

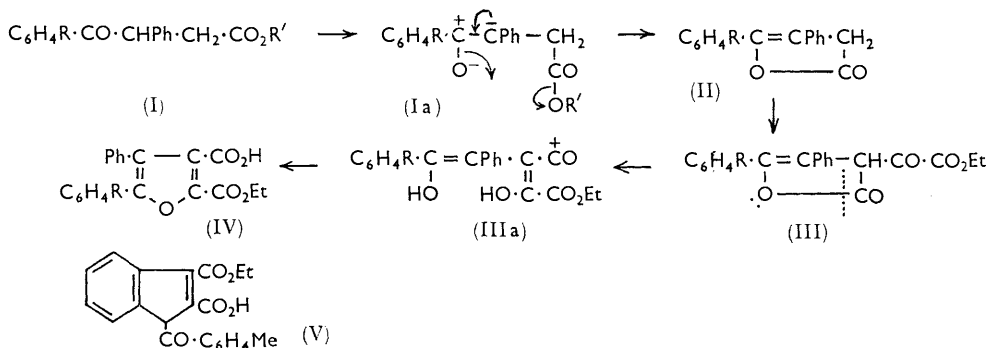
141. β -Aroylpropionic Acids. Part XVIII.* Their Conversion into 4,5-Diarylfuran-2,3-dicarboxylic Acids.

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Ethyl β -phenyl- β -*p*-toluoyl- and β -*p*-chlorobenzoyl-propionate, with ethyl oxalate in presence of potassium ethoxide, give 2-ethoxalyl-4-hydroxy-3-phenyl-4-*p*-tolyl- and *p*-chlorophenyl-but-3-enoic acid lactone, respectively. These are cyclised with sulphuric acid to the corresponding 5-aryl-2-ethoxycarbonyl-4-phenylfuran-3-carboxylic acids.

ETHYL β -PHENYL- β -*p*-TOLUOYLPROPIONATE (I; R = *p*-Me, R' = Et) with ethyl oxalate and potassium ethoxide¹ gave 2-ethoxalyl-3-phenyl-4-*p*-tolylbut-3-enoic acid lactone (III; R = *p*-Me). Its structure was established by the following facts: (i) The same product was obtained when the ethyl ester (I; R' = Et) was replaced by the methyl ester (I; R' = Me) or by 3-phenyl- γ -4-tolylbut-3-enoic acid lactone² (II; R = *p*-Me). This indicates that the alkoxide ion R'O⁻ is eliminated in the reaction. (ii) β -Aroyl- α - or β -arylpmpionic esters are converted into the 2,4- or 3,4-diarylbut-3-enoic acid lactones through the intermediate carbanion (Ia), when treated with potassium ethoxide. (iii) The infrared spectrum showed stretching frequencies at 1640, 1755, and 1785 cm.⁻¹, characteristic of enolic carbonyl groups,^{3a} α -keto-esters,^{3b} and β γ -unsaturated lactones,^{3b} respectively.

Warm 80% sulphuric acid converted the lactone (III; R = *p*-Me) into 2-ethoxycarbonyl-4-phenyl-5-*p*-tolylfuran-3-carboxylic acid (IV; R = *p*-Me). The reaction appears to proceed by intermediate formation of the carbonium ion (IIIa), as indicated by the green colour of the reaction mixture which disappeared at the end of the reaction. This colour is not given by the furan (IV) in 80% sulphuric acid.



The structure (IV; R = *p*-Me) assigned to the product is more probable than (V) for the following reasons: (i) The product decolorised alkaline potassium permanganate, a reaction which is given by furancarboxylic acids. (ii) On fusion with potassium hydroxide at 250–260°, it gives only the dibasic acid. However, at 290–300°, it was partially cleaved to give *p*-toluic acid. The failure to trace the presence of indene-2,3-dicarboxylic acid in the fusion product excluded structure (V), since indene-2,3-dicarboxylic acid is recovered unchanged when fused with alkali at 290–300°. (iii) It failed to respond to all ketonic reagents. (iv) Its infrared spectrum showed two bands, at 1760 and 1680 cm.⁻¹; the former is characteristic of the carboxylate group,^{3b} the slight shift to shorter wavelength being perhaps due to conjugation of the carboxylate group with the electro-negative carboxyl group.^{3b} The band at 1680 cm.⁻¹ is undoubtedly due to the carboxyl

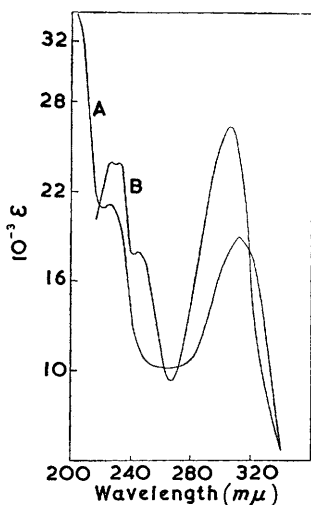
* Part XVII, *J.*, 1960, 3420.

