectively, in good yields (see Table):

$$RSO_2Na + CHX_3 \xrightarrow{KOH} RSO_2CHX_2 + NaX$$

I

II X = Cl
III X = Br

In the absence of base no reaction was observed making it likely that product formation takes place by reaction of the electrophilic dihalo carbene with the sulfinate anion.

Similarly, sodium tert. butylsulfinate reacts with chloroform to give IId. With bromoform, however, only a small yield of dibromo product could be isolated. The main product was the mono bromide t-$BuSO_2CH_2Br$ (26%, m.p. 101.5 - 102°) which arises from the dibromo compound IIId upon a further reaction with hydroxide ions. Such a reduction reaction was observed for α-halosulfones with thiolate[4] anions and also in some cases with alkoxides.[1]

With sodium benzylsulfinate, chloroform and aqueous base only 5% of the desired dichloromethyl sulfone IIe was found. The major product, trans styrenesulfonic acid ($\phi CH{=}CHSO_3H$) (yield 80%), is the result of a Ramberg-Bäcklund reaction[5] on the initially formed product IIe. This reaction may well offer a method for simple preparation of α,β-unsaturated sulfonic acids.

TABLE

RSO_2Na (I)	RSO_2CHCl_2 (II)		RSO_2CHBr_2 (III)	
R:	yield (%)	m.p.	yield (%)	m.p.
a. C_6H_5	87	81.5-83	77	114.5-115
b. p-$CH_3C_6H_4$	81	89.5-90	75	116-117
c. 2-naphthyl	70	93-94.5	48	114.5-115
d. $(CH_3)_3C$	55	71.5-72	7	90-95
e. $C_6H_5CH_2$	5	99.5-100		

The reactions were carried out as follows: A mixture of 0.1 mole of I, 0.1 mole of KOH, 0.3 mole of haloform and 75 ml of water was refluxed for 12 hours. After extraction with dichloromethane, drying over magnesium sulfate and removal of solvent, the crude product was obtained, which was then crystallized from ethanol.

REFERENCES

1. W. M. Ziegler and R. Connor, J. Amer. Chem. Soc., **62**, 2596 (1940).
2. E. Barr, W. M. Ziegler and R. Connor, ibid., **63**, 106 (1941).
3. G. Kresze, W. M. Schramm and G. Cleve, Chem. Ber., **94**, 2060 (1961).
4. F. G. Bordwell and B. B. Jarvis, J. Org. Chem., **33**, 1182 (1968).
5. L. A. Paquette, Accounts Chem. Res., **1**, 209 (1968); F. G. Bordwell, E. B. Hoyt, Jr., B. B. Jarvis and J. M. Williams, Jr., J. Org. Chem., **33**, 2030 (1968).