1287. *Preparation and Reactions of 2,2′-Di-iodoazobenzene*

By Brian T. Newbold

2,2′-Di-iodoazobenzene has been prepared in high yield from the corresponding azoxybenzene by the action of 98% sulphuric acid. Reduction of 2,2′-di-iodoazo- and -azoxy-benzene with zinc dust and sodium hydroxide gave azobenzene. 2,2′-di-iodoazobenzene resisted oxidation by 30% hydrogen peroxide in glacial acetic acid at 70—80°, but decomposed under more drastic conditions.

The most direct route for the synthesis of 2,2′-di-iodoazobenzene appears to be reduction of *o*-iodonitrobenzene, but this is very difficult under alkaline conditions without either decomposition or deiodination,[1-3] and all our attempts failed. Leffler and Wilson[4] prepared

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[1] B. T. Newbold, *J.*, 1961, 4260.

[2] J. F. Corbett and P. F. Holt, *J.*, 1963, 2385.

[3] B. T. Newbold and S. R. Baig, *J.*, 1964, 3488.

[4] J. E. Leffler and A. F. Wilson, *J. Org. Chem.*, 1960, **25**, 424.

2,2′-di-iodoazobenzene, m. p. 151—152·5°, from *o*-iodobenzoyl azide by the action of perbenzoic acid, but it was later reported[5] that this compound (synthesised from 2,2′-di-iodoazoxybenzene by means of lithium aluminium hydride) melted at 194°. Recently,[6] 2,2′-di-iodoazobenzene, m. p. 151°, was prepared from *o*-iodoaniline by use of active manganese dioxide.

We previously made 4,4′-di-iodoazobenzene from the azoxybenzene by treatment with concentrated sulphuric acid, and thought that the 2,2′-isomer might be similarly produced. In fact, 2,2′-di-iodoazoxybenzene reacted with 98% sulphuric acid to give a high yield of 2,2′-di-iodoazobenzene, m. p. 158—158·5°. Since the 4- and 4′-positions are available, it might be expected that Wallach rearrangement to 4-hydroxy-2,2′-di-iodoazobenzene would take place. However, the substance isolated could not be acetylated or benzoylated and did not dissolve in boiling 10% sodium hydroxide. The infrared spectrum did not indicate the presence of an OH group, but was very similar to that of 2,2′-di-iodoazoxybenzene. There was a sharp band at 6·88 μ, which may be attributed to the N=N group.[7] The product was shown to be 2,2′-di-iodoazobenzene when reduction with stannous chloride and hydrochloric acid produced only *o*-iodoaniline.

Attempts to convert 2,2′-di-iodoazoxybenzene into 2,2′-di-iodoazobenzene by reaction with zinc dust and sodium hydroxide gave only azobenzene. Similar treatment of 2,2′-di-iodoazobenzene gave the same result. In contrast, reduction of the latter with zinc dust and acetic acid in ethanol affords 2,2′-di-iodohydrazobenzene, which is oxidised to the azo-compound by peracetic acid.[8]

Previously,[9,10] it was shown that 2,2′-dichloro- and -dibromo-azobenzene are not easily oxidised to the azoxybenzenes by peracetic acid, and this might in part be due to shielding of the azo-group by the halogen atoms. We found that 2,2′-di-iodoazobenzene was largely unaffected by 30% hydrogen peroxide in glacial acetic acid at 70—80°. Moreover, attempted oxidations at higher temperatures with an excess of this agent caused complete decomposition. It seems likely that the azo linkage is sterically hindered by the bulky iodine atoms, which impede oxidation to the azoxybenzene.

EXPERIMENTAL

Melting points were determined on a calibrated Fisher-Johns apparatus. Infrared spectra were recorded on a Perkin-Elmer 137B spectrophotometer and ultraviolet and visible spectra on a Beckman DB spectrophotometer. All products, except 2,2′-di-iodoazobenzene, were identified by mixed m. p. and infrared spectroscopy.

2,2′-Di-iodoazoxybenzene.—This was prepared from *o*-iodonitrobenzene by the method of Cook and Jones,[11] orange-yellow plates, m. p. 148—149° (lit.,[11] 148°), $\lambda_{\text{max.}}$ (Nujol) 6·32, 7·45, 7·92, 8·78, 9·61, 9·82, 10·55, 10·78, 13·10, 13·30, 14·04, and 14·64 μ, $\lambda_{\text{max.}}$ (EtOH) 228 (ε 24,400) and 298—310 mμ. The centre of the latter band was at 304 mμ (ε 6740).

