Some Oxidation Reactions of Monochloramine

By **G. A. Jaffari** and **A. J. Nunn,*** School of Pharmacy, City of Leicester Polytechnic, Leicester

Certain primary aromatic amines treated with monochloramine under mild conditions gave the corresponding azobenzenes, often as both *cis*- and *trans*-isomers. Alcohols were oxidised to the respective carbonyl compounds in high yield.

CHLORAMINE has been reported to react with aliphatic amines to give the corresponding hydrazines.[1]

Whilst we were attempting the *N*-amination of 2-aminophenyl benzyl sulphide with monochloramine in the presence of sodium hydride at room temperature, 2,2′-dibenzylthioazobenzene was isolated, together with unchanged starting material. Although this azo-compound was obtained only in low yield (10%), it showed that chloramine was acting as an oxidant, behaviour previously unrecorded in the literature. Substituted anilines have usually been converted into azobenzenes by manganese dioxide [2,3], phenyl iodosoacetate [4], or lead tetra-acetate.[5] In all cases only the *trans*-isomer was obtained. 1-Chlorobenzotriazole has recently been

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[1] L. F. Audrieth and L. H. Diamond, *J. Amer. Chem. Soc.*, 1954, **76**, 4869.

[2] E. F. Pratt and T. P. McGovern, *J. Org. Chem.*, 1964, **29**, 1540.

[3] O. H. Wheeler and D. Gonzalez, *Tetrahedron*, 1964, **20**, 189.

[4] K. H. Pausacker, *J. Chem. Soc.*, 1953, 1989.

[5] K. H. Pausacker and J. G. Scroggie, *J. Chem. Soc.*, 1954, 4003.

employed to oxidise alcohols and hydrazo-compounds;[6] chloramine might be expected to behave in a similar fashion.

Treatment of aniline with chloramine under the same conditions as those used for 2-aminophenylbenzyl sulphide, and also in the absence of sodium hydride, gave *trans*-azobenzene in moderate yield (50%), together with a trace of *cis*-azobenzene, a small amount of 4-anilinoazobenzene (12%), and an amorphous, blue compound. The latter was probably a polymeric quinonedi-imine, or a partially reduced form of this.[7] A quantitative amount of ammonium chloride was isolated from the reaction mixture. The reactions were

$$2PhNH_2 + 2NH_2Cl \longrightarrow PhN{=}NPh + 2NH_4Cl$$

highly exothermic at the final stage, after the ether concentrate had been set aside for a few minutes at room temperature. A prolonged reaction time did not alter this, nor did it affect the yield. When the ether concentrate was quenched with water before the exothermic reaction had time to occur, chromatography showed that some unchanged aniline was present, together with *trans*-azobenzene (38%), a trace *cis*-azobenzene, some 4-anilinoazobenzene, and less of the blue polymer than in the unquenched experiment. Phenylhydrazine was absent.

The presence of electron-donating groups *ortho* or *para* to the amino-group should enhance its proneness to oxidation, whilst electron-withdrawing groups either on the aromatic nucleus, or on the nitrogen should make the oxidation of the amine more difficult. *p*-Toluidine was easily oxidised to 4,4′-dimethylazobenzene, separated as *cis*- and *trans*-isomers (14 and 28% respectively) by column chromatography; similarly *NN*-dimethyl-*p*-phenylenediamine gave both isomers of 4,4′-di(dimethylamino)azobenzene (10% of each); whilst *p*-ethoxyaniline was oxidised solely to *trans*-4,4′-diethoxyazobenzene (33%). Thus, in certain cases this method offers a convenient synthetic route to *cis*-azobenzenes, which otherwise are obtainable only in low yield by the irradiation of their *trans*-isomers. That the yields were all lower than that from aniline itself, may be explained by the greater susceptibility of these compounds to further oxidation to give coloured, polymeric quinonedi-imine type compounds. *p*-Chloroaniline gave *cis*- and *trans*-4,4′-dichloroazobenzene (20%of each). In all cases strong, exothermic reactions took place on concentration. In contrast *p*-cyanoaniline reacted to an extent of only 2% and *p*-nitroaniline, 2-aminopyridine, 2,4,6-tribromoaniline, benzamide, and acetanilide failed to react at all. This shows that electron-withdrawing groups inhibit the oxidation of the aromatic amino-group by chloramine. The reaction of chloramine with benzylamine gave benzaldehyde (30%) and benzylamine hydrochloride (30%).

