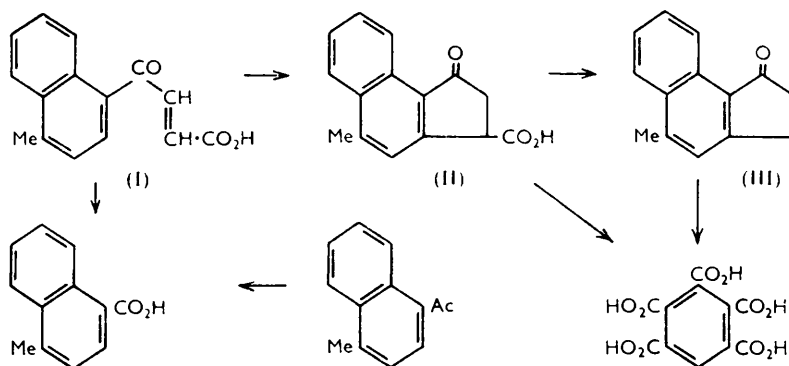


### 495. Reaction of 1- and 2-Methylnaphthalene with Maleic Anhydride.

By S. M. MAKAR, H. F. BASSILIOS, and A. Y. SALEM.

1- and 2-Methylnaphthalene react with maleic anhydride in ethylene chloride and in absence of excess of aluminium chloride to give methyl-naphthoylacrylic acids which are cyclised in molten aluminium chloride-sodium chloride at 100–120° by addition of the double bond to the naphthalene nucleus. The structure of the cyclised acids was established, and an easy and reliable method for oxidation of naphthalene derivatives to the carboxylic acids is described.

NAPHTHALENE reacts with maleic anhydride in presence of anhydrous aluminium chloride,<sup>1</sup> yielding  $\beta$ -1- and  $\beta$ -2-naphthoylacrylic acid which readily cyclise, in presence of excess of aluminium chloride, to 3-oxo-4 : 5-benzindane-1-carboxylic and 1-oxo-4 : 5-benzindane-3-carboxylic acid respectively by addition of the double bond to the 2-position in the former and to the 1-position in the latter case. The present paper extends these results to two methyl-naphthalenes. 1-Methylnaphthalene with a solution of the 1 : 2 maleic anhydride-aluminium chloride complex in ethylene dichloride readily affords  $\beta$ -(4-methyl-1-naphthoyl)acrylic acid (I) in a good yield. This acid is golden-yellow and decolorises dilute potassium permanganate solution and bromine in carbon tetrachloride. It provides 4-



methyl-1-naphthoic acid on oxidation with cold neutral permanganate solution, identical with that obtained by hypochlorite oxidation of 1-acetyl-4-methylnaphthalene. The acid (I) is cyclised in molten aluminium-sodium chloride at 100–120° to a saturated acid, which is proved to be 6-methyl-3-oxo-4 : 5-benzindane-1-carboxylic acid (II) by permanganate oxidation to benzenepentacarboxylic acid and not the tetracarboxylic acid, and by decarboxylation in quinoline in presence of copper chromite to 6-methyl-4 : 5-benzindan-3-one<sup>2</sup> (III). The indanone also affords benzenepentacarboxylic acid on permanganate oxidation.

Similarly,  $\beta$ -(6-methyl-2-naphthoyl)acrylic acid (IV) was obtained from 2-methylnaphthalene, but the crude product was a yellow sticky solid, probably owing to the presence of an isomeric acid. Crystallisation from benzene or acetic acid provided the pure acid (IV) in *ca.* 48% yield as golden-yellow needles, *m. p.* 169–170°. No isomer could be obtained from the mother-liquor, and permanganate oxidation gave only one methyl-naphthoic acid.

