equivalents of lithium aluminum hydride was used. A 40% ether solution of the glycidic ester was added to the solution of lithium aluminum hydride while the flask was being cooled by an ice bath. After the addition of the ester was completed the ice bath was removed and stirring was continued for 6–7 hr. at room temperature. The reaction mixture was then hydrolyzed, extracted with ether and the ether extracts dried over anhydrous sodium sulfate. The solvent was removed and the residue distilled *in vacuo*. Samples from the distillate were removed for elemental analysis and periodic acid titration.

Analysis of the Glycols.—The glycols were analyzed by allowing aqueous (or water-dioxane) solutions to stand with excess periodic acid for 1 hr. and determining the excess periodic acid in the usual manner, using standard solutions of sodium arsenite and iodine, the titration mixtures being buffered with excess sodium bicarbonate.[16] The values obtained from titration of duplicate and triplicate samples of the glycol are reproducible to ±0.2 %. However, due to the errors introduced during the isolation of the glycols by the extraction and distillation procedures a confidence of only about ±10% can be placed on the percentages of 1,2-glycols reported in this work. For example, the results obtained by different workers in the reduction of ethyl-3-methylglycidate were 49% and 53%, respectively. In three different reductions of ethyl 3,3-pentamethyleneglycidate the percentages of 1,2-glycol were 3.4, 4.3, and 4.8%.

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[16] K. G. Stone, "Determination of Organic Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 54.

The Reduction of Aromatic Nitro Compounds by Potassium Borohydride[1]

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Received February 5, 1962

It has been found that some *m*- and *p*-substituted nitrobenzenes carrying a substituent with a positive value of the Hammett sigma constant are reduced in good yield by potassium borohydride to the azoxy compounds. Nitrobenzenes with negative sigma constants are not reduced.

Few examples are to be found in the literature of the reduction of nitro compounds by complex borohydrides, and it is generally reported[2–5] that nitro groups are reduced either with difficulty or not at all by borohydrides.

Brown[6,7] has shown that the nitro group in ethyl *p*-nitrobenzoate is resistant to reduction by sodium borohydride–metal halide mixtures when the temperature is kept moderate. On the other hand the azido group[4] and the nitroso group[8] have been reduced by sodium borohydride.

As part of a research program requiring the synthesis of aromatic hydrazo compounds we have investigated further the reaction of borohydrides with aromatic nitro compounds. We have found that some substituents render an aromatic nitro group inert to reduction by potassium borohydride, while with other substituents the corresponding azoxy compound is formed in excellent yield. Most of our results are given in Table I. It can be seen that the difference between inertness and reducibility in the nitro group depends on the electronic effect of the substituent. Groups with a positive value of sigma constant enhance reduction of the nitro group to the azoxy group while the reverse is true of substituents with negative values. This means that in the formation of the azoxy compound at least one of the nitro groups of the pair involved needs to be made susceptible to attack by borohydride (or hydride) ion. It is evident that this attack is inhibited by electron donation from substituent to nitro group nitrogen.

The only exception in Table I is *p*-nitrobenzoic acid in pyridine solution. However, it can be seen that in general reduction in pyridine is not at all as extensive as in ethanol. In the case of *p*-nitroacetanilide in ethanol hydrolysis by the added potassium hydroxide occurs.

Some of the compounds used did not give identifiable products. Thus, both *m*- and *p*-dinitrobenzene gave large amounts of red-brown solids, which were rather insoluble in organic solvents and which could not be recrystallized. These solids left a residue on ignition. *p*-Fluoronitrobenzene in ethanol gave *p*-nitrophenetole, but in pyridine gave small amounts of products with melting point ranges between 82° and 264°. No recognizable product could be obtained from *p*-nitrobenzonitrile in ethanol and *p*-iodonitrobenzene in pyridine.

In two instances our data differ from data in the literature. Gore and Wheeler[9] have reported the λ_{max} of 4,4′-diiodoazoxybenzene in ethanol as 295 mμ. We find λ_{max} 342 mμ, which fits the order expected. Apparently, Gore and Wheeler measured the λ_{max} of *p*-iodonitrobenzene, for which we obtained 293 mμ.

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[1] From the M.S. degree thesis of H. E. Mallory, Texas Technological College, 1961. This work forms part of a program of research in hydrazoaromatic rearrangements. We are grateful for support by the Research Corporation and by the National Science Foundation (Grant No. NSF-G-14551).

[2] N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, 1956, pp. 776, 777.

[3] J. H. Billman and A. C. Diesing, *J. Org. Chem.*, **22**, 1068 (1957).

[4] J. H. Boyer and S. E. Ellzey, Jr., *ibid.*, **23**, 127 (1958).

[5] E. Schenker, *Angew. Chem.*, **73**, 81 (1961).

[6] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 3164 (1955).

[7] H. C. Brown, E. J. Mead, and B. C. Subba Rao, *ibid.*, **77**, 6209 (1955).

[8] J. H. Boyer and S. E. Ellzey, Jr., *ibid.*, **82**, 2525 (1960).

[9] P. H. Gore and O. H. Wheeler, *ibid.*, **78**, 2160 (1956).