Goldschmidt[8] found that aniline treated with an ethereal solution of hypochlorous acid at −15° gave *NN*-dichloroaniline, which decomposed explosively at room temperature in the absence of solvent. Subsequently Goldschmidt and Strohmenger[9] discovered that *o*-, *m*-, and *p*-nitroaniline, *m*-toluidine, and certain *C*-chloro-anilines behaved in a similar manner to give the corresponding substituted azobenzenes. Abramovitch and Davis[10] proposed that these decompositions proceeded *via* a nitrene intermediate. From the present work this possibility does not seem likely, since the reaction of 2-aminobiphenyl and chloramine gave only *cis*- and *trans*-2,2′-azobiphenyl and no carbazole. 2,2′-Diaminobiphenyl and chloramine gave mainly unchanged starting material, together with a small amount of benzo[*c*]cinnoline and some dark polymeric material. The mechanism of these chloramine oxidations is obscure.

In view of the above results some preliminary experiments were tried with certain other compounds. Under mild conditions, benzyl alcohol was easily oxidised by monochloramine to benzaldehyde in high yield, likewise diphenylmethanol with chloramine gave benzophenone; a quantitative amount of ammonium chloride was isolated in each case. Hydrazobenzene reacted readily with chloramine to give a high yield of azobenzene, but phenylhydrazine gave a much lower yield. The yields

$$PhCH_2{\cdot}OH + NH_2Cl \longrightarrow PhCHO + NH_4Cl$$

were of the same order as those obtained by Rees and Storr with 1-chlorobenzotriazole.[6]

EXPERIMENTAL

Ethereal Chloramine.—This was prepared by a modification of the method of Coleman and Hauser.[11] Powdered ammonium chloride (27 g.) suspended in ether (1 l) was cooled to −10°. Concentrated aqueous ammonia (42 ml.) was added to the mixture which was then vigorously stirred while commercial aqueous sodium hypochlorite (250 ml.; 1·8 M-solution) was added in small portions during 10 min., the internal temperature being kept between −15 and −10°. The ethereal layer was separated, washed once with saturated sodium chloride solution (250 ml.), and dried over granulated calcium chloride for 1 hr. at −15°. The filtered ethereal chloramine could be stored for several hours at −10°, or below. An aliquot was assayed iodometrically. Ether was evaporated from the mixture before the latter was titrated with thiosulphate. The ethereal chloramine solutions were normally in the range of 0·1—0·2M.

2,2′-Dibenzylthioazobenzene.—2-Aminophenyl benzyl sulphide (2·8 g., 0·013 mole) and sodium hydride (1 g. in oil suspension) were placed in ether (50 ml.); ethereal chloramine (0·01 mole) was added to the mixture which was then stirred at room temperature for 4 hr. The mixture was

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[6] C. W. Rees and R. C. Storr, *J. Chem. Soc.* (*C*), 1969, 1474.

[7] P. A. S. Smith, 'The Chemistry of Open-chain Organic Nitrogen Compounds,' vol. I, 1965, Benjamin, New York, p. 112.

[8] S. Goldschmidt, *Ber.*, 1913, **46**, 2728.

[9] S. Goldschmidt and L. Strohmenger, *Ber.*, 1922, **55** (*B*), 2450.

[10] R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 1964, **149**, 168.

[11] G. A. Coleman and C. R. Hauser, *J. Amer. Chem. Soc.*, 1928, **50**, 1193.

filtered and the filtrate was concentrated under reduced pressure to leave an oily residue which was taken up in methylene chloride and chromatographed on alumina. The first light petroleum (b.p. 40—60°) eluate gave unchanged 2-aminophenyl benzyl sulphide (1·68 g., 60%). The chloroform eluate yielded 2,2′-dibenzylthioazobenzene (0·28 g., 10%) as red crystals, m.p. 170° (decomp.) (lit.,[12] 223°) (Found: C, 72·8; H, 5·65; N, 6·6; S, 14·8. Calc. for $C_{26}H_{22}N_2S_2$: C, 73·1; H, 5·2; N, 6·6; S, 15·0%).

