

## Synthesis and Reactions of Some Highly Chlorinated Azobenzenes

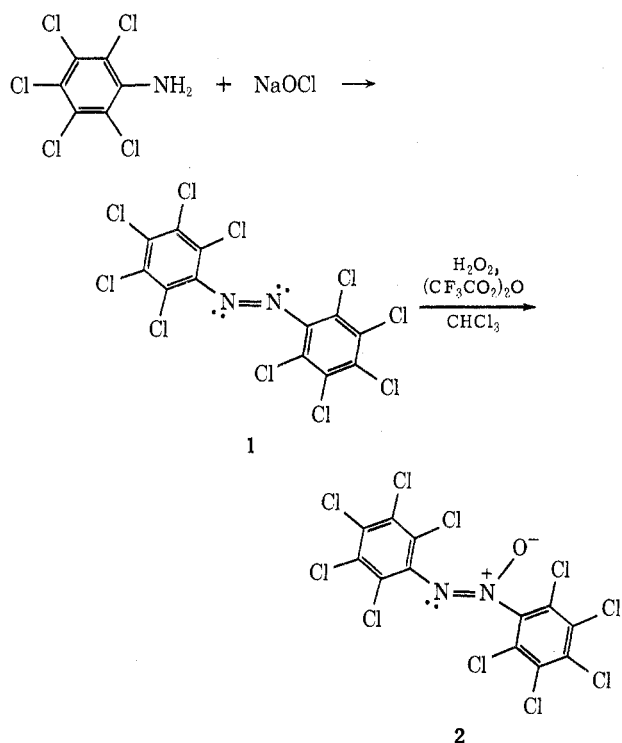
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Decachloroazobenzene (1) was synthesized in 56% yield directly from pentachloroaniline. 1 was oxidized to decachloroazoxybenzene (2) in 97% yield and also reduced to pentachloroaniline along with minor amounts of decachlorohydrazobenzene. A series of pentachloroazo- and -azoxybenzenes were also prepared and their nmr spectra determined. The nmr spectra of a series of pentadeuterioazo- and -azoxybenzenes indicated that in the pentachloroazoxy series the  $\alpha$  isomer had been formed exclusively. This was confirmed by mass spectroscopy.

Decachloroazobenzene (1) was first prepared in 1922 by refluxing heptachloroaniline in toluene.<sup>2</sup> More recently 1 was synthesized *via* oxidation of pentachloroaniline,<sup>3</sup> but yields were not given in either case. We now report the preparation of 1 in 56% yield by the reaction of pentachloroaniline with 5% aqueous sodium hypochlorite. This reaction appears to have some degree of generality at least when applied to highly halogenated aromatic amines.<sup>4</sup>



As expected, 1 is more sterically crowded than its fluoro analog. This was confirmed by their uv spectra, in which the extinction coefficient of decafluoroazobenzene was calculated as  $\epsilon$  20,000 ( $\lambda_{\max}^{\text{EtOH}}$  308 nm),<sup>4</sup> while that of 1 was only 8600 (301). Decafluoroazobenzene was first reported<sup>4</sup> to be inert toward a number of peracids; however, we readily obtained a 97% yield of decachloroazoxybenzene (2) by refluxing 1 in a mixture of trifluoroacetic anhydride, 98% hydrogen

peroxide, and chloroform.<sup>5,6</sup> Peracetic and performic acids had no effect on 1.

Exhaustive catalytic hydrogenation of both 1 and 2 gave pentachloroaniline. When the hydrogenation of 1 was stopped before completion, decachlorohydrazobenzene (3) was obtained, but was always contaminated with amine. This suggests that the reductions of 1 and 3 do not have widely different rates, a marked contrast with highly fluorinated analogs, which gave pure hydrazobenzenes from this reaction.<sup>4</sup> The reduction of 2 to 1 was never accomplished under these conditions. However, 3 did disproportionate on heating to give 1 and pentachloroaniline, although at a higher temperature than was necessary in the analogous reaction of hydrazobenzene.

