[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND SCHOOL OF PHARMACY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Derivatives of Sulfenic Acids. X. The Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with Alcohols

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2,4-Dinitrobenzenesulfenyl chloride (I) reacts with a series of primary, secondary and tertiary alcohols in accord with the equation: $(NO_2)_2C_6H_3SCl + ROH \rightleftarrows (NO_2)_2C_6H_3SOR - HCl$. Pyridine greatly facilitates formation of the 2,4-dinitrobenzenesulfenate esters, thereby permitting a general technique for the characterization of the alcohols.

Information concerning reactions of sulfenyl halides with alcohols is very scant. While 1-anthraquinonesulfenyl chloride or bromide reacts with methanol or ethanol to yield the expected alkyl 1-anthraquinonesulfenates[1] (equation 1, Ar = 1-anthraquinonyl), the literature[2] as well as experience in this Laboratory permit the conclusion that the reaction does not always take place in accord with the simple displacement formulated in equation 1. Even in rigorously dry alcohol, the disulfides are the major products in some cases[3]; and, for example, 2-nitrophenyl 2′-nitrobenzenethiosulfonate, 2-nitrobenzenesulfinic acid, as well as bis-(2-nitrophenyl) disulfide have been noted[4] as products of the alcoholysis of 2-nitrobenzenesulfenyl chloride.

$$\mathrm{ArSX + ROH \rightleftharpoons ArSOR + HX} \qquad (1)$$

In the case of 2,4-dinitrobenzenesulfenyl chloride (I), however, we had found[5] that reaction with excess dry methanol or ethanol led to good yields of the alkyl 2,4-dinitrobenzenesulfenates, in accord with equation 1 (Ar = 2,4-dinitrophenyl). Therefore, the recent report by Perold and Snyman[6] that reaction of I with absolute alcohol yielded about 80% of bis-(2,4-dinitrophenyl) disulfide, prompted us to re-examine our original work and to extend the study to other alcohols. It may now be stated with certainty that I reacts with dry methanol or ethanol (either in the absence or presence of inert solvents; compare reference 6) to form the alkyl sulfenates in yields approaching 90% of pure isolable products, and that similar reactions result from I and *n*-propyl, isopropyl and *n*-butyl alcohols. Only traces of a high-melting product, presumably bis-(2,4-dinitrophenyl) disulfide (dec. 240–280°) were encountered in these reactions.

Since reaction of I proceeded smoothly with various alcohols, suitable conditions were sought for a general method to characterize alcohols by use of the sulfenyl chloride. It was found that addition of pyridine to the reaction mixtures of I and the alcohols greatly facilitated the reactions, and permitted the convenient identification of primary, secondary and even tertiary alcohols. The use of pyridine fosters rapid completion of the reactions, permits high yields if some simple precautions are taken, and appears quite essential for the success of the reactions with the two tertiary alcohols studied (*t*-butyl and *t*-amyl). The group of alcohols studied in the present work is shown in Table I, and the general procedure is given in the experimental section.

The obvious role of pyridine in these reactions would appear to be neutralization of hydrogen chloride, thereby preventing reversal of reaction 1. While such an explanation accords with a similar one proposed by Cook and Donia[7] for the effect of added silver salts on the reactions of 2,4-dinitrobenzeneselenenyl bromide with alcohols, preliminary work on the reactions of sulfenyl halides with tertiary amines (with and without alcohols present) suggests that the role of pyridine may be more complex, and a complete study of its role in the reactions with alcohols has therefore been undertaken.[8]

Recrystallizations of the 2,4-dinitrobenzenesulfenate esters of Table I were effected from absolute ethanol or methanol. Under these conditions, alcohol interchange was not appreciable; and, indeed, isopropyl 2,4-dinitrobenzenesulfenate could be recovered unchanged even after refluxing for ten hours in absolute methanol. In the presence of hydrogen chloride, however, the isopropyl ester was converted to the methyl ester; and the methyl and ethyl esters were shown to be interconvertible, by boiling with a solution of hydrogen chloride in the appropriate alcohol.

