385. *Derivatives of* 6-*Bromo- and* 4 : 6-*Dibromo*-m-*toluidine.*

By G. D. PARKES and E. D'A. BURNEY.

THE action of bromine upon aceto-*m*-toluidide yields first 6-bromoaceto-*m*-toluidide and then (with 2 molecules of bromine) a mixture of 2 : 6- and 4 : 6-dibromoaceto-*m*-toluidide. The latter constituent is readily obtained pure by recrystallisation of the mixture from alcohol.

6-Bromo- and 4 : 6-dibromo-*m*-toluidine, obtained by hydrolysis of the acetyl compounds, are readily diazotised and the diazonium salts yield hydrazines on reduction, and couple and condense in a normal manner. The hydrazines form stable well-crystallised hydrazones, which react with bromine in a similar manner to other hydrazones (compare Chattaway and Parkes, this vol., p. 1005).

A number of other brominated derivatives of *m*-toluidine have been prepared, and their properties are here briefly recorded.

The following *m*-toluidides were prepared by suitable modifications of ordinary methods and crystallised from alcohol: o'-*nitrobenzo*-, pale yellow needles, m. p. 146° (Found: N, 10·7. $C_{14}H_{12}O_3N_2$ requires N, 10·9%); m'-*nitrobenzo*-, almost colourless needles, m. p. 114° (Found: N, 10·9%); p'-*nitrobenzo*-, pale yellow needles, m. p. 148° (Found: N, 10·8%); benzo-6-bromo-, white needles, m. p. 123° (Leulier and Arnoux, *Bull. Soc. chim.*, 1887, **47**, 730, give m. p. 98°) (Found: Br, 27·5. Calc.: Br, 27·6%); o'-*nitrobenzo*-6-*bromo*, pale yellow needles, m. p. 163° (Found: Br, 23·8. $C_{14}H_{11}O_3N_2Br$ requires Br, 23·9%); m'-*nitrobenzo*-6-*bromo*-, white leaflets, m. p. 185·5° (Found: Br, 23·8%); p'-*nitrobenzo*-6-*bromo*-, pale yellow needles, m. p. 258° (Found: Br, 23·9%); *benzo*-4 : 6-*dibromo*-, white needles, m. p. 131° (Found: Br, 43·6. $C_{14}H_{11}ONBr_2$ requires Br, 43·4%); o'-*nitrobenzo*-4 : 6-*dibromo*-, pale yellow needles, m. p. 203° (Found: Br, 38·7. $C_{14}H_{10}O_3N_2Br_2$ requires Br, 38·65%); m'-*nitrobenzo*-4 : 6-*dibromo*-, white needles, m. p. 207° (Found: Br, 38·8%); p'-*nitrobenzo*-4 : 6-*dibromo*-, yellow needles, m. p. 182·5° (Found: Br, 39·1%).

6-*Bromo*-m-*tolylurea*, prepared from 6-bromo-*m*-toluidine (9·3 g.) in warm *N*/2-hydrochloric acid (100 c.c.) and potassium cyanate (4·5 g.) in a little water, crystallised from benzene in white needles, m. p. 191° (Found: Br, 34·9. $C_8H_9ON_2Br$ requires Br, 34·9%). 4 : 6-*Dibromo*-m-*tolylurea* separated after several days from mixed solutions of 4 : 6-dibromo-*m*-toluidine (10·6 g.) and potassium cyanate (3·3 g.), each in 30 c.c. of glacial acetic acid; it crystallised from alcohol in white needles, m. p. 218° (Found: Br, 51·6. $C_8H_8ON_2Br_2$ requires Br, 51·95%).

The following compounds were prepared by heating urea with excess of the appropriate base until evolution of ammonia ceased: s.-*bis*-6-*bromo*-m-*tolylurea*, white needles, from alcohol, m. p. 276° (Found: Br, 40·6. $C_{15}H_{14}ON_2Br_2$ requires Br, 40·2%); s.-*bis*-4 : 6-*dibromo*-m-*tolylurea*, white needles, from glacial acetic acid, m. p. 297° (Found: Br, 57·4. $C_{15}H_{12}ON_2Br_4$ requires Br, 57·55%).

6-*Bromo*-m-*tolueneazo*-β-*naphthol*, prepared from diazotised 6-bromo-*m*-toluidine (7·5 g.) and β-naphthol (7 g. in 30 c.c. of 2*N*-sodium hydroxide), crystallised from alcohol in red needles, m. p. 143° (Found: Br, 23·5. $C_{17}H_{13}ON_2Br$ requires Br, 23·5%). 4 : 6-*Dibromo*-m-*tolueneazo*-β-*naphthol*, prepared similarly, formed bright red needles, from alcohol, m. p. 193° (Found: Br, 37·9. $C_{17}H_{12}ON_2Br_2$ requires Br, 38·1%).

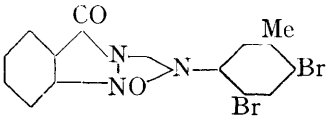
6-*Bromo*-m-*tolylhydrazine Hydrochloride*.—6-Bromo-*m*-toluidine (120 g. in 1200 c.c. of concentrated hydrochloric acid) was diazotised (45 g. of sodium nitrite in 300 c.c. of water) below 5°, and the diazonium solution poured into 270 g. of stannous chloride in 270 c.c. of concentrated hydrochloric acid, cooled in ice and salt. After 12 hours the precipitate of hydrochloride was collected and recrystallised from dilute hydrochloric acid, separating in white needles, m. p. 220°. 4 : 6-Dibromo-*m*-tolylhydrazine hydrochloride, prepared similarly, formed white needles, m. p. 225°.