Performic acid oxidation of pentachloroaniline gave pentachloronitrosobenzene<sup>7</sup> (4), in 30% conversion (~100% yield). This enabled a series of stable reddish orange pentachloroazobenzenes (Table I) to be prepared by the condensation of 4 with aniline, and four para-substituted anilines, in glacial acetic acid. Similar condensations could not be achieved with pentachloro- or pentafluoroaniline.

The 2,3,4,5,6-pentachloroazobenzenes were oxidized rapidly and almost quantitatively to their corresponding pale yellow azoxy derivatives by peroxytrifluoroacetic acid (Table I). Oxidation of these azobenzenes using the more common peracids (acetic, benzoic, etc.) was difficult and incomplete even after several days of reflux.

In addition to *cis-trans* isomerism<sup>8</sup> unsymmetrically substituted azoxy compounds, such as those in Table I, may also exist in two other isomeric forms, often designated  $\alpha$  and  $\beta$ , depending on the position of the oxygen in the azoxy group.<sup>9</sup> The nmr spectra (Table II) of the para-substituted azo- and azoxybenzenes exhibited simple A<sub>2</sub>B<sub>2</sub> quartets which indicated that only one of these isomers had been obtained. The ortho protons of the azoxybenzenes were shifted downfield, com-

(5) Under the proper conditions decafluoroazobenzene can also be oxidized with these reagents: J. M. Birchall, R. N. Haszeldine, and J. E. Kemp, *J. Chem. Soc. C*, 1519 (1970).

(6) Hedayatullah reported<sup>3</sup> that 1 was unreactive with trifluoroperacetic acid at 75°.

(7) D. Berry, I. Collins, S. Roberts, H. Suschitzky, and B. Wakefield, *J. Chem. Soc. C*, 1285 (1969).

(8) All of our azo and azoxy compounds were assumed to exist in the more stable *trans* configuration. Their mode of preparation makes this a reasonable assumption: H. Zollinger "Azo and Diazo Chemistry Aliphatic and Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1961, pp 59, 297.

(9) Although the  $\alpha$  and  $\beta$  designations can be confusing, they are used in this paper to simplify the discussion. The  $\alpha$  isomer has been defined as the one with the N-O function adjacent to the smaller or less highly substituted aryl group.<sup>10</sup> Consequently, in this paper the  $\alpha$ -azoxy isomer (where R = Br) will be the one named 4'-bromo-2,3,4,5,6-pentachloro-ONN-azoxybenzene.

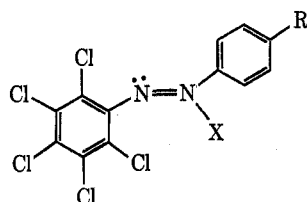
(10) G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970).

(1) Allied Chemical Corp. Research Fellow, 1963-1966.

(2) S. Goldschmidt and L. Strohmenger, *Ber.*, **55**, 2450 (1922).

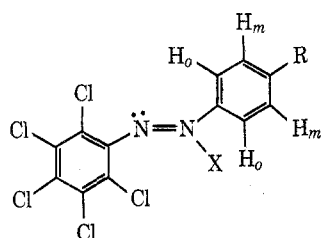
(3) M. Hedayatullah, C. Ollé, and L. Denivelle, *C. R. Acad. Sci., Paris, Ser. C.*, **264**, 106 (1967).

(4) J. Burdon, C. J. Morton, and D. F. Thomas, *J. Chem. Soc.*, 2621 (1965).

