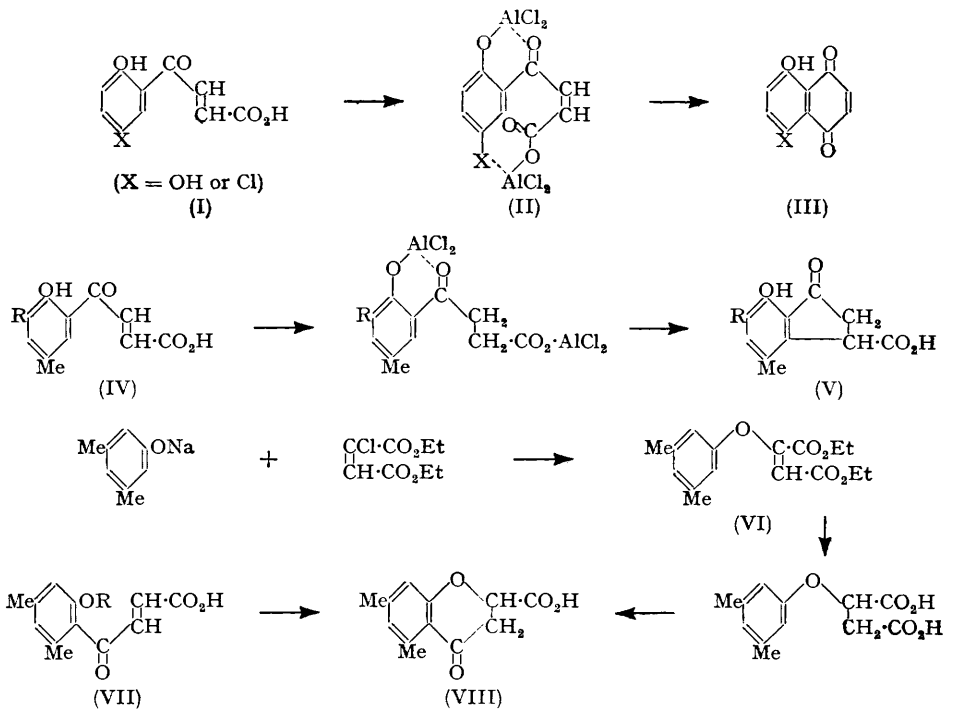
811. *Interaction of β-Aroylacrylic Acids and Aluminium Chloride.*

By G. Baddeley, S. M. Makar, and (Miss) M. G. Ivinson.

Whereas β-2 : 5-dihydroxy- and β-5-chloro-2-hydroxy-benzoylacrylic acid and their derivatives undergo intramolecular acylation (I ⟶ III), cyclisation of β-2-hydroxy-5-methyl- and β-2-hydroxy-3 : 5-dimethyl-benzoylacrylic acid is effected by intramolecular alkylation (IV ⟶ V); an explanation of this difference is offered.

β-2-Hydroxy-4 : 5-dimethylbenzoylacrylic acid is comparatively stable and β-2-hydroxy-4 : 6-dimethylbenzoylacrylic acid gives 5 : 7-dimethyl-4-oxochroman-2-carboxylic acid (VIII).

Quinol and its derivatives combine with maleic anhydride in the presence of excess of aluminium chloride to provide naphthazarins (III; X = OH) (Zahn and Ochwat, *Annalen*, 1928, **462**, 72; Winzer, *J.*, 1935, 336; Macbeth, Price, and Winzer, *J.*, 1935, 1982; Kuroda and Wada, *Proc. Imp. Acad. Japan*, 1936, **12**, 239; Brockmann and Müller, *Annalen*, 1939, **540**, 51), and a similar reaction occurs when quinol is replaced by 4-chloro-1-naphthol (Zahn and Ochwat, *loc. cit.*; Walden and Poppe, *Annalen*, 1937, **527**, 190) or by *p*-chlorophenol (see Experimental section). Although β-2 : 5-dihydroxyaroyl- and β-5-chloro-2-hydroxy-aroyl-acrylic acids (I; X = OH and Cl respectively) have not been isolated from the



products of these reactions, it is probable that they are intermediates since it is now shown that they undergo intramolecular acylation (I ⟶ III): β-2 : 5-dimethoxybenzoylacrylic acid was obtained from quinol dimethyl ether and maleic anhydride in methylene chloride and reacted with excess of aluminium chloride (*a*) in ethylene chloride at 80° and (*b*) at 200°, to give β-2-hydroxy-5-methoxybenzoylacrylic acid (I; X = OMe) and naphthazarin respectively. Similarly, β-5-chloro-2-methoxybenzoylacrylic acid gave β-5-chloro-2-hydroxybenzoylacrylic acid (I; X = Cl) and 5-chloro-8-hydroxy-1 : 4-naphthaquinone (III; X = Cl).

