Nuclear Magnetic Resonance and Mass Spectra of Nitrosobenzene Derivatives

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The synthesis of $[3.5-{}^{2}H_{2}]$ - and $[2.4.6-{}^{2}H_{3}]$ -nitrosobenzene is described. Chemical shifts for the aryl protons of nitrosobenzene and several 4-substituted derivatives have been measured. The mass spectra of nitrosobenzene and its deuterated derivatives are recorded; hydrogen interchange in the $C_6H_5^+$ fragment is discussed.

THE chemical shifts observed in the n.m.r. spectra of various substituted benzenes have been the subject of several recent investigations.1-3 Accurate values for the ortho, meta, and para shifts induced by a substituent are useful in studies on aromatic reactivity and in predicting the spectra of polysubstituted benzene deriv-We now report chemical shifts for nitrosoatives. benzene and certain 4-substituted derivatives.

The deuterated specimens of nitrosobenzene were prepared as follows: [2,4,6-2H₃]aniline was obtained by the exchange of aniline hydrochloride with deuterium oxide at 100°.⁴ Oxidation with peracetic acid⁵ $[2,4,6-^{2}H_{3}]$ nitrosobenzene. 4-Nitroaniline gave heated in a mixture of deuterosulphuric and deuterohydrochloric acids, obtained by decomposing sulphuryl chloride in deuterium oxide, to give 4-nitro-[2,6-²H₂]aniline. The n.m.r. spectrum of this material showed that deuteration had taken place, as expected, ortho to the amino-group. Deamination with hypophosphorous acid ⁶ then gave [3,5-²H₂]nitrobenzene. Reduction to the corresponding phenylhydroxylamine and mild oxidation, in the usual way, completed the synthesis of [3,5-2H2]nitrosobenzene. The n.m.r. spectra of these deuterated nitrosobenzenes were measured with 0.2Msolutions in cyclohexane. Dilution to 0.1M did not produce any significant change in the line positions and the values obtained therefore are effectively those of infinitely dilute solutions. A small amount of benzene was added to each solution to permit an accurate measurement of the shifts, relative to benzene, produced by the nitroso-group. The spectrum of [3,5-²H₂]nitrosobenzene showed two broadened singlets (relative areas 2:1) corresponding to the ortho and the para protons.

The line position of the meta protons was obtained from the broad singlet observed in the spectrum of

[2,4,6-²H₃]nitrosobenzene. This specimen contained appreciable quantities (see below) of the $[2,4-^{2}H_{2}]$ derivative. The ortho proton in this component gave a well-defined doublet (J = 8.3 c./sec.) which had the same chemical shift as the two-proton singlet of [3,5-2Ho]nitrosobenzene. The chemical shifts, relative to benzene,

TABLE 1

Chemical shifts (p.p.m.), from benzene, for nitrosobenzene and 4-substituted derivatives (<0.2M in cyclohexane) at 36°

	Shifts * for	on:	
4-Substituent	2	3	4
Н	-0.56	-0.26	-0.31
Me	-0.47(0.43)	-0.04(0.09)	
C1	-0.49(0.53)	-0.23(0.28)	
MeO	-0.55(0.52)	+0.32(0.17)	
Me ₂ N	— 0·48 (0·46)	+0.68(0.34)	
* Values in pare	ntheses are calc	ulated from ref. 2	(CL MeC

and Me₂N) and ref. 1 (Me). The signs of observed and calculated shifts agree throughout.

of the ortho, meta, and para protons of nitrosobenzene are in Table 1. The corresponding values for nitrobenzene, -0.95, -0.21, and -0.33, have been recorded by Spiesecke and Schneider.² Clearly the deshielding effect of the nitroso-group is much smaller than that of the nitro-group at the ortho positions. However, the difference is less marked at the *meta* and *para* positions. In nitrosobenzene, as in nitrobenzene, the *para* proton absorbs at lower field than the *meta* protons, suggesting mesomeric withdrawal of electrons from the para position

¹ P. Diehl, Helv. Chim. Acta, 1961, 44, 829, and references there cited.

² H. Spiesecke and W. G. Schneider, J. Chem. Phys., 1961, **35**, 731.