TABLE I  
 2,3,4,5,6-PENTACHLOROAZO- AND -AZOXYBENZENES<sup>a</sup>


b		Mp, °C	% yield	% calcd			% found		
R	X			C	H	Cl	C	H	Cl
H		117-118	85	40.64	1.41	50.09	40.93	1.58	50.20
H	O	148-150	>95	38.88	1.35	47.88	38.52	1.19	47.07
Br		179-181	40	33.23	0.92	6.46 <sup>c</sup>	32.99	0.82	6.34 <sup>c</sup>
Br	O	192-193	>95	32.05	0.89	6.24 <sup>c</sup>	31.92	1.00	6.34 <sup>c</sup>
CH <sub>3</sub>		234-237	41	42.35	1.90	48.14	42.06	2.17	48.64
CH <sub>3</sub>	O	159-161	>95	40.59	1.82	46.13	40.58	1.89	46.25
Cl		168-170	53	37.03	1.03	54.73	36.84	1.19	55.13
Cl	O	169-171	>95	35.37	0.98	52.56	35.25	0.99	51.98
OCH <sub>3</sub>		136-138	35	40.59	1.82	46.13	40.83	1.49	45.80
OCH <sub>3</sub>	O	158-159	>95	38.97	1.75	44.29	38.74	2.03	44.03

<sup>a</sup> We define the azoxybenzenes in this table as the  $\alpha$  isomers. <sup>b</sup> Registry numbers are, respectively, 35159-10-5, 35159-11-6, 35191-76-5, 35159-12-7, 35159-13-8, 35159-14-9, 35159-15-0, 35159-16-1, 35159-17-2, 35159-18-3. <sup>c</sup> % N was analyzed for in this compound instead of % Cl.

 TABLE II  
 NMR SPECTRAL DATA FOR THE  
 2,3,4,5,6-PENTACHLOROAZO- AND -AZOXYBENZENES IN CDCl<sub>3</sub>


R	X	Chemical shift, <sup>a</sup> Hz			J(H <sub>o</sub> -H <sub>m</sub> ),	$\Delta_{\text{azoxy-azo}}$	
		H <sub>o</sub>	H <sub>m</sub>	H <sub>CH<sub>3</sub></sub>		H <sub>o</sub>	H <sub>m</sub>
H		478 <sup>b</sup>	454 <sup>b</sup>			22	2
H	O	500 <sup>b</sup>	456 <sup>b</sup>				
Cl		476	453			20	-2
Cl	O	496	451		9		
Br		469	463		9	22	-2
Br	O	491	461		9		
OCH <sub>3</sub>		477	422	233 <sup>c</sup>	9	21	-3
OCH <sub>3</sub>	O	498	419	233 <sup>d</sup>	9		
CH <sub>3</sub>		474	443	148 <sup>e</sup>	8.5	20	0
CH <sub>3</sub>	O	494	443	148 <sup>f</sup>	8.5		

<sup>a</sup> The chemical shifts were found to be relatively insensitive to concentration. <sup>b</sup> Values given are the approximate centers of complex multiplets. <sup>c</sup> This singlet appears at 200 Hz in benzene. <sup>d</sup> This singlet appears at 195 Hz in benzene. <sup>e</sup> This singlet appears at 127 Hz in benzene. <sup>f</sup> This singlet appears at 122 Hz in benzene.

pared with the corresponding azobenzenes, by a constant  $21 \pm 1$  Hz.

Surprisingly few methods existed at the beginning of this work for distinguishing between  $\alpha$  and  $\beta$  isomers.<sup>11</sup> Consequently, model azo- and azoxybenzenes, which had one completely deuterated phenyl ring, were synthesized for further nmr studies. The  $\alpha$ - and  $\beta$ -azoxy isomers were then separated by column chromatography

(11) (a) G. M. Badger and G. E. Lewis, *J. Chem. Soc.*, 2151 (1953); (b) L. C. Behr, *J. Amer. Chem. Soc.*, **76**, 3672 (1954), and references therein; (c) L. C. Behr, E. G. Alley, and O. Levand, *J. Org. Chem.*, **27**, 65 (1962).