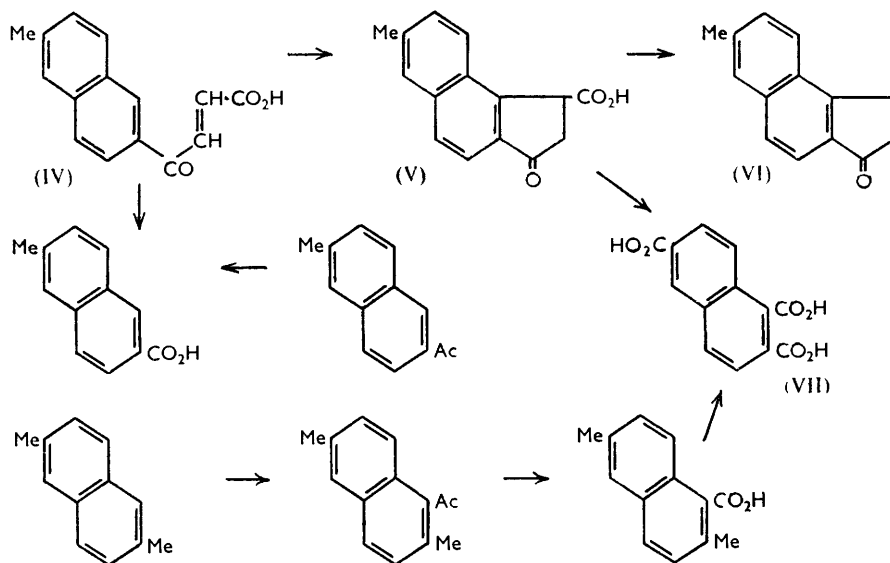
$\beta$ -(6-Methyl-2-naphthoyl)acrylic acid (IV) in molten sodium-aluminium chloride at 100–120° affords 3'-methyl-1-oxo-4 : 5-benzindane-3-carboxylic acid (V), oxidised by

<sup>1</sup> Baddeley, Makar, and Ivinson, *J.*, 1952, 3605.

<sup>2</sup> Mayer, Fritz, and Müller, *Ber.*, 1927, **60**, 2278.

nitric acid to naphthalene-1 : 2 : 6-tricarboxylic acid (VII). This acid is new, so it was prepared for comparison from 2 : 6-dimethylnaphthalene by acetylation in presence of aluminium chloride. The 1-acetyl-2 : 6-dimethylnaphthalene, thus obtained, was oxidised to the monocarboxylic acid by hypochlorite and thence by nitric acid to the previously obtained naphthalene-1 : 2 : 6-tricarboxylic acid.

Oxidation of alkyl and other side-chains in a naphthalene compound by nitric acid offers an easy and reliable method for production of naphthalenecarboxylic acids which have hitherto been difficult to prepare: mild oxidising agents such as potassium ferri-



cyanide react slowly and give poor yields of the carboxylic acid; strong oxidising agents such as potassium permanganate or chromic acid break the naphthalene nucleus. The procedure provided the corresponding naphthoic acid from 1- or 2-methylnaphthalene and the corresponding dicarboxylic acid from 2 : 6-dimethyl-, 1-acetyl-4-methyl-, and 2-acetyl-6-methyl-naphthalene. The known procedure for oxidation of benzene derivatives to benzenepolycarboxylic acids by nitric acid could not be applied to naphthalene derivatives (to give benzenepolycarboxylic acids by fission of the naphthalene nucleus); the product is frequently a polymer of a nitrated naphthalene derivative.

Like other oxo-4 : 5-benzindanecarboxylic acids, 3'-methyl-1-oxo-4 : 5-benzindane-3-carboxylic acid (V) is decarboxylated to 3'-methyl-1-oxo-4 : 5-benzindane (VI) in hot quinoline in presence of copper chromite.

#### EXPERIMENTAL

Analyses are by M. Sobotka, Graz, Austria.

