The Mechanism of Reduction of Nitrosobenzene by Alcohols

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Nitrosobenzene is easily reduced to azoxybenzene by alkaline aqueous solutions of alcohols. Combined kinetic and product studies indicate that this reduction involves a hydride transfer, probably from an alkoxide anion, to give the anion of phenylhydroxylamine which then combines rapidly with a second molecule of nitrosobenzene to form azoxybenzene. Only the latter reaction involves the formation of nitrosobenzene anion-radicals, (PhNO·)-. The one-electron reduction of nitrosobenzene could not be effected by hydrocarbons such as cumene or by symtrisubstituted phenols.

AZOXYBENZENE is usually prepared by boiling nitrobenzene with sodium methoxide in methanol and it was shown by Bamberger¹ that nitrosobenzene is much more easily reduced than nitrobenzene by this procedure. By using ethanol and sodium ethoxide Bamberger obtained 74-89% yields of azoxybenzene and also isolated 3-7% of N-formyl-N-phenylhydroxylamine, which was not produced in the methanol reaction. Potassium ethoxide in ether² can also effect reduction of nitrosobenzene, and good yields of azoxybenzene can also be obtained by the use of aqueous alcohol.³

Much more recently, Russell and Geels^{4,5} have found by electron spin resonance study that the nitrosobenzene radical-anion (PhNO)⁻ is formed during the reactions between nitrosobenzene and a whole series of alcohols containing sodium hydroxide or sodium alkoxides, and is produced in almost quantitative yield during the rapid reaction between nitrosobenzene and phenylhydroxylamine in ethanolic alkali, which yields azoxybenzene almost quantitatively (96%).

$$PhNO + RO^{-} \longrightarrow PhN O^{-} OR$$
(1)

$$PhN O^{-} + PhNO \longrightarrow PhN O^{+} (PhNO)^{-} (2)$$

$$2(PhNO)^{-} \xrightarrow{\qquad} PhN-NPh \qquad (3)$$

0-

$$PhN \xrightarrow{O^{\bullet}} PhN=O + \cdot OR$$
 (5)

They formulated ⁵ the reaction sequence given above and showed that azoxybenzene, in a strongly alkaline solution of dimethyl sulphoxide, dissociated slightly to the (PhNO)⁻ radical-anion evidently by reversal of reactions (3) and (4) above. Alkoxy-radicals, RO, formed by reaction (5), or their decomposition products, were considered to be potential reducing agents.

- A. Reissert, Ber., 1909, 42, 1364.
- 4 G. A. Russell and E. J. Geels, J. Amer. Chem. Soc., 1965, 87, 122
 - E. J. Geels, Ph.D. Thesis, Iowa State University, 1965.

The occurrence of an equilibrium (3), or its more generalised equivalent (6), is supported not only by

$$(Ar^{1}NO^{-})^{-} + (Ar^{2}NO^{-})^{-} \xrightarrow{} Ar^{1}N - NAr^{2} \qquad (6)$$

e.s.r. spectroscopy but also by a number of earlier studies of reactions between substituted nitrosobenzenes and substituted N-phenylhydroxylamines.⁶ For instance the reaction of *m*-carboxyphenylhydroxylamine and o-nitrosotoluene yields all four possible products that could be obtained from an intermediate $Ar^{1}N(OH)-N(OH)Ar^{2}$ by the dissociation (3). Again isotopic labelling experiments using both PhNH-18OH and Ph¹⁵NO have shown that there is complete mixing of both nitrogen and oxygen atoms in azoxybenzene formation.7

Though the work of Russell and Geels has established that the reaction between nitrosobenzene and phenylhydroxylamine in alkali involves a one-electron transfer [(7) followed by (3)] and the formation of free radicals, we considered that reactions (1), (2), and (5) of Geels mechanism were no more than speculative suggestions.

$$PhNHOH + 2OH^{-} \iff (PhNO)^{2-} + 2 H_2O$$

$$(PhNO)^{2-} + PhNO \implies 2(PhNO^{-})^{-}$$

$$(PhNO^{-})^{-}$$

Therefore we have examined in detail both the products and the rates of reduction of nitrosobenzene by several alcohols in the presence of bases. From this study we conclude that the reduction of nitrosobenzene by an alcohol occurs mainly by hydride transfer to give phenylhydroxylamine, or its anion, and that freeradical reactions are invoved only in the fast subsequent reactions between the anion of phenylhydroxylamine and a second molecule of nitrosobenzene. Thus though phenylhydroxylamine, like hydroxylamine itself, can be regarded as a powerful one-electron reducing agent, alcohols quite regularly tend to reduce other molecules by hydride transfer.