¹ Baddar and Warren, *J.*, 1939, 944; Baddar, Fleifel, and Sherif, *J.*, 1959, 1009.

² Baddar and Sherif, *J.*, 1960, 2309.

³ Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1956, pp. (a) 114, (b) 153, (c) 140, (d) 84, (e) 31, (f) 34.

group^{3c} and not to a carbonyl group,^{3a} since it was absent from the spectrum of the corresponding diethyl ester (see p. 709). (v) The ultraviolet spectrum (Figure) was similar to that of methyl 3,4,5-triphenylfuran-2-carboxylate (sample kindly provided by Professor G. Soliman, Faculty of Science, Alexandria University). (vi) The infrared spectra of the furan (IV) and of methyl 3,4,5-triphenylfuran-2-carboxylate include a weak band at 1620 and 1613 cm^{-1} , respectively, characteristic of a conjugated double bond;^{3e} their low intensities may be due to symmetry considerations.^{3f}



Absorption spectra of (A) 2-ethoxycarbonyl-4-phenyl-5-p-tolylfuran-3-carboxylic acid and (B) methyl 3,4,5-triphenylfuran-2-carboxylate.

When ethyl β -*p*-chlorobenzoyl- β -phenylpropionate (I; R = *p*-Cl, R' = Et) was subjected to the same series of reactions, it gave the lactone (III; R = *p*-Cl) and the furan (IV; R = *p*-Cl). The latter gave *p*-chlorobenzoic acid when refluxed with 10% aqueous potassium hydroxide.

EXPERIMENTAL

Infrared spectra were measured with a Perkin-Elmer Infracord spectrophotometer model 137, for Nujol mulls, and ultraviolet spectra with a Zeiss spectrophotometer model PMQ II, for EtOH or MeOH solutions.

Ethyl and methyl β -phenyl- β -*p*-toluoylpropionate were obtained from β -phenyl- β -*p*-toluoylpropionic acid⁴ in the usual manner. The ethyl ester (90%) had b. p. 197–198°/0.6 mm., n_D^{20} 1.5581 (Found: C, 76.9; H, 6.5. $\text{C}_{19}\text{H}_{20}\text{O}_3$ requires C, 77.0; H, 6.8%). The methyl ester had m. p. 109–110° [from benzene–light petroleum (b. p. 50–70°)] (Found: C, 76.5; H, 6.5. $\text{C}_{18}\text{H}_{18}\text{O}_3$ requires C, 76.6; H, 6.4%).

2-Ethoxalyl-3-phenyl-4-*p*-tolylbut-3-enoic Acid Lactone.—(i) Finely powdered potassium (1.9 g., 1 g.-equiv.) was covered with dry ether (100 ml.), allowed to react with ethanol (3.5 ml.), then treated with freshly distilled ethyl oxalate (7.3 g., 1 mol.), followed by ethyl β -phenyl- β -*p*-toluoylpropionate (14.8 g., 1 mol.). The mixture was left overnight, then refluxed for 6 hr. and worked up.¹ The yellow crystals (10 g.) left on the removal of ether crystallised from benzene–light petroleum (b. p. 50–70°) to give 2-ethoxalyl-3-phenyl- γ -4-tolylbut-3-enoic acid lactone, m. p. 134–135° (Found: C, 71.6; H, 5.2. $\text{C}_{21}\text{H}_{18}\text{O}_5$ requires C, 72.0; H, 5.2%). It gave a deep-red colour with concentrated sulphuric acid, and a green colour with ferric chloride solution. Its infrared spectrum showed absorption bands at 1640, 1755, and 1785 cm^{-1} . (ii) The same compound was obtained in inferior yields when the reaction was carried out with methyl β -phenyl- β -*p*-toluoylpropionate or 3-phenyl-4-*p*-tolylbut-3-enoic acid lactone² instead of the ethyl ester.

2-Ethoxycarbonyl-4-phenyl-5-*p*-tolylfuran-3-carboxylic Acid.—The above ethoxalyl ester (4 g.) was stirred with 80% (v/v) sulphuric acid (50 ml.) for 1 hr. at 50–60°, then for 2 hr. at

⁴ Baddar, Fleifel, and Sherif, *Egypt. J. Chem.*, in the press.

room temperature. The red solution changed gradually to green but the solution was colourless at the end of the reaction. The mixture was poured into cold water, filtered off, and dried (3.5 g.). On crystallisation from benzene–light petroleum (b. p. 50–70°) it gave 2-ethoxycarbonyl-4-phenyl-5-p-tolylfuran-3-carboxylic acid, m. p. 165–166° (Found: C, 71.95; H, 5.1. C₂₁H₁₈O₅ requires C, 72.0; H, 5.2%). It discharged the colour of alkaline potassium permanganate and gave a yellow colour with 80% (v/v) sulphuric acid. Its infrared spectrum showed bands at 1760 and 1680 cm.⁻¹.

Attempted cyclisation with concentrated sulphuric acid at 0–5° caused complete sulphonation.