Other β-aroylacrylic acids afford 3-oxoindane-1-carboxylic acids by intramolecular alkylation (*e.g.*, see IV ⟶ V) (Baddeley, Holt, and Maker, *J.*, 1952, 3289); β-2-hydroxy-

5-methylbenzoyl- and β-2-hydroxy-3 : 5-dimethylbenzoyl-acrylic acids (IV; R = H and Me respectively), which have now been obtained by reaction of maleic anhydride with *p*-cresol and *m*-4-xylenol respectively, behave in this way. This is not a general reaction of β-*o*-hydroxyaroylacrylic acids: β-2-hydroxy-4 : 5-dimethylbenzoylacrylic acid does not cyclise and β-2-hydroxy-4 : 6-dimethylbenzoylacrylic acid (VII; R = H), which is one of the products of interaction of *m*-5-xylenol and maleic anhydride, affords 5 : 7-dimethyl-4-oxochroman-2-carboxylic acid (VIII). This acid is the other product of the above interaction and was identified by comparison with an authentic sample obtained from the aryloxyfumaric acid (VI); it is unaffected by fusion with excess of reagent and is also obtained when β-6-ethoxy-2 : 4-dimethylbenzoylacrylic acid (VII; R = Et), in ethylene chloride at room temperature, stands in contact with excess of reagent. Similar ring closures, *e.g.*, 2 : 5 : 7-trimethylchromanone from 6-methoxy-2 : 4-dimethylphenyl propenyl ketone, have been reported by Auwers (*Annalen*, 1920, **421**, 1).

The following possibilities may determine whether ring-closure is effected as in (I ⟶ III) or as in (IV ⟶ V).

(*a*) *trans*-β-Aroylacrylic acids from interaction of maleic anhydride and aromatic compounds (Lutz, *J. Amer. Chem. Soc.*, 1930, **52**, 3405; 1933, **55**, 1168, 1593; *J. Org. Chem.*, 1941, **6**, 77) may be converted by aluminium chloride–hydrogen chloride into their *cis*-isomers (see Dippy, McGhie, and Young, *Chem. and Ind.*, 1952, 195) which, only when conserved by formation of a chelate ring as in (II), provide intramolecular acylation (II ⟶ III).

(*b*) Electromeric release of electrons by an oxyaluminochloride group (–O·$AlCl_2$ derived from –OH + $AlCl_3$ ⟶ –O·$AlCl_2$ + HCl) and a chlorine atom, when these are present as substituents in the benzene ring, is more fully developed and therefore of greater directing influence in nuclear acylation than in nuclear alkylation: resonance interaction of these substituents and carbonyl group in the products of *ortho*-acylation facilitates this reaction by occurring, though to a smaller extent, in the transition state; there is no corresponding resonance stabilisation of the transition state of *ortho*-alkylation. This difference between the two reactions also explains why acylation of *p*-cresol and *p*-chlorotoluene occurs *ortho* to the oxyaluminochloride group and chlorine atom respectively whereas alkylation of *p*-cresol occurs *ortho* to the methyl group (*J.*, 1944, 330). In keeping with the argument, bromination of *p*-cresol in the presence of aluminium chloride resembles alkylation (Baddeley and Plant, *J.*, 1943, 525).

