DIRECT *ortho*-MERCURATION REACTIONS OF AZOBENZENE AND *ortho*-SUBSTITUTED AZOBENZENES

PAUL V. ROLING *, DIANE D. KIRT, JOSEPH L. DILL, STEVEN HALL and CHERI HOLLSTROM

Department of Chemistry, Central Michigan University, Mt. Pleasant, MI 48859 (U.S.A.)

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Summary

The mercuration of azobenzene occurred exclusively in the *ortho*-position to yield 2-chloromercuriazobenzene and a mixture which on iodination gave 2,2'- and 2,6-diiodoazobenzene. Ten other *ortho*-substituted azobenzenes were mercurated and mercuration was found to occur predominately in an *ortho*-position. The regiospecificity of these reactions suggests that the mercury is directed into an *ortho*-position by coordination of the mercury to an azo nitrogen and then subsequent electrophilic substitution.

Introduction

Currently, there is much interest in the *ortho*-metalation reactions of azobenzene. A number of direct metalations of azobenzene have been described [1—5] and in all cases metalation occurs in the *ortho*-position, presumably by coordination of the metal to an azo nitrogen and subsequent substitution [1]. There have been reported two indirect *ortho*-mercuration reactions of azobenzene [4,5].

Synthetically the *ortho*-metalated azobenzenes and in particular the mercurials are very useful. The mercurials react readily with halogens to produce haloazobenzenes cleanly and in high yields [5]. These haloazobenzenes can be converted to numerous other derivatives [6]. Overall a great number of new and old *ortho*-substituted unsymmetrical and symmetrical azobenzenes can be synthesized thru *ortho*-metalated azobenzenes.

In this paper we describe the direct mercuration of azobenzene and the effects of various *ortho*-substituents on this mercuration reaction.

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* Author to whom correspondence should be addressed at his present address: Department of Chemistry, Texas A & M University, College Station, Texas 77843 (U.S.A.)

Results

For all mercuration reactions, mercuric acetate and the azobenzene were treated in refluxing methanol for 22 hours. The size of the runs was varied but the concentration of the azobenzene was always kept the same (0.44 M). In Table 1 are listed the results of the mercuration reactions. These results are the average of a number of runs (two to ten) for each azobenzene. All monomercurials were easily isolated as related in the experimental. Each monomercurial was determined to be pure by chromatography, melting point, and elemental analysis. The position of mercury substitution was determined by conversion of the mercurial to an iodoazobenzene. The iodo position was then identified by comparison with a known compound and/or by an NMR spectrum. In a few cases the iodo compound was further converted to another known compound. No attempt was made to maximize the yields of the iodination reactions of monomercurials.

The dimercurials, however, proved extremely difficult to isolate and purify. In most instances a mixture of dimercurials resulted and separation could not be effected. The dimercurials, with the exception of 2,2'-bis(chloromercuri)-6,6'-dimethylazobenzene, were therefore not isolated but iodinated, separated where mixtures of diiodo compounds existed, and each diiodo compound purified. The positions of the two mercury atoms were then determined by determining the positions in the iodo groups thru comparison with knowns and/or NMR spectra.

The mercuration of azobenzene (Scheme 1) yielded only one monomercury

TABLE 1

MERCURATION RESULTS [a]

Starting azobenzene				Yield [b] of products (%)					
Substituents			Recovery (%)	Monomercurials Substitution position		Dimercurials Substitution positions			Total
o	o	o'		o	o'	o,o'	o',o'	other	
—	—	—	40	40	—	3	3	0	46
CH$_3$	—	—	20	71	0	0	0	0	71
CH$_3$	—	CH$_3$	39	51	—	4	—	0	55
CH$_3$	CH$_3$	—	72	—	10	—	c	c	d
CH$_3$O	—	—	24	0	63	1	4	1 [e]	69
CH$_3$O	—	CH$_3$O	27	54	—	10	—	0	64
i-PrO	—	—	35	24	c	c	c	c	d
I	—	—	70	20	2	0	0	0	22
Cl	—	—	75	13	7	0	0	0	20
NO$_2$	—	—	93	5	1	0	0	0	6
CN	—	—	96	1	0	0	0	0	1

[a] The results listed here are for the equimolar reaction of an azobenzene and mercuric acetate in refluxing methanol for 22 h. [b] The % yields are based on the azobenzene. The dimercurials, except for that of 2,2'-dimethylazobenzene, were not isolated but the apparent mixtures of dimercurials were iodinated and the diiodo compounds separated. See further the Experimental Section. Dashes in a given column indicate that such a product is not possible. [c] Not determined due to a complicated mixture which was inseparable. [d] The total % yield of mercuration cannot be determined since not all products were isolated and characterized. See further the Experimental Section. [e] The diiodo compound isolated was 5,2'-diiodo-2-methoxyazobenzene.

product, 2-chloromercuriazobenzene (I). This mercurial on iodination gave 2-iodoazobenzene (IV) which in mixture melting point with authentic 2-iodoazobenzene [7] was undepressed. Also from this mercuration reaction there remained an insoluble, inseparable solid which on iodination gave a separable mixture of 2,2'- (V) and 2,6-diiodoazobenzene (VI). The melting point of the 2,2'-diiodoazobenzene (V) agreed with the literature value [8]. The 2,6-diiodoazobenzene (VI) was a new compound and was identified by its NMR spectrum and chemically by conversion to 2,6-dimethoxyazobenzene [6]. The insoluble, inseparable solid thus apparently contained a mixture of 2,2'- (II) and 2,6-bis-(chloromercuri)azobenzene (III).