4-Phenyl-5-p-tolylfuran-2,3-dicarboxylic Acid.—The above ester (1 g.) was refluxed for 1 hr. with 10% aqueous potassium hydroxide (50 ml.), then worked up as usual. *4-Phenyl-5-p-tolylfuran-2,3-dicarboxylic acid* (0.8 g.) had m. p. 230° (decomp.) (from xylene). It contains one molecule of water of crystallisation as shown by its infrared spectrum ^{3d} (sharp band at 3595 cm.⁻¹) and by analysis (Found: C, 67.0; H, 4.5. C₁₉H₁₄O₅.H₂O requires C, 67.05; H, 4.75%). This water was removed at 140°/0.6 mm. in 2 hr. [Found: C, 71.0; H, 4.5%; *M* (Rast), 313; equiv., 160. C₁₉H₁₄O₅ requires C, 70.8; H, 4.4%; *M* (dibasic), 322]. The band at 3595 cm.⁻¹ had disappeared. Attempts to obtain an anhydride were unsuccessful: furan-2,3-dicarboxylic acid also fails to give an anhydride.⁵ The *diethyl ester* was obtained by refluxing the monoethyl ester with absolute ethanol and concentrated sulphuric acid for 6 hr. and had m. p. 87–88° [from light petroleum (b. p. 50–70°)] (Found: C, 73.4; H, 5.8. C₂₃H₂₂O₅ requires C, 73.0; H, 5.9%), ν_{\max} 1745 and 1730 cm.⁻¹, characteristic of two carboxylate groups.^{3b}

Action of Potassium Hydroxide on 2-Ethoxycarbonyl-4-phenyl-5-p-tolylfuran-3-carboxylic Acid and 4-Phenyl-5-p-tolylfuran-2,3-dicarboxylic Acid.—The ester or acid was fused with potassium hydroxide at 290–300° for 1 hr., and the mixture was worked up as usual to give *p*-toluic acid, identified by m. p. and mixed m. p. 181°. At 250–260° no cleavage took place.

Ethyl β-p-Chlorobenzoyl-β-phenylpropionate.—This ester, obtained (90%) from the corresponding acid,² had b. p. 205–207°/5 mm. (Found: C, 68.0; H, 5.3; Cl, 11.3. C₁₅H₁₇ClO₃ requires C, 68.2; H, 5.4; Cl, 11.2%).

2-Ethoxalyl-3-phenyl-4-p-chlorophenylbut-3-enoic Acid Lactone.—The preceding ester was converted in the usual manner into the yellow lactone (40%), m. p. 135–136° [from benzene–light petroleum (b. p. 50–70°)] (Found: C, 64.6; H, 4.1; Cl, 9.7; OEt, 10.8. C₂₀H₁₅ClO₅ requires C, 64.8; H, 4.1; Cl, 9.6; OEt, 12.1%), ν_{\max} 1645, 1740, and 1760 cm.⁻¹, giving a deep-red colour with alcoholic ferric chloride solution, and a red colour with concentrated sulphuric acid.

2-Ethoxycarbonyl-5-p-chlorophenyl-4-phenylfuran-3-carboxylic Acid.—The chloro-ester (as I) (3 g.) was stirred in 85% (v/v) sulphuric acid (60 ml.) at 60–65° for 2 hr., left overnight, and worked up as usual. The product (2.5 g.) crystallised from benzene, to give 5-*p*-chlorophenyl-2-ethoxycarbonyl-4-phenylfuran-3-carboxylic acid, m. p. 192–193° (Found: C, 64.2; H, 4.0; Cl, 9.6. C₂₀H₁₅ClO₅ requires C, 64.8; H, 4.1; Cl, 9.6%). This discharged the colour of alkaline potassium permanganate, gave a yellow colour with concentrated sulphuric acid, and with refluxing 10% aqueous potassium hydroxide (1 hr.) gave *p*-chlorobenzoic acid, m. p. and mixed m. p. 239°.

3-p-Chlorophenyl-2-p-methoxyphenylbut-3-enoic Acid Lactone.—(i) A mixture of ethyl β-*p*-chlorobenzoyl-α-*p*-methoxyphenylpropionate,² potassium ethoxide [from potassium (1 g.) and absolute ethanol (2 ml.)], and ether (30 ml.) was left overnight, then refluxed for 5 hr. and worked up as usual.¹ The product was extracted with light petroleum (b. p. 50–70°) to remove unchanged ester, then with dilute sodium carbonate solution to remove traces of the acid. The insoluble residue crystallised from ethanol, to give 3-*p*-chlorophenyl-2-*p*-methoxyphenylbut-3-enoic acid lactone, m. p. and mixed m. p.² 140–141°. (ii) A solution of β-*p*-chlorobenzoyl-α-*p*-methoxyphenylpropionic acid² (1 g.) in acetic anhydride (10 ml.) was refluxed for 3 hr., cooled, and poured into water. The lactone was filtered off and washed with dilute sodium carbonate solution. On crystallisation from ethanol, it was obtained, in quantitative yield, with m. p. and mixed m. p. 140–141°.

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⁵ Paul, *Bull. Soc. chim. France*, 1941, 8, 369.