The following compounds were prepared by shaking equivalent quantities of the hydrazine hydrochloride and the aldehyde with anhydrous sodium acetate and glacial acetic acid: *benzaldehyde*-6-*bromo*-m-*tolylhydrazone*, white needles, from alcohol. m. p. 154° (Found: Br, 27·8. $C_{14}H_{13}N_2Br$ requires Br, 27·7%); o-*nitrobenzaldehyde*-6-*bromo*-m-*tolylhydrazone*, red prisms, from glacial acetic acid, m. p. 175·5° (Found: Br, 23·8. $C_{14}H_{12}O_2N_3Br$ requires Br, 23·95%); m-*nitrobenzaldehyde*-6-*bromo*-m-*tolylhydrazone*, orange-yellow prisms, m. p. 148° (Found: Br, 24·4%); p-*nitrobenzaldehyde*-6-*bromo*-m-*tolylhydrazone*, red prisms, m. p. 171·5° (Found: Br, 24·1%); *benzaldehyde*-4 : 6-*dibromo*-m-*tolylhydrazone*, yellow needles, m. p. 109° (Found: Br, 43·25. $C_{14}H_{12}N_2Br_2$ requires Br, 43·5%); o-*nitrobenzaldehyde*-4 : 6-*dibromo*-m-*tolylhydrazone*, orange-red needles, m. p. 180° (Found: Br, 38·9. $C_{14}H_{11}O_2N_3Br_2$ requires Br, 38·7%); m-*nitrobenzaldehyde*-4 : 6-*dibromo*-m-*tolylhydrazone*, orange-yellow prisms, m. p. 204° (Found: Br, 38·8%); p-*nitrobenzaldehyde*-4 : 6-*dibromo*-m-*tolylhydrazone*, orange-red needles, m. p. 221° (Found: Br, 38·6%).

α-*Bromo*-m-*nitrobenzaldehyde*-4 : 6-*dibromo*-m-*tolylhydrazone*.—5 G. of *m*-nitrobenzaldehyde-*m*-tolylhydrazone, suspended in 25 c.c. of glacial acetic acid, were treated with a solution of 6·3 g. of bromine in 10 c.c. of glacial acetic acid, added drop by drop with constant shaking. The green precipitate of α-*bromo*-m-*nitrobenzaldehyde*-4 : 6-*dibromo*-m-*tolylhydrazone* was washed with water and recrystallised from glacial acetic acid, separating in pale yellow needles, m. p. 191° (Found: Br, 48·6. $C_{14}H_{10}O_2N_3Br_3$ requires Br, 48·8%). The same compound was obtained by the action of bromine upon *m*-nitrobenzaldehyde-6-bromo-*m*-tolylhydrazone, and upon *m*-nitrobenzaldehyde-4 : 6-dibromo-*m*-tolylhydrazone.

The following were prepared similarly: α-*bromobenzaldehyde*-4 : 6-*dibromo*-m-*tolylhydrazone*, pale yellow needles, from alcohol, m. p. 122° (Found: Br, 53·4. $C_{14}H_{11}N_2Br_3$ requires Br, 53·7%); α-*bromo*-o-*nitrobenzaldehyde*-4 : 6-*dibromo*-m-*tolylhydrazone*, bright yellow needles, from glacial acetic acid, m. p. 151° (Found: Br, 49·0. $C_{14}H_{10}O_2N_3Br_3$ requires Br, 48·8%).

p-*Nitrobenzenyl*-4 : 6-*dibromo*-m-*tolylhydrazidine* was prepared by warming 5 g. of α-bromo-*p*-nitrobenzaldehyde-4 : 6-dibromo-*m*-tolylhydrazone, suspended in 50 c.c. of alcohol to which 5 c.c. of concentrated aqueous ammonia had been added. It crystallised from alcohol in brick-red prisms, m. p. 207° (Found: Br, 37·3. $C_{14}H_{12}O_2N_4Br_2$ requires Br, 37·4%). m-*Nitrobenzenyl*-4 : 6-*dibromo*-m-*tolylhydrazidine*, prepared similarly, formed pale violet prisms, from alcohol, m. p. 155° (Found: Br, 37·5. $C_{14}H_{12}O_2N_4Br_2$ requires Br, 37·4%).



5 G. of α-bromo-*o*-nitrobenzaldehyde-4 : 6-dibromo-*m*-tolylhydrazone were warmed with just sufficient alcohol for solution; on cooling, 3-*keto*-1 : 2-endo-4′ : 6′-*dibromo*-m-*tolylimino*-1 : 2-*dihydro*-1 : 2-*benz*isodiazole 1-*oxide* separated in yellow needles, exploding at 126° (Found: Br, 38·5. $C_{14}H_9O_2N_3Br_3$ requires Br, 38·9%).

THE DYSON PERRINS LABORATORY, OXFORD.

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