SCHEME 1
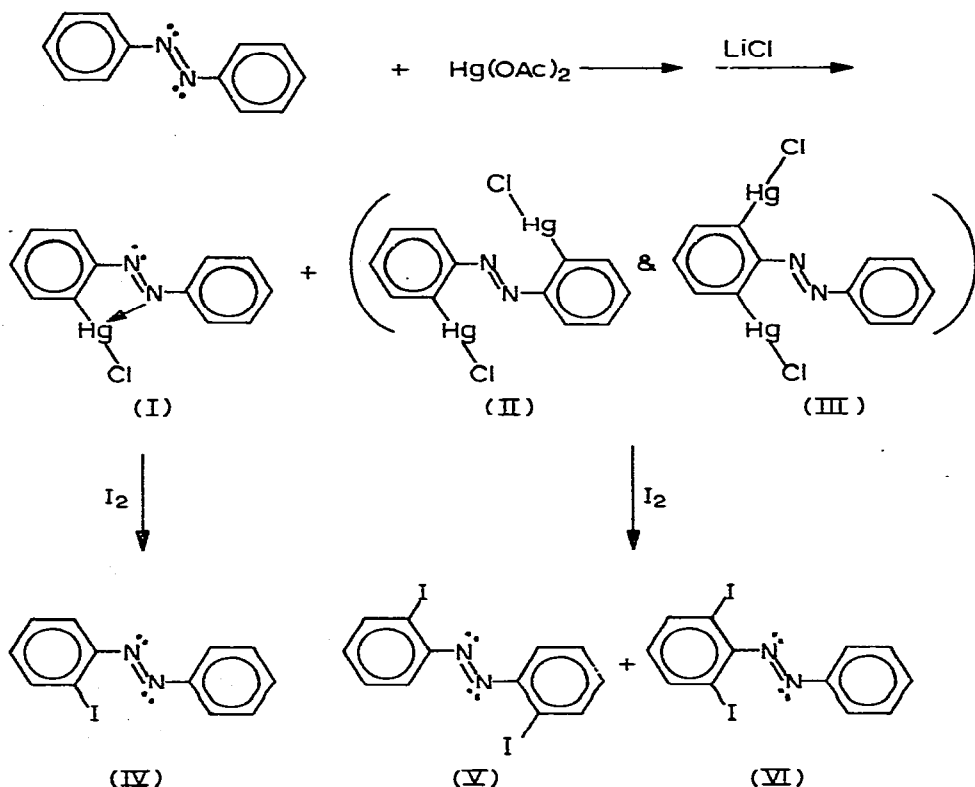
The NMR spectra of the iodoazobenzenes were particularly diagnostic for determining the position of the iodo group(s) on the aryl rings. With no substituents, azobenzene shows a multiplet at δ 7.8—8.2 ppm for the four *ortho*-protons and a second multiplet at δ 7.4—7.8 ppm for the four *meta*- and two *para*-protons [9]. This pair of characteristic looking multiplets was found to consistently occur whenever there was an unsubstituted ring present in a given compound. The NMR spectrum of 2-iodoazobenzene (IV) shows the two characteristic unsubstituted ring multiplets along with the signals for the 3,5,6-protons which are mostly buried underneath the multiplets and a triplet-of-doublets at δ 7.04 ppm which is assigned to the 4-proton. This assignment is

made on the following basis. The 4-proton is *meta* to the iodo group and should experience a fairly large shielding effect due to the iodo [10,11], moving the resonance for this proton above the δ 7.4—7.8 ppm area. The 6-proton is also *meta* to the iodo but would be a doublet-of-doublets (see below 2,2′-diiodoazobenzene). The other triplet-of-doublets for the 5-proton is *para* to the iodo group and should experience almost no effect by the iodo [10,11] and thus it should stay in the δ 7.4—7.8 ppm region.

The NMR spectrum of 2,2′-diiodoazobenzene (V) is simple. The high field (δ 7.09 ppm) triplet-of-doublets is assigned to the 4,4′-protons and the low field (δ 7.34 ppm) triplet-of-doublets is then due to the 5,5′-protons. The two doublet-of-doublets were assigned as a result of a decoupling experiment in which the low field (δ 7.98 ppm) doublet-of-doublets was tickled and this led to the collapse of the δ 7.09 ppm triplet-of-doublets to a doublet (J $7\frac{1}{2}$ Hz) and the collapse of the δ 7.34 ppm triplet-of-doublets to a triplet (J $7\frac{1}{2}$ Hz). Thus the low field (δ 7.98 ppm) doublet-of doublets is assigned to the 3,3′-protons leaving the δ 7.70 ppm doublet-of-doublets for the 6,6′-protons.

The NMR spectrum of 2,6-diiodoazobenzene (VI) is also simple showing the two multiplets characteristic of an unsubstituted ring, a triplet, and a doublet. The triplet is assigned to the 4-proton. The shielding of this 4-proton in 2,6-diiodoazobenzene is roughly twice that of the 4-proton in 2-iodoazobenzene. The doublet is assigned to the 3,5-protons. The large coupling constant (J 8 Hz) for the triplet and doublet is indicative that all three protons are *ortho* to each other.

The iodo compounds from the other mercuration reactions were identified by using the NMR criteria above.

In addition, 2-iodo-2′-methoxyazobenzene was further identified by methoxylation to give 2,2′-dimethoxyazobenzene and 2-chloro-2′-chloromercuriazobenzene was chlorinated to give 2,2′-dichloroazobenzene, known compounds.

The NMR methyl proton chemical shifts and the UV K-band absorption maxima (~320 nm) shifts helped to further confirm assignments of the products. Azobenzene is conformationally a planar molecule [12] *. Upon adding substituents to the *ortho*-positions the degree of twisting about the azo linkage varies depending upon the bulk of the substituents [13]. The addition of a substituent in the 2′-position of a 2-substituted azobenzene gives rise to only small shifts in the methyl proton resonances and positive K-band shifts over the parent 2-substituted azobenzenes, indicating that planarity has been disturbed very little compared to the parent 2-substituted azobenzene. However, when a iodo group was in the 6-position, planarity was disrupted resulting in a shielded methyl group (due to the anisotropic effect of the azo group). The K-band absorption was shifted to lower wavelength due to a loss in total conjugation over the entire system. When a chloromercuri group was in the 6-position, planarity was not disrupted, due to coordination of the mercury with an azo nitrogen. Therefore the methyl resonances were not shielded and K-band absorption moved to longer wavelengths.

2-Phenylazopyridine was mercurated but gave no detectable mercuration prod-

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* All azobenzenes considered in this paper are *trans*-compounds, except benzo[c]cinnolin, which has no choice but to be a *cis*-compound.

TABLE 2

RESULTS OF OTHER MERCURATION REACTION CONDITIONS

Substituent on starting azobenzene	Mercuric compound	Molar ratio of mercuric compound to azobenzene	Recovery of starting material (%)	Yield of products (%)	
				Monomer-curial(s)	Dimer-curial(s)
—	acetate	2	16	55	8 [a], 11 [b]
—	trifluoro-acetate	1	26	57	c
—	acetate [d]	1	19	55	9 [a], 11 [b]
2-I	acetate	2	52	33 [e], 4 [f]	0
2-I	acetate [d]	1	39	44 [e], 6 [f]	2 [g]

[a] Determined as 2,6-diiodoazobenzene (see Experimental). [b] Determined as 2,2′-diiodoazobenzene (see Experimental). [c] Not determined. [d] To this reaction (55 mmol of azobenzene) was added 0.20 ml of 70% perchloric acid. [e] 2-Chloromercuri-6-iodoazobenzene. [f] 2-Chloromercuri-2′-iodoazobenzene. [g] Determined as 2,2′,6-triiodoazobenzene (see Experimental).

ucts. However, a complex was isolated from the reaction mixture. This complex, 2-phenylazopyridine mercuric chloride (VII), was also made by adding together equal molar amounts of mercuric chloride dissolved in methanol and 2-phenyl-azopyridine dissolved in methanol. An instant crystallization of the complex resulted. The probable structure of this complex (VII) is shown.
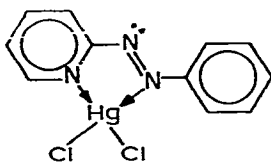

(VII)

Benzo[c]cinnolin yielded no detectable mercuration products.

