

PREPARATION AND SYNTHETIC USES OF [2-(ARYLAZO)PHENYL]-MERCURIALS

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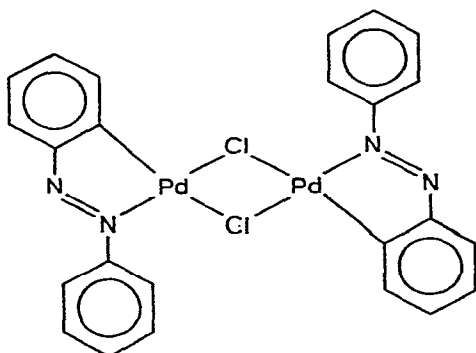
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SUMMARY

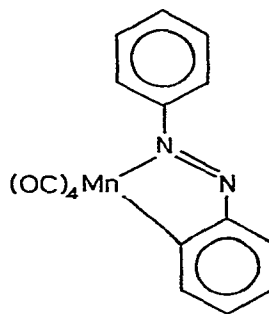
The straightforward preparation of the title compounds in good yield from readily available materials is described. The mercury-carbon bonds of these compounds are smoothly cleaved by halogens to produce the corresponding 2-haloazobenzene derivatives. Nitrosyl chloride reacts with [2-(phenylazo)phenyl]-mercuric chloride to give high yields of 2-phenylbenzotriazole 1-oxide, a reaction involving cyclisation of *ortho*-phenylazo and nitroso substituents. The substituents on the benzene rings retain their relative positions during the formation and reactions of the mercurials, making them ideal reagents for the syntheses of azobenzene derivatives.

INTRODUCTION

Azobenzene derivatives of transition metals have been known for some years. They are commonly prepared from the reaction between azobenzene itself and a metal complex¹⁻⁴, and most compounds involve both metal-nitrogen and metal-carbon bonds. Thus palladium(II) chloride² or sodium chloropalladite(II)³ react with azobenzene to produce (I).



(I)



(II)

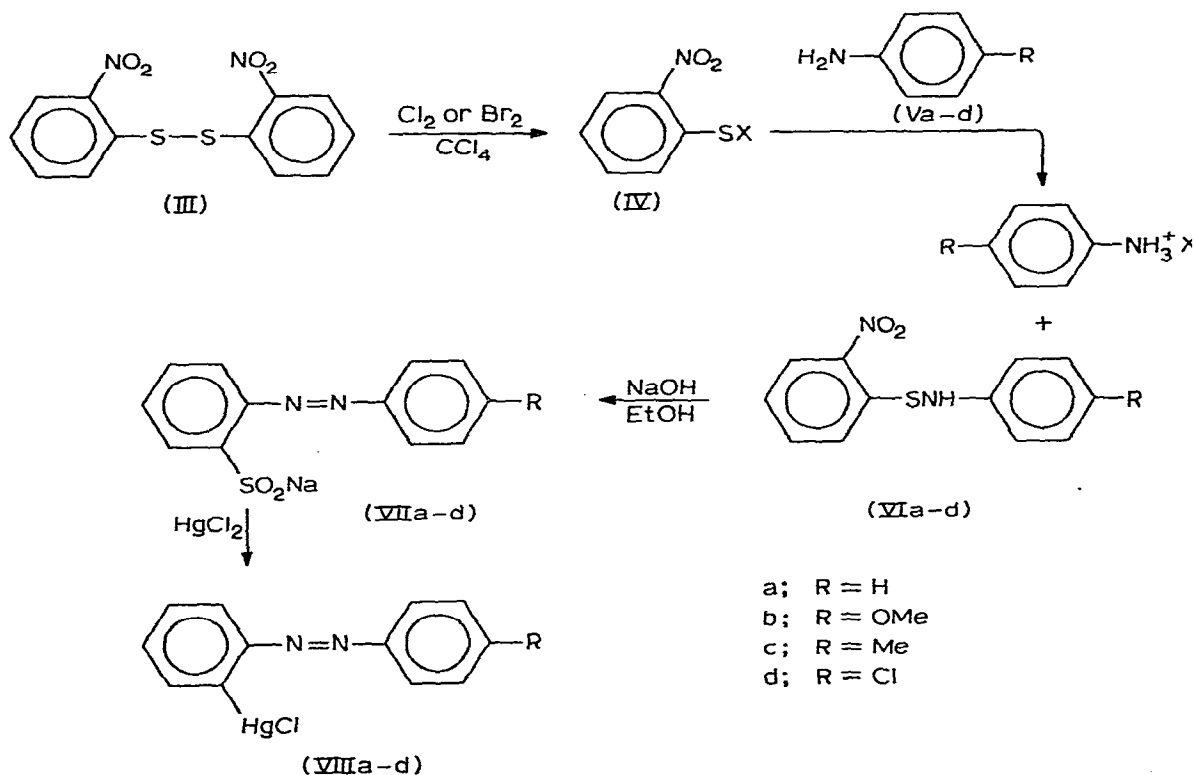
Such preparative reactions are unpredictable. Occasionally the reaction times are long² and the yields low^{1,4}. In some cases either no reaction occurs⁵ or the azobenzene ligand rearranges (see ref. 1 and refs. therein). A small number of compounds with only metal–nitrogen bonding⁶ (these may be precursors of the chelate *N,C*-bonded complexes), or metal–carbon bonding⁷ (often by ligand displacement from the chelates) have also been described.

