NOTE.

6-*Bromo*-2-*methoxy*-1-*naphthoic Acid.* By FRANK L WARREN, MUNIR GINDY, and FAWZY GHALI BADDAR.

THE preparation of 2-methoxy-1-naphthoic acid by the oxidation of 2-methoxy-1-naphthaldehyde with hydrogen peroxide or alkaline potassium permanganate (Rousset, *Bull. Soc. chim.*, 1896, **17**, 311) gave a very poor yield. The yield was increased when the oxidation with potassium permanganate was carried out in acetone solution. Bromination of the 2-methoxy-1-naphthoic acid in acetic acid solution gave mainly 1-bromo-2-methoxynaphthalene. This must be due to decarboxylation prior to bromination, since the same product was obtained by the action of bromine on 2-naphthyl methyl ether (cf. Davis, J., 1900, **77**, 38). The acid, therefore, was esterified, before bromination, with diazomethane, the yield being quantitative. The ester gave on bromination *methyl* 6-*bromo*-2-*methoxy*-1-*naphthoate.* The position of the bromine atom was determined by hydrolysing the bromination product to the free acid, which on decarboxylation with copper and quinoline gave a mixture of 6-bromo-2-naphthol and 6-bromo-2-methoxynaphthalene.

2-*Methoxy*-1-*naphthoic Acid.*—2-Methoxy-1-naphthaldehyde (35 g.; 1 mol.) was dissolved in acetone (400 c.c.) and mixed with sodium carbonate solution (20 g. in 100 c.c. of water), and potassium permanganate (30 g.; 1 mol.) slowly added at intervals. The excess of permanganate was destroyed with hydrogen peroxide, the solution filtered, and the manganese dioxide washed with a mixture of sodium carbonate solution and acetone. Acetone was removed, and the solution filtered from the unchanged material (2—3 g.). The acid crystallised from alcohol or benzene in colourless prisms, m. p. 176—177°. Rousset (*loc. cit.*) and Fuson, Farlow, and Stehman (*J. Amer. Chem. Soc.*, 1931, **53**, 4102) record m. p. 176°, whereas Froelicher and Cohen (J., 1922, **121**, 1657) give m. p. 133—134°. Yield, 26 g., *i.e.*, 68%.

Methyl 2-*Methoxy*-1-*naphthoate.*—The dry powdered acid (25 g.; 1 mol.) was slowly added to an ethereal solution of diazomethane (13 g.; 2·5 mols.), and the product was worked up in the usual way. The oily ester solidified on standing and then crystallised from ethyl or methyl alcohol in colourless prisms, m. p. 52—53°. Werner and Seybold (*Ber.*, 1904, **37**, 3661) give m. p. 52°. Yield, 85%.

Methyl 6-*Bromo*-2-*methoxy*-1-*naphthoate.*—Methyl 2-methoxy-1-naphthoate (10 g.; 1 mol.) was dissolved in acetic acid (75 c.c.), and the bromine solution (7·4 g., 1 mol., in 25 c.c. of acetic acid) added slowly while shaking. The solution, after being left for 5 hours in sunlight, was diluted with ice-cold water. The precipitate, repeatedly crystallised from dilute alcohol, gave *methyl* 6-*bromo*-2-*methoxy*-1-*naphthoate* in colourless leaflets, m. p. 112·5° (Found: C, 52·7; H, 3·7. $C_{13}H_{11}O_3Br$ requires C, 52·9; H, 3·7%). Yield, 37%.

6-*Bromo*-2-*methoxy*-1-*naphthoic Acid.*—The ester (6 g.) was refluxed with alcoholic sodium hydroxide (20 g. in 80 c.c. of 60% alcohol) for 1 hour. The precipitated acid, crystallised from benzene, gave 6-*bromo*-2-*methoxy*-1-*naphthoic acid* in colourless needles, m. p. 176—177° (Found: C, 51·3; H, 3·1; Br, 28·5. $C_{12}H_9O_3Br$ requires C, 51·2; H, 3·2; Br, 28·5%). Yield, nearly quantitative.

Decarboxylation of 6-*Bromo*-2-*methoxy*-1-*naphthoic Acid.*—A mixture of the acid (5·7 g.), quinoline (10 c.c.), and copper bronze (1·2 g.) was refluxed for 10 minutes and then extracted with benzene. The extract was washed with hydrochloric acid, and then with sodium hydroxide solution to remove phenolic substances. The phenolic product, repeatedly crystallised from benzene–light petroleum (b. p. 60—70°), gave 6-bromo-2-naphthol in colourless prismatic needles, m. p. 128°, undepressed on admixture with an authentic specimen (Found : Br, 36·2. Calc. for $C_{10}H_7OBr$: Br, 35·8%). The benzene solution was evaporated, and the residue extracted with light petroleum (b. p. 30—50°). The product, crystallised from methyl alcohol, gave 6-bromo-2-methoxynaphthalene in colourless needles, m. p. 108°, not depressed by an authentic specimen (Found : C, 56·0; H, 4·0; Br, 33·8. Calc. for $C_{11}H_9OBr$: C, 55·7; H, 3·8; Br, 33·7%).

1-Bromo-2-methoxynaphthalene was prepared by the bromination of 2-naphthyl methyl ether in glacial acetic acid solution (cf. Davis, *loc. cit.*). The product crystallised from light petroleum (b. p. 60—70°) in plates, m. p. 83—84°, identical with that of an authentic specimen.—FOUAD I UNIVERSITY, ABBASSIA, CAIRO, EGYPT. [*Received, August 5th,* 1941.]