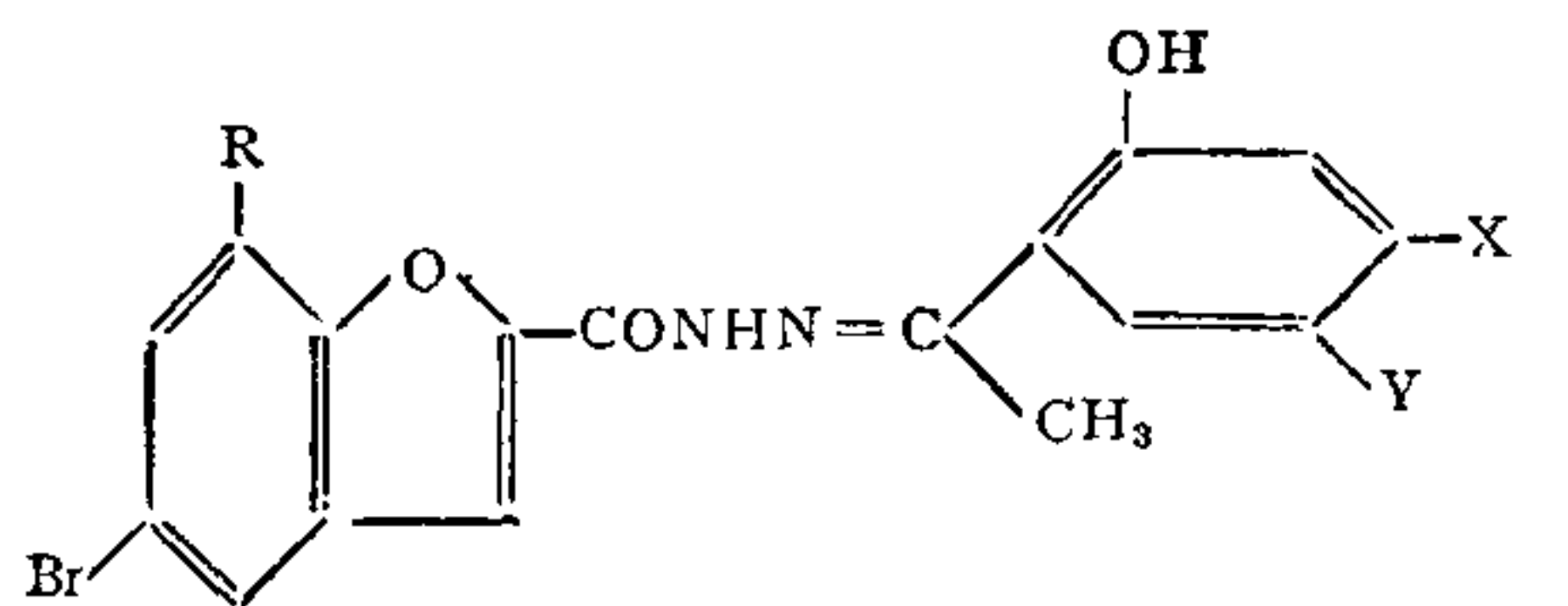


(.01 mole) in absolute ethanol (25 ml), 99% hydrazine hydrate (.015 mole) was added. The reaction mixture was refluxed for 4 hr. Ethanol and excess of hydrazine hydrate were removed under reduced pressure. The hydrazide which separated out was crystallized from ethanol, yield 80%, m.p. 175°, Anal. ($C_9H_7BrO_2N_2$). Found: C, 42.10; H, 2.50; N, 10.80; Required C, 42.35; H, 2.74; N, 10.98%.

5, 7-Dibromocoumarilic Acid Hydrazide.—This was prepared from 5, 7-dibromo-2-carbethoxy coumarone² by the above procedure, yield 75%, m.p. 228°, Anal. ($C_9H_6Br_2O_2N_2$). Found: C, 32.40; H, 1.75; N, 8.20; Required C, 32.33; H, 1.79; N, 8.30%.