Experimental

β-*Aroylacrylic Acids*.—(*a*) A warm solution of maleic anhydride (1 mol.) in methylene chloride was saturated with finely divided aluminium chloride and decanted into a solution of aromatic ether or diether in methylene chloride. The mixture was boiled under reflux until evolution of hydrogen chloride was comparatively slow and was then decomposed with ice. The organic layer was separated, washed with dilute mineral acid, and extracted repeatedly with sodium hydrogen carbonate solution. Acidification of the extracts gave the required acid which was isolated and recrystallised from acetic acid. The following β-aroylacrylic acids were prepared in this way:

β-2 : 5-Dimethoxybenzoyl-, m. p. 147° (Papa *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 3356); β-2 : 4-dimethoxybenzoyl-, m. p. 190—192° (*idem*, *ibid.*; Rice, *ibid.*, 1931, **53**, 3156); β-3 : 4-dimethoxybenzoyl-, m. p. 178° (Dave and Nargund, *Brit. Abs.*, 1939, A II, 267); β-6-*ethoxy*-2 : 4-*dimethylbenzoyl*-, golden-yellow needles, m. p. 175—176° (Found: C, 67·8; H, 6·4%; equiv., 246. $C_{14}H_{16}O_4$ requires C, 67·7; H, 6·5%; equiv. 248); and β-5-*chloro*-2-*methoxybenzoyl*-, pale yellow needles, m. p. 141—142° (Found: C, 54·9; H, 3·6; Cl, 15·0. $C_{11}H_9O_4Cl$ requires C, 54·9; H, 3·7; Cl, 14·8%). The last acid was demethylated by aluminium chloride (3 mol.) in boiling ethylene chloride and afforded β-5-*chloro*-2-*hydroxybenzoylacrylic acid* as yellow plates, m. p. 196—198° (Found: C, 52·9; H, 3·1; Cl, 16·4. $C_{10}H_7O_4Cl$ requires C, 53·0; H, 3·1; Cl, 15·7%). Similarly, β-2 : 5-dimethoxybenzoyl- afforded β-2-*hydroxy*-5-*methoxybenzoyl-acrylic acid* as red needles, m. p. 196—198° (Found: C, 59·4; H, 4·3. $C_{11}H_{10}O_5$ requires C, 59·5; H, 4·5%).

(*b*) A solution of maleic anhydride (1 mol.) and another of aromatic compound, each in ethylene chloride, were saturated with aluminium chloride and brought together. The mixture was set aside for a day at room temperature, or was warmed gently until reaction was complete,

and decomposed in the usual way. The solid product was isolated and recrystallised from acetic acid. The following β-aroylacrylic acids were prepared in this way:

β-2-*Hydroxy*-5-*methylbenzoyl*-, golden-yellow needles, m. p. 173—174° (Found: C, 63·8; H, 5·0%; equiv., 205. $C_{11}H_{10}O_4$ requires C, 64·0; H, 4·9%; equiv., 206); β-3 : 4-*dihydroxybenzoyl*-, needles, m. p. 218—220° (decomp.) (Found: C, 57·2; H, 4·1. $C_{10}H_8O_5$ requires C, 57·7; H, 3·9%). β-2-*Hydroxy*-4 : 5-*dimethylbenzoylacrylic acid*, yellow needles, m. p. 192—193° (Found: C, 65·1; H, 5·2%; equiv., 220. $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·5%; equiv., 220), was obtained in better yield when the three components were brought together in molecular proportions; it absorbed hydrogen (1 mol.), affording β-2-*hydroxy*-4 : 5-*dimethylbenzoylpropionic acid*, m. p. 153—154° (Found: C, 64·7; H, 6·1. $C_{12}H_{14}O_4$ requires C, 64·9; H 6·3%) which, by admixture, did not depress the m. p. of the product of interaction of *o*-4-xylenol and succinic anhydride. β-2-*Hydroxy*-3 : 5-*dimethylbenzoylacrylic acid*, red needles, m. p. 134—138° (Found: C, 65·4; H, 5·5) gave (i) 2-hydroxy-3 : 5-dimethylacetophenone, m. p. and mixed m. p. 53—54°, when boiled with dilute alkali and (ii) β-2-*hydroxy*-3 : 5-*dimethylbenzoylpropionic acid*, m. p. 147—148°, by hydrogenation (Found: C, 64·7; H, 6·3%; equiv., 221. $C_{12}H_{14}O_4$ requires equiv., 222). This acid was also prepared from *m*-4-xylenol and succinic anhydride. β-2-*Hydroxy*-4 : 6-*dimethylbenzoylacrylic acid*, yellow needles, m. p. 186—187° (Found: C, 65·2; H, 5·4%; equiv., 218), represented only 33% of the product of reaction; the remainder was 5 : 7-*dimethyl*-4-*oxochroman*-2-*carboxylic acid* and crystallised from acetic acid in colourless needles, m. p. and mixed m. p. 147—148° (Found: C, 65·6; H, 5·4%; equiv., 220) and was obtained in 45% yield when equimolecular proportions of the three components were used; it was recovered after fusion with aluminium chloride–sodium chloride at 150°. This acid gave no colour with ferric chloride; a solution in alkali at 60° was unaffected by addition of methyl sulphate; in methanolic hydrogen chloride it gave an alkali-insoluble *methyl* ester which separated from methanol in long needles, m. p. 67—68° (Found: C, 66·3; H, 5·9. $C_{13}H_{14}O_4$ requires C, 66·6; H, 6·0%); it was decarboxylated with copper chromite in quinoline and the product, 5 : 7-dimethylchromanone, gave a bromo-derivative, m. p. 158—159° (Found: Br, 65·0%).