Few reactions of these azobenzene derivatives have been studied. Complex (I) reacts with $\text{Mn}_2(\text{CO})_{10}$ to produce (II)⁵, and with Cl_2 to yield a mixture of chlorinated products⁸. In general, however, none of the compounds reported thus far is ideally suitable for further synthetic work, due either to expense or difficulty in preparation, or to unpredictability of its reactions. Furthermore, azobenzene derivatives are readily reduced by alkali metals⁹ and by Grignard or organolithium reagents¹⁰, ruling out this useful class of synthetic reagents.

We have examined a series of azobenzene–mercury derivatives, and report here the facile synthesis of [2-(arylaazo)phenyl]mercurials. The ready and specific cleavage of the mercury–carbon bond makes these compounds useful intermediates in synthetic reactions involving arylazo groups.

SCHEME 1

PREPARATIVE ROUTE TO 2-(ARYLAZO)-1-(HALOMERCURI)BENZENES



RESULTS AND DISCUSSION

[2-(Arylazo)phenyl]mercuric chloride derivatives, (VIII), were prepared according to the reaction sequence shown in Scheme 1. Overall yields were about 55%. The starting materials (III) and (V) are readily available, and the synthesis hinges on two key steps: the base-promoted rearrangement of the 2-nitrobenzenesulphenanilide (VI) to the sodium azobenzene-2-sulphinate (VII), and its subsequent treatment with HgCl_2 to give the chloromercuri derivative.

The rearrangement reaction has been closely examined by Brown¹¹ and explained in terms of an 8-step intramolecular route. It was reported that the reaction proceeds when the *para*-substituent, R, is H or MeO (both of which we have employed), but not when $\text{R} = \text{NO}_2$. We have extended the rearrangement to $\text{R} = \text{Cl}$ and Me. The *para*-nitro group has a very high Hammett σ constant (+0.78) compared to the other substituents (Cl, +0.22; H, 0.0; Me, -0.17; MeO, -0.27)¹². This suggests that although the few other groups with Hammett σ constants approaching that of *p*- NO_2 (e.g. COOR, CF_3 and CN) might also prevent this rearrangement, the vast majority of *para*-substituents will allow it and this step should be quite versatile.

The second critical process involves the formation and decomposition of a mercury arenesulphinate. This useful general reaction, originally developed by Peters¹³, has recently been examined in some detail¹⁴ and the intermediacy of the mercury sulphinate and subsequent loss of SO_2 to form an Hg-C bond is well established. For our compounds, this reaction proceeded readily in water, or, more conveniently, ethanol. No attempt was made to isolate the intermediate sulphinates.