E. Bamberger, Ber., 1902, 35, 732.
 A. Hantzsch and M. Lehmann, Ber., 1902, 35, 905.

⁶ E. Bamberger and E. Renauld, Ber., 1897, **30**, 2278; V. O. Lukashevich, Doklady Akad. Nauk S.S.S.R., 1938, **21**, 376 (Chem. Abs., 1939, **33**, 3769); Y. Ogata, M. Tsuchida, and Y. Takagi, J. Amer. Chem. Soc., 1957, **79**, 3397; Y. Ogata and J. Mibae, J. Org. Chem., 1962, **27**, 2048.

⁷ T. Oae, T. Fukumoto, and M. Yamagami, Bull. Chem. Soc. Japan, 1963, 36, 728; M. M. Shemyakin, V. I. Maimind, and B. K. Vaichunaite, Bull. Acad. Sci. U.S.S.R. 1957, 1284 (Chem. Abs., 1958, 52, 6231).

It is evident that the one-electron reduction of nitrosobenzene requires a strong reducing agent, because we have found that its reduction in alkali cannot be effected by cumene, or by 2,4,6-trisubstituted phenols which are easily oxidised by one-electron transfer.

We have also considered alternative, and side, reactions that could be involved in the reduction of nitrosobenzene by alcohols. Solutions of nitrosobenzene in aliphatic alcohols, under nitrogen, turn red on treatment with sodium hydroxide or the corresponding sodium alkoxide. If, after storage, these solutions are evaporated and then treated with light petroleum and water, the petrol solution contains azoxybenzene (25-38% from spectively) of the main reaction products, azoxybenzene and nitrobenzene, are quite distinct from that of nitrosobenzene (Figure 1). Moreover the aromatic reaction products can also be separated and estimated chromatographically to within $\pm 3\%$. To avoid complications from secondary reactions initial rates of disappearance of nitrosobenzene have been measured. In 50% aqueous ethanol the rate of consumption of nitrosobenzene proved to be a first order reaction and Table 1 shows that its rate is proportional to the hydroxide ion concentration of the solution while Table 2 shows that the composition of the reaction products is independent of the reaction temperature. From the data of Table 2,



t-butanol and *ca*. 80% from methanol or ethanol) together with small amounts of azobenzene and 2-hydroxy-*ONN*-azoxybenzene, PhNO:N·C₆H₄·OH (I),⁸ while the aqueous layers are deep red. The formation of aldehydes or ketones could not be established, but this is understandable since nitrosobenzene reacts with compounds containing the CH₂·CO group and again aliphatic aldehydes polymerise in strong alkali.

The red aqueous solutions, after acidification, yield the rather unstable tautomeric dimer (II) which Bamberger ⁹ had obtained by treating nitrosobenzene with concentrated sulphuric acid, and which can be reduced to p-aminodiphenylamine. This self-condensation (8) is so slow in alkaline aqueous t-butanol that this solvent can be used for the spectroscopic study of the reaction between nitrosobenzene and several primary and secondary alcohols.

Since the dimerisation (8) indicates that nitrosobenzene can be attacked by a nucleophilic group at the *para*-position the possibility of a reaction sequence such as (9) was considered, and 4,4'-di-t-butoxyazoxy benzene (IV) was synthesised, but no trace of it could be isolated from any reactions of nitrosobenzene with alkaline t-butanol. Hence reduction of nitrosobenzene through hydroximino-compounds such as (III) is improbable.

The reduction of nitrosobenzene by alkaline solutions of aqueous alcohols can be followed spectrographically since the absorption maxima (323 and 261 m μ re-⁸ For structure see E. Bamberger, *Ber.*, 1900, **33**, 1939; A. Angeli, *Gazzetta*, 1921, **51**, 35.

the reaction has a calculated activation energy of 13.5 ± 0.7 kcal., an activation enthalpy (ΔH^{\ddagger}) of 12.9 ± 0.7 kcal. and an entropy (ΔS^{\ddagger}) of -31 ± 2 e.u.



