313. *Studies in the Diphenyl Series. Part III. Cain's supposed 4'' : 4'''-Disubstituted Tetranitrobenzerythrenes.*

By Herbert H. Hodgson and Paul F. Holt.

Cain, Coulthard, and Micklethwait, treating their tetrazotised so-called 3 : 5' (now 3 : 3')-dinitrobenzidine by Ullmann's modification of Sandmeyer's process, obtained what they regarded as derivatives of benzerythrene (J., 1913, **103**, 2074). Suspicion of the structure of these substances was aroused by their relatively low m. p.'s, *e.g.*, the alleged 4'' : 4'''-dichlorotetranitrobenzerythrene had m. p. 203°, whereas 4 : 4'-dichloro-3 : 3'-dinitrodiphenyl has m. p. 237° (Hodgson and Gorowara, J., 1926, 1754), and the corresponding dibromo-compounds have m. p.'s 184° and 247° respectively. Further, those authors emphasised the fact of the simultaneous formation of azo-compounds which affected their nitrogen determinations (on which they seemed to rely almost entirely), and consequently impaired the validity of their conclusions. It was also remarkable that the decomposition of the above bisdiazonium compound by potassium thiocyanate should yield a benzerythrene derivative in the absence of copper, whereas with potassium iodide the normal replacement should take place with production of 4 : 4′-di-iodo-3 : 3′-dinitrodiphenyl.

At first, we thought that the Sandmeyer reaction had brought about the replacement of one diazonium group by halogen (or the cyano- or thiocyano-group) and of the other by hydrogen, a possibility suggested by molecular-weight determinations, but exhaustive purification by recrystallisation, first from acetic acid and subsequently from nitrobenzene, raised the m. p.'s of the so-called benzerythrenes to those of the pure 4 : 4′-disubstituted 3 : 3′-dinitrodiphenyls (where these were known).

The so-called 4″ : 4‴-dichlorotetranitrobenzerythrene was also reconverted into the original 3 : 3′-dinitrobenzidine by treatment with alcoholic ammonia under pressure. Reduction of the above benzerythrene and of authentic 4 : 4′-dichloro-3 : 3′-dinitrodiphenyl gave the same product, *viz.*, 4 : 4′-dichloro-3 : 3′-diaminodiphenyl, and elimination of the amino-groups left 4 : 4′-dichlorodiphenyl.

The supposed 4″ : 4‴-disubstituted tetranitrobenzerythrenes are therefore impure 4 : 4′-disubstituted 3 : 3′-dinitrodiphenyls, the impurities arising probably from the method of tetrazotising the 3 : 3′-dinitrobenzidine; in the cases of the chloro- and bromo-derivatives, Hodgson and Walker's method (J., 1933, 1620) affords very pure products owing to the suppression of subsidiary reactions.

EXPERIMENTAL.

Molecular-weight determinations were done cryscopically in nitrobenzene (naphthalene in one case), Rast's method being unsuitable.

General Procedure.—The methods of Cain, Coulthard, and Micklethwait were followed in all cases, 10 g. of 3 : 3′-dinitrobenzidine being used.

Alleged 4″ : 4‴-*Dichlorotetranitrobenzerythrene.*—(a) The diazonium solution was poured on copper-bronze and hydrochloric acid, the solid removed and extracted with boiling alcohol, the extract poured into water, and the precipitate crystallised from 50% aqueous acetic acid. The yellow crystals obtained were of poor quality and had m. p. 203° as given by C., C., and M. One recrystallisation from glacial acetic acid and five from nitrobenzene afforded pale yellow needles, m. p. 237°, identical (mixed m. p.) with authentic 4 : 4′-dichloro-3 : 3′-dinitrodiphenyl [Found : N, 9·0; Cl, 22·6; *M* (mean of 3 detmtns.) 310. Calc. : N, 8·9; Cl, 22·7%; *M*, 313].

