[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY DREXEL INSTITUTE OF TECHNOLOGY]

The Preparation of Some N-Substituted 2-Nitrobenzenesulfenamides[1]

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Nine previously unreported 2-nitrobenzenesulfenamides were prepared. Oxidations of 2-nitrobenzenesulfenamides were unsuccessful.

This paper presents the synthesis of some 2-nitrobenzenesulfenamides. Previous to this study, Zincke[2] and Lecher[3] had prepared substituted sulfenamides, and Billman[4] reported the use of *o*-nitrobenzenesulfenyl chloride as a reagent for the identification of amines. The present work was carried out to broaden the scope of Billman's work and also to test the compounds prepared as fungicides. The latter results will be reported elsewhere.

Nine 2-nitrobenzenesulfenamides were prepared by treating *o*-nitrobenzenesulfenyl chloride with the appropriate amine. The properties of these compounds are summarized in Table I. Several amines did not react with *o*-nitrobenzenesulfenyl chloride or formed liquid sulfenamides which could not be crystallized and which decomposed on distillation at reduced pressure. These included *n*-amyl, di-*n*-butyl, β-phenylethyl, diisopropyl, 3-methoxypropyl, and 3-isopropoxypropyl amines as well as piperidine.

The patent literature describes several examples wherein sulfenamides are oxidized to sulfonamides.[5–7] It was found that no sulfonamide or sulfinamide could be definitely characterized as the product of oxidation in this research. Oxidation of crude 2-nitrobenzenesulfenopiperidide with hydrogen peroxide in glacial acetic acid yielded the corresponding disulfide. This product was identified by mixture melting point and by sulfur analysis. Attempted oxidation with chromic anhydride in glacial acetic acid yielded only an oil which could not be identified. In another experiment, 2-nitrobenzenesulfeno-2, 4-dichloroanilide was treated with a 4% aqueous solution of potassium permanganate. In this case, unchanged starting material was recovered plus a small amount of oil which could not be identified. Hydrogen peroxide in acetone yielded the disulfide, as did nitric acid in glacial acetic acid. Aqueous permanganate in benzene gave unchanged sulfenamide and a solution of bleaching powder yielded an oil which could not be identified.

EXPERIMENTAL

All melting points are uncorrected. The properties and analyses of the 2-nitrobenzenesulfenamides are summarized in Table I.

o-Nitrobenzenesulfenyl chloride. This compound was prepared from *o,o'*-dinitrodiphenyl disulfide by the method described in *Organic Syntheses.*[8]

General procedure for the preparation of sulfenamides. To 0.26 mole of the appropriate amine dissolved in 250 ml. of anhydrous ethyl ether in a one liter 3-neck flask equipped with a stirrer, dropping-funnel, and a reflux condenser was added dropwise, a solution of 25 g. (0.132 mole) of *o*-nitrobenzenesulfenyl chloride in 250 ml. of ether. The amine hydrochloride formed was separated by filtration and washed with 50 ml. of ether. The ether extracts were combined and the solvent was removed by distillation. The oily liquid that resulted, crystallized on standing and was purified by crystallization from an appropriate solvent.

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TABLE I

2-NITROBENZENESULFENO DERIVATIVES

					Analyses			
				Crystallizing	Mol. Wt.		Sulfur	
	M.P., °C.	Yield, %	Color	Solvent	Calc'd	Found	Calc'd	Found
Benzylamide	59.5–60	70	Orange	Ligroin	260	263	12.3	12.5
m-Nitroanilide	192–193	55	Yellow	Acetone	291	285	11.0	11.0
2,4-Dichloroanilide	182–183	60	Yellow	Acetone	315	310	10.1	10.2
α-Phenylethylamide	57.5–58	77	Orange	90% Ethanol	274	268	11.7	11.5
Morpholide	89.5–90	90	Yellow	90% Ethanol	240	245	13.3	13.3
Dibenzylamide	107–107.5	85	Orange	Acetone	350	345	9.1	9.2
2-Biphenylamide	113.5–114	95	Yellow	Acetone	322	330	9.9	10.1
4-Biphenylamide	145–146	95	Orange	Benzene-petroleum ether	322	316	9.9	9.9
2-Methoxyanilide	115.5–116	95	Orange	Acetone	276	280	11.6	11.6

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[1] Abstracted from the M.S. thesis submitted by Nicholas Capron in partial fulfillment of the requirements for the degree of Master of Science.

[2] Zincke and Farr, *Ann.*, **391**, 55 (1912).

[3] Lecher and Holschneider, *Ber.*, **57**, 755 (1924).

[4] Billman and O'Mahony, *J. Am. Chem. Soc.*, **61**, 2340 (1939).

[5] Bann, *et al.*, British Patent 551,206 (to the Manchester Oxide Company, Ltd.), (February 11, 1943) [*Chem. Abstr.*, **38**, 1751 (1944)].

[6] Barber, British Patent 557,055 (to May and Baker, Ltd.), (November 2, 1943) [*Chem. Abstr.*, **39**, 2296 (1945)].

[7] Barber, British Patent 550,446 (to May and Baker, Ltd.), (January 8, 1943) [*Chem. Abstr.*, **38**, 1850 (1944)].

[8] *Org. Syntheses*, Col. Vol. II, 455 (1943).