$\beta$ -(4-Methyl-1-naphthoyl)acrylic Acid [4-(4-Methyl-1-naphthyl)-4-oxobut-2-enoic Acid].—Finely powdered aluminium chloride (60 g.) was gradually added to a stirred solution of maleic anhydride (24.5 g.) in anhydrous ethylene chloride (250 c.c.), and the mixture stirred for 0.5 hr. at room temperature. The resulting solution was then gradually decanted from undissolved aluminium chloride into a solution of 1-methylnaphthalene (35.5 g.) in ethylene chloride (100 c.c.). Reaction was instantaneous and the mixture, after 0.5 hr. at room temperature, was poured on ice and dilute hydrochloric acid. The organic solvent was removed by distillation and the yellow sticky residue, which solidified overnight, was separated, washed with water and dried under reduced pressure. Crystallisation from benzene provided  $\beta$ -(4-methyl-1-naphthoyl)acrylic acid (41 g.) as golden-yellow needles, m. p. 179—180° (Found: C, 75.2; H, 5.3%; equiv.,

239.  $C_{15}H_{12}O_3$  requires C, 75.0; H, 5.0%; equiv., 240). It afforded 4-methyl-1-naphthoic acid,<sup>3</sup> m. p. 174—175°, on oxidation with 0.1N-potassium permanganate in presence of 2N-sodium carbonate. The melting point was not depressed on admixture with 4-methyl-1-naphthoic acid obtained by oxidation of 1-acetyl-4-methylnaphthalene<sup>4</sup> with sodium hypochlorite.

$\beta$ -(6-Methyl-2-naphthoyl)acrylic Acid [4-(6-Methyl-2-naphthyl)-4-oxobut-2-enoic Acid].—This acid was the only identifiable product obtained from the interaction of 2-methylnaphthalene (1 mole) with maleic anhydride (1 mole) and aluminium chloride (2 moles) by the above procedure. The crude yellow sticky material (A) crystallised from acetic acid or 30 : 70 benzene-chloroform as golden-yellow needles, m. p. 169—170° (48% yield) (Found: C, 74.9; H, 5.2%; equiv., 240). Oxidation with cold potassium permanganate solution provided 6-methyl-2-naphthoic acid<sup>5</sup> which crystallised from acetic acid in colourless needles, m. p. and mixed m. p. 229—230°.<sup>5</sup>

Fractional crystallisation of a product (B) recovered from the mother-liquor of (A) by using acetic acid, chloroform, ethylene chloride, or ethanol provided in each case only impure samples of the same acrylic acid. Oxidation of product (B) with cold potassium permanganate solution provided an impure 6-methyl-2-naphthoic acid. Crystallisation of the semicarbazone also led to the same acrylic acid.

Isomerisation of  $\beta$ -(4-Methyl-1-naphthoyl)acrylic Acid.—This acid (12 g.) was gradually introduced into molten aluminium chloride (120 g.) and sodium chloride (18 g.) at 100—120°. The mixture was poured, after 1 hr., on ice and dilute hydrochloric acid. The pale brown product crystallised from acetic acid (charcoal), to give 6-methyl-3-oxo-4 : 5-benzindane-1-carboxylic acid (II) (8.2 g.) as pale yellow needles, m. p. 210° (Found: C, 75.0; H, 5.2%; equiv., 240.  $C_{15}H_{12}O_3$  requires C, 75.0; H, 5.0%; equiv., 240). Oxidation of this acid with boiling potassium permanganate solution in presence of sulphuric acid afforded benzenepentacarboxylic acid, m. p. and mixed m. p. 225—230° (decomp.) (pentamethyl ester,<sup>6</sup> m. p. and mixed m. p. 145—147°).

The acid (II) was decarboxylated by copper chromite in quinoline at 170—180°; the catalyst was removed by filtration, quinoline was separated by extraction with acid, and the residue was distilled with steam. It afforded 6-methyl-4 : 5-benzindane-3-one (III) as colourless needles,<sup>7</sup> m. p. 133—134° (Found: C, 85.8; H, 6.5. Calc. for  $C_{14}H_{12}O$ : C, 85.7; H, 6.1%) [semicarbazone, m. p. 266° (Found: N, 16.4.  $C_{15}H_{15}ON_3$  requires N, 16.6%)]. This indanone also provided benzenepentacarboxylic acid on vigorous oxidation with acid permanganate solution.