and identified by comparison of their melting points (Table III) with those of the known hydrogen analogs.<sup>12</sup>

Nmr spectral data for these deuterated compounds are also given in Table III. Once again the ortho hydrogens of the  $\alpha$ -azoxybenzenes were shifted downfield by  $21 \pm 1$  Hz, while the corresponding deshielding in the  $\beta$ -azoxybenzenes varied from 16 to 24 Hz. In addition, the methyl protons of the  $\beta$ -azoxybenzene were shifted by a slightly larger amount than the methyl protons of the  $\alpha$ -azoxybenzene.<sup>13</sup>

We had hoped that these differences in the nmr spectra of the  $\alpha$ - and  $\beta$ -azoxy isomers would be somewhat larger and more definitive; fortunately, however, mass spectroscopy provided complete confirmation of the assignments. The pertinent mass spectral data for the pentachloroazoxybenzenes is given in Table IV. It is known that the base peaks in the mass spectra of azoxybenzenes are produced by C-N cleavage  $\alpha$  to the N-oxide group.<sup>14</sup> As is evident from Table IV, the base ion<sup>15</sup> ( $C_6H_4R^+$ ) in every spectra resulted from the type of fragmentation expected for the  $\alpha$  isomer.

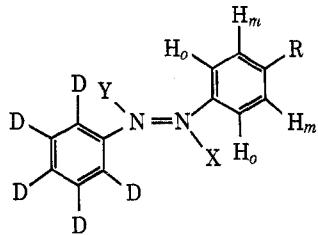
In addition, while no  $(M - Cl)^+$  ions were observed in the mass spectra of the pentachloroazobenzenes, with only one exception, this ion was the second most abundant peak in the spectra of the corresponding azoxy compounds (Table IV). It has been established that the formation of five-membered cyclic structures involving the oxygen of the N-O group is an important rearrangement in the mass spectra

(12) Assignments were also confirmed by mass spectroscopy.

(13) The methyl and methoxy protons of the  $\alpha$ -azoxybenzenes are apparently shifted upfield more from their corresponding azobenzenes when benzene is used as the solvent for determining the nmr spectra. For examples see footnotes c-f in Table II and D. Webb and H. Jaffé, *J. Amer. Chem. Soc.*, **86**, 2419 (1964).

(14) J. H. Bowie, R. G. Cooks, and G. E. Lewis, *Aust. J. Chem.*, **20**, 1601 (1967).

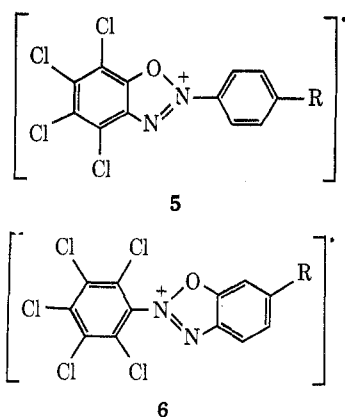
(15) Additional facile fragmentations due to the presence of the p-methoxy group led to other ions, such as  $C_6H_4O^+$ , which were observed in greater abundance in the mass spectra of this compound. For simplicity these low *m/e* ions were ignored in preparing Table IV.

