Sulfones from Sodium Benzenesulfinate

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Yields of sulfones from reaction of organic halides with sodium benzenesulfinate have been improved by use of higher alcohols or diols as solvents. Optimum reaction conditions for octadecyl phenyl sulfone were found. Diverse types of halides were tried to determine the applicability of the reaction. Four new sulfones were prepared.

REACTION of sulfinate salts with organic halides to give sulfones is well known (*6*). The usual reaction conditions involve boiling the reactants in ethanol and dilution with water to precipitate the product. Boiling times as short as seven to eight hours have been reported with reactive halides (*5*), and as long as 118 hours for less reactive alkyl halides (*1*). In the case of 2-chloroquinoline, a reaction time of eight days and a temperature of 100° C. (sealed tube) was required (*7*).

To shorten reaction time and avoid use of sealed tubes without sacrifice of yield, various solvents were tried for the reaction of octadecyl bromide with sodium benzenesulfinate. The results are shown in Table I. Crude phenyl octadecyl sulfone was obtained by drowning the reaction mixture in ice and water, filtering the solid product, and drying at 1 torr overnight. Substantial amounts of solvents were entrained in several cases, giving falsely high yields of crude product. All products were analyzed to determine purity by measurement of their infrared absorption at 1305 cm.$^{-1}$ in carbon tetrachloride solution, and yields corrected for purity are given in Table I. Dipropylene glycol gave the highest yields, but was hard to separate from the product; methoxyethanol and ethoxyethanol gave slightly lower yields, but allowed easier purification. Reaction times longer than four hours were not beneficial, and temperatures over 135° C. caused some decomposition. Other glycols tried were ethylene, diethylene, and propylene. Neither these, acetic acid, dimethylformamide, nor dimethyl sulfoxide were as good.

The scope of the reaction was investigated by trying different types of alkyl and aryl halides. Results are shown in Table II. In each case, 10 mmoles of halide (or 5 mmoles of dihalide) and 11 mmoles of sodium benzenesulfinate were used. Analysis of each crude product for sulfur was obtained. Purity was determined by dividing the per cent sulfur found by the calculated per cent sulfur, and the yields given in Table II are actual, corrected yields, although the melting points are those of crude samples. It was assumed that sodium halide and unreacted sodium benzenesulfinate would be removed during workup, which included a water-washing, and that the only significant impurity in the products was organic halide. Alkylation of sulfinate salts with soft alkylating agents, such as organic halides, in protic solvents gives negligible amounts of sulfinate esters (*3*).

Table I. Preparation of Octadecyl Phenyl Sulfone

Solvent	Temp., ° C.	Time, Hrs.	Yield, %
Ethanol	80	2	34
Methoxyethanol	125	2	78
Ethoxyethanol	135	2	68
Ethoxyethanol	125	4	7w
Dipropylene glycol	125	2	99

Table II. $R - X + C_6H_5SO_2^- \, Na^+ \rightarrow C_6H_5SO_2R + Na^+ \, X^-$

Run	*R*	*X*	Temp., ° C.	Time, Hrs.	M.P., ° C.	Yield, %
1	$(CH_3O)_2CHCH_2$—	Cl	135	6	. . .	0[a]
2	$CH_3(CH_2)_{11}$—	Br	135	6	. . .	0[b]
3	$HOCH_2CH_2$—	Br	135	6	[c]	0[a]
4	$HOCO(CH_2)_{10}$—	Br	125	4	53-66[d]	72
5	—$CH_2CH_2OCH_2CH_2$—	Cl	135	21	124-154	42
6	—$(CH_2)_2$—	Br	125	4	177-178[e]	83
7	—$(CH_2)_4$—	Br	125	2	90-107[f]	68
8	—$(CH_2)_5$—	Br	135	6	70-75[g]	64
9	—$(CH_2)_{10}$—	Br	125	4	55-60	84
10	3,4-Dimethylbenzyl—	Cl	135	6	67-87	80
11	4-Nitrobenzyl—	Cl	125	4	201-207[h]	87
12	2,4-Dinitrophenyl—	Cl	135	6	143-153[i]	88
13	2-Pyridyl—	Br	135	6	. . .	0[a,j]
14	5-Nitro-2-pyridyl—	Br	135	6	129-145[k]	76
15	2-Quinolyl—	Cl	125	4	153-161[l]	81

