517. *β-Aroylpropionic Acids. Part XVI.* The Conversion of γ-Oxo-γ-2-xanthenylbutyric Acid into 2,3-Benzoxanthone.*

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γ-Oxo-γ-2-xanthenylbutyric acid has been reduced to γ-2-xanthenylbutyric acid and then cyclised to 1′,2′,3′,4′-tetrahydro-4′-oxo-2,3-benzoxanthen. This is reduced to 1′,2′,3′,4′-tetrahydro-2,3-benzoxanthen, then dehydrogenated, and oxidised to 2,3-benzoxanthone. γ-2-Xanthenylbutyric ester has been condensed with diethyl oxalate, and the oxalyl derivative cyclised to 1′,2′-dihydro-2,3-benzoxanthen-3′,4′-dicarboxylic anhydride. This on dehydrogenation, decarboxylation, and oxidation gives 2,3-benzoxanthone.

CONTRARY to a report by Burtner and Brown[1] the Friedel–Crafts reaction of xanthen with succinic anhydride in benzene gave a mixture of γ-oxo-γ-2-xanthenylbutyric acid (I) and β-benzoylpropionic acid. However, condensation in acetylene tetrachloride afforded the keto-acid (I) in 96% yield. The structure of this keto-acid was established by its oxidation to xanthone-2-carboxylic acid[2] (XIII). Mild oxidation of either γ-oxo-γ-2-xanthenylbutyric acid (I) or its methyl ester by potassium permanganate in aqueous acetone yielded γ-oxo-γ-2-xanthonylbutyric acid (II; R = H) or its methyl ester respectively. Hydrolysis of the diketo-ester (II; R = Me) with 5% alcoholic potassium hydroxide gave the diketo-acid (II; R = H), but treatment with 10% aqueous sodium hydroxide led to a phenolic acid. This was probably due to the rupture of the heterocyclic ring, to give β-(4-hydroxy-3-*o*-hydroxybenzoylbenzoyl)propionic acid (III). Its structure was based on the fact that it cyclised back to the original ester (II; R = Me) on attempted methylation with methyl sulphate and potassium carbonate in acetone. A similar result was obtained with 2,2′-dihydroxybenzophenone, which was converted into xanthone on attempted methylation with alkaline methyl sulphate[3a] or on evaporation of its alkaline solution.[3b]

The structure of the acid (III) was further supported by its infrared spectrum. It showed a broad band at 3200—3125 and a weak sharp band at 3545 cm.$^{-1}$ (in $CHCl_3$), characteristic for the chelated and the free OH group, respectively.[4a] Two bands at 1695 and 1639 cm.$^{-1}$ (in Nujol) are characteristic for the side chain and the *o*-hydroxycarbonyl group, respectively.[4a]

Reduction of γ-oxo-γ-2-xanthenylbutyric acid (I) by Clemmensen's method, or less satisfactorily by the Wolff–Kishner method, gave γ-2-xanthenylbutyric acid (IV; R = H).

Conversion of the acid (V; R = H) into 2,3-benzoxanthone (XIV) was carried out by two routes: (*A*) The acid chloride of (IV; R = H) was best cyclised with anhydrous stannic chloride, affording a cyclic ketone, theoretically of structure (VII) or (XV). It was proved

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* Part XV, *J.*, 1960, 2309.

