629. *The Preparation and Isomerisation of β-Aroylacrylic Acids.*

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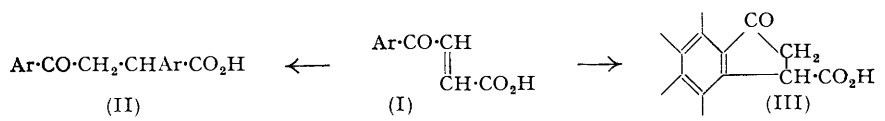
Experimental procedure for the preparation of β-aroylacrylic acids by interaction of maleic anhydride and an aromatic hydrocarbon through the agency of aluminium chloride is discussed. Several of these acids have been isomerised to 3-ketoindane-1-carboxylic acids; ring closure of β-2-alkylaroylacrylic acids is sometimes accompanied by intramolecular migration of the 2-alkyl group. Decarboxylation of these ketoindanecarboxylic acids affords a valuable method of preparing indan-1-one derivatives.

MALEIC ANHYDRIDE reacts with aromatic hydrocarbons at room temperature in the presence of aluminium chloride (2 mols. as $AlCl_3$), to provide β-aroylacrylic acids (I); these have the *trans*-configuration (Lutz, *J. Amer. Chem. Soc.*, 1930, **52**, 3405; 1933, **55**, 1168, 1593; *J. Org. Chem.*, 1941, **6**, 77). Other reactions can and frequently do interfere, but they are avoided when practical procedure is based on the following considerations: (i) β-Aroylacrylic acids, behaving like αβ-unsaturated ketones, combine with aromatic hydrocarbons in the presence of hydrogen chloride and excess of aluminium chloride to provide β-aroyl-α-arylpropionic acids (II) (Pummerer and Buchta, *Ber.*, 1936, **69**, 1005). (ii) Even when excess of aromatic hydrocarbon is avoided, excess of aluminium chloride is detrimental as it affords less pure β-aroylacrylic acids and, in some instances, isomeric products; for

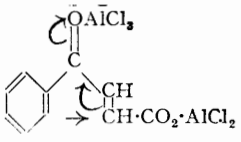
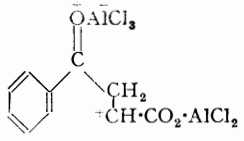


example, when durene, maleic anhydride, and aluminium chloride in the molecular ratio 1 : 1 : 4 are kept at room temperature for two days, 3-keto-4 : 5 : 6 : 7-tetramethylindane-1-carboxylic acid (X) is obtained in 85% yield (see Experimental section) by way of the intermediate β-2 : 3 : 5 : 6-tetramethylbenzoylacrylic acid (IX). The acid (IX), in methylene chloride, is not affected by excess of aluminium chloride if hydrogen chloride is swept from the solution by a stream of dry nitrogen, but (*a*) when hydrogen chloride is not removed, and especially (*b*) when the solution is saturated with dry hydrogen chloride, it affords the above indanone derivative acid in yields of (*a*) 20% and (*b*) 90% after one day. None of these complications arises if excess of aluminium halide, *i.e.*, more than 2 mols. per mol. of maleic anhydride, is avoided. β-Aroylacrylic acids are best prepared, therefore, by combining maleic anhydride with aluminium chloride (2 mols.) in methylene or ethylene chloride, decanting the solution from any undissolved aluminium chloride, and adding the aromatic hydrocarbon (1 mol.); yields are excellent. The success of this method rests on the high solubility of the complex $(CH{\cdot}CO)_2O,2AlCl_3$ and the low solubility of aluminium chloride in methylene or ethylene chloride; they enable the complex to be readily formed and easily freed from excess of aluminium halide. Fieser and Fieser (*J. Amer. Chem. Soc.*, 1935, **57**, 1679) obtained improved yields of β-aroylacrylic acids by employing trichloroethylene in place of carbon disulphide or nitrobenzene as solvent; their procedure, in which powdered aluminium chloride is added to a solution of aromatic hydrocarbon and maleic anhydride, exposes the reaction mixture to the action of the solid chloride and, therefore, cannot be recommended. Similar considerations have been applied in this laboratory to the preparation of β-aroylpropionic acids by interaction of succinic anhydride, aluminium halide, and aromatic hydrocarbons; this work will be reported later.

