688. *Interaction of Naphthalene and Maleic Anhydride through the Agency of Aluminium Chloride.*

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A mixture of β-1- and β-2-naphthoylacrylic acids is obtained in good yield only in the absence of excess of dissolved or of solid aluminium chloride; the acids are readily separated by crystallisation from ethylene chloride. They isomerise to 3-keto-4 : 5-benzindane-1-carboxylic acid (III) and 1-keto-4 : 5-benzindane-3-carboxylic acid (IV) respectively in the presence of hydrogen chloride and excess of aluminium chloride. In the past, the former has been mistaken for 3-ketoperinaphthane-1-carboxylic acid (VII) and also for β-2-naphthoylacrylic acid; an authentic sample of β-2-naphthoylacrylic acid has not been obtained previously. Decarboxylation of the ketobenzindanecarboxylic acids affords ready access to 4 : 5-benzindan-3- and -1-one (V and VI). The reactions are discussed.

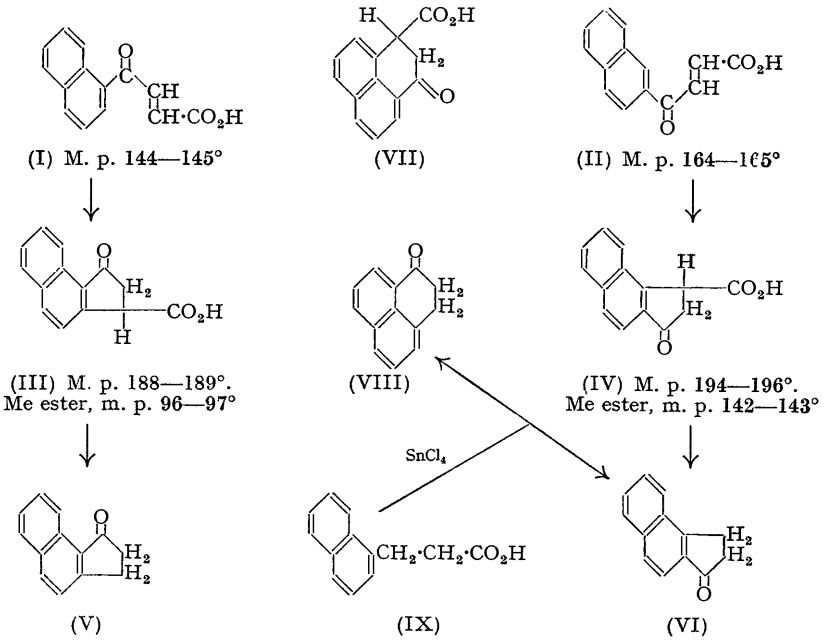
The precautions necessary to avoid side-reactions and thus to obtain good yields of β-aroylacrylic acids by interaction of an aromatic hydrocarbon with maleic anhydride in the presence of aluminium chloride have been enumerated in an earlier paper (*J.*, 1952, 3289); they demand absence of excess of, or undissolved, chloride and have now been successfully applied in the preparation of β-1- and β-2-naphthoylacrylic acids. Whereas acid chlorides and anhydrides of monobasic acids, when fully engaged by aluminium chloride in methylene or ethylene chloride as solvent, effect mainly α-substitution in naphthalene (*J.*, 1949, 998), yet phthalic, succinic and maleic anhydrides, under similar conditions, provide considerable β-substitution; this difference will be discussed in a further communication. The resulting mixtures of keto-acids can be separated by fractional crystallisation (*e.g.*, see Barnett and Campbell, *J.*, 1935, 1031) or by fractional precipitation by gradual addition of mineral acid to an aqueous solution of the sodium salts (see, *e.g.*, Newman, Taylor, Hodgson, and Garrett, *J. Amer. Chem. Soc.*, 1947, **69**, 1784).

The complex of maleic anhydride with aluminium chloride (2 mols. as $AlCl_3$), in solution in methylene or ethylene chloride, provides a ready reaction when decanted from undissolved halide into a solution of naphthalene in the same solvent; the resulting β-1- and β-2-naphthoylacrylic acids are conveniently separated by recrystallisation from ethylene chloride. Each is golden-yellow, affords a red solution in concentrated sulphuric acid, decolorises bromine in carbon tetrachloride, and is oxidised to the corresponding naphthoic acid by cold permanganate.