TABLE III  
 MELTING POINTS AND NMR SPECTRAL DATA FOR THE PENTADEUTERIOAZO- AND -AZOXYBENZENES IN CCl<sub>4</sub>


R	X	Y	Mp, °C <sup>b</sup>	Chemical shift, Hz			Δ <sub>azoxy-azo</sub>	
				H <sub>o</sub>	H <sub>m</sub>	H <sub>CH<sub>3</sub></sub>	H <sub>o</sub>	H <sub>m</sub>
CH <sub>3</sub>			68-70 (71-72) <sup>c</sup>	469	433	143	8.5	
OCH <sub>3</sub>			55-55.5 (54-56) <sup>c</sup>	472 <sup>d</sup>	417 <sup>d</sup>	229 <sup>d</sup>	9.0	
Br			88-89.5 (89) <sup>c</sup>	467	458		9.0	
CH <sub>3</sub>	O		64.5-66 (65) <sup>c</sup>	489	430	139	8.5	20
OCH <sub>3</sub>	O		50-51.5 (42-43) <sup>c</sup>	494 <sup>d</sup>	414	232 <sup>d</sup>	9.0	22
Br	O		91.5-93 (92-92.5) <sup>c</sup>	489	452		9.0	22
CH <sub>3</sub>		O	45-47 (46-48) <sup>c</sup>	489	428	137	8.5	20
OCH <sub>3</sub>		O	74-75 (66.5-67.5) <sup>c</sup>	496 <sup>d</sup>	415 <sup>d</sup>	232 <sup>d</sup>	9.0	24
Br		O	71-72 (73-73.5) <sup>c</sup>	483	451		9.0	16

<sup>a</sup> Registry numbers, are, respectively, 35159-19-4, 35261-92-8, 35159-20-7, 35159-21-8, 35159-22-9, 35159-23-0, 35159-24-1, 35159-25-2, 35159-26-3, 35159-27-4, 35159-28-5. <sup>b</sup> Melting points of the corresponding nondeuterated azo- and -azoxybenzenes are given in parentheses. <sup>c</sup> "Dictionary of Organic Compounds," J. R. A. Pollack and R. Stevens, Ltd., Oxford University Press, New York, N. Y., 1965: Vol. 1, p 419; Vol. 3, p 1647; Vol 5, pp 2130 and 2429. <sup>d</sup> The chemical shift is dependent somewhat on concentration, and the value given is that calculated for infinite dilution. The remaining chemical shifts are relatively insensitive to concentration. <sup>e</sup> H. Jaffé and C. S. Hahn, *J. Amer. Chem. Soc.*, **84**, 949 (1962).

of azoxybenzenes.<sup>14,16</sup> With the α isomer this rearrangement leads to an (M - Cl) ion such as **5** while the β isomer would yield an (M - H) ion such as **6**.



These two major mass spectral arguments, together with nmr and the remaining mass spectroscopy data, leave little doubt that only the α isomers of the pentachloroazoxybenzenes were formed.

### Experimental Section<sup>18</sup>

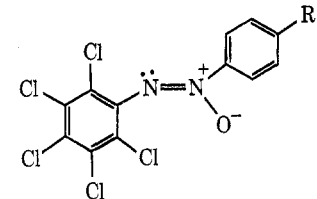
**Decachloroazobenzene (1).**—To a magnetically stirred slurry of 5 g of pentachloroaniline in 100 ml of 95% ethanol, 400 ml of 5% aqueous sodium hypochlorite was added. The heterogeneous mixture turned yellow immediately after addition. After 3 hr of stirring at room temperature, the reaction mixture turned red and

(16) Azoxybenzenes have been reported to form similar cyclic structures under other conditions.<sup>16,17</sup>

(17) A. I. Feinstein and E. K. Fields, *J. Org. Chem.*, **36**, 3878 (1971).

(18) All melting points are uncorrected. Elemental analysis were determined by Dr. C. S. Yeh, Purdue University. Ir spectra were obtained on a Beckman IR-8 spectrophotometer. Uv spectra were obtained on a Bausch and Lomb Spectronic 505 spectrophotometer. Nmr spectra were measured using a Varian A-60 spectrometer, with tetramethylsilane as an internal standard. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6A high resolution mass spectrometer.

