

Benzidine Rearrangement *via* a Cation Radical in Liquid Sulphur Dioxide

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The reactions of several hydrazobenzene derivatives in liquid sulphur dioxide gave products formed *via* intermediate cation radicals. The intermediates were studied by u.v. and e.s.r. spectroscopy.

SOME examples of benzidine rearrangement of aromatic hydrazo-compounds *via* cation radicals have been reported recently. The most clear-cut is the photo-rearrangement of tetraphenylhydrazine cation radical to *NN'*-diphenylbenzidine.¹ In the acid-catalysed rearrangement of the hydrazine, the participation of the same cation radical was demonstrated.² Tetrakis-*p*-methoxyphenylhydrazine and tetra-*p*-tolylhydrazine have been oxidized electrochemically to give stable radicals, which rearranged to the corresponding dihydrophenazines.³

¹ U. Svanholm and V. D. Parker, *J. Amer. Chem. Soc.*, 1972, **94**, 5507.

² U. Svanholm, K. Bechgaard, O. Hammerich, and V. D. Parker, *Tetrahedron Letters*, 1972, 3675.

During an investigation of oxidation with liquid sulphur dioxide, we found that triphenylamine dimerizes to *NNN'*-tetraphenylbenzidine cation radical in this medium.⁴ This result suggested the possibility of oxidative rearrangements of hydrazobenzenes in liquid sulphur dioxide. Furthermore the cation radical of the product is expected to be stable in this medium because of its low nucleophilicity and electron affinity (1.0 eV).⁵ On anodic oxidation or oxidation with a strong oxidant, further reactions of the products would be expected because of their lower ionization potential.

³ G. Cauquis, H. Delhomme, and D. Serve, *Tetrahedron Letters*, 1971, 4649.

⁴ T. Nagai, K. Katayama, and N. Tokura, *Chem. Letters*, 1973, 919.

⁵ J. M. Sichel, *Canad. J. Chem.*, 1973, **51**, 2124.

RESULTS AND DISCUSSION

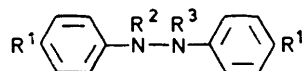
To discover the effects of substituents on ionization potential, a series of nine hydrazobenzenes were studied by cyclic voltammetry. The data are summarized in the Table. Inductive and steric effects and the stability

Reactions of hydrazobenzenes in liquid sulphur dioxide

Hydrazobenzene	$E_{p/2}$ (vs. s.c.e.)	Reaction time (h)	Yields of products (%)
(1)	0.445	24	(10) 10, (11) 40 ^b
(2)	0.64	48	(12) 15, (13) 65
(3)	0.75	12 ^a	(14) 10, (15) 55
(4)	0.25	72	(16) 5, (17) 34 ^c
(5)	0.67	48	(18) 75 ^d
(6)	0.64	72	No reaction
(7)	0.64	72	(19) 50 ^e
(8)	0.25	72	(20) 30, (21) 50
(9)	0.86	12 ^a	(22) 100

^a The reaction mixture was irradiated. ^b Polymeric products were also obtained (ca. 20%) yield. ^c Starting material (45%) was recovered. ^d The hydrazine was isolated in 15% yield. ^e No other isolable product.

of the cation radical formed seem to be the factors determining the values of $E_{p/2}$, as observed in the case



	R ¹	R ²	R ³
(1)	OMe	<i>p</i> -MeO·C ₆ H ₄	<i>p</i> -MeO·C ₆ H ₄
(2)	Me	<i>p</i> -Me C ₆ H ₄	<i>p</i> -Me C ₆ H ₄
(3)	H	Ph	Ph
(4)	Me	Me	Me
(5)	H	Me	Me
(6)	H	Me	H
(7)	H	Ph	H
(8)	Me	H	H
(9)	H	H	H

of tetra-alkylhydrazines.⁶ A *p*-methyl or -methoxy-group clearly decreases the $E_{p/2}$ values. The mono-substituted hydrazobenzenes, (6) and (7), have the lowest half-peak potentials; this can be explained by the inductive effect of the methyl group and the effect of the phenyl group on the stability of the cation radical formed. Disubstituted substances, (3) and (5), show $E_{p/2}$ values between those of hydrazobenzene (9) and the monosubstituted derivatives. In this case inductive and resonance effects compensate for steric effects, which are known to increase the half-peak potentials of hydrazines.⁶

The reactions of the hydrazobenzenes in liquid sulphur dioxide were performed at 20 °C in the absence of oxygen, and u.v. and e.s.r. spectra of the mixture were measured periodically. In some cases the e.s.r. spectra were not fully resolved, and were simulated on the assumption that the nitrogen and the attached methyl group and hydrogen coupling constants were equivalent. Products were isolated and characterized

⁶ S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, 1972, **94**, 7108.