Oxidation of Amines.—Aniline. Chloramine in ether (0·086 mole) at −10° was added to freshly redistilled aniline (7·95 g., 0·083 mole). The reaction mixture was stirred at room temperature for 12 hr. after which the ether was evaporated off at 25° under reduced pressure; when nearly all the solvent had been removed an exothermic reaction took place and the reaction mixture became dark. The gummy residue was treated with light petroleum (b.p. 40—60°) and filtered. The petroleum-insoluble residue was extracted with methylene chloride and filtered. The remaining residue was extracted with water and yielded ammonium chloride (3·6 g.). The petroleum filtrate was concentrated under reduced pressure and yielded an oily, orange residue (5·25 g.). This was examined by t.l.c. on silica, which showed that mainly *trans*-azobenzene, a trace of *cis*-azobenzene (R_F value the same as an authentic sample prepared by irradiation [13]), some 4-anilinoazobenzene, very little unchanged aniline, and a small amount of a blue polymer were present. G.l.c. on a 5% NGA column at 150° showed the same result, except that *cis*-azobenzene was absent owing to thermal isomerisation to *trans*-azobenzene (a separate experiment with authentic *cis*-azobenzene checked that this isomerisation did occur).

Preparative t.l.c. yielded *trans*-azobenzene (3·96 g., 50%) m.p. and mixed m.p. 68° (the *cis*-isomer could not be separated from the zone adjoining the *trans*-isomer) and 4-anilinoazobenzene (1 g., 12%), m.p. 85° (lit.,[14] 82°) (Found: C, 78·6; H, 6·1; N, 14·9%, *M* (mass spec.), 273. Calc. for $C_{18}H_{15}N_3$: C, 79·2; H, 5·5; N, 15·4%, *M*, 273), $\nu_{max.}$ (CCl_4) 400 cm.$^{-1}$ ($\Sigma_{max.}$ 14,560). The methylene chloride extract yielded a black residue (3 g.), which was shown by t.l.c. to consist mainly of blue polymer and very little *trans*-azobenzene. Chromatography on an alumina column, whereby the azobenzene was removed first with light petroleum and then the polymer eluted with methanol, gave a blue amorphous powder with no distinct m.p. [$\nu_{max.}$ (KBr) 1730, 1630, 1600, 1520, and 1500 cm.$^{-1}$].

In a parallel experiment the reaction mixture was quenched with water just before the exothermic stage and the product was worked up as before. T.l.c. on the residue from the light petroleum extract indicated the presence of unchanged aniline, *trans*-azobenzene, and 4-anilinoazobenzene, but no phenylhydrazine. Likewise g.l.c. on a 5% NGA column at 230 and at 150° gave an identical result. The residue was chromatographed over neutral alumina and the light petroleum eluate yielded *trans*-azobenzene (38%), m.p. and mixed m.p. 68°. The methylene chloride extract gave mainly polymeric material, t.l.c. and g.l.c. of which showed the presence of very little unchanged aniline and very little azobenzene. The absence of phenylhydrazine was confirmed by comparing the g.l.c. of pure phenylhydrazine with that of the reaction mixture. The i.r. spectra of both extracts showed no absorption comparable to that of pure phenylhydrazine. The aqueous extract yielded ammonium chloride (66%).

Both the quenched and unquenched reaction were carried out with chloramine dissolved in methylene chloride instead of in ether. The results were identical with those obtained above.

When the ratio of ethereal chloramine to aniline was increased to 5:1 and the experiment was conducted without being quenched, the result was identical with that for the 1 : 1 ratio. In another experiment the reaction mixture was stirred for 4 days at room temperature with the same result.

No exothermic reaction occurred and no residue was left, when ethereal chloramine alone was stirred at room temperature for 6 hr. and the solvent was removed under reduced pressure.

p-*Toluidine.*—Chloramine in ether (0·05 mole) at −10° was added to *p*-toluidine (3·6 g., 0·03 mole), and the reaction mixture was stirred at room temperature for 12 hr. The solvent was removed under reduced pressure at 25° and soon afterwards an exothermic reaction occurred. The residue was treated with benzene and filtered; the insoluble residue yielded ammonium chloride (1·6 g.). The benzene filtrate was concentrated and chromatographed on alumina. The first and yellow band eluted with light petroleum–benzene (7 : 1) yielded *trans*-4,4′-dimethylazobenzene (2·1 g., 30%), m.p. 144° (lit.,[15] 145°); $\nu_{max.}$ (Nujol) 1600, 1510, 1465, and 1380 cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 207, 236, and 333 mμ ($\Sigma_{max.}$ 16,000, 21,000, and 37,000). The second red band eluted with light petroleum–benzene (1 : 1) gave *cis*-4,4′-dimethylazobenzene (1·05 g., 15%), m.p. and mixed m.p. with an authentic sample prepared by irradiation,[13] 100° (lit.,[15] 105°); $\nu_{max.}$ (Nujol) 1620, 1610, 1590, 1570, 1520, 1465, and 1380 cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 207, 292, and 331 mμ ($\Sigma_{max.}$ 10,000, 8000, and 9000); M^+ *m/e* 210 ($C_{14}H_{14}N_2 = M^+$, 210).