 TABLE IV  
 MASS SPECTRA<sup>a</sup> OF THE 2,3,4,5,6-PENTACHLOROAZOXYBENZENES



Ion	R				
	H	<sup>79</sup> Br	CH <sub>3</sub>	<sup>35</sup> Cl	OCH <sub>3</sub>
M <sup>•+</sup>	368 (4.0)	446 (6.8)	382 (2.1)	402 (3.5)	398 (2.7)
M - Cl	333 (82)	411 (32)	347 (33)	367 (74)	363 (7.3)
M - N <sub>2</sub> Cl <sub>2</sub>	270 (56)	348 <sup>b</sup>	284 (28)	304 (38)	300 (9.1)
C <sub>6</sub> Cl <sub>5</sub>	247 (3.2)	247 (28)	247 (4.8)	247 (4.0)	247 (31)
C <sub>6</sub> Cl <sub>4</sub> N	226 (22)	226 (29)	226 (13)	226 (29)	226 (63)
ONC <sub>6</sub> H <sub>4</sub> R	107 (8.6)	185 (9.4)	121 (19)	141 (8)	137 (45)
C <sub>6</sub> H <sub>4</sub> R	77 (100)	155 (100)	91 (100)	111 (100)	107 (100) <sup>c</sup>

<sup>a</sup> Spectral data is given as *m/e* (% of base ion). <sup>b</sup> This particular ion appeared at very low abundance; however, this compound had a very prevalent (M - N<sub>2</sub>BrCl) ion at *m/e* 304 (32). <sup>c</sup> See ref 15.

tended to coagulate. Stirring was continued for a further 10 hr. Then the mixture was filtered and the red solid washed with water and crystallized from toluene to give 2.8 g (56%) of dimorphic crystals of decachloroazobenzene: mp 314-316° (lit.<sup>2</sup> mp 316-318°); uv max (dioxane) 233 nm (ε 30,800), 301 (8600), 270 (sh, 10,800); ir (mull) 6.60 (w), 7.38 (s), 7.58 (m), 8.16 (w), 13.18 (m), 13.55 (s), 13.68 (s), 14.22 μ (s).

*Anal.* Calcd for C<sub>12</sub>Cl<sub>10</sub>N<sub>2</sub>: C, 27.38; Cl, 67.33. Found: C, 27.43; Cl, 67.00.

**Decachloroazoxybenzene (2).**—To a stirred mixture of 1.0 g (1.9 mmol) of **1**, 15 ml of trifluoroacetic anhydride, and 100 ml of chloroform, 6 ml of 98% hydrogen peroxide (Columbia Organic Chemicals Co.) was added rapidly. After refluxing for 5 hr, the solvent was evaporated to give 1.0 g (97% yield) of **2** which recrystallized from chloroform-hexane as shiny, yellow flakes: mp 257-258°; uv max (dioxane) 231 nm (ε 33,000), 302 (3700); ir (mull) 6.60 (s), 6.88 (s), 7.45 (s), 7.68 (m), 8.18 (w), 12.98 (m), 13.10 (m), 13.95 (br s), 14.15 (s), 14.82 μ (w).

*Anal.* Calcd for C<sub>12</sub>Cl<sub>10</sub>N<sub>2</sub>O: C, 26.54; Cl, 65.35. Found: C, 26.16; Cl, 65.53.

**Reduction of 1.**—Stirred together in 100 ml of toluene and in an atmosphere of hydrogen was 0.3 g (0.6 mmol) of 1 and 0.7 g of 5% palladium on charcoal. After only 18.2 ml (0.81 mmol) of H<sub>2</sub> had been taken up, the reaction was stopped, the mixture was filtered, and the filtrate was evaporated to an orange mass which was chromatographed on acid-washed alumina. Three bands were eluted with toluene which were, in order of elution, 1 (trace); 0.1 g of decachlorohydrazobenzene (3); and 0.15 g of pentachloroaniline. 3 recrystallized from toluene as light yellow needles which darkened to a copper color at 150° and at 195° began to disproportionate to pentachloroaniline (identified by ir and melting point) and to a red liquid (1). Spectral data for 3: ir (mull) 2.92 (w), 6.28 (m), 7.08 (m), 7.28 (w), 7.45 (br m), 7.58 (m), 13.16 (br), 13.60  $\mu$  (br, w).