The compounds isolated from this procedure are listed in Table 1. The use of mercuric bromide or iodide (instead of HgCl_2) during the preparation produces the corresponding bromomercuri or iodomercuri derivatives, respectively. All of these

TABLE 1
AZOBENZENE-MERCURY DERIVATIVES

Compound	M.p. (°C)	Analysis found (calcd.) (%)			$\nu(\text{HgX})$ (cm^{-1})
		C	H	N	
$(\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_4)\text{HgI}$	148.5–150.5	28.26 (28.33)	1.58 (1.78)	5.37 (5.50)	205 ^a
$(\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_4)\text{HgBr}$	178–180	31.54 (31.22)	2.07 (1.96)	5.97 (6.07)	233 ^a
$(\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_4)\text{HgCl}$	200–202	34.62 (34.54)	2.42 (2.17)	6.75 (6.71)	325 ^b
$(p\text{-MeOC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4)\text{HgCl}$	205–207	35.21 (34.91)	2.45 (2.48)	6.48 (6.26)	330 ^b (322sh)
$(p\text{-MeC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4)\text{HgCl}$	200–202	36.42 (36.21)	2.50 (2.57)	6.44 (6.50)	328 ^b (325 sh)
$(p\text{-ClC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4)\text{HgCl}$	194–196	31.81 (31.91)	1.92 (1.79)	6.41 (6.20)	330 ^b
$(\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_4)_2\text{Hg}$	144–146	51.35 (51.20)	3.37 (3.22)	10.22 (9.95)	

^a Rigidex disc. ^b KBr disc.

compounds are bright red solids which crystallise readily as needles from benzene. Retention of the 1,2- and 1,4-substitution patterns of the two benzene rings is confirmed by observation of the characteristic out-of-plane C-H bending vibrations in their IR spectra¹⁵. The ¹H NMR spectra at 100 MHz is also interpreted simply in terms of this substitution pattern^{1,16}.

Four mercury derivatives of azobenzene have been previously reported in the literature. Ustynyuk and co-workers isolated [2-(phenylazo)phenyl]mercuric chloride* and [2-(phenylazo)phenyl]mercuric acetate from the cleavage of cyclopentadienyl[2-(phenylazo)phenyl]nickel by HgCl₂ and Hg(OAc)₂ respectively¹⁶. This nickel derivative, prepared in low yield from the reaction between nickelocene and azobenzene⁴, lacks the potential for specific unsymmetrical substitution of the two benzene rings afforded by our route. The other reported compounds, 4-(phenylazo)-2-(chloromercuri)phenol and 4-[(*p*-nitrophenyl)azo]-2-(chloromercuri)phenol, were prepared in moderate yield from the reaction between 2-(chloromercuri)phenol and the diazotised amines¹⁷. Mercuration of azoxybenzene by mercuric acetate, followed by treatment with sodium chloride, produces a mixture of *o*- and *p*-(ClHg)-C₆H₄-N=N(O)-Ph¹⁸. In contrast, we failed to observe any reaction between azobenzene itself and mercuric chloride, even after prolonged reflux in ethanol.

[2-(Phenylazo)phenyl]mercuric chloride was symmetrised to bis[2-(phenylazo)phenyl]mercury by refluxing in an acetone solution of triphenylphosphine.

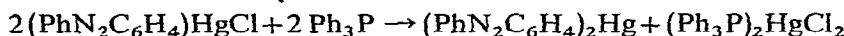
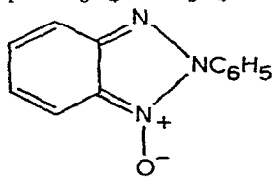


TABLE 2

CLEAVAGE PRODUCTS OF THE ORGANOMERCURIALS

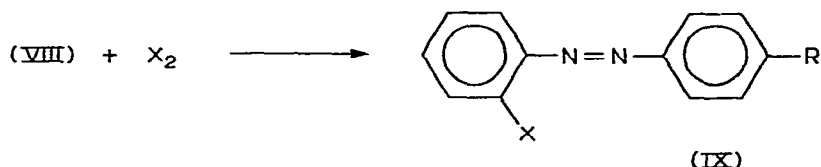
Compound	<i>M.p.</i> (°C)	Analysis found (calcd.) (%)			<i>Mol. wt.</i> found ^a (calcd.)
		C	H	N	
C ₆ H ₅ N=NC ₆ H ₄ I	61.5–62.5	46.78 (46.78)	3.12 (2.94)	9.07 (9.09)	308 (308)
<i>p</i> -MeOC ₆ H ₄ N=NC ₆ H ₄ I	81.5–83.5	46.24 (46.18)	3.36 (3.28)	8.35 (8.23)	338 (338)
<i>p</i> -MeC ₆ H ₄ N=NC ₆ H ₄ I	78–80	48.27 (48.45)	3.52 (3.44)	8.91 (8.70)	322 (322)
<i>p</i> -ClC ₆ H ₄ N=NC ₆ H ₄ I	100.5–102.5	41.92 (41.96)	2.36 (2.35)	8.33 (8.16)	342 (342)
<i>p</i> -MeC ₆ H ₄ N=NC ₆ H ₄ Br	58–60	56.86 (56.75)	4.08 (4.03)	10.34 (10.18)	274 ^b (274)
<i>p</i> -MeC ₆ H ₄ N=NC ₆ H ₄ Cl	38–40	67.56 (67.68)	4.76 (4.81)	12.14 (12.14)	230 ^c (230)
	85.5–87.5	68.03 (68.28)	4.40 (4.30)	20.15 (19.90)	211 (211)