It is also of interest to note that the sulfenate esters are sulfur analogs of organic peroxides (RSOR′ *vs.* ROOR′). In our experience, the 2,4-dinitrobenzenesulfenate esters of Table I are of entirely adequate stabilities to permit their use as derivatives for the alcohols; and the esters may also be employed conveniently in various synthetic operations. As might be expected from their structures, however, these substances can undergo thermal decomposition. Such a behavior was particularly evident in the case of *t*-butyl 2,4-dinitrobenzenesulfenate, which decomposed with attendant evolution of a gas at the melting point (118–119°). In view of such possible thermal dissociations, our general procedure for the preparation of the alkyl

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[1] K. Fries, *Ber.*, **45**, 2965 (1912).

[2] For a general review, *cf.* N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Revs.*, **39**, 269 (1946).

[3] Thus, *p*-chlorobenzenesulfenyl chloride and rigorously pure methanol yield 80–90% of bis-(*p*-chlorophenyl) disulfide. M. B. Sparke and N. Kharasch, succeeding paper in this series.

[4] T. Zincke and F. Farr, *Ann.*, **391**, 55 (1912).

[5] C. M. Buess, Doctoral Dissertation, University of Southern California (1949).

[6] G. W. Perold and H. L. F. Snyman, THIS JOURNAL, **73**, 2379 (1951).

[7] W. S. Cook and R. A. Donia, *ibid.*, **73**, 2275 (1951).

[8] It has been observed, for example, by M. L. Moore and T. B. Johnson [THIS JOURNAL, **57**, 1517 (1935)], and also in this Laboratory, that sulfenyl halides may react with dry pyridine to form disulfides. While the mechanism for such disulfide formation has not as yet been established, we suspect that a reactive pyridinium salt (ArSPyCl) may be involved as the first step. Reaction of such an intermediate with the sulfenyl chloride might yield disulfide: $\mathrm{ArSPyCl + ArSCl \rightarrow ArSSAr + PyCl_2}$ (?); and reaction with the alcohol could lead to the sulfenate ester: $\mathrm{ArSPyCl + ROH \rightarrow ArSOR + Py.HCl}$.

TABLE I

REACTION OF 2,4-DINITROBENZENESULFENYL CHLORIDE WITH ALCOHOLS

Alcohol	Alkyl 2,4-dinitrobenzene-sulfenate; Ar = 2,4-dinitrophenyl	Yield,[a] %	M.p.,[b] °C.	Analyses[g] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Methyl[c]	$ArSOCH_3$	95	122–123				
Ethyl[c]	$ArSOC_2H_5$	85	124–125				
n-Propyl	ArSO-*n*-C_3H_7	85	75– 76	41.85	41.84	3.90	3.87
Isopropyl	ArSO-*i*-C_3H_7	90	77– 78	41.85	41.93	3.90	4.16
n-Butyl	ArSO-*n*-C_4H_{10}	85	53– 54	44.11	44.32	4.44	4.77
s-Butyl	ArSO-*sec*-C_4H_{10}	80	71– 72	44.11	43.77	4.44	4.22
t-Butyl	ArSO-*t*-C_4H_{10}	80	118–119	44.11	44.39	4.44	4.45[e]
n-Amyl	ArSO-*n*-C_5H_{11}	85	31– 32[j]	46.14	45.98	4.93	5.01
Isoamyl	ArSO-*i*-C_5H_{11}	85	56– 57	46.14	46.18	4.93	5.23
t-Amyl	ArSO-*t*-C_5H_{11}	85	102–103	46.14	46.18	4.93	4.78[f]
n-Octyl	ArSO-*n*-C_8H_{17}	90	57– 58	51.21	51.21	6.14	6.20
Lauryl	ArSO-*n*-$C_{12}H_{25}$	85	73– 74	56.24	55.88	7.34	7.01
Cyclohexanol	ArSO-cyclo-C_6H_{11}[d]	85	133–134	48.31	48.37	4.73	4.79
Cholesterol	$ArSOC_{27}H_{45}$[d]	80	189–190	67.82	67.47	8.22	8.21
l-Menthol	$ArSOC_{10}H_{18}$	85	99–100[i]	54.23	54.33	6.25	6.21
Benzyl	$ArSOCH_2C_6H_5$[d,h]	95	142–143	50.96	51.13	3.29	3.41