p-*Chloroaniline.*—Ethereal chloramine (0·05 mole) and *p*-chloroaniline (3·2 g., 0·025 mole) were allowed to react as described above. After the exothermic reaction the residue was extracted with chloroform. The chloroform-insoluble residue gave ammonium chloride, the filtrate was chromatographed on alumina. The first fraction eluted with petroleum–benzene (3 : 1) gave *trans*-4,4′-dichloroazobenzene (1·26 g., 20%), m.p. 187° (lit.,[16] 188°); $\nu_{max.}$ (Nujol) 1595, 1580, 1485, 1470, and 1380 cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 206, 235, and 325 mμ ($\Sigma_{max.}$ 17,000, 23,000, and 42,000).

The second fraction eluted with light petroleum–benzene (1 : 1) yielded *cis*-4,4′-dichloroazobenzene (1·26 g., 20%), m.p. and mixed m.p. 129—130° with an authentic sample prepared by irradiation,[13] also same R_F values on t.l.c. plate (Found: C, 57·8; H, 3·75; N, 10·25. $C_{12}H_8Cl_2N_2$ requires C, 57·4; H, 3·2; N, 11·15%); $\nu_{max.}$ (Nujol) 1595, 1570, 1515, 1495, 1465, and 1380 cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 211 and 292 mμ ($\Sigma_{max.}$ 22,000 and 15,000); M^+ *m/e* 251 ($C_{12}H_8N_2Cl_2 = M^+$, 251).

NN-*Dimethylphenylenediamine.*—Ethereal chloramine (0·14 mole) and NN-dimethylphenylenediamine (0·07 mole) were allowed to react as described above. The first orange band eluted with light petroleum–ether (3 : 2) gave *trans*-4,4′-di-(dimethylamino)azobenzene (10%), m.p. 273° (lit.,[17]

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[15] A. H. Cook, *J. Chem. Soc.*, 1938, 876.

[16] J. Burns, H. McCombie, and H. A. Scarborough, *J. Chem. Soc.*, 1928, 2933.

[17] D. Vorlander and E. Wolferts, *Ber.*, 1923, **56**, 1238.

273°) (Found: C, 71·65; H, 7·9; N, 21·3. Calc. for $C_{16}H_{20}N_4$: C, 71·7; H, 7·5; N, 20·9%); $\nu_{max.}$ (Nujol) 1600, 1560, 1515, 1465, and 1330 cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 208, 255, and 325 mμ ($\Sigma_{max.}$ 3000, 2000, and 830).

The second and red band after elution with ether yielded cis-4,4'-*di-(dimethylamino)azobenzene* (12%), m.p. 220° (Found: C, 70·5; H, 7·5; N, 18·3. $C_{16}H_{20}N_4$ requires C, 71·7; H, 7·5; N, 20·9%); $\nu_{max.}$ (Nujol) 1600, 1560, 1515, 1465, and 1370 cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 206, 257, and 333 mμ ($\Sigma_{max.}$ 2000, 1000, and 750).

The third and purple band eluted with methanol gave a dark blue, polymeric solid with no distinct m.p.; $\nu_{max.}$ (Nujol) 1610, 1520, 1470, and 1380 cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 210 and 267 mμ.