*Anal.* Calcd for C<sub>12</sub>H<sub>2</sub>Cl<sub>10</sub>N<sub>2</sub>: C, 27.23; H, 0.38. Found: C, 27.13; H, 0.19.

**Reduction of 2.**—A solution of 0.5 g (0.9 mmol) of 2 dissolved in 80 ml of benzene and 40 ml of toluene was stirred with 1 g of 5% palladium on charcoal in an atmosphere of H<sub>2</sub>. Hydrogen uptake was very slow and, after 26 hr, the reaction was worked up as described above to yield 0.45 g of a white solid, melting between 160 and 240° and containing only a small amount of 3. The solid was mainly pentachloroaniline as determined by ir spectroscopy.

**Pentachloronitrosobenzene (4).**—A two-phase liquid system containing 5.0 g (19 mmol) of pentachloroaniline, 20 ml of 90% formic acid, 100 ml of chloroform, and 5 ml of 98% hydrogen peroxide was stirred under reflux for 6 hr. After the deep green mixture cooled, white granular crystals settled and were collected. The green filtrate was washed with water, dried, and evaporated to yield 3.4 g of crude pentachloroaniline. The filtered crystals, after recrystallization from toluene, afforded 1.5 g (30% conversion) of 4: mp 168–170°; ir (mull) 6.70 (w), 7.41 (s), 7.75 (s), 8.19 (m), 8.85 (w), 10.40 (w), 12.60 (w), 13.92  $\mu$  (s).

*Anal.* Calcd for C<sub>6</sub>Cl<sub>5</sub>NO: C, 25.78; Cl, 63.48. Found: C, 26.09; Cl, 63.57.

**A. Typical Condensation of 4 with an Amine.**—A solution of 1.0 g (3.6 mmol) of 4, 0.64 g (5.0 mmol) of 4-chloroaniline, and 70 ml of glacial acetic acid was refluxed for 3 hr. Water was added to the reaction mixture and the precipitated solid was collected *via* suction filtration. Elution of this material with benzene on a column (1 × 22 in.) of acid-washed alumina (110 g) produced 0.74 g (53%) of 2,3,4,4',5,6-hexachloroazobenzene and 0.25 g (25%) of pentachloroaniline. The product was recrystallized from ethanol: mp 168–170°; uv max (EtOH) 212 nm ( $\epsilon$  31,300), 226 (sh, 23,000), 307 nm (14,300); ir (mull) 6.35 (w),

6.73 (m), 7.13 (m), 7.44 (s), 7.61 (m), 8.71 (m), 9.11 (m), 9.90 (m), 11.30 (m), 12.00 (s), 13.72 (m), 13.85 (m), 13.92  $\mu$  (s).

**An Improved Condensation of 4 with Aniline.**—Aniline (0.5 g, 5 mmol) was added rapidly to a solution of 1.0 g (3.6 mmol) of 4 and 50 ml of toluene-acetic acid solution (4% glacial acetic acid in toluene) maintained at 40°. After 18 hr the reaction temperature was increased slowly to 75° over an additional 12-hr period. Evaporation of the solvent gave a red solid, which was chromatographed twice (acid-washed alumina, benzene). Obtained was 1.08 g (85%) of 2,3,4,5,6-pentachloroazobenzene: mp 117–118°; uv max (EtOH) 215 nm ( $\epsilon$  24,000), 229 (23,000), 293 (12,600); ir (mull) 3.28 (w), 6.71 (m), 7.44 (s), 7.65 (m), 8.15 (m), 8.70 (s), 11.28 (m), 12.88 (m), 13.10 (s), 13.78 (m), 13.95 (m), 14.72 (s), 15.05  $\mu$  (vr).