[a] Product soluble in H_2O. [b] Product oils out of H_2O. [c] Reported m.p. <25° C. (*4*). [d] Reported (*2*) m.p. 86° C. [e] Reported (*1*) m.p. 177.5-184° C. [f] Reported (*1*) m.p. 152.5-153.5° C. [g] Reported (*1*) m.p. 92.5-93.5° C. [h] Reported (*6*) m.p. 207° C. [i] Reported (*6*) m.p. 161° C. [j] Nonaqueous workup gave about 25% yield; see experimental part. [k] Reported (*8*) m.p. 151-153° C. [l] Reported (*7*) m.p. 160° C.

Many of the halides tried gave good yields of sulfones with reaction times as short as 2 hours. The products of Runs 5, 9, 10, and 13 were also obtained by an alternate treatment of the reaction mixture, as described below. Their analyses are shown in Table III, as they are new compounds.

EXPERIMENTAL

All organic halides were commercially available materials which were used without purification. Sodium benzenesulfinate was used as received from Aldrich. Analysis showed 0.51% water. Infrared determinations and spectra were run on a Beckman IR-5 instrument with sodium chloride optics under the direction of L. A. Small in this laboratory.

General Method of Preparation of Sulfones. A mixture of 10 mmoles of organic halide (or 5 mmoles of dihalide), 11 mmoles of sodium benzenesulfinate, and 10 ml. of ethoxyethanol were heated in a 25-ml. foil-sealed conical flask with magnetic stirring. Workup consisted of pouring the reaction mixture into 50 ml. of water, filtering the product, washing it with water, and vacuum drying overnight at <1 torr (Table II).

1,10-Bis(phenylsulfonyl)decane. The crude product prepared as above (Run 9) was recrystallized from ethyl acetate-hexane, and then recrystallized as in Table III. $\nu_{\text{min}}^{\text{KBr}}$ 3050, 2990, 2910, 2840, 1470, 1445, 1400, 1320, 1295, 1275, 1220, 1090, 1040, 928, 790, 733, 720, 685 cm.$^{-1}$.

Bis[2-(phenylsulfonyl)ethyl] Ether. After 17 hours' boiling under reflux, the reaction mixture was freed of solvent

Table III. Analyses of Sulfones—$C_6H_5SO_2R$

R	M.P., °C.[a]	Recrystallization from	Calcd., % C	Calcd., % H	Calcd., % S	Found, %[b] C	Found, %[b] H	Found, %[b] S
$—(CH_2)_{10}—$	72–73	Benzene-hexane	62.56	7.11	15.16	62.17	7.31	14.94
$—CH_2CH_2OCH_2CH_2—$	176.5–180	1,1,1-Trichloroethane–hexane[c]	54.23	5.08	18.07	54.14	4.75	18.06
3,4-Dimethylbenzyl—	93.5–95.5	2-Propanol–water	69.23	6.15	12.31	69.12	6.33	11.89
2-Pyridyl—	87–89	1,1,1-Trichloroethane–hexane[c]	60.27	4.10	14.61	60.28	4.18	14.34

[a] Melting points are those of analytical samples, determined with a Mel-Temp heated aluminum block in capillaries, and are corrected.
[b] Performed under the direction of L. A. Small in this laboratory. [c] With use of Darco KB carbon.

by means of a rotary evaporator. Extraction of the residue with 25 ml. of hot 1,1,1-trichloroethane and dilution of the extract with hexane gave the analytical sample (Table III). $\nu_{\text{min}}^{\text{KBr}}$ 3050, 2980, 2920, 1580, 1475, 1450, 1420, 1290, 1220, 1140, 1080, 1030, 1000, 930, 775, 742, 683 cm.$^{-1}$.

