NOTES.

The Nitration of Benzylpiperidine. By ROBERT ROBINSON and JOHN STEPHEN WATT.

A LARGE effect on the proportion of the *m*-isomeride produced in the nitration of benzylpiperidine was observed by Pollard and Robinson (J., 1927, 2770) as the result of the addition of soluble salts to the fuming nitric acid employed. Further work on this subject was contemplated, but it has not been found possible to reproduce the results. It is desirable to place this fact on record, and experiments will be undertaken with the view of discovering the cause of the anomaly, which may be the result of some elusive variation of detail in the conditions.

The method employed was that of Ing and Robinson (J., 1926, 1664), the nitration mixture being kept for 3 hours in the freezing mixture before being worked up, and after addition of potassium iodide to the solution of the bases 3 hours were allowed for the separation.

Benzyl-piperidine, g.	$RbNO_3$ added, g.	Hydriodide ppted., g.	Base equiv. to this hydriodide, g.	Total nitro-bases, g.	*m*-Nitro-compound, %.
15	—	16·2	10·2	17·7	57
15	3	17·5	11	18·4	59
9·5	9·5	10·5	6·6	10·9	60
10	10	10·2	6·4	11·7	55
3	3	3	1·9	3·7	51

The percentages in the last column are calculated from the weight of hydriodide only; by fractional crystallisation of the picrates of the remaining bases, further quantities of *m*-isomeride (5—10%) could be obtained.

The melting point of the crude hydriodide varied from 213° to 216°, and was raised to 221° after crystallisation. The m. p.'s of the hydriodides of the pure nitrobenzylpiperidines (Lellman and Pekrun, *Annalen*, 1890, **259**, 40) were: *o*-, 218°; *m*-, 221°; *p*-, 194·5°; and those of mixtures of equal quantities were: *o-p*, 179—182°; *o-m*, 192°; *p-m*, 179—180°.

The melting point of the hydriodide from the nitration product was not depressed by admixture with a specimen of the pure *m*-isomeride.—DYSON PERRINS LABORATORY, OXFORD. [*Received, March* 1*st*, 1931.]

The 3-*Fluoro*-2-, -4-, and -6-*amino- and* -2-, -4-, *and* -6-*halogeno-anisoles.* By HERBERT HENRY HODGSON and JOSEPH NIXON.

Preparation of the Amines.—3-Fluoro-2-, -4-, and -6-nitro-anisoles (Hodgson and Nixon, J., 1928, 1879) are reduced in the usual way with iron powder and aqueous (50%) acetic acid, and the resulting amines removed by steam distillation. Their hydrochlorides crystallise from dilute hydrochloric acid in colourless needles, and their sulphates from dilute sulphuric acid in pearly-white plates.

3-*Fluoro*-2-*aminoanisole* is a colourless oil, b. p. 208°/756 mm. (Found: N, 10·2. C_7H_8ONF requires N, 9·9%). 3-*Fluoro*-4-*aminoanisole* crystallises from water or aqueous alcohol in colourless needles, m. p. 50° (Found: N, 10·1%). 3-*Fluoro*-6-*aminoanisole* is a colourless oil, b. p. 215°/756 mm. (Found: N, 10·2%).

The following compounds were prepared from the amines by the Sandmeyer reaction. They are all colourless oils.

2-*Chloro*-3-*fluoroanisole*, b. p. 198°/757 mm. (Found: Cl, 22·2. C_7H_6OClF requires Cl, 22·1%). 4-*Chloro*-3-*fluoroanisole*, b. p. 196°/757 mm. (Found: Cl, 22·25%). 6-*Chloro*-3-*fluoroanisole*, b. p. 195°/757 mm. (Found: Cl, 22·15%). 2-*Bromo*-3-*fluoroanisole*, b. p. 220°/755 mm. (Found: Br, 39·2. C_7H_6OBrF requires Br, 39·0%). 4-*Bromo*-3-*fluoroanisole*, b. p. 215°/755 mm. (Found: Br, 39·1%). 6-*Bromo*-3-*fluoroanisole*, b. p. 208°/755 mm. (Found: Br, 39·1%). 2-*Iodo*-3-*fluoroanisole*, b. p. 240°/756 mm. (Found: I, 50·7. C_7H_6OIF requires I, 50·4%). 4-*Iodo*-3-*fluoroanisole*, b. p. 238°/756 mm. (Found: I, 50·5%). 6-*Iodo*-3-*fluoroanisole*, b. p. 236°/756 mm. (Found: I, 50·6%).

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