β-2-Naphthoylacrylic acid (II), in a molten mixture of aluminium and sodium chlorides at *ca.* 100°, affords a saturated isomeric acid which melts with decomposition at 194—196°; the following evidence shows it to be 1-keto-4 : 5-benzindan-3-carboxylic acid (IV). The product of decomposition at the melting point has the same properties, m. p. 120—121° and oxime of m. p. 226—227°, as has one of the products of interaction of β-1-naphthylpropionic acid (IX) and anhydrous stannic chloride (Cook and Hewitt, *J.*, 1934, 365) and is 4 : 5-benzindan-1-one (VI) as reduction provides 4 : 5-benzindane which was identified by its picrate and addition compound with 1 : 3 : 5-trinitrobenzene (*J.*, 1952, 807); Cook and Hewett (*loc. cit.*) were uncertain whether their product was (VI) or perinaphthan-1-one (VIII).

Similarly, β-1-naphthoylacrylic acid (I) affords a saturated isomeric acid, m. p. 188—189°; this provides 4 : 5-benzindan-3-one (V) on decarboxylation and is therefore 3-keto-4 : 5-benzindan-1-carboxylic acid (III). The isomerisation of β-1-naphthoylacrylic acid through the agency of aluminium chloride at 120—140° has been described previously (B.P. 273,321/1927; U.S.P., 1,702,002/1929); the product is identical with ours, but has been incorrectly referred to as dihydrophenalone-7-carboxylic acid (3-ketoperinaphthane-1-carboxylic acid) (VII) (Thomas, "Anhydrous Aluminium Chloride in Organic Chemistry," Reinhold Publ. Corp., New York, 1941, p. 492). The above isomerisations of β-1- and β-2-naphthoylacrylic acids have also been realised in the presence of hydrogen chloride and

excess of aluminium chloride in solutions in methylene chloride at room temperature (see Experimental); excess of or undissolved aluminium chloride must therefore be avoided, as in our procedure, in the preparation of naphthoylacrylic acids. In the past this precaution has not been taken and, in consequence, some confusion has arisen; we have been obliged to repeat much of the earlier work.



Oddy (*J. Amer. Chem. Soc.*, 1923, **45**, 2156) gradually added powdered aluminium chloride to a solution of naphthalene and maleic anhydride in benzene and subsequently heated the mixture at 60—70° for four hours. A product, m. p. 189—190° (methyl ester, m. p. 94—95°), was isolated and did not decolorise bromine in acetic acid solution; it is (III), but has been referred to as β-2-naphthoylacrylic acid (II). A small amount of a substance, m. p. 158—159°, was also isolated but was not investigated; it was an impure sample of β-2-naphthoylacrylic acid (m. p. 164—165°). Bogert and Ritter (*ibid.*, 1925, **47**, 526) modified Oddy's procedure; the temperature was kept below 20° during the addition of the chloride and the reaction mixture was refluxed on the steam-bath until evolution of hydrogen chloride was complete. The product was crystallised from toluene and afforded two acids, m. p. 150·2° and 188° respectively, which are referred to as β-1- and β-2-naphthoylacrylic acid respectively. The former is impure β-2-naphthoylacrylic acid and melts at 160—162° after further recrystallisation from ethylene chloride; the latter is (III). Preparation of β-1-naphthoylacrylic in nitrobenzene as solvent has been described (U.S.P. 1,702,002) and we have confirmed it; the yield is 35% and we were unable to isolate any β-2-naphthoylacrylic acid.

As ease of cyclisation of β-aroylacrylic acids is directly related to ease of electron release from the aromatic ring (*e.g.*, the rate of reaction increases with the number of methyl groups attached to this ring), and as the ketone group in β-1-naphthoylacrylic acid ensures that the electron density at the 2- is less than that at the 8-position, ring closure in this instance might be expected to be effected at the latter. It occurs exclusively at the 2-position, as does ring closure of α-naphthyl vinyl ketones (Mayer and Müller, *Ber.*, 1927, **60**, 2278), and appears all the more remarkable by comparison with the cyclisation of β-1-naphthylpropionic acid which occurs at the 8- as well as at the 2-position even though the latter is not encumbered by a carbonyl group in the 1-position. We have observed (*loc. cit.*) that cyclisation of β-aroylacrylic acids is greatly assisted by an *o*-methyl group and believe

that this is due to steric interaction between bulky *o*-substituent on the one hand and the carbonyl group in association with aluminium chloride on the other; this would hinder resonance interaction between the carbonyl group and the aromatic ring and render the latter more susceptible to electrophilic attack. It is possible that the 8-position in β-1-naphthoylacrylic acid acts as a bulky *o*-substituent and aids ring closure at the 2-position.