³ F. Langenbucher, R. Mecke, and E. D. Schmid, Annalen,

⁶ F. Langenberger, 1
1943, 669, 11.
⁴ A. P. Best and C. L. Wilson, J. Chem. Soc., 1946, 239.
⁵ J. D'Ans and A. Kneip, Ber., 1915, 48, 1136.
⁶ N. Kornblum and D. C. Iffland, J. Amer. Chem. Soc., 1949, 2107.

in the isolated molecule. Insofar as chemical reactivity and chemical shifts can be equated in aromatic systems, the nitroso-group behaves as a strong -M substituent.

The proton line positions of 1,4-disubstituted benzenes can be calculated with reasonable precision by algebraic addition of the ortho and meta chemical shifts for each substituent.1 The values observed for a series of 4-substituted nitrosobenzenes, in dilute cyclohexane solution, are recorded in Table 1 alongside those calculated using the chemical shifts reported ^{1,2} for the various Good agreement with the calculated **4-substituents**. values was observed except for protons ortho to the strongly electron-releasing methoxyl and dimethylamino-groups. The n.m.r. spectra of these nitrosobenzene derivatives, in deuterochloroform, are recorded in Table 2. The spectrum of 4-dimethylaminonitrosobenzene, in deuterochloroform, showed a well-defined doublet at τ 3.42, corresponding to the protons ortho

TABLE 2

N.m.r. spectra (τ values) of substituted nitrosobenzenes in deuterochloroform

		Protons	ons			
Substituents	2	3	4	Me		
2,4,6- ² H ₃		$2 \cdot 38$				
3,5- ² H,	2.08		2.29			
Me	$2 \cdot 20$	2.61		7.61		
Cl	$2 \cdot 14$	$2 \cdot 40$				
MeO	2.08	2.97		6.06		
Me_2N	ca. $2 \cdot 2$	3.38		6.91		

to the dimethylamino-group. However, the protons ortho to the nitroso-group gave a very broad and distorted doublet at ca. τ 2.2. A similar effect has been observed with acetone solutions by MacNicol et al.,⁷ who showed that rotation of the nitroso-group about the N-C bond is sufficiently slow at room temperature to make the 2 and the 6-proton non-equivalent. They attributed this effect to a powerful mesomeric interaction between the two substituents [as (I) \leftarrow (II)]. We have found, however, that the spectrum of 4-dimethylaminonitrosobenzene in cyclohexane shows no significant broadening of the low-field doublet. In mixtures of deuterochloroform and cyclohexane broadening was again observed and increased steadily with increasing concentrations of deuterochloroform (Table 3). Presumably an increase in solvent polarity favours the dipolar form (II) and thus reduces the ease of rotation of the nitroso-group.



Smith⁸ has published a list of substituent effects in 1,4-disubstituted benzenes, including certain nitroso-

benzene derivatives. The values for 4-diethylaminonitrosobenzene, in carbon tetrachloride, were used to calculate the ortho (-0.48) and meta (+0.11) chemical

TABLE 3

N.m.r.	spectrum	\mathbf{of}	4-dimethylan	nino nitr osol	oenzene	in
deı	uterochlorof	lorm	-cyclohexane	mixtures:	mean	line
wie	lths (c./sec.) at	half-height for	r the aryl d	oublets	

olvent composition by vol.	Line widths f	or protons
$CDCl_3 * : C_6H_{12}$	2	3
5:0	ca. $5 \cdot 0$	2.6
4:1	4.3	$2 \cdot 2$
3:2	3.5	$2 \cdot 0$
2:3	$3 \cdot 1$	$2 \cdot 2$
1:4	$2 \cdot 5$	$2 \cdot 3$

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* The half-width of the CHCl₃ signal was 1.1 c./sec. throughout. The line positions of protons 2 and 3 did not change significantly with varying solvent composition.

shifts, relative to benzene, for the nitroso-group. The ortho shift is in reasonable agreement with our results but the *meta* shift is not. The electron-releasing effect of the diethylamino-group (see above) may explain this discrepancy.