Other conditions for mercuration were looked at and these are summarized in Table 2. An increase in yields of products was brought about by the use of mercuric trifluoroacetate instead of mercuric acetate. The same result occurred by adding a small amount of perchloric acid to a molar ratio of mercuric acetate and azobenzene or by using a 2 : 1 molar ratio of mercuric acetate to azobenzene. The use of perchloric acid is by far the best way of increasing yields since very little is needed compared to the expensive mercuric trifluoroacetate or the excess mercuric acetate.

Discussion

For the *ortho*-mercuration reaction, the results (see total % yields in Table 1) indicate an electrophilic substitution mechanism. Enhanced reaction with mercuric trifluoroacetate and with mercuric perchlorate also indicate electrophilic substitution. Both mercuric salts are more ionic than the acetate [14], thus producing a better electrophile. Then too, Cross and Tennent [5] observed no reaction with the covalent mercuric chloride.

SCHEME 2

coordination complex

σ-complex

π-complex
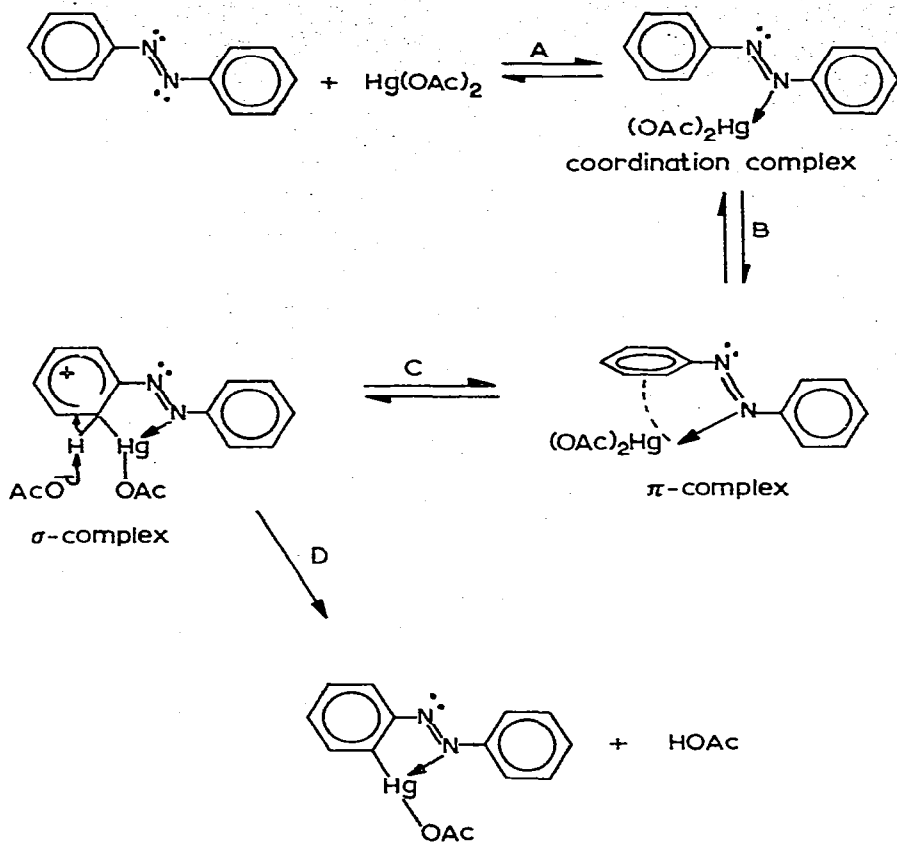
The regiospecificity of the mercuration reactions leads us to conclude that the mercury is directed into an *órtho*-position by coordination of the mercury to an azo nitrogen (Scheme 2 A) and then subsequent electrophilic substitution (Scheme 2 B—D). Support of mercury coordination (Step A) is found in the 1 : 1 complex, formed between mercuric chloride and 2-phenylazopyridine. Also the NMR and UV data show mercury—nitrogen coordination in the mercurials. Attempts were made to detect these coordination complexes by NMR, IR, and UV, but to no avail. Either the concentration of the coordination complexes was too small or the spectral change too minute to detect. The isolation of a palladium azobenzene coordination complex has been reported [15].

Support of Steps B—D is given by the lack of mercuration of benzo[c]cinnolin (VIII), a *cis*-azobenzene, which should be able to coordinate with mercury (Step A), but cannot proceed beyond that point in the reaction (Scheme 2). If mercuration were to occur on this compound, then it would be thru an uncomplexed mechanism. The relative reactivity of azobenzene and benzo[c]cinnolin (VIII) to electrophilic attack should be similar. π-Complexes for mercury have not been reported but π-complexes for other metals are known [16].

The effect of a 2-substituted group on azobenzene can be two-fold: steric and
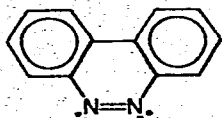
(VIII)

electronic. The R group can sterically hinder coordination of the mercury at the 1-nitrogen. Electronically, donating R groups will activate the aryl ring on which they are substituted and activate the 1'-nitrogen principally thru resonance. This means better mercury coordination (Scheme 2, Step A) and faster substitution (Steps B—D). Electron-withdrawing R groups will have the opposite effects.

Mercuration of 2-methylazobenzene in the 6-position follows the steric and electronic effects outlined above. However, the high yield of monomercurial in the case of 2,2'-dimethylazobenzene suggests that the steric hindrance by the methyl group is not a very large factor in the reaction.

In the case of 2-iodoazobenzene presumably steric hindrance by the iodo to block 1-nitrogen coordination is large, leaving the 1'-nitrogen to direct mercuration into the 6-position of the deactivated aryl ring. By lessening the steric requirement as in 2-chloroazobenzene more coordination can occur with the 1-nitrogen thus we find more mercuration of the unsubstituted aryl ring. The case is the same with 2-nitro- and 2-cyano-azobenzene as with 2-iodo- above, only ring deactivation is greater.

