NOTES.

The Fluorination of Trimethylamine. By J. THOMPSON and H. J. EMELÉUS.

THE vapour-phase fluorination of trimethylamine has been investigated by passing the vapour in a stream of nitrogen over a bed of cobaltic fluoride at temperatures ranging from 130° to 220°, and at atmospheric pressure. The issuing product was passed over sodium fluoride to remove hydrogen fluoride produced by the reaction and through a trap cooled with liquid air. The condensate was then introduced into a vacuum system for examination by trap-to-trap distillation and fractional condensation.

The product was a complex mixture, the components boiling from *ca.* −120° to 120° and having molecular weights ranging from *ca.* 70 to 310. Under the reaction conditions investigated one component of molecular weight 171 was found to constitute 40—70% of the condensate in the cooled trap and has been identified as the *bistrifluoromethylnitrogen monofluoride* (*perfluorodimethylamine*), $N(CF_3)_2F$ (Found: N, 8·0, 7·9, 7·9; F, 77·6, 78·1, 77·2; *M*, 171. C_2NF_7 requires N, 8·2; F, 77·8%; *M*, 171). Several samples of this substance have been prepared and submitted to careful purification and there appears to be little doubt of its identity. The other components have not yet been isolated, but the compounds $N(CF_3)_3$, $N(CF_3)F_2$, and more complex cyclic compounds may possibly be present. The vapour pressure of perfluorodimethylamine has been measured over the range −70° to −40° and is represented by the equation $\log_{10} p = 7{\cdot}000 - 972{\cdot}7/T$. The calculated boiling point is −37·0°, the latent heat of vaporisation at the boiling point 4450 cals./mol., and Trouton's constant 18·9. Chemically the compound is stable: it does not attack glass or mercury, is not hydrolysed by water at 20°, and can be recovered unchanged from 50% aqueous potassium hydroxide at room temperature. It appears not to have the basicity usually associated with amines, for, in addition to its being practically insoluble in water and unaffected by hydrogen fluoride, it is not dissolved by 50% aqueous sulphuric acid. Chemically, therefore, the compound is more closely related to nitrogen trifluoride than to the amines.

Fluorine was determined by heating the compound with metallic potassium in a Carius tube for two hours at 500° (cf. Elving and Ligget, *Ind. Eng. Chem., Anal.*, 1942, **14**, 449; Kimball and Tufts, *ibid.*, 1947, **19**, 150), steam-distilling the fluorine as fluorosilicic acid, and titrating this with 0·05N-thorium nitrate (Willard and Winter, *ibid.*, 1933, **5**, 7). Nitrogen was determined by a modification of the Dumas method. A weighed amount of the sample was condensed into an evacuated tube, which was assembled directly between the copper oxide tube and the carbon dioxide source. The tube containing the sample was surrounded by a bath of melting chloroform, which gave a convenient concentration of the compound in the carbon dioxide stream as it passed through the cooled trap and over the heated copper oxide. Free nitrogen was collected in the usual way, the analysis being conducted on a semi-micro scale.—UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, August 17th*, 1949.]

Derivatives of 7-Hydroxy-2-methylchromone. By J. S. H. DAVIES and W. L. NORRIS.

IN connection with an investigation on the pharmacological effects of certain complex chromones on smooth muscle, it became of interest to prepare and examine some 6- and 8-substituted derivatives of 7-methoxy-2-methylchromone.

2 : 4-Dimethoxy-5-allylacetophenone (5-allylresacetophenone dimethyl ether; Baker and Lothian, *J.*, 1935, 628) with ethyl acetate and powdered sodium gave 2 : 4-*dimethoxy-ω-acetyl-5-allylacetophenone*, but, when cyclisation with hydrobromic acid in glacial acetic acid or with hydriodic acid was attempted, halogen-containing resins were obtained. Saturation of the allyl group with bromine before attempted cyclisation, and subsequent treatment with zinc dust or sodium iodide in acetone failed to improve the result. However, as was expected, starting with 2 : 4-*dimethoxy*-5-n-*propylacetophenone*, 7-*methoxy*-2-*methyl*-6-n-*propylchromone* was obtained *via* 2 : 4-*dimethoxy-ω-acetyl*-5-n-*propylacetophenone*.