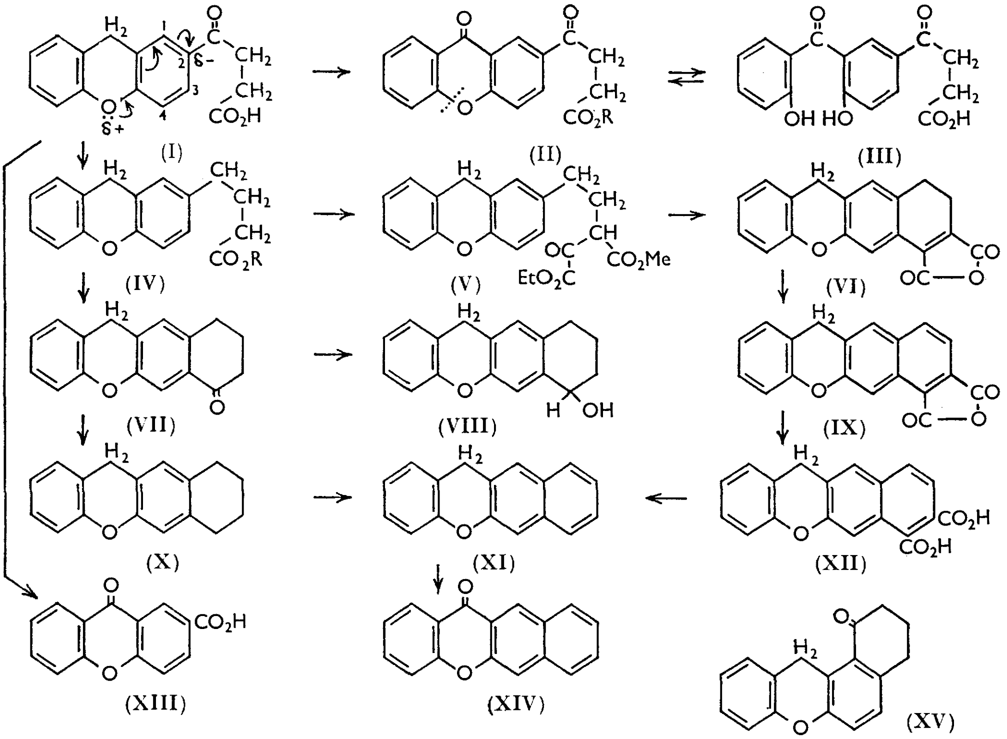
[1] Burtner and Brown, U.S.P. 2,480,220/1949.

[2] Anschütz, Stoltenhoff, and Voeller, *Ber.*, 1925, **58**, 1736.

[3] (*a*) Unpublished work by Baddar and El-Assal; (*b*) Richter, *J. prakt. Chem.*, 1883, **28**, 285.

[4] Bellamy, " The Infra-Red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1956, pp. (*a*) 84 and (*b*) 114.

to be (VII) by Clemmensen reduction to the tetralin (X), which on dehydrogenation followed by oxidation gave 2,3-benzoxanthone [5] (XIV). Reduction of the ketone (VII) by lithium aluminium hydride gave the alcohol (VIII) in a quantitative yield. (*B*) The methyl ester (IV; R = Me) was condensed with diethyl oxalate in presence of potassium ethoxide to give the oxalyl derivative (V), which was directly cyclised with 70% sulphuric acid to the anhydride [6] (VI). This was dehydrogenated with 40% palladised charcoal or merely by heat to 2,3-benzoxanthen-3′,4′-dicarboxylic anhydride (IX), and was then successively hydrolysed to the dicarboxylic acid (XII), decarboxylated by copper-bronze in quinoline to 2,3-benzoxanthen (XI), and oxidised to the same 2,3-benzoxanthone [5] (XIV).



The electrophilic substitution of the xanthen molecule in position 2 (see I) indicates that the electromeric shift initiated by the oxygen of the heterocyclic ring is stronger than that initiated by the methylene group.

EXPERIMENTAL

Infrared spectra were measured with a Perkin–Elmer Infracord 137 instrument, with a sodium chloride prism, for Nujol mulls unless otherwise stated.

γ-Oxo-γ-2-xanthenylbutyric Acid (I).—Powdered anhydrous aluminium chloride (33·0 g., 2·2 mol.) was added to a stirred ice-cold mixture of succinic anhydride (13·0 g., 1·2 mol.) and xanthen (20·0 g., 1 mol.) in acetylene tetrachloride (200 ml.), then stirring was continued for 4 hr. at room temperature. The product was worked up as usual (29·8 g., 96%), then crystallised from benzene–ethanol to give γ-oxo-γ-2-xanthenylbutyric acid, m. p. 210—212° (Found: C, 72·15; H, 5·3. Calc. for $C_{17}H_{14}O_4$: C, 72·3; H, 5·0%) (lit.,[1] m. p. 202°). It failed to give a 2,4-dinitrophenylhydrazone or a semicarbazone. It had two strong bands at 1695 and 1725 cm.$^{-1}$ characteristic of the carbonyl and the carboxyl group,[7] respectively.

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[5] Dilthey and Quint, *J. prakt. Chem.*, 1934, **141**, 306.
[6] Baddar and Warren, *J.*, 1939, 944.
[7] Bellamy, *op. cit.*, p. 140.