⁷ G. Cauquis, H. Delhomme, and D. Serve, *Tetrahedron Letters*, 1971, 4113.

⁸ A. Neugebauer and S. Bamberger, *Chem. Ber.*, 1972, **105**, 2058.

by comparing physical data with those of authentic samples (Table).

Tetrakis-*p*-methoxyphenylhydrazine (1) reacted with sulphur dioxide in the dark affording rapidly the corresponding cation radical, which was identified by its u.v. absorption at 380, 550, and 640 nm and its e.s.r. spectrum, which consisted of 5 lines (a_N 7.1 mT).³ After 20 min the absorption started to decay, and a new band, attributable to 5,10-dihydro-2,7-dimethoxy-5,10-bis-*p*-methoxyphenylphenazine (10) cation radical [λ_{max} 490, 535, and 650 nm; a_N (2) 6.2, a_H (2) 2.1 mT] appeared and increased in intensity. When the hydrazine (1) reacted with trifluoroacetic acid, a mixture of the phenazine (10) (30%) and bis-*p*-methoxyphenylamine (11) (45%) was obtained. Spectroscopic studies suggested the initial formation of the cation radical of (1), which disappeared during 60 min with the appearance of the dication of dihydrophenazine (435, 585, and 640 nm) and the cation radical of bis-*p*-methoxyphenylamine.⁷

The behaviour of tetra-*p*-tolylhydrazine (2) in liquid sulphur dioxide is similar to that of the methoxy-analogue (1). The cation radical of (2),³ first formed, disappeared during the reaction, and absorption assignable to the cation radical of 5,10-dihydro-2,7-dimethyl-5,10-di-*p*-tolylphenazine (12)³ increased. The reaction of (2) with trifluoroacetic acid gave the dication of (12)³ and di-*p*-tolylamine (13) cation radical,⁷ and products (12) and (13) were isolated in 25 and 50% yields, respectively. For the reaction of tetraphenylhydrazine (3), irradiation was found to be necessary. A solution of (3) in liquid sulphur dioxide [λ_{max} 390 nm, attributable to the charge transfer complex of (3) with sulphur dioxide] was irradiated with a Halos PIH 300 W high-pressure mercury lamp in the presence of a small amount of phenanthrene. Absorption at 480 and 570 nm assignable to the cation radical of (3)¹ was observed after 20 min. In 4 h this absorption started to decrease and a new band at 770 nm appeared and continued to increase in intensity. The e.s.r. spectrum of this solution consisted of six lines [a_N (2) = a_H (1) = 5.5 mT], suggesting the formation of the cation radical of *NNN'*-triphenyl-*p*-phenylenediamine (14).⁸

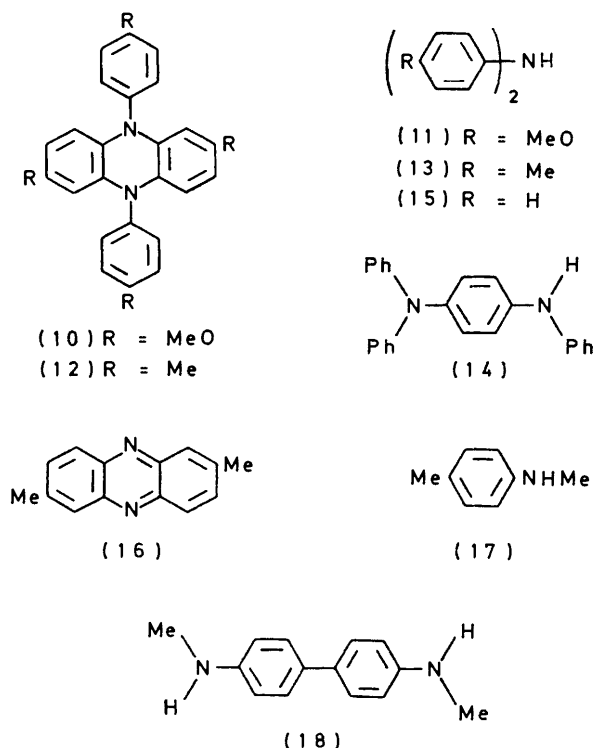
NN'-Dimethyl-*pp'*-hydrazotoluene (4) in liquid sulphur dioxide afforded a mixture of 2,7-dimethylphenazine (16) and *N*-methyl-*p*-toluidine (17). The intermediate cation radical of 5,10-dihydro-2,5,7,10-tetramethylphenazine was observed by u.v. (430 nm) and e.s.r. (a_N 9.6 mT) spectroscopy. The formation of (16) through the cation radical of the dihydrophenazine has been found before, in the acid-catalysed rearrangement of (4).⁹ From *NN'*-dimethylhydrazobenzene (5), only *NN'*-dimethylbenzidine (18) was isolated; this is also the major product in the acid-catalysed reaction of (5).¹⁰

⁸ A. Neugebauer and S. Bamberger, *Chem. Ber.*, 1972, **105**, 2058.