[a] Yields listed are for the crude, dry products, based on amount of sulfenyl chloride (I) used. Since some of I was generally converted to insoluble residue, R_1 (*cf.* Experimental), the stated yields would be increased somewhat if this were taken into account. Losses of 10–15% were usually incurred in recrystallizations to products melting within 2–3° (and often within only 1°) of the melting points recorded for the analytical samples. All of the above products were obtained by the general procedure, using pyridine. [b] Melting points were made on a Fisher–Johns apparatus. Mixed-melting points between the methyl and ethyl derivatives, and the *n*-propyl and isopropyl compounds gave sharp depressions. Melting of the *t*-butyl derivative was accompanied by evolution of a gas. [c] The methyl and ethyl esters were reported previously in reference 6. [d] These products were best recrystallized from approximately equal volumes of absolute alcohol and benzene. The other products were all recrystallized from absolute alcohol. [e] *Anal.* Calcd. N, 10.30. Found: N, 10.44. [f] *Anal.* Calcd. N, 9.78. Found: N, 9.54. [g] The microanalyses were performed by Mr. J. Pirie of this Laboratory, except for the *n*-propyl, isopropyl and *n*-butyl derivatives which were kindly analyzed by Misses C. Brauer and J. Sorenson of Northwestern University. [h] Decomposition to tars was sometimes noted in this case if the product was not carefully washed and recrystallized. [i] In these cases, a colorless, crystalline, hygroscopic precipitate (probably pyridine–hydrochloride) formed on adding the pyridine to the solution of alcohol in ethylene chloride. While the identity of this product was not established, it was water soluble, and did not interfere with the isolation of the sulfenate esters. [j] The product in this case was an oil which crystallized only with some difficulty.

2,4-dinitrobenzenesulfenates avoids prolonged heating.

Experimental

Starting Materials.—2,4-Dinitrobenzenesulfenyl chloride (I) was prepared by catalytic chlorinolysis of 2,4-dinitrophenyl disulfide[9]; m.p. 95–96°. Ethylene chloride was the Matheson white-label reagent, redistilled and dried over barium oxide and/or calcium hydride. Baker and Adamson C.P. pyridine was distilled from barium oxide, and then kept over calcium hydride. Absolute methanol was prepared by a procedure similar to the one of Lund and Bjerrum.[10] Absolute ethanol was prepared by the method of Manske.[11] The other alcohols were refractionated, reagent-grade products—tested for dryness with calcium hydride.

General Procedure for Characterizing Alcohols.—To a dry 50-ml. erlenmeyer flask, there was added 10 ml. of ethylene chloride and 1.0 g. of 2,4-dinitrobenzenesulfenyl chloride. The mixture was swirled and heated gently to effect solution; then the alcohol (1 ml. of liquid or 1 g. of solid) was added, the flask again swirled, and 1 ml. of pyridine added. A distinct deepening of the yellow color was generally observed as the pyridine dissolved in the solution; and, in some cases, *cf.*, footnote *i*, Table I, a white, needle-like precipitate (probably pyridine hydrochloride) was noted. The reaction appears to be complete immediately after adding the pyridine (negative test with starch–iodide paper or solution); but the reaction mixture was swirled and let stand 15–30 minutes to assure precipitation of any insoluble residue which may have formed. The mixture was filtered, and the residue (R_1) washed on the filter plate with a few ml. of hot ethylene chloride. The bright yellow R_1 (the amount of which varied somewhat with the alcohol used—being from 0–15% of the total weight of sulfenate ester obtained, in various runs) was discarded; and the filtrate aspirated to dryness (water-pump, room temperature). The residue from the filtrate was extracted with three to five 10-ml. portions of cold water, and the crude sulfenate ester collected and air-dried on the suction filter plate. After further drying in the vacuum desiccator (charged with calcium sulfate), or in the heating pistol at 56° (acetone), the crude products were recrystallized from hot absolute ethanol; or, in some cases (*cf.* footnote *d*, Table I), from alcohol–benzene mixtures. If the crude products were washed well, and dried, the melting points were generally within a few degrees of the purified samples of Table I.[12]