2-*Aminobiphenyl*.—Chloramine and 2-aminobiphenyl were allowed to react as described above. Neither of the two spots nor the streak which were obtained on t.l.c. of the reaction mixture were comparable to carbazole run under the same conditions. Chromatography of the mixture on an alumina column gave first an orange-yellow band (eluted with petroleum) which yielded *trans*-2,2'-azobiphenyl (10%), m.p. 144° (lit.,[18] 144·5°), and second a crimson band (eluted with ether) which yielded cis-2,2'-*azobiphenyl* (10%), m.p. 42—43° (Found: C, 86·1; H, 5·75; N, 8·4. $C_{24}H_{18}N_2$ requires C, 86·3; H, 5·45; N, 8·4%).

p-*Ethoxyaniline*.—Chloramine in ether (0·05 mole) at −10° was added to *p*-ethoxyaniline (7·3 g., 0·05 mole) and the mixture was treated as described above. After the exothermic reaction was complete the residue was treated with water to remove ammonium chloride and the insoluble residue was dissolved in methanol and chromatographed on alumina. The yellow band eluted with light petroleum gave *trans*-4,4'-diethoxyazobenzene (4·7 g., 33%), m.p. 157—159° (lit.,[4] 160°); $\lambda_{max.}$ (EtOH) 205, 241, and 356 mμ ($\Sigma_{max.}$ 9000, 7000, and 17,000). No *cis*-isomer was detected on the column.

Benzylamine.—Chloramine in ether (0·14 mole) was added to benzylamine (10 g., 0·09 mole). The reaction mixture was stirred and after 0·5 hr. a white precipitate appeared. The stirring was continued at room temperature for 12 hr. after which the ammonium chloride (2·5 g.) was filtered off and the filtrate was concentrated under reduced pressure. The residue was treated with light petroleum and yielded benzylamine hydrochloride (30%), m.p. 254° (Found: C, 58·0; H, 7·2; N, 9·8. Calc. for $C_7H_{10}NCl$: C, 58·8; H, 7·05; N, 9·8%). The light petroleum filtrate yielded benzaldehyde (30%) which was isolated as its 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 235°.

2,2'-*Diaminobiphenyl*.—Chloramine (2 mol.) and 2,2-diaminobiphenyl (1 mol.) were allowed to react as described above. The residues from the ether and methylene chloride extractions were examined by t.l.c. and showed the presence of a large proportion of unchanged 2,2'-diaminobiphenyl, a little benzo[*c*]cinnoline (*ca.* 10%), and polymeric material. Column chromatography on neutral alumina was unsuccessful.

p-*Cyanoaniline*.—The amine (5·11 g., 0·045 mole) was allowed to react with chloramine (0·052 mole). The methylene chloride extract chromatographed on neutral alumina with light petroleum–ether (1 : 1) as eluant mixture gave unchanged *p*-cyanoaniline (4·25 g., 83%) and 4,4'-dicyanoazobenzene (100 mg., 2%), m.p. 270° (lit.,[19] 270°).

Attempted Oxidation.—p-Nitroaniline, 2,4,6-tribromoaniline, benzamide, acetanilide, 2-aminopyridine, t-butylamine when treated with ethereal chloramine solution as described above were recovered unchanged (95%).

Oxidation of other Compounds.—*Benzyl alcohol*. A mixture of benzyl alcohol (5·4 g., 0·05 mole) and ethereal chloramine (0·06 mole) was stirred overnight at room temperature. After removal of the solvent under reduced pressure, an exothermic reaction occurred. The residue was extracted with benzene, the ammonium chloride (1·5 g.) was filtered off, and the filtrate was concentrated to yield benzaldehyde (4 g., 74%) which was identified as its 2,4-dinitrophenylhydrazone, m.p. 235°.

Diphenylmethanol.—The alcohol (4·6 g., 0·02 mole) and ethereal chloramine (0·04 mole) when treated in a like manner yielded ammonium chloride (1·2 g.), and benzophenone (4 g., 87%), m.p. 48°; the 2,4-dinitrophenylhydrazone, m.p. 238°, also confirmed by mixed m.p. and i.r. spectroscopy.

Hydrazobenzene.—Chloramine in ether (0·02 mole) at −10° was added to hydrazobenzene (4 g., 0·021 mole). The reaction was treated as above and gave only azobenzene (3·5 g., 90%), m.p. and mixed m.p. 68°. No exothermic reaction took place and only ammonium chloride (1·1 g.) was isolated.

Phenylhydrazine.—Freshly distilled phenylhydrazine (10 g., 0·09 mole) and ethereal chloramine (0·14 mole) were allowed to react as before and yielded azobenzene (2·0 g., 24%) as confirmed by mixed m.p. and u.v. spectroscopy.

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