Wallach Rearrangement of 2,2′-Di-iodoazoxybenzene.—To 2,2′-di-iodoazoxybenzene (2·00 g.) was added 98% sulphuric acid (100 ml.), the mixture was warmed on a hot plate for 5 min., and allowed to stand for 1 hr., with occasional shaking. Dilution with an excess of water and cooling overnight in a refrigerator gave a brown precipitate which was washed with water and dried (P_2O_5). Extraction with ethanol–benzene gave a red extract, which was evaporated, to yield 2,2′-di-iodoazobenzene, reddish-brown needles, m. p. 157—160° (82%). Three recrystallisations from ethanol gave red needles, m. p. 158—158·5° (Found: I, 56·7; N, 6·5. Calc. for $C_{12}H_8I_2N_2$: I, 58·5; N, 6·5%), $\lambda_{\text{max.}}$ (Nujol) 6·34, 6·40, 7·73, 8·01, 8·17, 8·65, 9·63, 9·85, 10·48, 13·00, 13·20, and 13·98 μ, $\lambda_{\text{max.}}$ (KBr) 6·88 μ, $\lambda_{\text{max.}}$ (EtOH) 221, 250, 326, 475 mμ (ε 23,700, 11,400, 12,500, 340).

Reductions of 2,2′-Di-iodoazoxybenzene.—2,2′-Di-iodoazoxybenzene (0·50 g.) was dissolved

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[5] P. H. Gore and O. H. Wheeler, *J. Org. Chem.*, 1961, **26**, 3296.

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

[7] R. J. W. Le Fèvre, M. F. O'Dwyer, and R. L. Werner, *Austral. J. Chem.*, 1953, **6**, 341.

[8] B. T. Newbold, unpublished results.

[9] P. E. Gagnon and B. T. Newbold, *Canad. J. Chem.*, 1959, **37**, 366.

[10] B. T. Newbold, *J. Org. Chem.*, 1962, **27**, 3919.

[11] A. H. Cook and D. G. Jones, *J.*, 1939, 1311.

in ethanol (25 ml.), and 40% sodium hydroxide (2 ml.) added, followed by zinc dust (2·0 g.). The mixture was refluxed for 1 hr., after which all colour had disappeared. The supernatant liquid was decanted and the residue extracted twice with hot ethanol (30 ml.). The liquid and the extracts were filtered, and the combined filtrate boiled for 30 min. in air. The solution became deep orange and was diluted with water, to give orange crystals of azobenzene, m. p. 62—65° (66%). Several recrystallisations from ethanol gave orange plates, m. p. 66—67°.

2,2′-Di-iodazoxybenzene (0·50 g.) was treated with an excess of stannous chloride in concentrated hydrochloric acid, to give only *o*-iodoaniline. Acetylation yielded *o*-iodoacetanilide.

Reductions of 2,2′-*Di-iodoazobenzene*.—To 2,2′-di-iodoazobenzene (0·150 g.) in ethanol (25 ml.) was added 40% sodium hydroxide (2 ml.) and zinc dust (2·0 g.). The mixture was refluxed for 30 min. and treated as described above, to yield azobenzene, m. p. 61—64° (65%). Recrystallisation from aqueous ethanol gave orange plates, m. p. 66·5°.

Reduction of 2,2′-di-iodoazobenzene with stannous chloride and hydrochloric acid gave *o*-iodoaniline.

Oxidations of 2,2′-*Di-iodoazobenzene*.—A solution of 2,2′-di-iodoazobenzene (0·172 g.) in glacial acetic acid (50 ml.) was heated to 65°, 30% hydrogen peroxide (5 ml.) was added, and this temperature maintained for 1 hr. Hydrogen peroxide (5 ml.) was then added, and the solution heated to 70—80° for 23 hr. Further 5-ml. additions of hydrogen peroxide were made after 19 and 21 hr. The orange-red solution was diluted with water and cooled overnight, to give a pink precipitate. Recrystallisation from ethanol–benzene gave 2,2′-di-iodoazobenzene, red needles, m. p. 158—159° (78%).

2,2′-Di-iodoazobenzene (0·134 g.) was dissolved in glacial acetic acid (50 ml.), 30% hydrogen peroxide (5 ml.) was added, and the solution refluxed. Further 5-ml. additions of hydrogen peroxide were made after ¼, 1¼, 2¼, and 4½ hr. The solution was refluxed for 9 hr., and treated as described above, but no product was isolated.

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