^a By mass spectrometry. ^b Using ⁷⁹Br. ^c Using ³⁵Cl.

* We report a different melting-point for this compound.

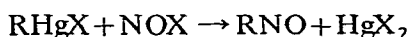
This is a standard method for symmetrising arylmercuric salts¹⁹. The chloride was also symmetrised in high yield simply by passing its solution down an ion-exchange column packed with the iodide form of Amberlyst A26. This method takes advantage of the highly coloured organic moiety for product detection during elution. Iodide is another recognised symmetrising agent, and the reaction in this case probably proceeds via nucleophilic attack of I^- at mercury. A similar reaction has recently been reported using KI adsorbed on alumina²⁰. In its chloride form, the ion-exchange resin was less effective.

The mercury-carbon bonds in all these compounds are readily cleaved by halogens to produce the corresponding 2-halo-4'-R-azobenzene derivatives, (IX).

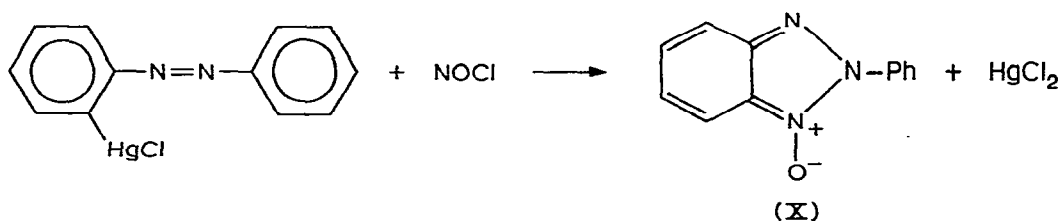


The products of these reactions are listed in Table 2. The IR and 1H NMR spectra of these compounds again confirm retention of the ring-substitution patterns. Of the compounds listed, only 2-iodoazobenzene²¹ and 2-bromo-4'-methylazobenzene²² have been previously reported, and this reaction provides a useful high-yield route to specific and unsymmetrically substituted azobenzene derivatives. The reaction between chlorine and the palladium derivative, (I), leads to a mixture of *ortho*-chlorinated azobenzenes containing from one to four chlorine atoms⁸. This probably happens because until all four *ortho*-hydrogen atoms are removed, the azobenzene derivatives formed can react with $PdCl_2$ and the process will continue.

Organomercurials are reported to react with nitrosyl halides to produce C-nitroso derivatives²³.



We have examined the reaction of [2-(phenylazo)phenyl]mercuric chloride, (VIIIa), with $NOCl$ in chloroform solution. The reaction proceeds smoothly to form 2-phenylbenzotriazole 1-oxide, (X), in high yield.



This reaction represents one of the simplest routes to (X), and again carries the potential for specific substitution at either aromatic ring. The C-nitroso compound is presumably produced as an intermediate, prior to cyclisation, adding weight to the argument that the same intermediate may be involved in other routes to (X)²⁴. For example, it has been suggested²⁵ that the isolation of (X) from the sodium sulphide

reduction of 2-nitroazobenzene proceeds via such a route. A similar mechanism, followed by the removal of oxygen from (X), may well operate in the reaction of 2-nitroazobenzene with triethyl phosphite to produce 2-phenylbenzotriazole, rather than the cyclisation of an intermediate nitrene as postulated²⁶. The cyclisation of *o*-dinitrosobenzene, a process similar to the above, is well documented²⁷.

EXPERIMENTAL

Analytical data for the mercury compounds is included in Table 1, and for their organic cleavage products in Table 2. Mass spectra were recorded on an AEI MS12 mass spectrometer. Melting points were determined on a Reichert Kofler Hot-Stage instrument and are uncorrected.