The composition of the deuterated nitrosobenzenes was determined by mass spectroscopy. In agreement with earlier work⁹ nitrosobenzene was found to fragment readily to give the ion, $C_6H_5^+$ (m/e 77), producing the base peak (relative intensity 100%) of the spectrum. Further fragmentation to $C_4H_3^+$ (m/e 51) (62%) also occurred. Metastable peaks at m/e 55.4 and 33.8 confirmed this step-wise breakdown. A minor peak at m/e 93 (12%) corresponded to loss of nitrogen from the molecular ion $(m/e \ 107)$ (65%). Measurement of the spectra of the deuterated nitrosobenzenes in the region m/e 107—110 gave the following compositions (%): dideuteronitrosobenzene; C₆H₃D₂NO (63·4), C₆H₄DNO (31.7), and C₆H₅NO (4.9) and trideuteronitrosobenzene; $C_6H_2D_3NO$ (58.5), $C_6H_3D_2NO$ (33.4), C_6H_4DNO (7.5), and C₆H₅NO (0.7). Similar results were obtained from measurements of the peaks at m/e 77—80. Both deuteroderivatives gave an array of metastable peaks in the region m/e 32-37 arising from fragmentations corresponding to the change $C_6H_5^+ \longrightarrow C_4H_3^+$ described above. No strong normal peaks were present in this region and identification of all the expected metastable peaks was possible. The spectrum of dideuteronitrosobenzene showed a fragmentation, m/e 79 \rightarrow 53 (metastable peak at 35.6), which must have involved loss of either C_2H_2 or C_2D from the ion $C_6H_3D_2^+$. Examination of the m/e 53 ion at high resolution established its composition as C₄HD₂ and confirmed the first possibility. The loss of C2H2 was unexpected since the original 3,5-dideuterated material contained no neighbouring CH groups. It seemed possible therefore that hydrogen and deuterium in the $C_6H_3D_2^+$ ion had become

⁷ D. D. MacNicol, R. Wallace, and J. C. D. Brand, Trans. Faraday Soc., 1965, **61**, 1.
⁸ G. W. Smith, J. Mol. Spectroscopy, 1964, **12**, 146.
⁹ J. Collin, Bull. Soc. roy. Sci. Liège, 1954, **23**, 201.

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interchanged before fragmentation; other fragmentations (see Experimental) supported this.¹⁰ The point is best illustrated with the spectrum of our trideuteronitrosobenzene. Eight metastable peaks were identified corresponding to all possible modes of breakdown of the tri-, di-, and mono-deuterated C_6 ions (Table 4). If it is assumed that hydrogen and deuterium become randomly distributed in the C₆ ions before fragmentation, then it is possible to calculate statistically the probability (P inTable 4) for loss of C_2H_2 , C_2HD , and C_2D_2 from each deuterated ion. This involves the additional, reasonable assumption that replacement of hydrogen by deuterium does not effect the rate of fragmentation. Since the relative abundances of the C_6 ions are known from the composition (see above) of the original trideuteronitrosobenzene, the overall probability of a particular fragmentation can be calculated. For example, the fragmentations $80 \longrightarrow 53$ and $78 \longrightarrow 51$ have, respectively, the highest (0.6×0.585) and lowest (0.4×0.075) overall probabilities for our deuterated mixture. In

TABLE 4

Fragmentation of the C_6 ions from trideuteronitrosobenzene

			Fragment		
Ions	Fragmentation	M *	lost	\mathbf{P} †	Ι†
ſ	$80 \longrightarrow 54$	36.5	C_2H_2	0.1	5
$C_{6}H_{9}D_{3}$	80 53	35.2	C_2HD	0.6	1
0 2 0	$80 \longrightarrow 52$	33.8	$C_2 D_2$	0.3	3
ć	79 > 53	35.6	C_2H_2	0.3	4
$C_{a}H_{3}D_{2}$	79 - 52	34.2	$C_{2}HD$	0.6	2
79	79 > 51	$32 \cdot 9$	$\overline{C_2}D_2$	0.1	7
C ₆ H₄D {	78 52	34.7	C_2H_2	0.6	6
	78 51	$33 \cdot 4$	C,HD	0.4	8

* M is the observed metastable peak (m/e); the calculated values agree to within 0.1 m/e. † The probability, P, and intensity, I, are defined in the text.

Table 4 the various fragmentations have been assigned a number (I) representing their probabilities in decreasing numerical order. Accurate measurement of the intensities of the observed metastable peaks was not possible but inspection showed that their relative intensities fell in the same order (I) calculated for the fragmentation probabilities. This appears to provide convincing evidence for randomisation of hydrogen atoms in the $C_6H_5^+$ ion derived from nitrosobenzene.