2-Methoxyazobenzene presents what at first sight appears unusual, mercuration of the unsubstituted ring. However, a possible explanation is that the oxygen and nitrogens form bidentate chelates (Fig. 1 A and B). Complex A, in order to mercurate would have to break chelation whereas complex B could mercurate the unsubstituted ring without initially breaking the chelation. By substitution of an isopropoxy group for the methoxy the steric requirements about the oxygen are increased and complexes A and B should not be as easy to form. Normal substitution, as with 2-methylazobenzene, should occur. Mercuration of 2-isopropoxyazobenzene occurs in the 6-position.

The one observed deviation from *ortho*-mercuration, the 5-substitution is 5,2'-diiodo-2-methoxyazobenzene, is an interesting case. The suggestion here would be that azobenzene is not activated enough to undergo mercuration without coordination (coordination is in effect a lowering of the entropy of activation),
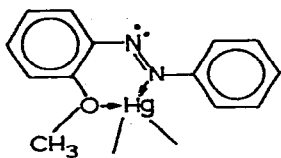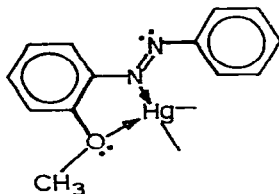
(A) (B)

Fig. 1. Mercuration products of 2-methoxyazobenzene.

but by the activation of the aryl ring by a methoxy group non-coordinative mercuration can occur. The same deviation from *ortho*-mercuration possibly occurred with 2,6-dimethylazobenzene, in view of the many inseparable products found.

Experimental

All NMR spectra were recorded on a Varian T-60 Spectrometer in 5—10% CDCl$_3$ solutions with TMS as the internal standard. All UV spectra were recorded on a Beckman DB Spectrophotometer in 95% ethanol solutions.

The activated alumina (activity about 1) used in this work was supplied by Fisher Alcoa F-20. That termed alumina (activity about 3) was made by shaking 1000 g of F-20 activated alumina with 75 ml of water. Alumina (A = 2) of activity 2 was made as above but with only 50 ml of water. The ligroin used was of boiling range 63—75°C.

Melting points were taken on a Mel-Temp apparatus and are uncorrected. All microanalyses were carried out by the Galbraith Laboratories, Inc., Knoxville, Tenn.

Mercuration reaction

In a round-bottomed flask equipped with a reflux condenser surmounted with a calcium chloride drying tube, were placed equal molecular amounts of the azobenzene and mercuric acetate and enough reagent grade methanol to make the reaction 0.44 M in the azobenzene (a typical example is 10.0 g (55 mmol) of azobenzene, 18.0 g (56 mmol) of mercuric acetate and 125 ml of methanol). This mixture was stirred by means of a magnetic stirrer and refluxed for 22 h. At the end of the reflux period, the reaction mixture was allowed to cool to room temperature and then lithium chloride (typically 5.0 g or 120 mmols) dissolved in hot methanol was added and the resulting thick mixture stirred for about 10 min, whereupon it was poured into water ($\frac{1}{2}$ l). The resulting precipitate was filtered and the filtrate extracted with ether until the extracts were colorless. The ether was evaporated and the resulting residue added to the filtered precipitate to give the reaction solid, which contained mercurials and the starting azobenzene.

The yields of mercuration products are given in Table 1, while individual work-ups are described in detail below.

Workups of the mercuration reactions

Azobenzene. The solid was extracted with four 100-ml portions of ligroin. The extracts were chromatographed on 100 g of alumina and elution with 9 : 1 ligroin/benzene gave azobenzene, crystallized from ligroin, m.p. 65—67°C (lit. [17] 68°C). Further elution with benzene removed the major band at the top of the column (a few very minor band· were noted but discarded) which was 2-chloromercuriazobenzene. Crystallization from benzene/ligroin gave yellow-orange crystals of 2-chloromercuriazobenzene, m.p. 202—204°C (lit. [5] 200—202°C). UV λ_{max} (nm) 230 (ϵ 15 600), 332 (17 700), 449 (430).

The solid was then extracted with hot benzene until the extracts were nearly colorless. Concentration and subsequent crystallization gave the main yield of

2-chloromercuriazobenzene. The remaining insoluble solid was iodinated (see Iodination reaction below) and the diiodo compounds chromatographed on 200 g of activated alumina. Elution with 8 : 2 ligroin/benzene gave a slow separation of first a pinkish band of 2,2'-diiodoazobenzene and second an orange band of 2,6-diiodoazobenzene.

The 2,2'-diiodoazobenzene was crystallized from benzene to give pinkish needles, m.p. 158—159°C (lit. [8] 158—158.5°C). NMR triplet-of-doublets at δ (ppm) 7.09 (2H, 4,4'-protons, J $7\frac{1}{2}$ Hz, J 2 Hz), triplet-of-doublets 7.34 (2H, 5,5'-protons, J $7\frac{1}{2}$ Hz, J $1\frac{1}{2}$ Hz), doublet-of-doublets 7.70 (2H, 6,6'-protons, J $7\frac{1}{2}$ Hz, J 2 Hz), doublet-of-doublets 7.98 (2H, 3,3'-protons, J $7\frac{1}{2}$ Hz, J $1\frac{1}{2}$ Hz).

2,6-Diiodoazobenzene was crystallized from ligroin to give red-orange crystals, m.p. 118—119°C. NMR triplet at δ (ppm) 6.65 (1H, 4-proton, J 8 Hz), doublet 7.87 (2H, 3,5-protons, J 8 Hz), multiplet 7.4—7.7 (3H, 3',4',5'-protons), multiplet 7.8—8.2 (2H, 2',6'-protons). UV λ_{max} (nm) 216 (ϵ 22 700), 278 (11 600), 310(sh) (8500), 437 (350). (Found: C, 33.41; H, 1.79; N, 6.47. $C_{12}H_8I_2N_2$ calcd.: C, 33.20; H, 1.85; N, 6.45%.)

2-Methylazobenzene. The solid was extracted with ligroin until the extracts were almost colorless. These were chromatographed on 100 g of alumina. Elution with 9 : 1 ligroin/benzene gave 2-methylazobenzene, a red oil, b.p. 97—103°C/0.3 mmHg (lit. [18] b.p. 180—181°C/20 mmHg).

The solid was then extracted with hot benzene until the extracts were colorless. At this point no solid remained. The extracts were concentrated and the 2-chloromercuri-6-methylazobenzene crystallized, m.p. 209—210°C. NMR singlet at δ (ppm) 2.75 (3H, CH$_3$), multiplet 7.2—7.7 (6H, 3,4,5,3',4',5'-protons), multiplet 7.9—8.1 (2H, 2',6'-protons). UV λ_{max} (nm) 233 (ϵ 11 900), 342 (14 700), 452 (470). (Found: C, 36.19; H, 2.42; N, 6.37. $C_{13}H_{11}N_2HgCl$ calcd.: C, 36.20; H, 2.57; N, 6.49%.)