Isomerisation of β-2-naphthoylacrylic acid to 1-keto-4 : 5-benzindane-3-carboxylic acid is consistent with the formation of 1 : 2-benzanthraquinone from *o*-2-naphthoylbenzoic acid (Brand and Trebing, *Ber.*, 1923, **56**, 2547); ring closure in such instances usually occurs at the 1- rather than at the 3-position (cf. *J.*, 1950, 994; Buckley, *J.*, 1945, 561, 564).

Experimental

β-1- *and* β-2-*Naphthoylacrylic Acids.*—Aluminium chloride (280 g.) was gradually added to a stirred solution of maleic anhydride (98 g.) in methylene chloride (300 c.c.). The mixture was stirred for 0·5 hour and the solution was slowly decanted from a little undissolved aluminium chloride into a solution of naphthalene (128 g.) in methylene chloride (150 c.c.); reaction was very fast and the product was poured on ice. The organic layer was separated and shaken with concentrated hydrochloric acid; it deposited yellow crystals (108 g.), m. p. 135—155°, which were separated. The filtrate slowly deposited yellow crystals (56 g.), m. p. 120—130°, which afforded golden-yellow needles of β-1-naphthoylacrylic acid, m. p. 144—145° (Found : C, 74·2; H, 4·6. Calc. for $C_{14}H_{10}O_3$: C, 74·3; H, 4·4%), from glacial acetic acid or ethylene chloride. This product afforded α-naphthoic acid, m. p. and mixed m. p. 160—161°, by oxidation with potassium permanganate.

β-2-*Naphthoylacrylic acid* was the main constituent of the first batch of crystals and crystallised from ethylene chloride in golden-yellow plates, m. p. 164—165° (Found : C, 74·5; H, 4·6%). This, like β-naphthoic acid, is readily purified since its sodium salt is sparingly soluble in sodium carbonate solutions; it afforded β-naphthoic acid, m. p. and mixed m. p. 181—183°, by oxidation with permanganate.

Isomerisation of β-1-*Naphthoylacrylic Acid.*—This acid (9 g.) was gradually added to a molten mixture of aluminium chloride (90 g.) and sodium chloride (13·5 g.) at 115°. After an hour, the mixture was poured into ice and dilute hydrochloric acid, and the pale brown product was separated by filtration and extracted with boiling water; the extracts deposited colourless needles of 3-keto-4 : 5-benzindane-1-carboxylic acid (5·9 g.), m. p. 188—189° (Found : C, 74·6; H, 4·1%; equiv., 225. Calc. for $C_{14}H_{10}O_3$: C, 74·3; H, 4·4%; equiv., 226). The methyl ester crystallised from methanol in long colourless needles, m. p. 96—97° (Found : C, 74·6; H, 5·0. Calc. for $C_{15}H_{12}O_3$: C, 75·0; H, 5·0%). The acid 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 4 : 5-benzindan-3-one, m. p. and mixed m. p. 101—103°.

Isomerisation of β-2-*Naphthoylacrylic Acid.*—Procedure was similar to that described above. The acid (5 g.) afforded 1-*keto*-4 : 5-*benzindan*-3-*carboxylic acid* (2·5 g.) which crystallised from glacial acetic acid in colourless crystals, m. p. 194—196° (decomp.) (Found : C, 74·2; H, 4·6%). The yield improved from 50 to 64% when isomerisation was effected at 90—95° for 1·5 hours. The methyl ester separated from methanol in needles, m. p. 142—143° (Found : C, 74·8; H, 4·9%). The acid readily decomposed at 200° and afforded 4 : 5-benzindan-1-one which crystallised from methanol in pale yellow needles, m. p. 120—121°. With concentrated sulphuric acid it provided a yellow solution with a green fluorescence. Reduction by the Clemmensen method afforded 4 : 5-benzindane (picrate, m. p. and mixed m. p. 108—109°; addition compound with 1 : 3 : 5-trinitrobenzene having m. p. and mixed m. p. 119—120°).

The isomerisations described above also occur in the presence of hydrogen chloride and excess of aluminium chloride in methylene chloride at room temperature.

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