Hydrazones (Table I).—An ethanolic solution of ketone (.01 mole), hydrazide (.01 mole) and sulphuric acid (0.1 ml) was refluxed for 2 hr. The reaction mixture was cooled and filtered. The solid thus obtained was crystallized from ethanol-acetic acid mixture.

TABLE I
Hydrazones



No.	R	X	Y	Yield %	M.P. °C	% Nitrogen	
						Found	Required
1.	H	OH	Br	80	280	6.00	5.98
2.	H	OH	NO ₂	76	270	9.55	9.67
3.	H	H	Cl	85	256	6.70	6.87
4.	H	H	CH ₃	72	164	7.00	7.23
5.	H	CH ₃	Cl	65	242	6.70	6.64
6.	Br	OH	Br	75	234	5.25	5.11
7.	Br	OH	NO ₂	78	238	8.10	8.18
8.	Br	H	Cl	82	232	5.50	5.75
9.	Br	H	CH ₃	68	205	6.04	6.00
10.	Br	CH ₂	Cl	74	224	5.60	5.59

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- Melting points are taken in capillaries and are uncorrected.
- Rajeshwar Kurdukar and Subba Rao, N. V., *Proc. Indian Acad. Sci., Sec. A*, 1963, 58 (6), 336

SYNTHESIS OF SUBSTITUTED AZOXY-BENZENES

A SURVEY of chemical literature shows that nitrobenzenes have been reduced to a variety of products by means of different reducing agents.¹⁻¹⁰ With an alkaline medium, the formation of azoxy compound was favoured. Reduction with sodium and potassium methoxides proved to be efficient.

Very little work has been done to reduce substituted nitrobenzenes in neutral medium, with zinc in presence of ammonium chloride in aqueous-alcohol medium. In 1966,¹¹ we reduced *o*-nitro-acetanilide by the above method and got *o*-azoacetanilide and *o*-azoxyacetanilide in good yield.

In the present work we have developed the methods for the reduction of *ortho*- and *para*-toluenes, *o*- and *p*-chloronitrobenzenes, *o*- and *p*-nitrophenols with zinc and ammonium chloride in aqueous-alcohol medium to the respective azoxy compounds in good yield.

EXPERIMENTAL

In a preliminary survey, some of the variables affecting the reduction were studied. The variables examined were temperature, time, concentration of reactants and rate of stirring. A set of standard conditions were set up as follows:

To *o*-nitrotoluene (25 g) and ammonium chloride (15 g) stirred vigorously in alcohol (200 ml 50%) in a three-necked flask at 40° C, zinc dust (25 gm) was added slowly over a period of 30 min. The reaction mixture was kept stirred for about 2 hr more and then filtered. The residue was extracted with alcohol. The alcohol extract was mixed with filtrate and distilled to remove most of the alcohol, then subjected to steam distillation. The distillate was acidified and extracted with ether to recover unreacted *o*-nitrotoluene (6.9%). The acidified distillate after removing unreacted material with ether was made alkaline and then extracted with ether to get amino compound, *o*-toluene (1.5%). The mixture from steam distillate remaining in the distillation flask was filtered to give a brownish-yellow residue of 2-2'-dimethyl-azoxybenzene (52%) which was crystallised from ethanol as yellow needles m.p. and mixed m.p. 58-59° C (Lit. 60° C).

All the products were identified by mixed m.p., carbon, hydrogen and nitrogen analysis and by infrared spectroscopy with a Perkin-Elmer infracord 137 B spectrophotometer.