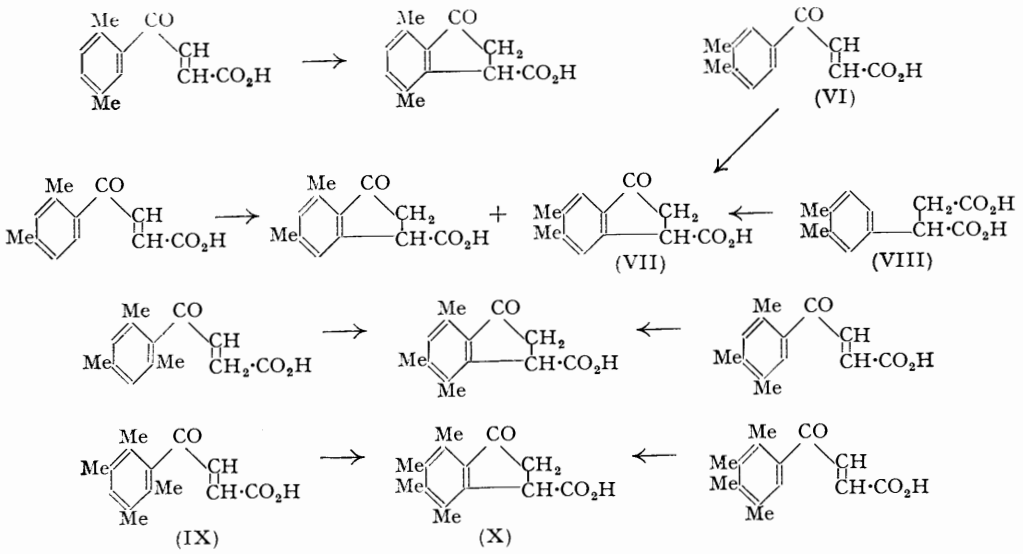
The yellow β-aroylacrylic acids obtained by interaction of maleic anhydride with toluene, *o*-, *m*-, and *p*-xylene, mesitylene, *pseudo*cumene, prehnitene, and durene severally afford colourless, isomeric 3-ketoindane-1-carboxylic acids (III) which do not decolorise cold aqueous permanganate or bromine in carbon tetrachloride. For example, β-3 : 4-dimethylbenzoylacrylic acid (VI) affords an isomeric acid which provides 5 : 6-dimethylindan-1-one on decarboxylation and is identical with the product of interaction of 3 : 4-dimethylphenylsuccinic acid (VIII) and sulphuric acid; it is, therefore, 3-keto-5 : 6-

dimethylindane-1-carboxylic acid (VII); Speight, Stevenson, and Thorpe (*J.*, 1924, 2190) showed that 3-ketoindane-1-carboxylic acid is obtained from phenylsuccinic acid and sulphuric acid.

We are unaware of any previous reference to the conversion of β-aroylacrylic acids into 3-ketoindane-1-carboxylic acids; it resembles the conversion of aryl vinyl ketones into indanones by the action of sulphuric acid or of aluminium and hydrogen chlorides in boiling carbon disulphide (*e.g.*, Smith and Pritchard, *J. Amer. Chem. Soc.*, 1940, **62**, 771) and is the intramolecular counterpart of (I ⟶ II). The electronic displacements can be represented as in (IV), but the dependence of the reaction on the presence of hydrogen chloride indicates that ring closure is preceded by addition of a proton to form a carbonium ion (V). As

(IV)   (V)

expected, ease of ring closure increases with the number of alkyl groups attached to the benzene ring: whereas β-benzoylacrylic acid does not cyclise and the 4-methyl derivative does so to a small extent, higher homologues provide ketoindanecarboxylic acids in good yield. Recently we reported (*J.*, 1952, 2415) that ring closure of *o*-2-alkylaroylbenzoic acids through the agency of aluminium chloride is sometimes *preceded* by intramolecular migration of the 2-alkyl group and that this enables even *o*-2 : 6-dialkylaroylbenzoic acids to afford anthraquinone derivatives. Similar migrations occur in β-aroylacrylic acids but in no instance has an isomeric β-aroylacrylic acid been isolated; ring closure has always intervened. Our results are formulated in the annexed scheme.