TABLE I

PRODUCTS OF REACTION

Substituent	Sigma const.[a]	Solvent	Vol., ml.	Mole, substrate	Mole, KBH_4	Products	%	M.p., °C	M.p., lit.
p-F	+0.062	C_2H_5OH	75	0.07	0.20	p-Nitrophenetole	87		
p-Cl	+ .227	C_2H_5OH	250	.032	.093	Azoxy compound	78	154–155	155–156[9]
						p-Nitrophenetole	5		
		Pyr.	100	.032	.185	Azoxy compound	63		
p-Br	+ .232	C_2H_5OH	165	.025	.074	Azoxy compound	72	172–173	172[9]
						p-Nitrophenetole	15		
		Pyr.	100	.025	.185	Azoxy compound	62		
p-I	+ .276	C_2H_5OH	150	.02	.111	Azoxy compound	70	198–199	198[9]
						p-Nitrophenetole	6		
p-COOH	+ .265[b]	C_2H_5OH	100	.029	.093	Azoxy compound[c]	100	350–353	
		Pyr.	100	.029	.093	p-Nitrobenzoic acid	88	240–243	
m-Cl	+ .373	C_2H_5OH	250	.032	.093	Azoxy compound	97	94–95	96[9]
		Pyr.	100	.032	.093	Azoxy compound	9		
						m-Chloronitrobenzene	76		
m-Br	+ .391	C_2H_5OH	250	.025	.075	Azoxy compound	93	109–110	111[9]
		Pyr.	100	.025	.093	Axoxy compound	16		
						m-Bromonitrobenzene	73		
m-I	+ .352	C_2H_5OH	250	.02	.093	Axozy compound	97	118–119	120–121[9]
m-CHO	+ .355	C_2H_5OH	250	.033	.185	m-Azoxybenzylalcohol[d]	71	82–83	
m-OC_2H_5	+ .150	C_2H_5OH	25	.006	.006	m-Axozyphenetole	49	49–50	49–50[e]
p-OC_2H_5[f]	− .250	C_2H_5OH	100	.017	.017	p-Nitrophenetole	91		
		Pyr.	100	.028	.185	p-Nitrophenetole	82		
		Pyr.	100	.028	.270	p-Nitrophenetole	71		
p-NH_2	− .660	C_2H_5OH	500	.075	.10	p-Nitroaniline	90		
		Pyr.	100	.038	.148	p-Nitroaniline	84		
p-NHAc	− .015	C_2H_5OH	100	.028	.093	p-Nitroaniline	88		
		Pyr.	100	.028	.074	p-Nitroacetanilide	81		
p-OH	− .475	C_2H_5OH	100	.036	.093	p-Nitrophenol	99		
		Pyr.	100	.036	.074	p-Nitrophenol	98		
m-NH_2	− .161	C_2H_5OH	250	.038	.074	m-Nitroaniline	96		

[a] H. H. Jaffé, *Chem. Rev.*, **53,** 191 (1953). [b] 0.132 for p-COO^-. [c] *Anal.* Calcd. for $C_{14}H_{10}N_2O_5$: C, 58.75; H, 3.52; N, 9.78. Found: C, 58.61; H, 3.38; N, 10.22. [d] *Anal.* Calcd. for $C_{14}H_{14}N_2O_3$: C, 65.11; H, 5.46; N, 10.84. Found: C, 65.01; H, 5.58; N, 11.01. [e] Ref. 10a, p. 819. [f] Reduction with lithium aluminum hydride in ether gave a 20% yield of 4,4′-diethoxyazoxybenzene.

The melting point of 4,4′-azoxybenzoic acid is given as 240° dec.[10] This is the melting point of p-nitrobenzoic acid. Repetition of the arsenite reduction[10] of this acid gave the azoxy compound, melting point 350–355° dec. after crystallization from dimethylformamide.

Experimental[11]

Materials.—The potassium borohydride was from Metal Hydrides, Inc. m-Nitrophenetole was prepared from m-nitrophenol.[12] All other nitro compounds and the pyridine were from Distillation Products Industries, Rochester, New York. Ethanol was stock 95%.

Method.—A slurry of the potassium borohydride was heated to reflux (ethanol) or to 90° (pyridine) and stirred. A small amount of solid potassium hydroxide was added in the ethanol cases. The nitro compound was added either in solution or as a slurry. Heating was continued for 24 hr., except for 48 hr. in the ethanol cases of the p-F—, m-OC_2H_5— and p-OC_2H_5— substituents listed in Table I. Half of the solvent was then removed under reduced pressure and the cooled mixture was poured onto a slurry of concentrated hydrochloric acid and ice. The precipitated product was filtered, washed, dried, and recrystallized. Where necessary the composition of the solid product mixture was determined spectroscopically in 95% ethanol solution, using extinction coefficients obtained in our own laboratory. A Beckman Model DK-2 recording spectrophotometer was used.

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(10) (a) I. Heilbron, "Dictionary of Organic Compounds," Vol. I, Oxford University Press, 1946, p. 205. (b) H. Loesner, *J. prakt. Chem.*, **(2) 50,** 563 (1894).

(11) Melting points are uncorrected. A Kofler hot stage was used for 4,4′-azoxybenzoic acid. Analyses by Schwarzkopf Microanalytical Laboratories, Woodside, New York.

(12) J. R. H. Whiston, *J. Soc. Chem. Ind.* (London), **43,** 369T (1924). We thank Miss Julie Tsai for this preparation and for carrying out the borohydride reduction.