[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE ALKYLATION OF MERCAPTANS BY MEANS OF SULFONIC ESTERS

BY HENRY GILMAN AND NATHANIEL J. BEABER

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In connection with studies involving the interaction of organic sulfur compounds and organomagnesium halides it was necessary to prepare a variety of sulfides. When the hydrogen of a mercapto (—SH) group is to be replaced by alkyl, two classes of compounds are generally used: alkyl halides and salts of alkyl sulfates. Sulfonic esters have been used to a decidedly limited extent in a replacement reaction of this type, despite the fact that these esters find a wide application in the preparation of ethers from the analogous hydroxyl compounds.

Dimethyl sulfate has been used in the preparation of methyl sulfides.[1] The inherent advantages of cost, smoothness of reaction and high yield of pure product justify the use of dimethyl sulfate as the best reagent for replacing the mercapto hydrogen by methyl.

However, the recent availability of diethyl sulfate and a variety of alkyl esters of *p*-toluenesulfonic acid[2] should extend the application of sulfonic esters in the alkylation of mercaptans. It is shown that the yields of sulfides prepared by means of alkyl *p*-toluenesulfonates are at least equal to those obtained from dialkyl sulfates. In most preparations, however, the latter are to be preferred because of the present significant advantage in cost when one considers the alkylating content of the respective esters. Furthermore, the disadvantages of the costly and volatile alkyl halides disappear in large part when alkyl groups of high molecular weight are to be introduced.

Halogen-alkyl *p*-toluenesulfonates are available.[3] However, it is shown that these esters are deserving of very little consideration in the preparation of halogen-alkyl sulfides. It is possible to prepare such sulfides by better methods.[4]

Experimental Part

A small excess of ester was added to the sodium hydroxide solution of mercaptan. Generally, about a 20% excess of a 15–25% solution of sodium hydroxide was used. An excess of alkali is helpful in breaking down to

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[1] Friedländer, *Ann.*, **351,** 390 (1907). Auwers and Arndt, *Ber.*, **42,** 537 (1909). Mayer, *Ber.*, **42,** 3046 (1909). Zincke and co-workers, *Ber.*, **48,** 1242 (1915); *Ann.*, **406,** 127 (1914), etc. Pollack and co-workers, *Monatsh.*, **39,** 129, 179 (1918). Brand and co-workers, *J. prakt. chem.*, **107,** 358 (1924), etc. Fricke and Spilker, *Ber.*, **58,** 24 (1925).

[2] Gilman and Beaber, THIS JOURNAL, **47,** 518 (1925).

[3] Clemo and Perkin, *J. Chem. Soc.*, **121,** 642 (1922). Also Gilman and Beaber, THIS JOURNAL, **45,** 839 (1923).

[4] Fromm and Kohn, *Ber.*, **54,** 320 (1921).

sulfides[5] the sulfonium-sulfides which are formed by the addition of sulfonic esters.

With dialkyl sulfates it is desirable to add the ester slowly to avoid the vigorous reaction which often sets in when too much ester is present. The mixture is refluxed for two to three hours after the addition of ester. The oily layer is separated, dissolved in ether, and this solution is washed

Table I

Reaction of Mercaptans with Sulfonic Esters

Mercaptan	G.	Moles	Ester[a]	G.	Moles	Sulfide	G.	Yield %	Boiling point, °C.[b]
n-Butyl	25	0.28	Ethyl	60	0.3	Ethyl *n*-butyl[c]	18.5	78.4	143–145
Benzyl	25	.2	Ethyl	44	.22	Ethyl benzyl	26	85.5	220–223
Thiophenol	22	.2	Ethyl	40	.2	Ethyl phenyl	18	65.2	202–205
Thiocresol[d]	50	.4	Dimethyl sulfate	58	.45	Methyl *p*-tolyl	44.5	80.6	104–105 20 mm.
Thiocresol	100	.8	Diethyl sulfate	121	.85	Ethyl *p*-tolyl[e]	95.5	83.4	101–103 2 mm.
Thiocresol	62	.5	Ethyl	110	.55	Ethyl *p*-tolyl	69	91	219–220[f]
Thiocresol	24.8	.2	*n*-Propyl	47.1	.22	*n*-Propyl *p*-tolyl[g]	28.5	85.8	234–235
Thiocresol	62	.5	*n*-Butyl	125	.51	*n*-Butyl *p*-tolyl[h]	82	91	135–138 15 mm.

[a] The esters, unless otherwise mentioned, are those of *p*-toluenesulfonic acid.

[b] The temperatures recorded in this paper are uncorrected.

[c] This sulfide was oxidized to ethyl *n*-butyl sulfone which is best crystallized from hot petroleum ether: m. p., 50–50.5°.

Anal. Calcd. for $C_6H_{14}O_2S$: S, 21.33. Found: 21.46.

[d] Performed by James E. Kirby. All of the methyl *p*-tolyl sulfide obtained in this experiment was oxidized by hydrogen peroxide. The yield of sulfone was 90%.