FIGURE 1 Visible absorption spectrum of nitrosobenzene and its decomposition products in aqueous alcohol

In aqueous t-butanol the reduction rate was of first order with respect to [ethanol] provided that the solvent contained over 25% of water (Table 3A) but when less ⁹ E. Bamberger, H. Büsdorf, and H. Sand, *Ber.*, 1898, **31**, 1513; cf. H. Wieland and F. Kögl, *ibid.*, 1922, **55**, 1800. F

TABLE 1

Reduction of nitrosobenzene in 50% aqueous ethanol (by vol.)

Initial $[PhNO] = 0.01M$; temp.,	20.2° .	
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[NaOH]	Percentage y	ields ($\pm 3\%$)	10 ⁵ Initial rate/[OH-]
M	Azoxybenzene	Nitrobenzene	(sec. ⁻¹)
0.02	82	12	6.6
0.04	85	15	5.9
0.08	87	13	6.0
0.16	92	8	6.0

TABLE 2

Temperature dependence of the reduction of nitrosobenzene by ethanol

Initial $[PhNO] = 0.01 M$; $[OH^{-}] = 0.04 \text{M};$	solvent = 50%
EtOH by vol.		, -

	Percentage y	Initial rate		
lemp. Azoxybenzene		Nitrobenzene	$(mole 1.^{-1} sec.^{-1})$	
6.05°	93	7	$4.9 imes10^{-7}$	
11.00	91	9	$1\cdot 1~ imes~10^{-6}$	
15.65	91	7	$1.8 imes10^{-6}$	
21.10	85	15	$2{\cdot}4~ imes~10^{-6}$	
25.25	93	7	$3\cdot5$ $ imes$ 10-6	
30.00	93	7	$5\cdot3~ imes~10^{-6}$	
3 4·3 0	91	10	$6{\cdot}2~ imes~10^{-6}$	
41.85	106	6	$1.2 imes10^{-5}$	

TABLE 3

Reduction of nitrosobenzene by ethanol in aqueous t-butanol

Initial [PhNO] = 0.01 m; [NaOH] = 0.04 m; temp., 25.25° .

A, Each reaction mixture (20.0 ml.) contained 10.0 ml. of $98\cdot8\%$ aqueous t-butanol and the specified volumes of ethanol and water.

	Percenta	ge yields			
Solvent		3%) Nitro-	Initial - Rate/[EtOH]		
Ml. H ₂ O	benzene	benzene	(sec1)		
0.4	94	16	$2{\cdot}0$ $ imes$ 10^{-6}		
5.0	88	12	$6\cdot0$ $ imes$ 10 ⁻⁷		
7.0	86	8	$5\cdot8~ imes~10^{-7}$		
9 ·0	92	8	$6\cdot1~ imes~10^{-7}$		
	ent Ml. H ₂ O 0·4 5·0 7·0 9·0	$\begin{array}{c} & {\rm Percenta} \\ (\pm 1) \\ {\rm ent} & {\rm Azoxy-} \\ {\rm MI.} \ {\rm H_2O} & {\rm benzene} \\ 0.4 & 94 \\ 5.0 & 88 \\ 7.0 & 86 \\ 9.0 & 92 \\ \end{array}$	$\begin{array}{c} & {\rm Percentage yields} \\ (\pm 3\%) \\ {\rm ent} & {\rm Azoxy-} & {\rm Nitro-} \\ {\rm MI.}\ {\rm H_2O} & {\rm benzene} & {\rm benzene} \\ 0.4 & 94 & 16 \\ 5.0 & 88 & 12 \\ 7.0 & 86 & 8 \\ 9.0 & 92 & 8 \end{array}$		

B, Each reaction mixture (20 ml.) contained 25% of EtOH by vol. (= 4.27m). The remaining solvent was t-butanol containing the percentages of water indicated.

		Percenta	uge yields	
Water		Azoxy-	Nitro-	Initial rate
% by vol.	$[H_2O]$ (M)	benzene	benzene	(mole 1. ⁻¹ sec. ⁻¹)
12.3	6.8	98	5	$7.6 imes10^{-6}$
15.7	8.7	95	11	$4\cdot 9 imes10^{-6}$
28.0	15.6	91	9	$2\cdot 8 imes10^{-6}$
$33 \cdot 4$	$18 \cdot 8$	88	9	$2{\cdot}4~ imes~10^{-6}$
40.2	22.3	93	8	$2{\cdot}1~ imes~10^{-6}$
52.5	29.2	95	9	$2{\cdot}6$ $ imes$ 10^{-6}

water than this was present the rate increased (Table 3B), possibly on account of the shift of the equilibrium $ROH + OH^{-} \implies RO^{-} + H_2O$.