2,2'-Dimethylazobenzene. The solid was extracted with ligroin until the extracts were nearly colorless. These were chromatographed on alumina and elution with 9 : 1 ligroin/benzene yielded 2,2'-dimethylazobenzene. Crystallization from ligroin gave orange crystals, m.p. 53—54°C (lit. [19] m.p. 54°C). NMR singlet at δ (ppm) 2.68 (6H, CH$_3$), multiplet 7.0—7.4 (6H, 3,4,5,3',4',5'-protons), multiplet 7.4—7.7 (2H, 6,6'-protons).

The solid was further extracted with hot benzene until colorless and these extracts chromatographed on the alumina column above. Elution with chloroform gave a large orange band of 2-chloromercuri-6,2'-dimethylazobenzene followed immediately by a red band of 2,2'-bis(chloromercuri)-6,6'-dimethylazobenzene, eluted with 95 : 5 chloroform/methanol. The 2-chloromercuri-6,2'-dimethylazobenzene was crystallized from benzene to yield orange crystals, m.p. 211—212°C. NMR singlet at δ (ppm) 2.78 (3H, CH$_3$), singlet 2.82 (3H, CH$_3$), multiplet 7.3—7.6 (7H, aryl protons). UV λ_{max} (nm) 233 (ϵ 11 400), 342 (13 800), 453 (790). (Found: C, 37.80; H, 2.89; N, 6.25. $C_{14}H_{13}N_2HgCl$ calcd.: C, 37.76; H, 2.94; N, 6.29%.)

The 2,2'-bis(chloromercuri)-6,6'-dimethylazobenzene was crystallized from chloroform/benzene, m.p. 270—271°C. (Found: C, 24.99; H, 1.77; N, 4.18. $C_{14}H_{12}N_2Hg_2Cl_2$ calcd.: C, 24.72; H, 1.78; N, 4.12%.)

2,6-Dimethylazobenzene. Workup was exactly as that for 2,2'-dimethylazobenzene above. The ligroin extracts recovered the 2,6-dimethylazobenzene, b.p.

106—114°C/0.3 mmHg (lit. [20] b.p. 175—176°C/16 mmHg). NMR singlet at δ (ppm) 2.33 (6H, CH$_3$), multiplet 6.9—7.1 (3H, 3,4,5-protons), multiplet 7.2—7.5 (3H, 3',4',5'-protons), multiplet 7.7—8.0 (2H, 2',6'-protons). UV λ$_{max}$ (nm) 312 (ε 11 700), 453 (600).

The benzene extracts gave 2-chloromercuri-2',6'-dimethylazobenzene, m.p. 206—208°C. NMR singlet at δ (ppm) 2.40 (6H, CH$_3$), multiplet 7.1—7.7 (7H, aryl protons). UV λ$_{max}$ (nm) 226(sh) (ε 14 500), 320 (11 400), 460 (750). (Found: C, 37.77; H, 3.03; N, 6.41. C$_{14}$H$_{13}$N$_2$HgCl calcd.: C, 37.76; H, 2.94; N, 6.29%.)

The final solid was iodinated, but the resulting iodo compounds were not further investigated due to the NMR indication of a number of products, all in small, equal yields. The methyl region showed eight peaks.

2-Methoxyazobenzene. The solid was extracted with 100 ml of ligroin and this was chromatographed on 100 g of alumina. 2-Methoxyazobenzene was eluted with 1 : 1 ligroin/benzene and crystallization from ligroin gave red crystals, m.p. 34—36°C (lit. [19] m.p. 40°C).

The remaining solid was extracted with hot benzene until the extracts were colorless and the benzene concentrated. Crystallization was effected from benzene/ligroin to give 2-chloromercuri-2'-methoxyazobenzene, m.p. 161—161.3°C. NMR singlet at δ (ppm) 4.10 (3H, CH$_3$O), multiplet 6.9—8.3 (8H, aryl protons). UV λ$_{max}$ (nm) 234 (ε 11 800), 326 (8200), 368 (7800), 450(sh) (980). (Found: C, 35.26; H, 2.30; N, 6.50. C$_{13}$H$_{11}$N$_2$OHgCl calcd.: C, 34.90; H, 2.47; N, 6.26%.)

The remaining solid was iodinated (see Iodination reaction below). There resulted on workup an oil which was dissolved in 95 : 5 ligroin/benzene and chromatographed on a column of 150 g of alumina (A = 2). Elution with 11 : 9 benzene/ligroin produced three partially separated bands, collected in about 150 ml portions. Band 1 gave a red oil and after fractional crystallization from benzene/ligroin yielded dark red crystals of 2,2'-diiodo-6-methoxyazobenzene and light orange crystals of 5,2'-diiodo-2-methoxyazobenzene.

2,2'-Diiodo-6-methoxyazobenzene, m.p. 98—99°C; NMR singlet at δ (ppm) 3.86 (3H, CH$_3$O), multiplet 6.9—7.8 (6H, aryl), doublet-of-doublets 8.00 (1H, 3'-proton, *J* 8 Hz, *J* 2 Hz). (Found: C, 33.42; H, 2.07; N, 5.99. C$_{13}$H$_{10}$N$_2$OI$_2$ calcd.: C, 33.65; H, 2.17; N, 6.04%.)

5,2'-Diido-2-methoxyazobenzene, m.p. 161.5—162.5°C; NMR singlet at δ (ppm) 4.00 (3H, CH$_3$O), doublet at 6.87 (1H, 3-proton, *J* 8 Hz), multiplet at 7.0—8.1 (6H, benzene). (Found: C, 33.67; H, 2.33; N, 5.89. C$_{13}$H$_{10}$N$_2$OI$_2$ calcd.: C, 33.65; H, 2.17; N, 6.04%.)

Band 2 gave a red oil which proved inseparable and was determined to be a mixture of 2,2'-diiodo-6-methoxyazobenzene and 5,2'-diiodo-2-methoxyazobenzene by NMR.

Band 3 gave an orange solid which was crystallized from benzene/ligroin to give orange crystals of 2,6-diiodo-2'-methoxyazobenzene, m.p. 130—131°C. NMR singlet at δ (ppm) 4.00 (3H, CH$_3$O), triplet at 6.67 (1H, 4-proton, *J* 8 Hz), multiplet at 6.9—8.1 (4H, 2',3',4',5'-protons), doublet 7.90 (2H, 3,5-protons, *J* 8 Hz). (Found: C, 33.89; H, 2.09; N, 6.04. C$_{13}$H$_{10}$N$_2$OI$_2$ calcd.: C, 33.65; H, 2.17; N, 6.04%.)