4-*O*-Allylresacetophenone (Baker and Lothian, *loc. cit.*) with sodium and ethyl acetate gave ω-acetyl-4-*O*-allylresacetophenone, and this on cyclisation furnished 7-*allyloxy*-2-*methylchromone*. Claisen re-arrangement of this chromone in dimethylaniline solution gave 7-*hydroxy*-2-*methyl*-8-*allylchromone*, the *methyl ether* of which was hydrogenated to 7-*methoxy*-2-*methyl*-8-n-*propylchromone*. This product was also prepared from 4-*O*-methyl-3-allylresacetophenone (obtained from 4-*O*-allylresacetophenone by the method of Baker and Lothian, *loc. cit.*).

Experimental.—(Analyses are by Drs. Weiler and Strauss, Oxford; m. p.s are uncorrected.)

2 : 4-*Dimethoxy-ω-acetyl-5-allylacetophenone.* 2 : 4-Dimethoxy-5-allylacetophenone (11 g.) was boiled under reflux with powdered sodium (3·8 g.) and dry ethyl acetate (75 c.c.) for 3 hours. The solvent was removed in a vacuum, and the residue was acidified with acetic acid–ice. 2 : 4-*Dimethoxy-ω-acetyl-5-allylacetophenone* (8·7 g., 66·5%) formed colourless needles, m. p. 85·5—86·5°, from ethanol (Found: C, 68·9; H, 7·0. $C_{15}H_{18}O_4$ requires C, 68·7; H, 6·9%).

2 : 4-*Dimethoxy*-5-n-*propylacetophenone.* A solution of 2 : 4-dimethoxy-5-allylacetophenone (38·5 g.) in methanol (250 c.c.) was shaken with hydrogen and palladium–charcoal (6 g.; 10%) at room temperature and pressure. Absorption of hydrogen was rapid. After filtration and removal of the solvent, 2 : 4-*dimethoxy*-5-n-*propylacetophenone* formed colourless, prismatic needles (35·3 g., 91%), m. p. 65·5—66·5°, from light petroleum (b. p. 60—80°) (Found: C, 70·3; H, 8·1. $C_{13}H_{18}O_3$ requires C, 70·2; H, 8·2%).

2 : 4-*Dimethoxy-ω-acetyl*-5-n-*propylacetophenone.* 2 : 4-Dimethoxy-5-*n*-propylacetophenone (4·5 g.) was boiled under reflux with powdered sodium (1·5 g.) and dry ethyl acetate (40 c.c.) for 3 hours. Isolated as above, 2 : 4-*dimethoxy-ω-acetyl-5-n-propylacetophenone* formed colourless prisms (2·85 g., 53%), m. p. 68·5—69·5°, from ethanol (Found: C, 68·1; H, 7·8. $C_{15}H_{20}O_4$ requires C, 68·1; H, 7·6%)

7-*Methoxy*-2-*methyl*-6-n-*propylchromone*. The foregoing diketone (2·0 g.) in glacial acetic acid (25 c.c.) containing hydrobromic acid (2 c.c.) was boiled under reflux for 15 minutes. The mixture was poured on ice and extracted with ether. Removal of this solvent and crystallisation of the residue from light petroleum (b. p. 60—80°) gave 7-*methoxy*-2-*methyl*-6-n-*propylchromone* as golden-yellow, irregular prisms, m. p. 106—106·5° (Found: C, 72·2; H, 6·7. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%).