Isomerisation of  $\beta$ -(6-Methyl-2-naphthoyl)acrylic Acid.—By the procedure described above, this acid (10 g.) afforded 3'-methyl-1-oxo-4 : 5-benzindane-3-carboxylic acid (6.7 g.) which crystallised from acetic acid in pale yellow prisms, m. p. 204—205° (Found: C, 75.0; H, 5.3%; equiv., 239). It formed a 2 : 4-dinitrophenylhydrazone, did not decolorise cold permanganate or bromine in carbon tetrachloride, and was oxidised by 8% nitric acid solution (w/v) in a sealed tube at 150° to 1 : 2 : 6-naphthalenetetracarboxylic acid (VII), m. p. and mixed m. p. 298—300° (decomp.) (Found: C, 60.3; H, 3.2%; equiv., 87.  $C_{13}H_8O_8$  requires C, 60.0; H, 3.0%, equiv., 86.7). The trimethyl ester (prepared by ethereal diazomethane) crystallised from methanol in needles, m. p. and mixed m. p. 139—140° (Found: C, 63.5; H, 5.0.  $C_{16}H_{14}O_8$  requires C, 63.6; H, 4.7%). The authentic samples of 1 : 2 : 6-naphthalenetetracarboxylic acid and its trimethyl ester were prepared by acetylation of 2 : 6-dimethylnaphthalene.<sup>8</sup> The 1-acetyl-2 : 6-dimethylnaphthalene, m. p. 71—72° (picrate, m. p. 139—140°; semicarbazone, m. p. 193—194°), thus obtained was oxidised by sodium hypochlorite solution to 2 : 6-dimethyl-1-naphthoic acid which crystallised from acetic acid in colourless needles,<sup>9</sup> m. p. 203—204°. Oxidation of this acid with 8% nitric acid at 150° afforded the required tricarboxylic acid.

<sup>3</sup> Mayer and Sieglitz, *Ber.*, 1922, **55**, 1839.

<sup>4</sup> Dziejowski and Mahusinska, *Bull. intern. Acad. polon., A*, 1938, 316; *Brit. Chem. Abs.*, 1939, A (II), 23.

<sup>5</sup> Kon and Weller, *J.*, 1939, 792.

<sup>6</sup> Ruzicka and Rudolph, *Helv. Chim. Acta*, 1927, **10**, 919; Jacobsen, Stromberg, and Peterson, *J. Amer. Chem. Soc.*, 1949, **71**, 1384; Fleischer and Retze, *Ber.*, 1923, **56**, 228.

<sup>7</sup> Mayer, Fritz, and Müller, *Ber.*, 1927, **60**, 2278.

<sup>8</sup> Clar, Wallenstein, and Avenarius, *Ber.*, 1929, **62**, 950; Dziejowski, Stec, and Zagala, *Bull. intern. Acad. polon., A*, 1928, 324.

<sup>9</sup> Lesser and Gad, *Ber.*, 1927, **60**, 244.

It was also obtained by direct oxidation of 1-acetyl-2 : 6-dimethylnaphthalene with 8% nitric acid.

Like other indanonecarboxylic acids,<sup>10</sup> 3'-methyl-1-oxo-4 : 5-benzindane-3-carboxylic acid (V) was decarboxylated by copper chromite in quinoline; it gave 3'-methyl-4 : 5-benzindane-3-one which crystallised from hot water in colourless needles, m. p. 112—113° (Found: C, 85.6; H, 6.4%) [semicarbazone, m. p. 276° (decomp.) (Found: N, 16.1%)].

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<sup>10</sup> Baddeley and Makar, *J.*, 1952, 3289, 3605.

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