Isomerisation of aryl ketones is a consequence of steric interaction between an acyl group and a bulky *ortho*-substituent as this partly inhibits mesomeric release of electrons from the aromatic ring to the acyl group and thereby makes the former more susceptible to attack by a proton. This does not occur in derivatives of indan-1-one because the five-membered ring ensures (i) comparatively little steric interaction between carbonyl group and a bulky substituent in the 7-position and (ii) coplanarity of the benzene ring and the carbonyl group (*J.*, 1944, 232; *Nature*, 1939, **144**, 444); therefore, migration of an alkyl group may precede or accompany the cyclisation of a β-aroylacrylic acid but cannot occur once the 3-ketoindane-1-carboxylic acid is formed.

All the above 3-ketoindane-1-carboxylic acids are readily decarboxylated by copper chromite in quinoline at 160—190° and afford the corresponding indanones in 65—70% yield; in consequence, the interaction of maleic anhydride and an aromatic hydrocarbon provides a valuable means of preparing derivatives of indan-1-one.

Interaction of maleic anhydride with quinol in the presence of excess of aluminium chloride follows a different course and affords naphthazarin (Zahn and Ochwat, *Annalen*, 1928, **462**, 72); in order to explain this remarkable difference; we are investigating the action of aluminium chloride on β-*o*-hydroxyaroylacrylic acids.

Experimental

β-Aroylacrylic Acids.—Powdered maleic anhydride was added to a suspension of finely powdered aluminium chloride (2·5 mols.) in methylene or ethylene chloride, and the mixture agitated for 0·5 hour at room temperature. The solution was decanted from undissolved aluminium chloride, and an aromatic hydrocarbon (1 mol.) was added. After 0·5 hour, the reaction mixture was decomposed with dilute hydrochloric acid, solvent was removed by distillation, and the solid product recrystallised from benzene–light petroleum (1 : 1) or aqueous acetic acid. The following β-aroylacrylic acids were prepared in this way (yields in parentheses) :

β-Benzoyl- (85%), m. p. 96—97° (Rice, *J. Amer. Chem. Soc.*, 1923, **45**, 222); β-*p*-methylbenzoyl- (70%), m. p. 137—138° (von Pechmann, *loc. cit.*); β-2 : 5-dimethylbenzoyl- (89%), m. p. 89—90° (Papa, Schwenk, and Villani, *J. Amer. Chem. Soc.*, 1948, **70**, 3356); β-2 : 4-dimethylbenzoyl- (91%), m. p. 117—118° (Kozniewski and Marchlewski, *Chem. Zentr.*, 1906, II, 1189); β-3 : 4-*dimethylbenzoyl-* (76%), m. p. 122—123° (Found : C, 70·6; H, 5·9. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%); β-2 : 4 : 6-trimethylbenzoyl- (83%), m. p. 140—141° (*idem, ibid.*); β-2 : 4 : 5-trimethylbenzoyl- (80%), m. p. 148—149° (*idem, ibid.*); β-2 : 3 : 5 : 6-*tetramethylbenzoyl-* (83%), m. p. 182—183° (Found : C, 72·2; H, 6·8. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%); and β-2 : 3 : 4 : 5-*tetramethylbenzoyl-* (76%), m. p. 122—123° (Found : C, 72·5; H, 6·9%).

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 homogeneous melt was continuously stirred and brought to a selected temperature, and the organic acid gradually added. After a selected time the mixture was cooled and decomposed by ice and dilute hydrochloric acid, and the organic material separated and recrystallised from water.