**A Typical Oxidation of the 2,3,4,5,6-Pentachloroazobenzenes.**—A two-phase liquid system of 0.3 g (0.85 mmol) of 2,3,4,5,6-pentachloroazobenzene, 3 ml of trifluoroacetic anhydride, 2 ml of 98% hydrogen peroxide, and 20 ml of CHCl<sub>3</sub> was stirred at reflux for 2 hr. The red solution faded to a light yellow almost immediately. On cooling, the mixture was washed with water; the organic layer separated and was evaporated to give 0.3 g (96% yield) of crude 2,3,4,5,6-pentachloroazoxybenzene. The product was recrystallized three times from hexane as fine, yellow needles: mp 148–150°; uv max (EtOH) 214 nm ( $\epsilon$  50,000), 260 (11,900); ir (mull) 6.99 (s), 7.43 (s), 12.92 (s), 13.85 (s), 14.90  $\mu$  (s).

**Pentadeuterioazo- and -azoxybenzenes.**—Pentadeuterionitrosobenzene (obtained from Merck Sharp and Dohme of Canada Ltd.) was condensed with the appropriately substituted aniline in acetic acid-benzene solution. The resulting pentadeuterioazobenzenes were oxidized in chloroform with peracetic acid solution, prepared from glacial acetic acid and 98% hydrogen peroxide. The  $\alpha$  and  $\beta$  isomers of each azoxy mixture were partially resolved by elution chromatography on alumina and brought to constant melting point by repeated recrystallizations (methanol) of the initial and final chromatographic fractions.

**Registry No.**—1, 35159-27-4; 2, 35159-28-5; 3, 35191-77-6; 4, 13665-49-1; pentachloroaniline, 527-20-8.

**Acknowledgment.**—The authors are indebted to the Allied Chemical Corp. for financial support of the work and to R. G. Cooks for his assistance with the mass spectra interpretation.

## Studies on 4-Quinazolinones. V.<sup>1</sup> Reductive Ring Cleavage by Metal Hydrides

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Metal hydride reductions of some substituted 4-quinazolinones have been studied under various conditions. Though the reduction was found to be facile in the *N*-methylated compounds under ordinary conditions irrespective of the substitution at position 2, the C=N function in those with a free NH group proved to be extremely resistant to the reducing agents and led to unusual products under forcing condition. 2,3-Disubstituted 4-quinazolinones and only the 3-phenyl derivative among the monosubstituted ones studied underwent ring cleavage at the bond between C<sub>2</sub> and the tertiary nitrogen. Reduction of the carbonyl group could only be brought about by lithium aluminum hydride in tetrahydrofuran under reflux in all cases.

While the carbonyl function of indoloquinazolinones is known<sup>3</sup> to be fully reduced by lithium aluminum hydride at room temperature, 1-methyl-2-benzyl-4-quinazolinone (1), a naturally occurring alkaloid<sup>4</sup> known

as arborine, under the same condition afforded<sup>5</sup> only its 2,3-dihydro derivative 2. We therefore investigated the metal hydride reduction of a series of variously substituted simple 4-quinazolinones under different conditions, and the results are summarized in Scheme I.

The reduction of 2-benzyl-3-methyl-4-quinazolinone (3a) with the same reagent at room temperature re-

(1) Paper IV: S. C. Pakrashi, J. Bhattacharyya, and A. K. Chakravarty, *Indian J. Chem.*, **9**, 1220 (1971).

(2) Senior Research Fellow, CSIR, New Delhi.

(3) I. J. Pachter, R. F. Raffauf, C. E. Ulyot, and O. Ribeiro, *J. Amer. Chem. Soc.*, **82**, 5187 (1960).

(4) D. Chakravarti, R. N. Chakravarti, and S. C. Chakravarti, *J. Chem. Soc.*, 3337 (1953).

(5) A. Chatterjee and S. Ghosh Mazumdar, *J. Amer. Chem. Soc.*, **76**, 2459 (1954).