Interaction with Aluminium Chloride.—This chloride (10 g.) and sodium chloride (1·5 g.) (both per g. of organic acid) were powdered together and heated by an oil-bath to 140°. The melt was continuously stirred in an atmosphere of dry nitrogen, the organic acid was gradually added, and the mixture was brought to a selected temperature. After a selected time the mixture was cooled and decomposed by ice, and the organic material was separated and purified:

(*a*) β-2 : 5-Dimethoxybenzoylacrylic acid, after 1 hr. at 200°, gave naphthazarin which sublimed at 160—170°/0·1 mm.; this was reduced by stannous chloride to dihydronaphthazarin, m. p. 154° (Wheeler and Edwards, *J. Amer. Chem. Soc.*, 1916, **38**, 387), and oxidised in sodium hydroxide solution (0·5%) by air to naphthapurpurin, m. p. 222° (Kuroda, *Proc. Imp. Acad. Japan*, 1939, **15**, 226).

(*b*) β-5-Chloro-2-hydroxybenzoylacrylic acid, after 2 hr. at 200°, gave 5-chloro-8-hydroxy-1 : 4-naphthaquinone, m. p. 199° (Guareschi, *Ber.*, 1886, **19**, 1156) (Found: C, 57·6; H, 2·4; Cl, 17·2. Calc. for $C_{10}H_5O_3Cl$: C, 57·5; H, 2·4; Cl, 17·0%). It depressed the m. p. of the starting material on admixture.

(*c*) β-2-Hydroxy-5-methylbenzoylacrylic acid, after 1 hr. at 180°, gave 4-*hydroxy*-7-*methyl*-3-*oxoindane*-1-*carboxylic acid*, prisms, m. p. 149—150°, from water (Found: C, 63·9; H, 5·0%; equiv., 206. $C_{11}H_{10}O_4$ requires C, 64·0; H, 4·9%; equiv., 206). It gave a dark blue colour with ferric chloride and was decarboxylated to 7-hydroxy-4-methylindanone, m. p. 109—110° [*p*-nitrophenylhydrazone, m. p. 296—298° (Auwers, *Ber.*, 1911, **44**, 3692); acetate m. p. 108—109°; and benzoate, m. p. 124—125° (Auwers, Hilliger, and Wulf, *Annalen*, 1922, **429**, 190)].

(*d*) β-2-Hydroxy-4 : 6-dimethylbenzoylacrylic acid, after 1 hr. at 130°, gave 5 : 7-dimethyl-4-oxochroman-2-carboxylic acid. (This isomerisation was also effected in warm ethylene chloride by aluminium chloride–hydrogen chloride.)

5 : 7-*Dimethyl*-4-*oxochroman*-2-*carboxylic Acid* (VIII).—A mixture of the sodium salt of *m*-5-xylenol and ethyl chlorofumarate in excess of the xylenol, after 3 hr. at 200°, gave the aryloxyfumarate (VI), b. p. 166°/0·08 mm.; hydrolysis gave 3 : 5-*dimethylphenoxyfumaric acid* which separated from acetic acid in needles, m. p. 237—239° (Found: C, 61·0; H, 5·1%; equiv., 117. $C_{12}H_{12}O_5$ requires C, 61·0; H, 5·1%; equiv. 118); and reduction with sodium amalgam gave the corresponding succinic acid from which (VIII) was obtained by the action of cold concentrated sulphuric acid.

FACULTY OF TECHNOLOGY, UNIVERSITY OF MANCHESTER. [*Received, September 4th*, 1953.]