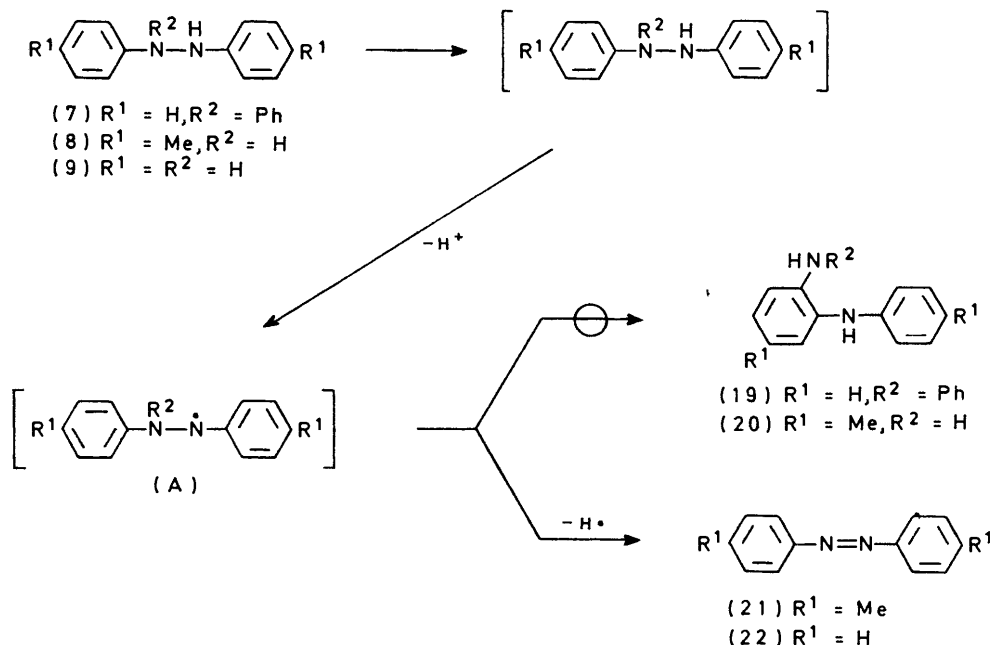
⁹ H. J. Shine and J.-D. Cheng, *J. Org. Chem.*, 1971, **36**, 2787; 1975, **40**, 703.

¹⁰ G. Wittig and J. E. Grolig, *Chem. Ber.*, 1961, **94**, 2148.

When triphenylhydrazine (7) was dissolved in liquid sulphur dioxide, e.s.r. [$a_N(2) = a_H(2) = 5.7$ mT] and



u.v. (685 nm) spectra assignable to *NN'*-diphenyl-*o*-phenylenediamine (19) cation radical were obtained, and



the diamine (19) was isolated in 50% yield. This result is in contrast with the acid-catalysed reaction of (7), from which *N*-phenylbenzidine was isolated in good

¹¹ P. F. Holt and B. P. Hughes, *J. Chem. Soc.*, 1954, 764.

¹² G. Cauquis, B. Chabaud, and M. Genies, *Bull. Soc. chim. France*, 1973, 3482.

yield.¹¹ To explain the formation of (19) in liquid sulphur dioxide the following scheme appears the most reasonable. The cation radical of (7), which appears to be unstable, undergoes rapid deprotonation to afford a stable triphenylhydrazyl (A). The nitrogen atom with the higher radical electron density may then attack a phenyl ring intramolecularly at the *ortho*-position. Migration of hydrogen and subsequent abstraction of hydrogen would then give (19). The formation of the hydrazyl radical (A) has also been postulated in the anodic oxidation of triphenylhydrazine (7).¹²