2,2'-Dimethoxyazobenzene. The solid was extracted with 100 ml of benzene and this extract chromatographed on 100 g alumina. Elution with benzene gave

2,2'-dimethoxyazobenzene, crystallized from benzene, m.p. 153—155°C (lit. [19] m.p. 155°C). Further elution with 1 : 1 benzene/chloroform gave, after crystallization from benzene, 2-chloromercuri-6,2'-dimethoxyazobenzene, m.p. 214—215°C. (Found: C, 35.39; H, 3.15; N, 5.82. $C_{14}H_{13}N_2OHgCl$ calcd.: C, 35.23; H, 2.75; N, 5.87%.)

The solid was then extracted with hot benzene until the extracts were colorless. Chromatography as above gave the main part of the 2-chloromercuri-6,2'-dimethoxyazobenzene. The remaining solid was iodinated to yield a residue which on chromatography on alumina and elution with 1 : 1 ligroin/benzene gave, after crystallization from benzene/ligroin, 2,2'-diiodo-6,6'-dimethoxyazobenzene, m.p. 159—160.5°C. NMR singlet at δ (ppm) 3.83 (6H, CH$_3$O), multiplet 7.0—7.3 (4H, 4,5,4',5'-protons), doublet-of-doublets 7.63 (2H, 3,3'-protons, J 5 Hz, J 3 Hz). (Found: C, 34.13; H, 2.47; N, 5.62. $C_{14}H_{12}N_2O_2I_2$ calcd.: C, 34.03; H, 2.45; N, 5.67%.)

2-Isopropoxyazobenzene. The solid was extracted with 100 ml of ligroin and this was chromatographed on alumina. 2-Isopropoxyazobenzene was eluted with 1 : 1 ligroin/benzene, b.p. 130—135°C/0.65 mmHg (lit. [6] b.p. 130—135°C/0.65 mmHg). UV λ_{max} (nm) 220(sh) (ϵ 10 600), 319 (13 400), 350(sh) (10 400), 440 (870). A few very small bands remained on the column and were not further investigated. The remaining solid was extracted with hot benzene until almost colorless extracts were obtained. These extracts were chromatographed on alumina and elution with 1 : 3 benzene/chloroform removed the major band, which on crystallization from benzene/ligroin gave 2-chloromercuri-6-isopropoxy-azobenzene, m.p. 208—209°C. UV λ_{max} (nm) 234(sh) (ϵ 12 000), 340 (11 700), 372(sh) (10 100), 462(sh) (820). (Found: C, 37.77; H, 3.05; N, 5.79. $C_{15}H_{15}N_2$-OHgCl calcd.: C, 37.90; H, 3.18; N, 5.89%.)

The remaining solid was not further investigated since it appeared to be a complex mixture by melting point range and chromatography.

2-Iodoazobenzene. The solid was extracted with ligroin until the extracts were nearly colorless. These extracts were chromatographed on alumina and elution with 9 : 1 ligroin/benzene gave 2-iodoazobenzene, crystallized from ligroin, m.p. 60—61.5°C (lit. [7] m.p. 62°C). NMR triplet-of-doublets at δ (ppm) 7.04 (1H, 4-proton, J 7½ Hz, J 2 Hz), multiplet 7.4—7.8 (5H), multiplet 7.8—8.2 (3H). UV λ_{max} (nm) 222 (ϵ 16 700), 250 (9400), 320 (17 300), 456 (380).

Elution with 1 : 1 benzene/chloroform removed 2-chloromercuri-6-iodoazo-benzene, crystallized from benzene, m.p. 249—250°C. UV λ_{max} (nm) 226 (ϵ 18 400), 252(sh) (7000), 342 (14 700), 460 (290). (Found: C, 26.60; H, 1.39; N, 5.13. $C_{12}H_8N_2HgClI$ calcd.: C, 26.53; H, 1.48; N, 5.15%.)

Further elution with chloroform gave 2-chloromercuri-2'-iodoazobenzene, crystallized from benzene, m.p. 196—197°C. UV λ_{max} (nm) 210 (ϵ 19 200), 328 (13 600), 443 (790). (Found: C, 26.66; H, 1.56; N, 5.20. $C_{12}H_8N_2HgClI$ calcd.: C, 26.53; H, 1.48; N, 5.15%.)

The solid was further extracted with hot benzene until the extracts were almost colorless. These extracts were chromatographed on 300 g of alumina as described above to yield the main portions of the two above described mercurials. The residual solid then contained no further azobenzenes.

In a large scale (40 g of 2-iodoazobenzene) mercuration reaction with perchloric acid, the residual solid was iodinated (see Iodination reaction below) and

the iodo compounds chromatographed on activated alumina. Elution with 4 : 1 ligroin/benzene gave first a small band for 2,2'-diiodoazobenzene and second a small band for 2,6-diiodoazobenzene. A third band (somewhat pinkish in color) closely followed. Crystallization of the material from this third band gave deep red crystals of 2,6,2'-triiodoazobenzene, m.p. 120—121°C. NMR triplet at δ (ppm) 6.72 (1H, 4-proton, J 7½ Hz), triplet-of-doublets 7.20 (1H, 4'-proton, J 7½ Hz, J 2 Hz), triplet-of-doublets 7.48 (1H, 5'-proton, J 7½ Hz, J 2 Hz), doublet-of-doublets 7.83 (1H, 6'-proton, J 7½ Hz, J 2 Hz), doublet 7.96 (2H, 3,5-protons, J 7½ Hz), doublet-of-doublets 8.12 (1H, 3'-proton, J 7½ Hz, J 2 Hz). (Found: C, 25.91; H, 1.09; N, 4.99. $C_{12}H_7N_2I_3$ calcd.: C, 25.74; H, 1.26; N, 5.00%.)

2-Chloroazobenzene. The workup follows exactly that of 2-iodoazobenzene yielding recovered starting material, 2-chloroazobenzene, m.p. 27—28°C (lit. [21] m.p. 33°C); 2-chloro-2'-chloromercuriazobenzene, m.p. 184—185°C; 2-chloro-6-chloromercuriazobenzene, m.p. 259—260°C. (Found: C, 32.04; H, 1.80; N, 6.20. $C_{12}H_8N_2HgCl_2$ calcd. for 2-chloro-2'-chloromercuriazobenzene: C, 31.91; H, 1.79; N, 6.20%.) (Found: C, 32.07; H, 1.72; N, 6.19. $C_{12}H_8N_2HgCl_2$ calcd. for 2-chloro-6-chloromercuriazobenzene: C, 31.91; H, 1.79; N, 6.20%.)