In 50% aqueous ethanol tetrabutylammonium hydroxide proved to be a slightly stronger basic catalyst than sodium hydroxide but triethylamine was much less effective (relative rates 6.8; 4.5; 0.18) and, in 100% ethanol, triethylamine was quite ineffective. The comparative reducing powers of alcohols are given in Table 4 and Figure 2. The reduction of nitrosobenzene by

cyclohexanol and 1-deuteriocyclohexanol was also followed in 50% aqueous t-butanol; the relative rates (1.5 and 0.46 at 25.25°) correspond to a primary kinetic

TABLE 4

Product yields and rates for reduction of nitrosobenzene by alcohols at $25{\cdot}25^{\circ}$

A, Initial [PhNO] = 0.01M; [OH⁻] = 0.04M.

	Percenta	ge yields	
	(±	3%)	Rate constant
Alcohol	Azoxy-	Nitro-	k3 ª
(50% v/v in water)	benzene	benzene	(mole ² sec. ⁻¹ l. ²)
Methanol	83	6	$1.5 imes10^{-5}$
Ethanol	93	7	$5\cdot2~ imes~10^{-4}$
n-Propanol	79	16	$6\cdot4$ $ imes$ 10 ⁻⁴
Isopropanol	92	5	$6.0 imes10^{-4}$
t-Butanol			Zero
2,2,2-Trifluoroethanol			Zero

B, Initial [PhNO] = 0.01M; [OH⁻] = 0.08M; solvent = 51°_{0} Aqueous t-butanol.

	γ_0 rieids					
	[Alco-	(± 3)	%)	k_3^{a}		
	hol	Azoxy-		(mole	2	
Alcohol	(M)	benzene	R ₂ CO	sec1 l	.²)	Ke ^b
Benzhydrol	0.10	83	80	9.7×1	0-3	$2 \cdot 1$
4,4'-Dinitrobenzhydrol	0.01	84	97	1.9×1	0-1	590 .0
4,4'-Dichlorobenzhydrol	0.10			$2{\cdot}6 imes 1$	0-2	14.2
4,4'-Dimethoxybenz-						
hydrol	0.10			$1{\cdot}2 imes 1$	0^{-2}	2.4
Benzyl alcohol	0.10		91	$2{\cdot}4 imes 1$	0-2	4.6
4-Nitrobenzyl alcohol	0.01			$2{\cdot}3 imes 1$	0-1	47.0
3-Nitrobenzyl alcohol	0.02			1.5 imes 1	0-1	43.1
4-Bromobenzyl alcohol	0.10			$5\cdot5 imes1$	0-2	10.6
4-Methylbenzyl alcohol	0.10			1.9×1	0-2	3.9
4-Methoxybenzyl alcohol	0.10			2.7 imes]	10-2	2.7
a - d[PhNO]/dt = k	.[PhN	OIROHI	[OH-].	^b Acie	lity	. rela-

tive to isopropanol; see ref. 10.

isotope effect, $k_{\rm H}/k_{\rm D} = 3.3$ which is low for a proton transfer process, but rational for either hydride transfer or for homolytic hydrogen transfer.



FIGURE 2 Hammett plots of reaction velocities for nitrosobenzene reduction $(\log_{10} k_3)$ and of relative acidities $(\log_{10} K_e)$ for a series of substituted benzyl alcohols. Full circles 2 + $\log_{10} k_3$; open circles $\log_{10} K_e$

In view of the high alkalinity of the reacting solutions it proved to be impossible to ascertain whether nitrosobenzene oxidised aliphatic primary alcohols to aldehydes. With benzyl alcohol however the formation of benzaldehyde was estimated quantitatively by the addition

¹⁰ J. Hine and M. Hine, J. Amer. Chem. Soc., 1952, 74, 5266.

of 2,4-dinitrophenylhydrazine and separation of benzaldehyde 2,4-dinitrophenylhydrazone. Again, with benzhydrol, oxidation to benzophenone was established by the isolation of this ketone in 80% yield together with 83% of azoxybenzene, as calculated from equation (10).

$$Ph_2CH \cdot OH + 2PhNO = Ph_2CO + PhN(O) \cdot NPh + H_2O.$$
 (10)

A careful search was made for the presence of benzpinacol which would result from hydrogen atom transfer [equations (11) and (12)] but none could be detected.

$$-O-CPh_2-H + PhNO \longrightarrow -O-\dot{C}Ph_2 + (PhN-O)^- (11)$$

$$2^{-}O-\dot{C}Ph_{2}+2H^{+}\longrightarrow (HOC-Ph_{2})_{2}$$
(12)

Again from 4,4'-dinitrobenzhydrol as much as 97% of dinitrobenzophenone was isolated. We therefore regard the hydrogen atom transfer mechanism of equation (11) to be improbable.