In the reactions of hydrazotoluene (8) and hydrazobenzene (9), radical species were not observed, but the products suggested the participation of hydrazine cation radicals. For the formation of *o*-semidine (20) and azotoluene (21), the participation of the corresponding hydrazyl radicals (A) would be expected. When the reaction of (9) was performed under irradiation, azobenzene (22) was obtained quantitatively. As the reductive scission product (*N*-methylaniline or aniline) was not obtained in the reactions of (8) and (9), hydrogen abstraction from hydrazyl radicals may be effected not by hydrazines, but by an ambient anion. In the anodic oxidation of (9), azobenzene and aniline are reported to be obtained in low yields.¹³

EXPERIMENTAL

E.s.r. spectra were obtained with a JEOL JNM 4P100 instrument, u.v. spectra with a Varian Techron 635 spectrometer, ¹H n.m.r. spectra with a JEOL 3H-60 instrument and mass spectra with a Hitachi RMU-6H spectrometer

The details of the apparatus used for the reactions in liquid sulphur dioxide have been described previously.¹⁴

¹³ S. Wawzonek and T. W. McIntyre, *J. Electrochem. Soc.*, 1967, **114**, 1025.

¹⁴ T. Nagai, T. Miyazaki, Y. Sonoyama, and N. Tokura, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1968, **6**, 3087.

Materials.—Tetrakis-*p*-methoxyphenyl-, tetra-*p*-tolyl-, and tetraphenyl-hydrazine were prepared by the method of ref. 15. *NN'*-Dimethylhydrazotoluene,⁹ *NN'*-dimethylhydrazobenzene,⁹ *N*-methylhydrazobenzene,¹⁸ triphenylhydrazine,¹¹ and hydrazotoluene¹⁷ were prepared by reported methods.

Cyclic Voltammetry.—The cyclic voltammetry studies were carried out with a one-compartment cell, with a Vycor bridge separating the saturated calomel reference electrode (s.c.e.) from the bulk solution. A Beckmann platinum electrode (No. 39273) was the working electrode, and a platinum foil served as auxiliary electrode. The scan rate was 40.8 mV s⁻¹ and voltammograms were recorded with a Moseley 3S X-Y recorder. Acetonitrile was used as solvent and lithium perchlorate (0.4 mol l⁻¹) as supporting electrolyte.

Reactions of Hydrazines in Liquid Sulphur Dioxide.—Into a quartz cell containing the hydrazo-compound (2.0 × 10⁻⁴ mol l⁻¹) sulphur dioxide (5.5 ml) was distilled in the dark at -70 °C. The solution was frozen (liquid nitrogen) and evacuated three times at 10⁻⁵ mmHg, and the vessel was allowed to warm to 20 °C. The formation

¹⁵ F. A. Neugebauer and P. H. H. Fischer, *Chem. Ber.*, 1965, **98**, 844.

¹⁶ R. B. Carlin, R. G. Nelb, and R. C. Odioso, *J. Amer. Chem. Soc.*, 1951, **73**, 1002.

¹⁷ R. B. Carlin and G. S. Wich, *J. Amer. Chem. Soc.*, 1958, **80**, 4023.

of cation radicals was followed by u.v. and e.s.r. spectroscopy. When irradiation was necessary, the reaction was performed at 0 °C. For example, a solution of tetraphenylhydrazine (47.0 mg) and phenanthrene (5.4 mg) in liquid sulphur dioxide (20 ml) in a Pyrex tube was irradiated with a Halos PIH 300 W high-pressure lamp. In the reaction of hydrazobenzene a 300 W tungsten lamp was used. The products (10),¹⁸ (12),¹⁸ (14),¹⁹ (16),⁹ (18),²⁰ (19),²¹ and (20)¹⁷ were isolated by column chromatography and characterized by comparing physical data with those of authentic samples.

*Reaction of Tetrakis-*p*-methoxyphenylhydrazine with Trifluoroacetic Acid.*—To a solution of trifluoroacetic acid (949 mg) in methylene chloride (15 ml) was added the hydrazine (1) (228 mg) of methylene chloride (15 ml) during 10 min, and the mixture was kept at room temperature for 80 min. For the measurement of u.v. and e.s.r. spectra, a solution of (1) in trifluoroacetic acid was used.

We thank Drs. H. Tamura and T. Iwakura for advice.

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¹⁸ F. A. Neugebauer and H. Fischer, *Chem. Ber.*, 1971, **104**, 886.

¹⁹ P. Welzel, *Chem. Ber.*, 1970, **103**, 1318.

²⁰ G. Wittig and J. E. Groling, *Chem. Ber.*, 1961, **94**, 2148.

²¹ J. Bourson, *Bull. Soc. chim. France*, 1970, 1867.