TABLE I
Nitro compounds successfully reduced to azoxy compounds

Sl. No.	Nitro compounds	Weight of the nitro compound taken (gm)	Weight of the zinc powder (gm)	Ratio of alcohol/water (cc/cc)	Weight of ammonium chloride taken (gm)	Temperature (°C)	Formula of the azoxy compound	Yield of the azoxy compound (%)
1	<i>o</i> -Nitrotoluene ..	25	25	100 100	15	40	C ₁₄ H ₁₄ ON ₂	52
2	<i>p</i> -Nitrotoluene ..	10	10	120 50	10	55	C ₁₄ H ₁₄ ON ₂	57.5
3	<i>o</i> -Nitrophenol ..	25	20	100 150	15	30	C ₁₂ H ₁₀ O ₃ N ₂	53.4
4	<i>p</i> -Nitrophenol ..	25	20	100 130	15	55	C ₁₂ H ₁₀ O ₃ N ₂	61.9
5	<i>o</i> -Chloronitrobenzene ..	25	35	150 200	25	55	C ₁₂ H ₈ O ₂ N ₂ Cl ₂	57.2
6	<i>p</i> -Chloronitrobenzene ..	25	35	200 200	15	30	C ₁₂ H ₈ O ₂ N ₂ Cl ₂	62.7

TABLE II
Analysis of azoxy compounds

Sl. No.	Azoxy compound	M.P. °C	Nitrogen %		Carbon %		Hydrogen %	
			Calculated	Found	Calculated	Found	Calculated	Found
1	2-2' Dimethyl-azoxy-benzene	58-59	12.38	12.26	74.32	74.58	6.23	6.29
2	4-4' Dimethyl-azoxy-benzene	69-70	12.38	12.31	74.32	74.61	6.23	6.28
3	2-2' Dihydroxy-azoxy-benzene	154-155	12.18	12.29	62.61	62.35	4.33	4.17
4	4-4' Dihydroxy-azoxy-benzene	224-225	12.18	12.32	62.61	62.85	4.38	4.15
5	2-2' Dichloro-azoxy-benzene	55-56	10.48	10.35	53.95	53.65	3.02	3.08
6	4-4' Dichloro-azoxy-benzene	156-157	10.48	10.57	53.95	53.58	3.02	3.07

These experiments indicate that: (1) The temperature of reaction is of critical importance between 30-55° C, higher temperature favours the formation of tar material while lower temperature decreases the yield of azoxy compound. (2) Prolonging the reaction beyond 2½ hr has no effect on the yield, which drops with shorter reaction time. (3) 7.5% ammonium chloride appears to be the optimum concentration. The conversions drop off slightly with higher concentration of ammonium chloride and falls rapidly with less than 6% ammonium chloride. (4) Under the conditions studied increasing the quantity of Zn increases the conversions upto the point where 2 moles of zinc were used per mole of substituted nitrobenzenes. Decreasing the quantity of zinc reduces the yield. (5) The importance of adequate mixing is shown by the linear relationship between the rate of stirring and the conversion. For some of the compounds studied, it is necessary to alter some of the conditions to obtain satisfactory yield. The results of successful reductions are shown in Table I and the analysis of resulting compounds is shown in Table II. *m*-Nitrotoluene, *m*-nitrophenol and *m*-nitrochloro-

benzene were also reduced by the same process but the yields of the respective azoxy compounds were very poor and less than 10%. The nitro compounds whose attempted reduction was unsuccessful include *m*-dinitrobenzene, *p*-nitro aniline, 2-nitro-4-methyl aniline and 2-chloro-4-nitro-aniline.

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1. Klinger, P. and Pitschke, T., *Ber.*, 1885, 18, 2552.
2. Elbs, K., *Chem. Ztg.*, 1893, 17, 209.
3. Zechmeister, L. and Rein, P., *Ann.*, 1928, 468, 117.
4. Loesner, H. J., *Prakt. Chem.*, 1894, 50, 563.
5. Gaudry, R. and Keistead, K. F., *Can. J. Research*, 1949, 27, 890.
6. Bigelow, H. E. and Palmer, A., *Org. Synthesis*, 1943, 2, 59.
7. Galbraith, H. W. et al., *J. Am. Chem. Soc.*, 1951, 73, 1323.
8. Paul, E. et al., *Can. J. Chem.*, 1957, 35, 1304.
9. Brain, T., Newbold and Raymond, P., Le-Blanc, *J. Org. Chem.*, 1962, 27, 312.
10. —, — and —, *J. Chem. Soc.*, 1965, p. 1546.
11. Kunwar Bahadur, Rao, K. R. K., and Sinha, S. K., *Jour. Indian Chem. Soc.*, 1966, 43, 725.