Table 5A shows that the benzhydrol reaction is of the

TABLE 5

Reduction of nitrosobenzene with benzhydrol in aqueous t-butanol at 25.25°

A, Initial [PhNO] = 0.01 m contains 51% water by	a; [Ph ₂ 0 vol.	CHOH] =	= 0.10 M.	The	solvent
[NaOH] (M) 10 ⁵ Initial rate/[OH-]	0.04	0.08	0.10	0.12	0.16
(sec. ⁻¹)	$2 \cdot 0$	1•7	1.6	1.6	$1 \cdot 6$
B, Initial [Ph ₂ CHOH] = contains 51% water by	0·10м; vol.	[OH-] =	= 0.08м.	The	solvent
[PhNO] (M) 10 ⁴ Initial rate/[PhNO] (se	c. ⁻¹)	$\begin{array}{c} 0{\cdot}010\\ 1{\cdot}4 \end{array}$	$0.01 \\ 1.4$	5	$0.020 \\ 1.4$

TABLE 6

Variation of rate of nitrosobenzene reduction with benzhydrol concentration at 25.25°

Initial [PhNO] = 0.01M; [OH⁻] = 0.10M; solvents as for Table 5. [Ph₂CHOH] (M) 0.025 0.050 0.075 0.100

 10^5 Initial rate/[Ph₂CHOH] 2.7 2.2 1.9 1.6

first order with respect to hydroxide anions when benzhydrol is present in excess, and Table 5B that it is also of first order with respect to nitrosobenzene. Table 6

$$\begin{array}{c} -O - CPh_2 - H + N = O \longrightarrow O = CPh_2 + HN - O \\ Ph & Ph \\ \end{array}$$
(13)

Bimolecular reaction of the Alkyloxide anion

$$HO^{-} + HO^{-}CPh_{2} - H + N=O \longrightarrow H_{2}O + O=CPh_{2}$$

$$HO^{-} + HN^{-}O^{-} (14)$$

$$HO^{-} + HN^{-}O^{-} (14)$$

$$HO^{-} + HN^{-}O^{-} (14)$$

shows that in aqueous t-butanol the reaction order with respect to benzhydrol is less than unity with alkali in excess, but in this solvent mixture the complete ionisation

¹¹ P. D. Bartlett and J. D. McCollum, J. Amer. Chem. Soc., 1956, **78**, 1441.

¹² J. Hutton and W. A. Waters, Chem. Comm., 1966, 634.

of the benzhydrol cannot safely be assumed [cf. equation (13) above]. All these results are consistent with the conclusion that the oxidations of both benzyl alcohol and benzhydrol occur by hydride transfer [reactions (13) or (14) followed by (6) and (7)] and not homolytically.

The variation with temperature of the rate of reduction of nitrosobenzene by benzhydrol in this solvent corresponds to a reaction having $E_{\rm A}$ 10·9 \pm 0·4 kcal., ΔH^{\ddagger} , 10·3 \pm 0·4 kcal., and ΔS^{\ddagger} -33 \pm 1 e.u.; these values are very similar to those found by Bartlett and Mc-Collum¹¹ for the hydride transfer from alcohols to the triphenylmethyl cation in acid solution.

$$H - O^{-}CR_{2} - H + CPh_{3}^{+} \longrightarrow H^{+} + O = CR_{2} + HCPh_{3}$$
(15)

Figure 2 gives plots of log k_3 , where $-d[PhNO]/dt = k_3[PhNO][Alcohol][OH⁻]$, against Hammett's σ constant for the reductions of nitrosobenzene by a number of substituted benzyl alcohols together with plots of the logarithm of the relative acidities, K_e , of these alcohols in isopropanol ($K_e = [A^-]/[Pr^iO^-][HA]^-$) as measured by the indicator method of Hine and Hine.¹⁰ The similarity in the slopes of the log K_e and log k_3 plots in Figure 2 may indicate that the rate of oxidation of an alcohol by nitrosobenzene depends on the ease of formation of its anion.