2-Nitroazobenzene. The solid was extracted once with 100 ml of 3 : 1 ligroin/benzene and this chromatographed on alumina (A = 2). Elution with 2 : 1 ligroin/benzene gave, after crystallization from benzene/ligroin, 2-nitroazobenzene, m.p. 67—68°C (lit. [22] 70.5—71°C).

The remaining solid was dissolved in hot benzene. The cooled solution was then chromatographed on alumina (A = 2). Elution with benzene produced more 2-nitroazobenzene. Further elution with chloroform gave two small bands. The first band gave 2-chloromercuri-6-nitroazobenzene, crystallized from chloroform, m.p. 277—278°C. (Found: C, 31.31; H, 1.71; N, 9.10. $C_{12}H_8N_3O_2HgCl$ calcd.: C, 31.18; H, 1.74; N, 9.90%.)

The second band gave 2-chloromercuri-2'-nitroazobenzene, crystallized from chloroform, m.p. 224—225°C. No elemental analysis was obtained of this compound due to the extremely small quantities available. Instead the iodo compound was made and this analyzed correctly (see below).

2-Cyanoazobenzene. The solid was extracted with ligroin until the extracts were colorless. These extracts were chromatographed on alumina with the 2-cyanoazobenzene being eluted with 1 : 1 ligroin/benzene to give, on crystallization from ligroin, orange crystals, m.p. 60—62°C (lit. [6] m.p. 61.5—63°C). UV λ_{max} (nm) 217(sh) (ϵ 15 700), 234 (12 400), 243(sh) (10 100), 249(sh) (7300), 324 (19 100), 337(sh) (18 000), 354(sh) (9600), 452 (420).

The remaining solid was extracted with hot benzene until they were colorless. These extracts were added to the column above and elution with 2 : 3 benzene/chloroform removed the major band (a few preceding very minor bands were discarded). Crystallization from benzene gave 2-chloromercuri-6-cyanoazobenzene, m.p. 300—302°C. UV λ_{max} (nm) 220 (ϵ 17 100), 247 (12 900), 338 (17 700), 352(sh) (16 100), 370(sh) (8900), 450 (390). (Found: C, 35.51; H, 1.63; N, 9.47. $C_{13}H_8N_3HgCl$ calcd.: C, 35.51; H, 1.82; N, 9.50%.)

The remaining solid on iodination gave no azobenzenes.

2-Phenylazopyridine. The solid was extracted with ligroin until the extracts were nearly colorless. These were chromatographed on alumina and elution with benzene gave 2-phenylazopyridine, crystallized from benzene/ligroin in Dry ice/

acetone bath, m.p. 30—31°C (lit. [23] m.p. 32—34°C).

The remaining solid was extracted with hot chloroform until the extracts were colorless, evaporated, and crystallized from benzene to give 2-phenylazopyridine mercuric chloride complex, m.p. 205—207°C. (Found: C, 28.98; H, 2.01; N, 9.16. $C_{11}H_9N_3HgCl_2$ calcd.: C, 29.06; H, 2.00; N, 9.24%.)

Benzo[c]cinnolin. The solid all dissolved in benzene. Chromatography of the above solution on alumina gave, with elution with 1 : 1 benzene/chloroform, only starting material, crystallized from benzene/ligroin, m.p. 158—159°C (lit. [24] m.p. 156^c C).

Iodination reaction

The mercurial (1.0 g), iodine (2 g, 8 mmol) and 50 ml of chloroform were stirred for 1 h (for dimercurated compounds stirring was continued for 24 h). Then 5 ml of a saturated sodium thiosulfate solution was added and this stirred until the color of the chloroform layer changed from purple to orange (about 2 min). The layers were immediately separated (if left together too long sulfur dissolved in the chloroform layer and had to be removed by repeatedly dissolving the iodo compound in acetone thus leaving the sulfur undissolved), the chloroform evaporated and the residue chromatographed on alumina.

The data for iodination reactions are listed below as follows: Iodo compound (mercurial iodinated), chromatography elution solvent, crystallization solvent, m.p. or b.p., % yield, NMR, UV, analysis (previously described data is not repeated here).

2-Iodoazobenzene (2-chloromercuriazobenzene), 90%.

2-Iodo-6-methylazobenzene (2-chloromercuri-6-methylazobenzene), ligroin, b.p. 140—155°C/0.2 mmHg, 75%, NMR singlet at δ (ppm) 2.20 (3H, CH$_3$), triplet 6.65 (1H, 4-proton, J 7$\frac{1}{2}$ Hz), doublet-of-doublets 7.00 (1H, 5-proton, J 7$\frac{1}{2}$ Hz, J 2 Hz), multiplet 7.3—7.5 (3H, 3',4',5'-protons), doublet-of-doublets 7.67 (1H, 3-proton, J 7$\frac{1}{2}$ Hz, J 2 Hz). multiplet 7.8—8.1 (2H, 2',6'-protons), UV λ_{max} (nm) 220 (ϵ 18 100), 278(sh) (8800), 310 (11 900), 456 (380). (Found: C, 48.20; H, 3.37; N, 8.82. $C_{13}H_{11}N_2I$ calcd.: C, 48.47; H, 3.44; N, 8.70%.)

2,2'-Dimethyl-6-iodoazobenzene (2-chloromercuri-6,2'-dimethylazobenzene) ligroin, ligroin, m.p. 39—40°C, 50%, NMR singlet at δ (ppm) 2.31 (3H, 2-CH$_3$), 2.68 (3H, 2'-CH$_3$), triplet 6.82 (1H, 4-proton, J 7$\frac{1}{2}$ Hz), multiplet 7.0—7.4 (4H, 5,3',4',5'-protons), multiplet 7.6—8.0 (2H, 3,2'-protons), UV λ_{max} 220 (ϵ 16 500), 320 (10 600), 457 (360). (Found: C, 50.04; H, 3.87; N, 8.27. $C_{14}H_{13}N_2I$ calcd.: C, 50.02; H, 3.90; N, 8.33%.)

2,2'-Diiodo-6,6'-dimethylazobenzene (bis-2,2'-(chloromercuri)-6,6'-dimethylazobenzene), 4 : 1 ligroin/benzene, ligroin, m.p. 102—103°C, 60%, NMR singlet at δ (ppm) 2.45 (6H, CH$_3$), triplet 6.90 (2H, 4,4'-protons, J 8 Hz), apparent broadened doublet-of-doublets 7.23 (2H, 5,5'-protons, J 8 Hz), apparent broadened doublet-of-doublets 7.88 (2H, 3,3'-protons, J 7$\frac{1}{2}$ Hz). (Found: C, 36.52; H, 2.63; N, 6.08. $C_{14}H_{12}N_2I_2$ calcd.: C, 36.39; H, 2.62; N, 6.06%.)

