The further experimental work may lead to a decision between these alternatives, although actual measurements of base strength may be required.

Summary

The oxidation of pinacol with aqueous solutions of sodium periodate has been found to obey simple bimolecular reaction kinetics. The variation of the rate with the pH of the reaction mixture may be interpreted accurately on the basis of reaction between pinacol and the monovalent periodate ion catalyzed by both acid and base.

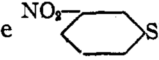
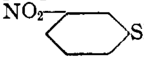
The reversal of the relative rates of oxidation of pinacol and ethylene glycol on shifting from an acidic to a basic reaction medium may be interpreted either on the basis of the configuration of the hydroxyl groups or on the relative base strengths of the two glycols.

URBANA, ILLINOIS RECEIVED AUGUST 13, 1938

[CONTRIBUTION FROM THE GRADUATE SCHOOL OF DUQUESNE UNIVERSITY]

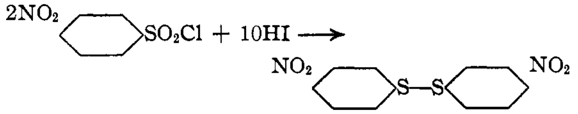
Some Unsymmetrical Aryl Sulfides[1]

BY NOEL E. FOSS,[2] JOHN J. STEHLE, HOWARD M. SHUSETT AND DAVID HADBURG

Zincke and Lenhart[3] and Foss, Dunning and Jenkins[4] have prepared a number of unsymmetrical aryl sulfides of the general type SR, where R may be various phenolic groups, and NO_2 may be in either the ortho or para position. The present investigation is concerned with the preparation of m-nitrophenyl sulfur phenols, SR, where R may be p-hydroxyphenyl, resorcyl, or β-hydroxynaphthyl.

The new nitro derivatives were chemically characterized by the preparation of their acetates and bromine substitution products. Two of the series were further identified by the synthesis of their benzyl and benzoyl derivatives, as well as by the reduction of the nitro compounds to the amino compounds.

The general scheme consists in preparing m,m'-dinitrodiphenyl disulfide by the following reaction



m-Nitrophenylsulfur chloride was prepared by allowing chlorine to react on the m,m'-dinitrodiphenyl disulfide by the method of Zincke and Lenhart[3] and subsequently condensed with the respective phenols. The reactions with phenol are represented by the scheme

$$NO_2C_6H_4SSC_6H_4NO_2 \xrightarrow{Cl_2} 2NO_2C_6H_4SCl$$

$$NO_2C_6H_4SCl + C_6H_5OH \longrightarrow NO_2C_6H_4SC_6H_4OH \xrightarrow{H_2} NH_2C_6H_4SC_6H_4OH$$

Experimental

m,m'-Dinitrodiphenyl disulfide was prepared by a modification of the method of Ekbom.[5] Two moles of the m-nitrobenzenesulfonyl chloride were reduced directly by the addition of the calculated amount of 45% hydriodic acid (ten moles). The reaction proceeded smoothly as evidenced by the precipitation of iodine crystals. After refluxing for several hours on the water-bath, the mixture was cooled and sodium bisulfite added until the iodine had been entirely reduced. The crude crystalline material was washed with water and recrystallized from hot acetone. Yellow crystals melting at 81–82° were obtained. The yield of pure product was about 80%.

Condensation of m-Nitrophenylsulfur Chloride with Phenols.—m-Nitrophenylsulfur chloride was prepared from m,m'-dinitrodiphenyl disulfide and condensed with the respective phenol according to the method described by Foss, Dunning and Jenkins.[4] In the case of the resorcinol derivative, 1,3-dihydroxy-2,6-*bis*-(3-nitrophenylthio)-benzene is formed principally unless the resorcinol is kept in excess during the reaction. The crude condensation products were recrystallized from sodium hydroxide and hydrochloric acid. The mononitro derivative also could be recrystallized from hot alcohol. These yellow compounds were insoluble in water, fairly soluble in hot alcohol, and very soluble in acetone and ether.

Acetylation.—The hydroxynitrosulfides and hydroxyaminosulfide were acetylated in the regular manner by refluxing with acetic anhydride and anhydrous sodium acetate. The pale yellow acetyl derivatives were very insoluble in cold water and slightly soluble in hot water,

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[1] Taken in part from theses presented by J. J. Stehle, H. M. Shusett, and D. Hadburg in partial fulfilment of the requirements for the degree of Master of Science in the Graduate School of Duquesne University.

[2] Present address: Burroughs Wellcome & Co. (U. S. A.), Inc., Tuckahoe, New York.