Reaction of I with Excess Methanol or Ethanol in Absence of Solvent and Pyridine; and with Other Alcohols in Absence of Pyridine.—Many runs were made to assure that I reacts with excess methanol or ethanol (in the absence of other solvents and pyridine) to give the corresponding esters (compare ref. 6). Thus: 500 mg. of I in rigorously dry methanol (10 ml.) was refluxed for 15 minutes. The hot solution was separated from 5 mg. of insoluble material, the filtrate was chilled, and needles of the product collected and dried; 363 mg., m.p. 120–121°. Dilution of the filtrate with water gave 68 mg. more of the ester; total yield 431 mg., 88%. The melting point after recrystallization (methanol) was 122–123° (uncor.); lit. 124.8–125.2° (cor., for the sublimed product[6]). The ethyl ester was obtained similarly (m.p. 123–124°, 85% yield); mixed m.p. with the methyl ester, 112–119°. Attempts to obtain maximum

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[9] N. Kharasch, G. I. Gleason and C. M. Buess, THIS JOURNAL, **72**, 1796 (1950).

[10] H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931); *cf.* L. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., Inc., Boston, Mass., 1941, p. 360.

[11] R. H. Manske, THIS JOURNAL, **53**, 1106 (1931); *cf.* ref. 11, p. 359.

[12] If wet reagents were used in the general procedure, the sulfenate esters were still obtainable; but the yields were reduced, and the amounts of insoluble residue were considerably increased—especially with the tertiary alcohols. Such a competing hydrolysis of I, leading to bis-2,4-dinitrophenyl disulfide and other products stemming from the intermediate 2,4-dinitrobenzenesulfenic acid is, of course, expected; but it should be noted that the pyridine-catalyzed procedure can be readily controlled to give good yields of the sulfenate esters even if moderate precautions to dry the reagents are taken.

yields with *n*-propyl, isopropyl and *n*-butyl alcohols were not made; but the corresponding alkyl 2,4-dinitrobenzenesulfenates were readily obtained by direct reactions of I and excess of the dry alcohols, by procedures similar to the ones for the methyl and ethyl esters, above. Yields of products (without working up the mother liquors) were: *n*-propyl (m.p. 75–76°, 56%); isopropyl (m.p. 77–78°, 53%)—mixed melting point with the *n*-propyl ester, 56–60°; *n*-butyl (m.p. 53–54°, 68%). Attempts to obtain a similar ester from *t*-butyl alcohol (without using pyridine) were not successful.

Hydrogen Chloride-catalyzed Reactions of the Sulfenate Esters with an External Alcohol.—The methyl ester was recovered (85% yield) unchanged (m.p. and mixed m.p.) after refluxing 1 g. of the ester in 50 ml. of absolute ethanol for 3 hours. The isopropyl ester was similarly recovered after refluxing a solution in absolute methanol for ten hours.

With hydrogen chloride present, rapid alcohol interchange occurred. Thus, into a solution of 200 mg. of pure ethyl 2,4-dinitrobenzenesulfenate, in 25 ml. of absolute methanol at 30°, a gentle stream of dry hydrogen chloride was passed. The solution was refluxed for two minutes, and most of the solvent distilled rapidly. The cooled residual mixture was filtered, yielding 11 mg. of methyl 2,4-dinitrobenzenesulfenate; yellow needles, m.p. 122–123°. The mixed m.p. with authentic methyl ester was not depressed; mixed m.p. with ethyl ester (m.p. 123–124°) was 110–115°. Dilution of the filtrate with water gave 48 mg. more of methyl ester; total yield 84%. The reverse conversion was effected in 83% yield. Similarly, isopropyl 2,4-dinitrobenzenesulfenate (m.p. 77–78°) yielded the methyl ester (m.p. 121–122°) by refluxing with excess methanol, saturated with hydrogen chloride.