3,4-Dimethylbenzyl Phenyl Sulfone. The crude reaction mixture obtained as in Run 10, Table II, was diluted with 50 ml. of water and 20 ml. of 1,1,1-trichloroethane. The lower layer was freed of solvent, and the oil remaining was crystallized from ethyl acetate-hexane and recrystallized as in Table III. $\nu_{\text{min}}^{\text{KBr}}$ 2910, 1445, 1285, 1260, 1240, 1155, 1125, 1083, 885, 795, 775, 750, 735, 707, 685 cm.$^{-1}$.

2-(Phenylsulfonyl)pyridine. The reactants in methoxyethanol were boiled under reflux for 16 hours. Longer reaction time up to 3 days caused no further apparent change. Extraction of the mixture, after removal of solvent, with 25 ml. of 1,1,1-trichloroethane and dilution with hexane and ethyl acetate gave material which was recrystallized as in Table III. $\nu_{\text{min}}^{\text{KBr}}$ 3080, 1578, 1448, 1427, 1303, 1252, 1162, 1127, 1089, 1071, 990, 785, 777, 758, 744, 733, 706, 680 cm.$^{-1}$.

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LITERATURE CITED

(1) Field, L., Boyd, E.T., *J. Org. Chem.* **29**, 3273 (1964).
(2) Koenig, N.H., Swern, D., *J. Am. Chem. Soc.* **79**, 4235 (1957).
(3) Meek, J.S., Fowler, J.S., *J. Org. Chem.* **33**, 3422 (1968).
(4) Schultz, H.S., Freyermuth, H.B., Buc, S.R., *Ibid.*, **28**, 1140 (1963).
(5) Shriner, R.L., Greenlee, S.O., *Ibid.*, **4**, 247 (1939).
(6) Suter, C.M., "The Organic Chemistry of Sulfur," pp. 667–672, Wiley, New York, 1944.
(7) Tröger, J., Meinecke, H., *J. Prakt. Chem.* **106**, 203 (1923); *CA* **18**, 376^5 (1924).
(8) Winter, H.C., Reinhart, F.E., *J. Am. Chem. Soc.* **62**, 3509 (1940).

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Nitration of 1,3-Dibromobenzene

Synthesis of 1,5-Dibromo-2,4-dinitrobenzene and 1,3-Dibromo-2,4,6-trinitrobenzene

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Nitration of 1,3-dibromobenzene has been effected in mixed acids and in solutions of potassium nitrate in 30% oleum. Simplified procedures for the preparation of 1,3-dibromo-2,4-dinitrobenzene and 1,3-dibromo-2,4,6-trinitrobenzene have been developed. In each case, the yield was 75% or higher, and the products were isolated easily from the reaction mixture.

METHODS for the preparation of 1,5-dibromo-2,4-dinitrobenzene (I) and 1,3-dibromo-2,4,6-trinitrobenzene (II) have either involved time-consuming multistep procedures or produced complex mixtures from which the products have been difficult to isolate. Jackson and Cohoe (*3*) prepared I by the nitration of 1,3-dibromobenzene in fuming nitric acid and mixtures of fuming nitric and sulfuric acids at elevated temperatures. The yields and detailed description of products were not given. However, Korner and Contardi (*6*) found that a similar procedure using fuming nitric acid gave I along with 1,3-dibromo-2,4-dinitrobenzene (III) and two mononitro derivatives. They also reported that I was converted to II when reheated in this medium. Jackson and Earle (*4*) found that by treating 1,3-dibromo-2,4,6-trinitrobenzene and 1,3,5-tribromo-2,4,6-trinitrobenzene with alcoholic sodium sulfite, they were reduced to I and II, respectively. However, their effort to find a more facile synthesis for II by nitrating I in boiling mixtures of fuming nitric and sulfuric acids was not successful. Along with II, this procedure gave 1,3-dinitro-4,5,6-tribromobenzene (IV) as the main product.

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[1] Deceased.