(b) The supposed benzerythrene (2 g.) was heated with alcohol (2 c.c.) and aqueous ammonia (9 c.c.; *d* 0·888) in a sealed tube at 180° for 6 hours; the scarlet reaction product (m. p. 263°) crystallised from nitrobenzene in scarlet needles, m. p. 275°, identical (mixed m. p.) with authentic 3 : 3′- dinitrobenzidine (Found : N, 20·5. Calc. : N, 20·4%). This product (0·3 g.), suspended in glacial acetic acid (5 c.c.), was poured into an ice-cooled solution of sodium nitrite (0·2 g.) and concentrated sulphuric acid (2 c.c.), and the mixture was stirred for 15 minutes, poured into excess of alcohol, and finally heated to the b. p. The precipitate of 3 : 3′-dinitrodiphenyl produced by dilution with water crystallised from 50% aqueous acetic acid in orange-yellow needles, m. p. 200° (lit. 200°), identical (mixed m. p.) with a specimen prepared from *m*-nitroaniline (Found : N, 11·6. Calc. : N, 11·5%).

(c) Both the impure and the authentic product in (a) (10 g.) were separately refluxed for 2½ hours with glacial acetic acid (30 c.c.), water (30 c.c.), and iron filings (12 g.), the mixtures made alkaline with aqueous ammonia, and the solids filtered off, dried, and extracted with boiling benzene. Passage of dry hydrogen chloride through the extracts gave in each case the *dihydrochloride* of 4 : 4′-*dichloro*-3 : 3′-*diaminodiphenyl*, which crystallised from hydrochloric acid in colourless micro-plates, m. p. 267° (Found : Cl, 43·4. $C_{12}H_{10}N_2Cl_2,2HCl$ requires Cl, 43·5%). Addition of aqueous ammonia gave the *base*, which crystallised from aqueous alcohol in white leaflets, m. p. 133·5° (Found : N, 11·2; Cl, 28·0. $C_{12}H_{10}N_2Cl_2$ requires N, 11·1; Cl, 28·1%); the *diacetyl* derivative crystallised from 50% aqueous acetic acid in micro-plates, m. p. 254° (Found : N, 8·5; Cl, 20·9. $C_{16}H_{14}O_2N_2Cl_2$ requires N, 8·3; Cl, 21·1%), and the *dibenzoyl* derivative also in micro-plates, m. p. 260° (Found : Cl, 15·2. $C_{26}H_{18}O_2N_2Cl_2$ requires Cl, 15·4%). Deamination of the above base by the usual procedure gave 4 : 4′-dichlorodiphenyl, which crystallised from 50% aqueous acetic acid in colourless clusters, m. p. and mixed m. p. 148° (lit. 148°) (Found : Cl, 31·7. Calc. : Cl, 31·8%).

Alleged 4'' : 4'''-*Dibromotetranitrobenzerythrene*.—The procedure was as in (a) for the chloro-analogue, except that the residue was extracted with glacial acetic acid instead of alcohol, and the extract poured into water; the resulting yellow precipitate crystallised from 50% aqueous acetic acid in fine yellow needles, m. p. 250° (C., C., and M. give 247°). Four crystallisations from nitrobenzene raised the m. p. to 259°, and the product was identical (mixed m. p.) with that prepared by the method of Hodgson and Walker (*loc. cit.*) (Found : N, 7·0; Br, 39·6; *M*, 401. Calc. : N, 7·0; Br, 39·8%; *M*, 402).

4 : 4'-*Dicyano*-3 : 3'-*dinitrodiphenyl*.—By the procedure as for the supposed benzerythrene compound, this *substance* was obtained after four crystallisations from nitrobenzene in red leaflets, m. p. 280° (C., C., and M. give m. p. 195—198°) (Found : N, 19·1; *M*, 291. $C_{14}H_6O_4N_4$ requires N, 19·0%; *M*, 294).

4 : 4'-*Dithiocyano*-3 : 3'-*dinitrodiphenyl*.—The *product* obtained by C., C., and M.'s procedure, followed by three crystallisations from nitrobenzene, formed yellow clusters, m. p. 307° (C., C., and M. give m. p. 301°) [Found : N, 15·7; S, 18·0; *M* (cryoscopic from naphthalene), 350. $C_{14}H_6O_4N_4S_2$ requires N, 15·6; S, 17·9%; *M*, 358].

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