We also attempted to search for hydride transfer from cycloheptatriene to nitrosobenzene, but as briefly reported ¹² found also that these two compounds interacted additively. The formation of a little nitrobenzene (6-15%) in these reactions merits brief comment. Whilst the higher values may possibly be ascribed to leakage of air into our reacting solutions it is clear that there are some minor side reactions which may be homolytic in type. One of these may well be the rapid autoxidation of phenylhydroxylamine in alkali ^{5,13} which probably involves the (PhNO·)⁻ radical-anion. An alternative is that reactions (1) and (2) (R = H) yield a little of the radical (V) which could ionise to the radical-ion of nitrobenzene (VI) and it has been shown

$$\begin{array}{ccc} PhN-O & & & (PhN-O)^- + H^+ & (16) \\ & & & & \\ OH & O & \\ & & (V) & (VI) \end{array}$$

that this anion rapidly reduces nitrosobenzene.

$$(PhNO_2)^- + PhNO \longrightarrow PhNO_2 + (PhNO)' - (17)$$

EXPERIMENTAL

The nitrosobenzene used in this work was crystallised colourless material, m. p. $67-68^{\circ}$. All the alcohols were purified to correct b. p. or m. p.

Decomposition under Nitrogen with Sodium Alkoxides in Anhydrous Alcohols.—An oxygen-free solution of nitroso-

¹³ Y. Ogata, Y. Sawaki, J. Mibae, and T. Morimoto, J. Amer. Chem. Soc., 1964, **86**, 3854; Y. Ogata and T. Morimoto, J. Org. Chem., 1965, **30**, 597.

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benzene (0.20M) with sodium t-butoxide (0.22M) in anhydrous t-butanol soon became bright red. After acidification (2N-HCl) an equal volume of water was added, butanol was removed under reduced pressure, and the residue was extracted with ether. The extract, after evaporation, was triturated with light petroleum and the resulting solution was chromatographed on alumina using graded elution with light petroleum-benzene-ether mixtures. It yielded azoxybenzene (38%), m. p. and mixed m. p. $35-36^{\circ}$, 2-hydroxy-ONN-azoxybenzene,⁸ (5%), m. p. 75-76° (Found: C, 67.3; H, 4.9; N, 13.0. Calc. for C₁₂H₁₀N₂O₂: C, 67.3; H, 4.7; N, 13.1%). 4,4'-Di-t-butoxyazoxybenzene (see below) could not be detected. The remainder of the reaction product was a black solid insoluble in petroleum. A similar reaction at 40° between 0.15m-nitrosobenzene and only 0.10m-sodium t-butoxide yielded 25% azoxybenzene, 1% of azobenzene, and only a trace of the 2-hydroxyazoxybenzene. No pure product could be isolated from the deep red aqueous solution that remained after the ether extraction.

The reaction of nitrosobenzene (0.05M) with sodium ethoxide (0.25M) in ethanol gave an orange solution which contained azoxybenzene (75%) but no azobenzene. In methanol a similar reaction occurred, but a reaction between nitrosobenzene (0.30M) and sodium hydroxide (0.30M) in methanol gave a deep red solution, which when treated with water and extracted with light petroleum gave azoxybenzene (78%) and an aqueous solution which, on cautious acidification at 0° under nitrogen, deposited a pale yellow powder, m. p. 150-152° (M, 214), soluble in alkali and unstable to sunlight. This, after reduction with alkaline aqueous sodium sulphite, yielded p-aminodiphenylamine, m. p. and mixed m. p. 66-67° (Found: C, 78.3; H, 6.4; N, 15.0. Calc. for C₁₂H₁₂N₂: C, 78.2; H, 6.6; N, 15.2%). By synthesis ⁹ and comparison of spectra the yellow product was proved to be the dimer (II) which Bamberger had obtained by adding nitrosobenzene to concentrated sulphuric acid at 0°.