(*a*) β-2 : 5-Dimethylbenzoylacrylic acid (10 g.), after 1 hour at 135°, provided 3-*keto*-4 : 7-*dimethylindane*-1-*carboxylic acid* (8·7 g.), m. p. 160—161° (Found : C, 70·4; H, 6·0%; equiv., 203. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%; equiv., 204). It formed a 2 : 4-dinitrophenylhydrazone, did not decolorise cold permanganate or bromine in carbon tetrachloride, and was oxidised by nitric acid (*d* 1·1) at 180° to benzene-1 : 2 : 3 : 4-tetracarboxylic acid, m. p. and mixed m. p. 244—246° (decomp.) (tetramethyl ester, m. p. and mixed m. p. 130—131°) (Read and Purves, *J. Amer. Chem. Soc.*, 1952, **74**, 117; Smith and Carlson, *ibid.*, 1939, **61**, 228; Fieser and Peters, *ibid.*, 1932, **54**, 4347). The isomerisation can be effected by aluminium chloride (3 mols.), but the initial acid is recovered when the chloride (2 mols.) is used. Sulphuric acid (75%) at 100° caused partial decomposition.

(*b*) β-2 : 4-Dimethylbenzoylacrylic acid (2 g.) and sulphuric acid (85%) gave 3-*keto*-4 : 6-*dimethylindane*-1-*carboxylic acid*, m. p. 157—158° (Found : C, 70·5; H, 6·0%; equiv., 204), in poor yield; it was oxidised by nitric acid to benzene-1 : 2 : 3 : 5-tetracarboxylic acid, m. p. and mixed m. p. 250—252° (tetramethyl ester, m. p. and mixed m. p. 107—109°) (Read and Purves, *loc. cit.*; Smith and Byrkit, *ibid.*, 1933, **55**, 4308; Nürsten and Peters, *J.*, 1950, 733). The acrylic acid (5 g.) with aluminium chloride at 135° during 1 hour gave a product (4 g.) from which 3-keto-4 : 6- (3·3 g.) and 3-*keto*-5 : 6-*dimethylindane*-1-*carboxylic acid* (0·2 g.), m. p. and mixed m. p. 172—174° (Found : C, 70·1; H, 6·0%), were obtained by repeated recrystallisation from water. The latter was also obtained by the action of sulphuric acid (85%) at 100°, and of aluminium chloride at 100° on β-3 : 4-dimethylbenzoylacrylic acid, and in yields of *ca.* 15% by the action of sulphuric acid, phosphoric oxide in boiling toluene, or aluminium chloride–sodium chloride on 3 : 4-*dimethylphenylsuccinic acid*. This acid was obtained as colourless needles, m. p. 198—199° (Found : C, 65·3; H, 6·5. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·3%), from 3 : 4-dimethylbenzaldehyde as described by Lapworth and Baker (*Org. Synth.*, 1927, **7**, 20; 1928, **8**, 88) for the preparation of phenylsuccinic acid from benzaldehyde. α-*Cyano*-β-3 : 4-*dimethylphenylacrylic acid*, which was obtained as intermediate, crystallised from ethanol in pale yellow plates, m. p. 205—206° (Found : C, 71·5; H, 5·2. $C_{12}H_{11}O_2N$ requires C, 71·6;

H, 5·5%). 3-Keto-5 : 6-dimethylindane-1-carboxylic acid was oxidised by nitric acid (*d* 1·1) to benzene-1 : 2 : 4 : 5-tetracarboxylic acid, m. p. and mixed m. p. 284—287° (tetramethyl ester, m. p. and mixed m. p. 140—142°) (Read and Purves, *loc. cit.*; Fieser and Campbell, *J. Amer. Chem. Soc.*, 1938, **60**, 2635; Feist, *Ber.*, 1911, **44**, 135). 3-Keto-4 : 6-dimethylindane-1-carboxylic acid did not provide the 5 : 6-isomer when heated with aluminium chloride.