[3] Zincke and Lenhart, *Ann.*, **400**, 1 (1924).

[4] Foss, Dunning and Jenkins, THIS JOURNAL, **56**, 1978 (1934).

[5] Ekbom, *Ber.*, **24**, 335 (1891).

TABLE

Condensation with	Derivative	Formula	M. p., °C.	% Sulfur Found	% Sulfur Calcd.
Phenol		$NO_2C_6H_4SC_6H_4OH$	83.0-83.5	12.88	12.97
	Monoacetyl	$NO_2C_6H_4SC_6H_4(O_2CCH_3)$	66-67	11.04	11.08
	Dibromo	$NO_2C_6H_4SC_6H_2(Br)_2(OH)$	136-137	7.90	7.89
	Monobenzyl	$NO_2C_6H_4SC_6H_4(OCH_2C_6H_5)$	105-106	9.53	9.50
	Monobenzoyl	$NO_2C_6H_4SC_6H_4(O_2CC_6H_5)$	102.0-102.5	9.31	9.13
	Amino	$NH_2C_6H_4SC_6H_4OH$	84.0-84.5	14.69	14.76
Resorcinol		$NO_2C_6H_4SC_6H_3(OH)_2$	150.5-151.5	12.33	12.18
	Diacetyl	$NO_2C_6H_4SC_6H_3(O_2CCH_3)_2$	77-78	9.23	9.23
	Dibromo	$NO_2C_6H_4SC_6H(Br)_2(OH)_2$	128-130	7.90	7.89
β-Naphthol		$NO_2C_6H_4SC_{16}H_6OH$	106	10.76	10.78
	Monoacetyl	$NO_2C_6H_4SC_{10}H_6(O_2CCH_3)$	85.0-85.5	9.25	9.45
	Monobenzyl	$NO_2C_6H_4SC_{10}H_6(OCH_2C_6H_5)$	136-137	8.09	8.28
	Monobenzoyl	$NO_2C_6H_4SC_{10}H_6(O_2CC_6H_5)$	110.0-110.5	7.85	7.99
	Amino	$NH_2C_6H_4SC_{16}H_6OH$	193	11.81	11.99
	Acetylaminoacetyloxy	$(NHCOCH_3)C_6H_4SC_{10}H_6(O_2CCH_3)$	163-164	9.06	9.12
Resorcinol (2 moles:1 mole)		$(NC_2C_6H_4S)_2C_6H_2(OH)_2$	179-180	15.32	15.41
	Diacetyl	$(NO_2C_6H_4S)_2C_6H_2(O_2CCH_3)_2$	109.5-110.5	12.54	12.52
	Monobromo	$(NO_2C_6H_4S)_2C_6H(Br)(OH)_2$	189-190	13.14	12.95

The acetylated hydroxy compounds were easily soluble in the usual organic solvents. The acetylated hydroxyamino compounds were sparingly soluble in alcohol and benzene, and very soluble in chloroform.

Bromination.—The hydroxynitrosulfides were brominated by adding the calculated amount of bromine to a glacial acetic acid solution of the compound. Recrystallization from dilute alcohol yielded canary yellow crystals. The bromo derivatives were insoluble in water, slightly soluble in benzene, and fairly soluble in alcohol.

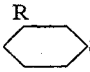
It was found impossible to prepare the bromo substitution product of the β-hydroxynaphthyl derivative by this method. Subsequent analysis and determination of melting point indicated that the compound formed corresponded to the original *m,m'*-dinitrodiphenyl disulfide. No explanation for the phenomenon is attempted.

Benzylation and Benzoylation.—The benzyl and benzoyl derivatives were prepared in the usual manner by the well known Schotten-Baumann reaction. Recrystallization from alcohol yielded canary yellow crystals which were found to be insoluble in water, slightly soluble in alcohol and chloroform, and very soluble in benzene.

Reduction to the Amines.—One part of nitrosulfide dissolved in ten parts of 95% ethyl alcohol was reduced by hydrogen with 0.01 part of Adams[6] platinum black as catalyst. The amino derivatives were insoluble in water, fairly soluble in benzene and alcohol, and very soluble in chloroform.

The accompanying table lists the compounds together with their melting points and analyses.

Summary

Eighteen compounds have been prepared. They are of the general type , where R may be NO_2 or NH_2, and R' may be the *p*-hydroxyphenyl, resorcyl, or β-hydroxynaphthyl radical. Some bromo derivatives, acetates, benzoates, and benzyl derivatives have been made.

PITTSBURGH, PA. RECEIVED JULY 21, 1938

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[6] Adams, *Org. Syntheses*, **8**, 92 (1928).