Acknowledgment.—We are indebted to the Flora-Synth Laboratories for a grant in support of this work; and to Mr. George Suld for checking yields and melting values for the products of Table I. The helpful coöperation of Professor E. R. Brady of the School of Pharmacy is also gratefully acknowledged.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Rearrangement of Benzyl Sulfides to Mercaptans and of Sulfonium Ions to Sulfides Involving the Aromatic Ring by Alkali Amides[1,2]

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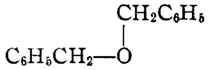
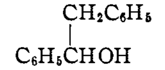
Certain benzyl sulfides and sulfonium ions were rearranged by alkali amides to form mercaptans and sulfides, respectively. Determination of the structures of the products showed that the type of rearrangement realized involved substitution at the ortho position of the benzene ring like that observed previously with benzyl quaternary ammonium ions. The Stevens 1,2-shift observed with benzyl ethers was not realized. The generality of the ortho substitution type of rearrangement is pointed out.

In general benzyl ethers and benzyl quaternary ammonium ions have exhibited different types of rearrangement with alkali amides. For example, dibenzyl ether (I) undergoes the Stevens 1,2-shift to form carbinol II with potassium amide in refluxing ethyl ether[3] or with sodium amide in liquid ammonia,[4] whereas dibenzyldimethylammonium ion (III) undergoes a rearrangement involving substitution at the ortho position of the benzene ring to form tertiary amine IV with sodium amide in liquid ammonia.[5,6] An interesting series of the latter type of rearrangement has been realized starting with quaternary ammonium ion V and ending with the completely substituted product, the first product being tertiary amine VI.



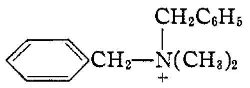
$$C_6H_5CH_2{-}O{-}CH_2C_6H_5$$

I

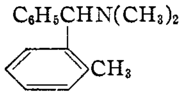


$$C_6H_5CH(OH){-}CH_2C_6H_5$$

II



III



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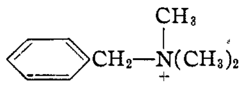
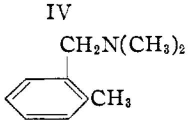


V



VI

In the present investigation a study was made of the possible rearrangement of certain benzyl sulfides and sulfonium ions with alkali amides. Since benzyl sulfides have more of a formal resemblance to benzyl ethers than to quaternary ammonium ions, the sulfides might be expected to exhibit the Stevens 1,2-shift especially with potassium amide in refluxing ether. However, dibenzyl sulfide (VII) was found to undergo with this reagent the type of rearrangement involving substitution at the ortho position of the benzene ring to form mercaptan VIII (79%). The structure of the product was established by independent synthesis from *o*-tolylmagnesium bromide and benzaldehyde. The 2,4-dinitrophenyl thioether of the mercaptan obtained from this synthesis was identical with that prepared from the rearranged mercaptan. The mechanism of the rearrangement involves presumably the isomerization of an intermediate carbanion in which the benzene ring functions as an acceptor, similar to that proposed for the analogous rearrangement of quaternary ammonium ions.[5]

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[1] Supported by the Office of Naval Research.

[2] Paper III on Isomerization of Carbanions. Presented in part at Conference on Reaction Mechanism, Northwestern University, August, 1950.

[3] C. R. Hauser and S. W. Kantor, THIS JOURNAL, **73**, 1437 (1951). For the use of lithium phenyl in this rearrangement see G. Wittig and co-workers, *Ann.*, **550**, 260 (1942); **557**, 205 (1947).

[4] A. J. Weinheimer and C. R. Hauser, unpublished result.

[5] S. W. Kantor and C. R. Hauser, THIS JOURNAL, **73**, 4122 (1951).

[6] It should be mentioned that quaternary ammonium ion III has exhibited the Stevens 1,2-shift with fused sodium amide at 140-150°; T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 1932 (1932). Certain quaternary ammonium ions also exhibit the 1,2-shift with other bases including lithium phenyl; G. Wittig, R. Mangold and G. Felletschin, *Ann.*, **560**, 116 (1948).