

NOTES.

The Preparation of Naphthastyril from 8-Bromo-1-naphthoic Acid. By H. GORDON RULE and ROBERT R. H. BROWN.

A SOLUTION of 20 g. of 8-bromo-1-naphthoic acid (Rule and Barnett, J., 1932, 179) in 300 c.c. of concentrated aqueous ammonia containing 0.4 g. of copper bronze, 5.0 g. of ammonium nitrate, and 0.4 g. of potassium chlorate (compare Groggins and Stirton, *Ind. Eng. Chem.*, 1933, 25, 169) was heated in a small glass-lined rotating autoclave at 130—150° for 1 hour. The yellow crystalline solid was filtered off after cooling, washed with cold water, and recrystallised from 2.5 l. of water, giving 10 g. of pure naphthastyril, m. p. 181°. An additional 1 g. was obtained by concentrating the mother-liquor (total yield, 82%).

In the absence of ammonium nitrate and potassium chlorate the yield was about 15% less. When the operation was carried out in an open vessel, the yields varied from 52 to 67%.

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The Preparation of Camphorquinone. By W. C. EVANS, J. M. RIDGION, and J. L. SIMONSEN. CAMPHORQUINONE, obtained usually by the hydrolysis of isonitrosocamphor, can be readily prepared by the oxidation of camphor by Riley's method (E.P. 354,798) with selenium dioxide. A mixture of camphor (5 g.), selenium dioxide (6 g.), and acetic anhydride (5 c.c.) was heated at 140—150° for 3—4 hours. The cooled solution was filtered, the selenium washed with acetic acid, and the orange-yellow filtrate carefully neutralised with potassium hydroxide solution. The camphorquinone (5.22 g.) had m. p. 190—195°, and 198° after recrystallisation from ligroin (Found: C, 72.4; H, 8.6. Calc. for C₁₀H₁₄O₂: C, 72.3; H, 8.4%). The identity was confirmed by the preparation of the semicarbazone, decomp. 228—229°, and the *p*-bromophenylhydrazone, m. p. 215—216° (Found: Br, 23.9. Calc.: Br, 23.8%) (compare Lapworth and Chapman, J., 1901, 79, 381). Dioxan may be used in place of acetic anhydride as a solvent, but the yield is less satisfactory and the product more difficult to purify. (Commercial dioxan contains aldehydic impurities which can be removed by distillation over solid potassium hydroxide).

The method described provides also the simplest route from camphor to camphoric anhydride, since Forster and Holmes (J., 1908, 93, 252; compare Holleman, *Rec. trav. chim.*, 1904, 23, 171) have shown the latter to be formed in quantitative yield by the oxidation of the diketone with hydrogen peroxide.

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The Action of Bromine on 2- and 6-Chloro- and 2- and 6-Iodo-3-bromophenols. By HERBERT H. HODGSON and JOSEPH NIXON.

BROMINE reacts normally with 2- and 6-chloro-3-bromophenol to form 2-chloro-3:4:6-tribromo- and 6-chloro-2:3:4-tribromo-phenol respectively, but converts both 2- and 6-iodo-3-bromophenol into 2:3:4:6-tetrabromophenol. 3:4:6-Tribromo-2-iodophenol can be obtained, but is converted into the tetrabromophenol on long standing in the reaction liquor. No migrations have been detected.

2-Chloro-3-bromophenol, obtained from 3-bromo-2-aminophenol, crystallised from alcohol in colourless needles, m. p. 60° (Found : Cl + Br, 55.4. C_6H_4OClBr requires Cl + Br, 55.7%). It (2 g.) was converted by bromine (1 c.c.) in chloroform (20 c.c.) into *2-chloro-3 : 4 : 6-tribromophenol*, which formed colourless needles, m. p. 96°, from alcohol (Found : Cl + Br, 75.1. $C_6H_2OClBr_3$ requires Cl + Br, 75.4%).

2-Chloro-5-bromophenol, obtained from 5-bromo-2-aminophenol, crystallised from alcohol in colourless needles, m. p. 60° (Found : Cl + Br, 55.3%). On dibromination as above, it gave *6-chloro-2 : 3 : 4-tribromophenol*, which separated from alcohol in colourless needles, m. p. 98° (Found : Cl + Br, 75.2%). This compound was also obtained by chlorination (in chloroform) of Kohn and Strassmann's dibromination product of *m*-bromophenol (see Hodgson, Walker, and Nixon, J., 1933, 1053).