The preparation of [2-(phenylazo)phenyl]mercuric chloride, (VIIIa)

To a cooled solution of *o*-nitrobenzenesulphenyl chloride (5.02 g, 26.5 mmoles) in dry ether (60 ml) was added aniline (5.08 g, 54.5 mmoles) with constant stirring²⁸. The white precipitate of aniline hydrochloride was removed by filtration, and the solvent was evaporated from the filtrate to leave an orange viscous liquid. Two crystallisations from petroleum ether (b.p. 60–80°) gave orange crystals of *o*-nitrobenzenesulphenanilide (VIa) (5.44 g, 84%. M.p. 90–92°, lit.²⁹ 94°).

This material (22.2 mmoles) was added to a solution of sodium hydroxide (0.89 g, 22.2 mmoles) in water (5.5 ml) and ethanol (25 ml). The mixture was refluxed for 6 h. After adding a further 25 ml of water, the solution was cooled to 0° and bright orange crystals of sodium *o*-azobenzenesulphinate²⁹ (VIIa) were deposited (4.64 g, 78%). A solution of (VIIa) (2.39 g, 8.9 mmoles) in ethanol (25 ml) was added to a solution of mercuric chloride (2.65 g, 9.8 mmoles) in hot ethanol (100 ml). An immediate precipitate was produced, and the mixture was refluxed for 30 min. Sulphur dioxide was evolved. Cooling and concentration of the orange solution yielded orange needles of [2-(phenylazo)phenyl]mercuric chloride (VIIIa) (2.5 g, 70%. M.p. 200–202° *ex* benzene, lit.¹⁶ 151–154°).

[2-(Phenylazo)phenyl]mercuric bromide

Prepared as above but using mercuric bromide instead of the chloride. The ethanol solution of (VIIa) (3.38 g, 12.6 mmoles) and HgBr₂ (4.57 g, 12.7 mmoles) was refluxed for 2½ h. Concentration and cooling produced red needles of the product (4.24 g, 72%, M.p. 178–180° *ex* benzene).

[2-(Phenylazo)phenyl]mercuric iodide

As above from (VIIa) (4.03 g, 15.0 mmoles) and HgI₂ (6.81 g, 15.0 mmoles). The normal procedure gave orange needles of the product, (6.70 g, 87%. M.p. 148.5–150.5° *ex* benzene).

{2-[(4-Methoxyphenyl)azo]phenyl}mercuric chloride, (VIIIb)

The reaction was carried out according to the method described for (VIIIa) above. *o*-Nitrosulphenyl bromide (2.33 g, 9.9 mmoles; from the reaction of bromine and *o*-nitrophenyl disulphide)²⁸ and *p*-anisidine (2.51 g, 20.4 mmoles) was produced 2.32 g, (85%) of (VIb) as orange crystals (M.p. 140.5–141.5°, lit.¹¹ 141.5–142.5°). This

material (1.64 g) was treated with sodium hydroxide¹¹ to produce 1.66 g (94%) of (VIIb). Treatment of (VIIb) (1.14 g, 4.2 mmoles) with mercuric chloride afforded orange needles of the product (1.28 g, 74%. M.p. 205–207° *ex* benzene).

{2-[(4-methylphenyl)azo]phenyl}mercuric chloride, (VIIIc)

In the same way, *o*-nitrosulphenyl bromide (3.64 g, 15.5 mmoles) and *p*-toluidine (3.31 g, 30.9 mmoles) reacted to give 3.71 g, (92%) of (VIc) as golden prisms (m.p. 137–139°, lit.²⁸ 133°). To 1.50 g of this product was added a solution of sodium hydroxide (0.74 g) in a 5/1 ethanol/water mixture (30 ml) and the mixture was refluxed for 5½ h to produce (VIIc) (95% conversion). This material (1.35 g, 47.8 mmoles) was treated with mercuric chloride (1.37 g, 51.6 mmoles) in ethanol (300 ml) and, after 1½ h reflux, produced orange needles of the product (1.79 g, 87%. M.p. 200–202° *ex* benzene).