(*c*) β-2 : 4 : 6-Trimethylbenzoylacrylic acid (4·7 g.), after 3 hours at 135° or 1 hour at 150°, gave 3-*keto*-4 : 6 : 7-*trimethylindane*-1-*carboxylic acid* (3·9 g.), m. p. 189—190° (Found: C, 71·3; H, 6·5%; equiv., 220. $C_{13}H_{14}O_3$ requires C, 71·6; H, 6·4%; equiv., 218). It is a saturated acid, forms a 2 : 4-dinitrophenylhydrazone, is oxidised by nitric acid (*d* 1·1) at 220° to benzenepentacarboxylic acid, m. p. and mixed m. p. 225—230° (decomp.) (pentamethyl ester, m. p. and mixed m. p. 145—147°) (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), and is identical (m. p. and mixed m. p.) with the product of interaction of β-2 : 4 : 5-trimethylbenzoylacrylic acid with sulphuric acid (85%) or aluminium chloride at 100°.

(*d*) β-2 : 4 : 5-Trimethylbenzoylacrylic acid, after 1 hour at 100° or at 150°, provided only 3-keto-4 : 6 : 7-trimethylindane-1-carboxylic acid.

(*e*) β-2 : 3 : 5 : 6-Tetramethylbenzoylacrylic acid (5 g.), after 1 hour at 105°, gave 3-*keto*-4 : 5 : 6 : 7-*tetramethylindane*-1-*carboxylic acid* (4·5 g.), m. p. 216—217° (from water) (Found: C, 72·2; H, 6·8. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%). It is identical (m. p. and mixed m. p.) with the product of isomerisation of β-2 : 3 : 4 : 5-tetramethylbenzoylacrylic acid after 1 hour at 110°, and affords mellitic acid, m. p. 286—288° (sealed tube) (hexamethyl ester, m. p. 187—188°) (Fieser and Fieser, "Organic Chemistry," D. C. Heath & Co., Boston, U.S.A., 1950, p. 705), by oxidation with nitric acid.

(*f*) β-Benzoylacrylic acid partly decomposed during unsuccessful attempts to isomerise it at 105° or 145° (1 hour); β-*p*-toluoylacrylic acid, after 2 hours at 120°, afforded only 5% of an isomeric saturated acid, m. p. 146—147° (Found: C, 69·7; H, 5·2. $C_{11}H_{10}O_3$ requires C, 69·5; H, 5·3%), which is probably 3-*keto*-6-*methylindane*-1-*carboxylic acid*.

Decarboxylation of 3-*Ketoindane*-1-*carboxylic Acids*.—The acid (2 g.) and copper chromite (0·5 g.) in quinoline (10 c.c.) were heated in an atmosphere of nitrogen; evolution of carbon dioxide commenced at 160—165° and was complete after 3—4 hours at 180—190°. After cooling, the mixture was diluted with ether (100 c.c.) and filtered, the quinoline extracted with dilute acid, the ether removed by evaporation, the residue distilled with steam, and the indanone separated and crystallised from acetic acid. The following derivatives of indan-1-one were prepared in this manner (yields in parentheses): 4 : 7-Dimethyl- (64%), needles, m. p. 78—79° (Plattner and Wyss, *Helv. Chim. Acta*, 1941, **24**, 483) (phenylhydrazone, needles, m. p. 131—132°, from ethanol) (Maureu, *Bull. Soc. chim.*, 1893, **9**, 568); 5 : 7-*dimethyl*- (65%), prisms, m. p. 75—76° (Found: C, 82·1; H, 7·4. $C_{11}H_{12}O$ requires C, 82·5; H, 7·5%); 5 : 6-*dimethyl*- (43%), plates, m. p. 83—84° (Found: C, 82·1; H, 7·6%); 4 : 5 : 7-trimethyl- (68%), pale yellow needles, m. p. 110—111° (oxime, plates, m. p. 227—228°, from ethanol) (Aitken, Badger, and Cook, *J.*, 1950, 333, give m. p.s 104—105° and 223—224° respectively); 4 : 5 : 6 : 7-tetramethyl- (71%), yellow plates, m. p. 152—153° (oxime, plates, m. p. 214—215°, from ethanol) (Aitken, Badger, and Cook, *loc. cit.*, give m. p.s 149—150° and 211—213° respectively).

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