Reactions of Nitrosobenzene with Sodium Hydroxide in Aqueous Alcohols .--- These were also performed under nitrogen and were worked up as described above to give the product yields listed in Tables 1-4. There was no reaction between nitrosobenzene and sodium hydroxide in t-butanolwater (9:1 v/v) after 12 hr. at 70°. For the reactions of Table 4B the alcohol and nitrosobenzene were dissolved in t-butanol containing 2% of water and then mixed with an equal volume of aqueous sodium hydroxide. After the reaction with benzyl alcohol was complete a known fraction of the reaction mixture was treated with an excess of 2,4-dinitrophenylhydrazine in 5M-sulphuric acid and then a known weight of benzophenone 2,4-dinitrophenylhydrazone was added. The dinitrophenylhydrazones were extracted into benzene and the solution was washed with aqueous sulphuric acid, evaporated at 90°/0.2 mm., redissolved in a little benzene and then subjected to t.l.c. on alumina. The 2 bands corresponding to the dinitrophenylhydrazones of benzaldehyde and benzophenone were dissolved in equal volumes of benzene and their absorptions at $365 \text{ m}\mu$ were compared: a control analysis was performed similarly. The estimated yield of benzaldehyde, calc. from equation (10), was 91%. From the reactions with benzhydrol the resulting ketone was separated chromatographically from

azoxybenzene and both were estimated by weight. The yield of azoxybenzene was 83% and of benzophenone 80%, with recovery of 4% of unchanged benzhydrol. A careful search was made for both benzpinacol and benzpinacolone, but chromatographic plate separation yielded no material with $R_{\rm F}$ values corresponding to those of authentic samples of these substances. From the reaction with 4,4'-dinitrobenzhydrol the corresponding ketone separated almost quantitatively from the reaction mixture; it was collected and weighed.

The yields of azoxybenzene and nitrobenzene listed in Tables 1—4 were estimated by diluting aliquots of reacted mixtures with ethanol and measuring their absorptions at 323 and 261 m μ respectively. Unchanged nitrosobenzene gave an absorption maximum at 281.5 m μ . The kinetic measurements of initial rates of reduction of nitrosobenzene were made by following the decrease of absorption at 680 m μ (compare Figure 1), due correction being made for the absorption of reaction products.

Measurements of the Relative Acidities of Substituted Benzyl Alcohols and Benzhydrols in Isopropanol.—These were performed in duplicate at $25 \cdot 25^{\circ}$ by the competitive indicator technique of Hine and Hine ¹⁰ using 4-nitrodiphenylamine as indicator and measuring its extinction coefficient at 500 mµ. The results, shown in part in Figure 2 and listed in Table 4B, were concordant to within 1%.

Other Reactions.—4,4'-Di-t-butoxyazoxybenzene. 4-Fluoronitrobenzene was converted into 4-t-butoxynitrobenzene¹⁴ which was then refluxed for 26 hr. with an equal weight of sodium hydroxide in aqueous methanol. The product was extracted into benzene and this solution was evaporated to give a yellow solid which, crystallised from aqueous methanol, had m. p. 103—104° (65%) (Found: C, 70·3; H, 7·7; N, 8·0. C₁₈H₂₆N₂O₃ requires C, 70·2; H, 7·7; N, 8·2%). Its n.m.r. spectrum showed a multiplet of 8 benzenoid protons at τ 1·65—3·25 and a sharp singlet of 18 aliphatic protons at τ 8·63; its u.v. spectrum in ethanol had λ_{max} . 350 mµ (ε 1430) and 241 mµ (ε 1250). Formation of this compound was not detected, by t.l.c., in the reaction product from nitrosobenzene and sodium t-butoxide.

Attempted reactions between nitrosobenzene and other possible reducing agents. Nitrosobenzene and 2,4,6-tri-tbutylphenol (each 0.04M) and sodium hydroxide (0.10M) were dissolved in deoxygenated 51% aqueous t-butanol and the rate of loss of nitrosobenzene at 20° was measured at 680 mµ. The optical density dropped from 0.22 to 0.07 in 10 days. Organic products were then extracted into benzene and examined by t.l.c. which established the presence of a high concentration of unchanged tri-t-butyl phenol. Similar results were obtained with mesitol.

Decomposition of nitrosobenzene under nitrogen in alkaline 51% aqueous t-butanol with tetralin, triphenylmethane, and cumene at $25 \cdot 25^{\circ}$ all proceeded at rates comparable with that of the spontaneous decomposition of nitrosobenzene in the same solvent. With cumene alone there was no detectable change of absorption at 680 m μ in 15 hr. at 25°.

One of us (J. H.) thanks the S.R.C. for a research student-ship.

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¹⁴ K. Bowden and P. N. Green, J. Chem. Soc., 1954, 1795.