{2-[(4-Chlorophenyl)azo]phenyl}mercuric chloride, (VIIIId)

As before, *o*-nitrosulphenyl bromide (3.82 g, 16.3 mmoles) was allowed to react with *p*-chloroaniline (4.01 g, 39.4 mmoles) in dry ether to yield yellow crystalline (VIId) (3.79 g, 83%. M.p. 142–144°, lit.³⁰ 144°). A 5/1 ethanol/water solution of this material was refluxed with sodium hydroxide for 6 h to produce (VIIId) (99% conversion). This material (2.31 g, 7.6 mmoles) was treated with mercuric chloride (2.06 g, 7.6 mmoles) in ethanol (200 ml) to produce, after refluxing for 1½ h, orange needles of the product (3.0 g, 89%. M.p. 194–196° *ex* benzene).

Bis[(2-phenylazo)phenyl]mercury

(a). To a suspension of [2-(phenylazo)phenyl]mercuric chloride (VIIIa) (4.34 g, 10.4 mmoles) in hot acetone (150 ml) was added a solution of triphenylphosphine (2.73 g, 10.4 mmoles) in acetone (20 ml). A clear orange solution resulted. Removal of the solvent and ether extraction left white solid bis(triphenylphosphine)-mercury(II) chloride, (Ph₃P)₂HgCl₂ (3.99 g, 96%. IR. and m.p. (267–270°) identical to those of an authentic sample³¹). Concentration of the ether extracts yielded orange crystals of the title product (2.65 g, 95%. M.p. 144–146° *ex* ethanol).

(b). A 15 cm × 2 cm chromatography column was packed with Amberlyst A26 resin in water, then converted to its iodide form by running through a solution of KI. Excess potassium halide was removed by water washing, and the column solvent was then replaced by methanol (200 ml) followed by benzene (200 ml). A solution of [2-(phenylazo)phenyl]mercuric chloride (0.79 g, 1.9 mmoles) in benzene (7.5 ml) was added to the column and eluted with benzene (200 ml) followed by ethanol (100 ml) until the eluant was colourless. Evaporation of the combined eluants produced bis[2-(phenylazo)phenyl]mercury (0.52 g, 96%).

Halogen cleavage reactions

To a solution of iodine (0.52 g, 2.0 mmoles) in ethanol (30 ml) was added [2-(phenylazo)phenyl]mercuric iodide (1.05 g, 2.0 mmoles) in ethanol (20 ml). After 10 min reflux the iodine colour disappeared. Removal of solvent and extraction of the residue by benzene, followed by filtration and removal of the benzene and crystallisation from ethanol, produced red crystals of 2-iodoazobenzene (0.53 g, 87%. M.p. 61.5–62.5°, lit.²¹ 62°). Similarly prepared were: 2-iodo-4'-methoxyazobenzene (86%.

M.p. 81.5–83.5°) from (VIIIb) and iodine; 2-iodo-4'-methylazobenzene (89% M.p. 78–80°) from (VIIIc) and iodine; 2-iodo-4'-chloroazobenzene (98% M.p. 100.5–102.5°) from (VIId) and iodine; 2-bromo-4'-methylazobenzene (90% M.p. 58–60° lit.³⁰ 60.5–61.5°) from (VIIIc) and bromine, and 2-chloro-4'-methylazobenzene (76% M.p. 38–40°, *ex* water/ethanol) from (VIIIc) and chlorine.

The preparation of 2-phenylbenzotriazole 1-oxide, (X)

Nitrosyl chloride gas was bubbled through a stirred suspension of [2-(phenyl-azo)phenyl]mercuric chloride, (VIIIa), (2.29 g, 55.2 μ moles) in chloroform (100 ml). After $\frac{1}{2}$ h the mixture had turned to a deep orange-red liquid containing a pale precipitate of mercuric chloride. The reaction was continued for a further hour when the solution was filtered and the filtrate extracted with water (2 $\times$ 50 ml). The chloroform fraction was dried (MgSO₄) and concentrated to an orange viscous liquid which was dissolved in the minimum amount of dry ether. On cooling to 0° this solution yielded pale yellow prisms of 2-phenylbenzotriazole 1-oxide, (X) (0.89 g, 77% M.p. 85.5–87.5°, lit.³² 85°, lit.³⁸ 88.5°).