2,6-Dimethyl-2'-iodoazobenzene (2-chloromercuri-2',6-dimethylazobenzene) ligroin, ligroin, m.p. 39—40°C, 53%, NMR singlet at δ (ppm) 2.50 (6H, CH$_3$), multiplet 6.9—7.8 (6H, 3,4,5,4',5',6'-protons), doublet-of doublets 7.96 (1H, 3'-proton), UV λ_{max} (nm) 224(sh) (ϵ 13 600), 239(sh) (9900), 324 (12 300),

370(sh) (4100), 462 (490). (Found: C, 50.10; H, 4.06; N, 8.50. $C_{14}H_{13}N_2I$ calcd.: C, 50.01; H, 3.89; N, 8.33%.)

2-Iodo-2'-methoxyazobenzene (2-chloromercuri-2'-methoxyazobenzene), m.p. 99—100°C (lit. [6] 99—100°C), 66%, UV λ_{max} (nm) 213 (ϵ 20 100), 240 (9500), 321 (10 700), 367 (12 400), 454 (710).

2,2'-Dimethoxy-6-iodoazobenzene (2-chloromercuri-6,2'-dimethoxyazobenzene), 1 : 1 ligroin/benzene, benzene/ligroin, m.p. 104—105°C, 99%, NMR singlet at δ (ppm) 3.78 (3H, 2-CH$_3$O), singlet 4.00 (3H, 2'-CH$_3$O), multiplet 6.9—7.8 (7H, aryl protons). (Found: C, 45.84; H, 3.60; N, 7.48. $C_{14}H_{13}N_2O_2I$ calcd.: C, 45.67; H, 3.56; N, 7.61%.)

2-Iodo-6-isopropoxyazobenzene (2-chloromercuri-6-isopropoxyazobenzene), distilled thru short path distillation apparatus at 0.7 mmHg pressure and an oil bath temperature of 160°C, 60%, NMR doublet at δ (ppm) 1.22 (6H, CH$_3$, J 6 Hz), septet 4.40 (1H, methine, J 6 Hz), multiplet 6.6—7.3 (2H, 4,5-protons), multiplet 7.5—7.8 (4H, 3,3',4',5'-protons), multiplet 7.8—8.2 (2H, 2',6'-protons), UV λ_{max} 220 (ϵ 24 300), 274 (9800), 314 (8900), 456 (540). (Found: C, 49.53; H, 4.28; N, 7.65. $C_{15}H_{15}N_2OI$ calcd.: C, 49.20; H, 4.13; N, 7.65%.)

2,2'-Diiodoazobenzene (2-chloromercuri-2'-iodoazobenzene), 100%.

2,6-Diiodoazobenzene (2-chloromercuri-6-iodoazobenzene), 85%.

2-Chloro-6-iodoazobenzene (2-chloro-6-chloromercuriazobenzene), ligroin, ligroin, m.p. 50.5—51.5°C, 69%, NMR triplet at δ (ppm) 6.88 (1H, 4-proton, J 8 Hz), multiplet 7.2—8.2 (7H, rest of aryl protons, resembles azobenzene peaks). (Found: C, 42.04; H, 2.27; N, 8.22. $C_{12}H_8N_2ClI$ calcd.: C, 42.07; H, 2.35; N, 8.18%.)

2-Iodo-6-nitroazobenzene (2-chloromercuri-6-nitroazobenzene), benzene, benzene/ligroin, m.p. 60.5—61.5°C, 50%, NMR triplet at δ (ppm) 7.16 (1H, 4-proton, J 8 Hz), multiplet 7.4—8.4 (7H, rest of aryl protons; the two characteristic multiplets of azobenzene are seen with a few extra doublets therein), UV λ_{max} 222 (ϵ 21 400), 304 (13 600), 448 (450). (Found: C, 40.75; H, 2.11; N, 11.72. $C_{12}H_8N_3O_2I$ calcd.: C, 40.82; H, 2.28; N, 11.90%.)

2-Iodo-2'-nitroazobenzene (2-chloromercuri-2-nitroazobenzene), benzene, benzene/ligroin, m.p. 140.5—141°C, 52%, NMR triplet-of-doublets at δ (ppm) 7.17 (1H, 4-proton, J 7 Hz, J 2 Hz), multiplet 7.0—8.2 (7H, aryl protons), UV λ_{max} (nm) 211 (ϵ 19 300), 248(sh) (10 400), 323 (12 800), 454 (320). (Found: C, 40.62; H, 2.08; N, 11.59. $C_{12}H_8N_3O_2I$ calcd.: C, 40.82; H, 2.28; N, 11.90%.)

2-Iodo-6-cyanoazobenzene (2-chloromercuri-6-cyanoazobenzene), 1 : 1 ligroin/benzene, ligroin, m.p. 65—67°C (lit. [6] 73—74°C). The mixture melting point with authentic material was undepressed and the NMR spectra of the two are identical. UV λ_{max} (nm) 224(sh) (ϵ 18 100), 260 (8700), 316 (12 300), 456 (370).

Chlorination of 2-chloro-2'-chloromercuriazobenzene

Into a solution of 0.10 g (0.22 mmol) of 2-chloro-2'-chloromercuriazobenzene and 50 ml of chloroform was bubbled rapidly chlorine gas for 15 min. Then 10 ml of aqueous saturated sodium thiosulfate solution was added. This mixture was stirred 5 min, separated, and the chloroform evaporated. The residue was chromatographed on 25 g of alumina and elution with ligroin gave 0.04 g (72%), crystallized from ligroin, of 2,2'-dichloroazobenzene, m.p. 127—129°C (lit.

[25] 136.5°C). A mixture melting point with authentic 2,2'-dichloroazobenzene (made by the procedure of Tussell et al. [26]) was undepressed (127—129°C).

Methoxylation of 2-iodo-2'-methoxyazobenzene

By the method B previously described [6], 0.15 g (0.44 mmol) of 2-iodo-2'-methoxyazobenzene was treated with sodium methoxide (22 mmol) in 25 ml of methanol. On chromatography of the product on alumina and elution with benzene there resulted 0.06 g (56%) 2,2'-dimethoxyazobenzene. Crystallization from ligroin/benzene gave 0.04 g (37%) of 2,2'-dimethoxyazobenzene, m.p. 154—155°C (lit. [19] 155°C).

Acknowledgement

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