[e] When 15–50g. lots of this sulfide were oxidized by nitric acid or acidified potassium permanganate, the yield of sulfone was quite low.

[f] The ethyl *p*-tolyl sulfide distilled at 122–125° (20 mm.).

[g] *n*-Propyl *p*-tolyl sulfide boils at 120° (15 mm.); d_4^{20}, 0.9755.

Anal. Calcd. for $C_{10}H_{14}S$: S, 19.28. Found: 19.49.

n-Propyl *p*-tolyl sulfone was prepared in two ways. The yield by oxidation of 0.1 mole with hydrogen peroxide was 85.9%; when prepared from 0.2 mole of sodium *p*-toluenesulfinate and 0.23 mole of *n*-propyl iodide, the yield was 36.6%.

[h] The time of refluxing with ester in this experiment was 1.5 hours.

At atmospheric pressure, the sulfide distils at 249–250° with slight decomposition. This distillate on standing deposited a small quantity of fine, white needles which were identified as *p*-toluenesulfonic acid; d_4^{20}, 0.9615.

Anal. Calcd. for $C_{11}H_{16}S$: S, 17.77. Found: 18.1.

n-Butyl *p*-tolyl sulfone was prepared by two methods: oxidation of the sulfide by hydrogen peroxide gave a 61.3% yield; refluxing an alcoholic solution of sodium *p*-toluenesulfinate with *n*-butyl bromide for ten hours gave a 25.2% yield. The sulfone boiled at 175–177° (4 mm.); d_4^{20}, 1.1020.

Anal. Calcd. for $C_{11}H_{16}O_2S$: S, 15.09. Found: 15.07, 15.27.

Some of this sulfone, prepared in connection with another study, shows no indication of crystallizing after two years.

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[5] Kehrmann and co-workers, *Ber.*, **55**, 2346 (1922), etc. **Also Brand and Stallmann**, *J. prakt. Chem.*, **107**, 358 (1924).

with water, dried with potassium carbonate and then distilled in a vacuum. In most cases the yield is only slightly decreased by distilling the oily layer directly after separation.

The identity of the sulfide was confirmed by converting it to the corresponding sulfone which, in turn, was compared with the known sulfone. Several oxidizing agents have been used for the preparation of sulfones from sulfides. However, it is doubtful whether any of these oxidizers equal in value a 30% solution of hydrogen peroxide. It is necessary only to dissolve the sulfide in glacial acetic acid, add about a 50% excess of the hydrogen peroxide, digest the mixture on a steam plate for a few hours and then pour into water. In this way the sulfone is precipitated in a very high degree of purity and the yield is excellent. In addition to its value as one of the best means of identifying sulfides, it has the merit of being superior to the preparation of sulfones from alkali sulfinates, when the extra cost is secondary to a high yield of pure compound.

Preparation of β-Chloro-ethyl *p*-Toluyl Sulfide, ($CH_3C_6H_4SCH_2CH_2Cl$).—Forty-seven g. or 0.35 mole of β-chloro-ethyl *p*-toluenesulfonate was added to a solution containing 24.8 g. or 0.2 mole of *p*-thiocresol and 8.5 g. or 0.21 mole of sodium hydroxide in 15 cc. of water. After the mixture had been stirred on the water-bath for two hours the cooled reaction product was extracted with ether. The ether extract, dried by potassium carbonate, was concentrated and gave 8 g. or a 29.2% yield of di-*p*-tolyl-dithio-ethane ($CH_3C_6H_4SCH_2CH_2SC_6H_4CH_3$). This compound was identified by conversion into the known disulfone.

The mother liquor from the dithio-ethane was distilled in a vacuum and gave 9 g. or a 24.1% yield of β-chloro-ethyl *p*-tolyl sulfide, distilling at 150–152° (20 mm.). In addition, 5 g. of unchanged ester was obtained.

The chloro-ethyl sulfide was identified by oxidation to the corresponding chloro-sulfone by means of hydrogen peroxide. Crystallized from 80% alcohol, it melted at 78–78.5°. Fromm and Kohn[4] previously prepared the sulfide and the sulfone. However, their chlorosulfone prepared from the chlorosulfide by oxidation with potassium permanganate in dil. sulfuric acid solution melted at 71°.

In an attempt to prepare β-chloro-ethyl *p*-tolyl sulfide by using 0.12 mole of sodium carbonate in 50 cc. of water with 0.1 mole of *p*-thiocresol and an equivalent amount of chloro-ester, 62% of di-*p*-tolyl-dithio-ethane was obtained in addition to some unaltered *p*-thiocresol.

An 80% yield of diphenyl-dithio-ethane ($C_6H_5SCH_2CH_2SC_6H_5$) was obtained when a mixture of 0.22 mole of thiophenol, 0.3 mole of sodium hydroxide and 0.22 mole of β-chloro-ethyl benzene-sulfonate was refluxed for three hours. The dithio-ethane was identified by conversion to the corresponding disulfone.

Summary

Mercaptans can be alkylated in good yields by refluxing an alkaline solution with an equivalent quantity of dialkyl sulfate or alkyl *p*-toluenesulfonate.

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