7-*Allyloxy*-2-*methylchromone*. 4-*O*-Allylresacetophenone (38·4 g.) was boiled under reflux for 1½ hours with powdered sodium (13·8 g.) and dry ethyl acetate (100 c.c.). Isolation furnished the β-diketone as an oil (52·7 g.), some of which (12 g.) was boiled under reflux with glacial acetic acid (40 c.c.) containing a few drops of concentrated hydrochloric acid. After the solution had been poured on ice and extracted with ether, and the solvent had been removed, the residue was crystallised from aqueous methanol, with the aid of a little alumina, yielding 7-*allyloxy*-2-*methylchromone* (4 g., 41%) as colourless, prismatic needles, m. p. 92° (Found: C, 72·5; H, 5·6. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6%).

7-*Hydroxy*-2-*methyl*-8-*allylchromone*. The allyloxychromone (5 g.) in dimethylaniline (5 c.c.) was boiled under reflux for 1¼ hours. After cooling and the addition of benzene (10 c.c.), 7-*hydroxy*-2-*methyl*-8-*allylchromone* separated as a light yellow, crystalline powder (3·67 g., 73%), which formed yellow prisms, m. p. 194—195°, from ethanol (Found: C, 72·0; H, 5·7. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6%).

7-*Methoxy*-2-*methyl*-8-*allylchromone*. Methyl sulphate (7·3 g.) was added dropwise to a cooled, stirred solution of 7-hydroxy-2-methyl-8-allylchromone (12·35 g.) in alcoholic sodium ethoxide, prepared from sodium (1·32 g.) and dry ethanol (50 c.c.). After attaining room-temperature, the solution was boiled under reflux for 15 minutes to complete the reaction. The mixture was poured into water, and the product isolated with ether. Two crystallisations from benzene–light petroleum (b. p. 60—80°) gave 7-*methoxy*-2-*methyl*-8-*allylchromone* (8·7 g., 66%) as slightly pink plates, m. p. 102—103° (Found: C, 72·7; H, 6·2. $C_{14}H_{14}O_3$ requires C, 73·0; H, 6·1%).

7-*Methoxy*-2-*methyl*-8-n-*propylchromone*. The methoxy-allylchromone (8·7 g.) in methanol (75 c.c.) was hydrogenated at room-temperature and pressure in the presence of palladium–charcoal (3·0 g., 10%). Hydrogen uptake was rapid and the yellow oil, obtained after the solution had been filtered and the solvent removed, rapidly solidified. Crystallised from aqueous methanol, it gave 7-*methoxy*-2-*methyl*-8-n-*propylchromone* (7·2 g., 82%), m. p. 106—108°; a further crystallisation from methanol yielded colourless prisms, m. p. 110—111° (Found: C, 72·1; H, 6·6. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%).

4-O-*Methyl*-3-n-*propylresacetophenone*. 4-*O*-Methyl-3-allylresacetophenone (13·6 g.) in methanol (70 c.c.) was hydrogenated as above, theoretical absorption of hydrogen being rapidly attained. The filtered solution was concentrated, and 4-O-*methyl*-3-n-*propylresacetophenone* (11·4 g., 83%) separated as colourless prisms, m. p. 87—89° (Found: C, 69·0; H, 7·5. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%).

ω-*Acetyl*-4-O-*methyl*-3-n-*propylresacetophenone*. 4-*O*-Methyl-3-*n*-propylresacetophenone (5 g.) in ethyl acetate (50 c.c.) was boiled under reflux for 3 hours with powdered sodium (2·3 g.), and gave ω-*acetyl*-4-O-*methyl*-3-n-*propylresacetophenone* as colourless prisms (2·5 g., 42%), m. p. 86—88°, from light petroleum (b. p. 60—80°) (Found: 67·3; H, 7·0. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·3%). Cyclisation of the product (1·4 g.) with glacial acetic acid containing a few drops of concentrated hydrochloric acid gave 7-methoxy-2-methyl-8-*n*-propylchromone (0·6 g., 46·2%), which crystallised from methanol in colourless prisms, m. p. 110—111°, identical with the product described above from 7-methoxy-2-methyl-8-allylchromone.—British Schering Research Institute Alderley Edge. [*Received, August 29th,* 1949.]