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REFERENCES

- 1 M. I. Bruce, M. Z. Iqbal and F. G. A. Stone, *J. Chem. Soc. A*, (1970) 3204.
- 2 A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, 87 (1965) 3272.
- 3 H. Takahashi and J. Tsuji, *J. Organometal. Chem.*, 10 (1967) 511.
- 4 J. P. Kleiman and M. Dubeck, *J. Amer. Chem. Soc.*, 85 (1963) 1544.
- 5 R. F. Heck, *J. Amer. Chem. Soc.*, 90 (1968) 313.
- 6 (a) A. L. Balch and D. Petridis, *Inorg. Chem.*, 8 (1969) 2247;
(b) R. Murray, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 811;
(c) S. Otsuka, T. Yoshida and Y. Tatsuno, *J. Chem. Soc. D*, (1971) 67;
(d) R. S. Dickson and J. A. Ibers, *J. Amer. Chem. Soc.*, 94 (1972) 2988.
- 7 (a) D. L. Weaver, *Inorg. Chem.*, (1970) 2250;
(b) B. Crociani, T. Boschi, R. Pietropaolo and U. Belluco, *J. Chem. Soc. A*, (1970) 531.
- 8 D. R. Fahey, *J. Organometal. Chem.*, 27 (1971) 283.
- 9 V. Kalyanaraman and M. V. George, *J. Organometal. Chem.*, 47 (1972) 225.
- 10 H. Gilman and J. C. Bailie, *J. Org. Chem.*, 2 (1937) 84.
- 11 C. Brown, *J. Amer. Chem. Soc.*, 91 (1969) 5832.
- 12 H. H. Jaffé, *Chem. Rev.*, 53 (1953) 191.
- 13 W. Peters, *Ber. Deut. Chem. Ges.*, 38 (1905) 2567.
- 14 J. R. Brush, P. G. Cookson and G. B. Deacon, *J. Organometal. Chem.*, 34 (1972) C1; and refs. therein.
- 15 L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen, London, 2nd. ed., 1966, Ch. 5.
- 16 Yu. A. Ustynyuk, I. V. Barinov and E. I. Sirotkina, *Dokl. Akad. Nauk, SSSR*, 187 (1969) 112.
- 17 S. F. Chang and I. E. Liener, *Nature*, 203 (1964) 1065.
- 18 T. Ukai and Y. Ito, *J. Pharm. Soc. Jap.*, 73 (1953) 821; *Chem. Abstr.*, 48 (1954) 9945i.
- 19 G. E. Coates and A. Lauder, *J. Chem. Soc.*, (1965) 1857.
- 20 R. J. Cross and C. M. Jenkins, *J. Organometal. Chem.*, 56 (1973) 125.
- 21 G. M. Badger, R. J. Drewer and G. E. Lewis, *Aust. J. Chem.*, 17 (1964) 1036.
- 22 Y. Nomura, *Bull. Chem. Soc. Jap.*, 34 (1961) 1648.
- 23 (a) A. Baeyer, *Ber. Deut. Chem. Ges.*, 7 (1874) 1638;
(b) L. I. Smith and F. L. Taylor, *J. Amer. Chem. Soc.*, 57 (1935) 2460;
(c) P. Tarrant and D. E. O'Connor, *J. Org. Chem.*, 29 (1964) 2012.

- 24 P. N. Preston and G. Tennant, *Chem. Rev.*, 72 (1972) 627.
- 25 W. Lwowski (Ed), *Nitrenes*, Interscience, 1970, p. 176.
- 26 J. I. G. Cadogan, *Quart. Rev., Chem. Soc.*, 22 (1968) 222.
- 27 H. Feuer (Ed.), *The Chemistry of the nitro and nitroso groups*, Part 1, Interscience, 1969.
- 28 T. Zincke and F. Farr, *Justus Liebigs Ann. Chem.*, 391 (1912) 57.
- 29 M. P. Cava and C. E. Blake, *J. Amer. Chem. Soc.*, 78 (1956) 5444.
- 30 A. Baruffini and F. Gialdi, *Farmaco, Ed. Sci.*, 14 (1959) 771; *Chem. Abstr.*, 54 (1960) 8695d.
- 31 R. C. Evans, F. G. Mann, H. S. Peiser and D. Purdie, *J. Chem. Soc.*, (1940) 1209.
- 32 N. Zinin, *Justus Liebigs Ann. Chem.*, 114 (1860) 217.
- 33 (a). A. Werner and E. Stiasny, *Ber. Deut. Chem. Ges.*, 32 (1899) 3256;
(b). E. Bamberger and R. Hübner, *Ber. Deut. Chem. Ges.*, 36 (1903) 3822.