3-Bromo-2-iodophenol, obtained from 3-bromo-2-aminophenol, crystallised from 90% formic acid in colourless needles, m. p. 85° (Found : Br + I, 68.9. C_6H_4OBrI requires Br + I, 69.2%).

Bromination of 3-Bromo-2-iodophenol.—(a) Solutions of the phenol (0.5 g. in 5 c.c.) and of bromine (0.8 g. in 3 c.c.) in glacial acetic acid were mixed, warmed to 50°, and kept for 2 hours at room temperature; *3 : 4 : 6-tribromo-2-iodophenol* separated in colourless needles, m. p. 125° (Found : Br + I, 80.0. $C_6H_2OBr_3I$ requires Br + I, 80.3%). The mother-liquor on dilution with water gave *2 : 3 : 4 : 6-tetrabromophenol*, which crystallised from 90% formic acid in colourless needles, m. p. and mixed m. p. with an authentic specimen, 113—114° (Found : Br, 77.8. Calc. : Br, 78.0%).

(b) When the bromination was repeated, 15 c.c. of glacial acetic acid being used, and the mixture kept for 18 hours, no crystals separated, but on dilution with water *2 : 3 : 4 : 6-tetrabromophenol* was precipitated.

3 : 4 : 6-Tribromo-2-iodophenol was also prepared from *3 : 4 : 6-tribromo-2-aminophenol*, itself prepared from *3 : 4 : 6-tribromo-2-nitrophenol* (Hodgson, Walker, and Nixon, *loc. cit.*); m. p. and mixed m. p. 125° (Found : Br + I, 80.0%).

5-Bromo-2-iodophenol, prepared from 5-bromo-2-aminophenol, crystallised from alcohol in colourless needles, m. p. 55° (Found : Br + I, 69.0%). On bromination by methods (a) and (b) it gave only *2 : 3 : 4 : 6-tetrabromophenol*, m. p. and mixed m. p. 113—114°.

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An Instance of the Action of Air in determining the Course of Bromination. By JOHN HANNON and J. KENNER.

THE conversion of *2 : 2'*-ditolyl into its $\omega\omega\omega_1\omega_1$ -tetrabromo-derivative was described by Kenner and Turner (J., 1909, 95, 2102), but at the same time it was stated that only those experiments were successful in which the bromination was spread over 2 days. The difficulty thus indicated was again encountered when the study of the matter was resumed, until it occurred to us that interruption of the operation might have permitted re-access of air to the bromination mixture, and to connect this with the favourable influence of air on the yield of benzyl bromide from toluene (Andrich and Le Blanc, *Z. wiss. Photochem.*, 1916, 15, 148, 183) and with the earlier discovery by Luther and Goldberg (*Z. physikal. Chem.*, 1906, 56, 43) that its presence is inimical to the nuclear chlorination of benzene. When, therefore, access of dry air was allowed through the reflux condenser during the interval (13½ hours) between the bromination, initially at 110° and finally at 140°, of *2 : 2'*-ditolyl, b. p. 254—259°, for 2 working days, a transparent final product was consistently obtained and some crystals developed in the upper portions of the bromination flask. After removal of hydrogen bromide by solid potassium hydroxide in a vacuum desiccator, the gum was readily converted into a mass of crystals by nucleation and rubbing with dry ether. Yield, 60% of the theoretical.

o-Iodocyanobenzene, m. p. 54—55° (Found : N, 6.4. C_7H_4NI requires N, 6.1%), reacted with copper powder at 275° to furnish *2 : 2'-dicyanodiphenyl*, m. p. 176—177° (Found : N, 13.9. $C_{14}H_8N_2$ requires N, 13.7%). It was identified by alkaline hydrolysis to diphenic acid, m. p. 229°, but could not be converted by Stephen's method into *2 : 2'-dialdehydodiphenyl*, which is thus best prepared in the manner described by Kenner and Turner (*loc. cit.*). Its dioxime forms colourless prisms, m. p. 186—187° (Found : N, 11.8. Calc. for $C_{14}H_{12}O_2N_2$: N, 11.7%) (compare Mayer, *Ber.*, 1911, 44, 2304).—THE COLLEGE OF TECHNOLOGY, MANCHESTER. [Received, December 4th, 1933.]