EXPERIMENTAL

 $[2,4,6^{-2}H_3]$ Nitrosobenzene.—Acetic acid (18 ml.) and 30% hydrogen peroxide (6 ml.) were heated at 85° for 1 hr. then cooled. The resulting peracetic acid ⁵ was added slowly with stirring to $[2,4,6^{-2}H_3]$ aniline hydrochloride ⁴ (1 g.) in water (40 ml.) containing potassium hydrogen carbonate (35 g.) at -5° . After 2 hr. at 0 to -5° the $[2,4,6^{-2}H_3]$ nitrosobenzene was collected, washed with N-hydrochloric acid, and purified by steam distillation and crystallisation from aqueous ethanol. The product (0.38 g.) had m. p. 68° , undepressed when mixed with nitrosobenzene.

4-Nitro-[2,6-²H₂]aniline.—Sulphuryl chloride (2·7 ml.) and deuterium oxide (2·7 g.) were cautiously heated, with exclusion of moisture, until hydrolysis was complete. 4-Nitroaniline (1 g.) was added and the mixture heated under reflux for 20 min. 4-Nitro-[2,6-²H₂]aniline, m. p. 148—148·5°, was isolated after dilution of the cooled mixture with water. However the acidic solution was suitable for use directly in the deamination step (see below). The n.m.r. spectrum (in acetone) showed a broad singlet, τ 1·96 (3,5-protons). A weak doublet (J = 9.5 c./sec.), τ 3·22, was attributed to the presence a small amount of 4-[2-²H]aniline.

 $[3,5^{-2}H_2]$ Nitrosobenzene.-4-Nitro- $[2,6,^{-2}H_2]$ aniline was diazotised and deaminated with hypophosphorus acid.⁶ The n.m.r. spectrum of the resulting $[3,5^{-2}H_2]$ nitrobenzene (in deuterochloroform) showed broad singlets at τ 1.83 (2,6protons) and 2.33 (4-proton). Reduction to the correspondingly deuterated phenylhydroxylamine and oxidation of this to $[3,5^{-2}H_2]$ nitrosobenzene, m. p. 67-68°, was effected in the usual way.

N.m.r. Spectra of Nitrosobenzenes.—Specta were run on a Varian A-60 spectrometer (on permanent loan to Professor D. H. R. Barton, F.R.S., from the Wellcome Trust). The colourless, dimeric nitroso-derivatives were warmed in cyclohexane to give blue-green solutions of the monomers. Recrystallisation of the dimers did not occur at room temperature. 4-Dimethylaminonitrosobenzene was only sparingly soluble in cyclohexane but a solution, saturated a 36°, gave a satisfactory n.m.r. spectrum.

Mass Spectra of Nitrosobenzenes.—Spectra were run by Mr. P. R. Boshoff with an Associated Electrical Industries M.S.9, double focusing, mass spectrometer. Samples were directly inserted on a probe heated at $50-75^{\circ}$; an ionising potential of 70 ev was used throughout.

[3,5-²H₂]*Nitrosobenzene*. The following fragmentations (m/e values) were established by detection of the appropriate metastable peaks (given in parentheses): 79 \longrightarrow 53 (35.6), 79 \longrightarrow 52 (34.2), 79 \longrightarrow 51 (32.9), 78 \longrightarrow 52 (34.7), 78 \longrightarrow 51 (33.3), and 77 \longrightarrow 51 (33.8). The peak at m/e 53 (loss of C₂H₂ from C₆H₃D₂) was shown to arise from the ion C₄HD₂⁺ by accurate weighing (Found: M, 53.03630. Calc. for C₄HD₂: M, 53.03603 and for C₄H₃D: M, 53.03758).

4-Dimethylaminonitrosobenzene. The molecular ion (m/e150) gave the base peak (100%) of the spectrum. The peak at m/e 120 (42%) corresponded to loss of NO (metastable peak m/e 96.0) from the molecular ion.

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¹⁰ A similar process has been observed in the fragmentation of biphenyl, see J. G. Burr, J. M. Searborough, and R. H. Shudde, J. Phys. Chem., 1960, **64**, 1359. For a discussion of the carbon skeleton of $C_{\rm eH_5^+}$ see J. Momigny, L. Brakier, and L. D'Or, Bull. Classe Sci., Acad. roy. Belg., 1962, **48**, 1002.