The *methyl ester*, prepared in 86% yield by refluxing the acid (2·0 g.) with methyl sulphate (1·8 g.) and potassium carbonate (3·0 g.) in acetone (50 ml.) for 15 hr., had m. p. 113—114° [from light petroleum (b. p. 70—80°)] (Found: C, 72·5; H, 5·7. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%). Refluxing the ester with 10% sodium hydroxide solution for 15 min. gave back the acid in a quantitative yield. The ester had two strong bands at 1680 (C=O) and 1755 cm.$^{-1}$ (CO_2R).[8]

Oxidation of γ-Oxo-γ-2-xanthenylbutyric Acid (I) *to Xanthone-2-carboxylic Acid* (XIII).—A solution of the keto-acid (2·5 g.) in 10% aqueous potassium hydroxide (200 ml.) was heated on a boiling-water bath, and treated portionwise with powdered potassium permanganate (6·6 g.) during 1 hr. The product was worked up as usual, then crystallised from ethanol to give xanthone-2-carboxylic acid [2] (1·9 g.), m. p. and mixed m. p. 303—304° (Found: C, 70·0; H, 3·1. Calc. for $C_{14}H_8O_4$: C, 70·0; H, 3·4%). The methyl ester, prepared as above, had m. p. and mixed m. p. 217—218° (from benzene) (lit.,[2] m. p. 185°) (Found: C, 70·3; H, 4·0. Calc. for $C_{15}H_{10}O_4$: C, 70·9; H, 4·0%).

γ-Oxo-γ-2-xanthonylbutyric Acid (II; R = H).—A stirred suspension of γ-oxo-γ-2-xanthenylbutyric acid (3·0 g.) in 1 : 3 aqueous acetone (100 ml.) was treated portionwise with powdered potassium permanganate (4·2 g.) during 30 min. The product was worked up as usual, then crystallised from acetic acid to give *γ-oxo-γ-2-xanthonylbutyric acid* (2·9 g., 93%), m. p. 195—197° (Found: C, 68·7; H, 4·2. $C_{17}H_{12}O_5$ requires C, 68·9; H, 4·1%). It failed to give a 2,4-dinitrophenylhydrazone.

The methyl ester was prepared by methylation of the acid as above (93% yield) and by oxidation of methyl γ-oxo-γ-2-xanthenylbutyrate (2·0 g.) with potassium permanganate (2·6 g.) in 3 : 7 aqueous acetone. The latter product was a mixture of methyl γ-oxo-γ-2-xanthonylbutyrate (0·7 g.) (soluble in benzene) and xanthone-2-carboxylic acid (0·5 g.) (insoluble in benzene). The *ester*, crystallised from benzene–light petroleum (b. p. 60—80°), had m. p. 124—125° (Found: C, 69·7; H, 4·8. $C_{18}H_{14}O_5$ requires C, 69·7; H, 4·55%). Its infrared spectrum showed two strong overlapping bands at 1690 and 1666 cm.$^{-1}$, characteristic of the two carbonyl groups. Its *2,4-dinitrophenylhydrazone* formed red crystals, m. p. 241—242°, from acetic acid (Found: N, 11·5. $C_{24}H_{18}N_4O_8$ requires N, 11·4%).

Hydrolysis of Methyl γ-Oxo-γ-2-xanthonylbutyrate.—(i) The ester was hydrolysed with boiling 5% alcoholic potassium hydroxide for 45 min., to give γ-oxo-γ-2-xanthonylbutyric acid in quantitative yield. (ii) Hydrolysis with boiling 10% aqueous sodium hydroxide for 45 min. gave (probably) *β-(4-hydroxy-3-o-hydroxybenzoylbenzoyl)propionic acid* (III), m. p. 148—149° (pale greenish-yellow needles from benzene) (Found: C, 65·5; H, 4·7. $C_{17}H_{14}O_6$ requires C, 65·0; H, 4·5%), showing a weak sharp band at 3545 cm.$^{-1}$ (in $CHCl_3$), a broad band at 3200—3125 cm.$^{-1}$ (in $CHCl_3$), and bands at 1695 and 1639 cm.$^{-1}$. Attempts to methylate this dihydroxy-acid with methyl sulphate and potassium carbonate in acetone gave back the ester (II; R = Me).

γ-2-Xanthenylbutyric Acid (IV; R = H).—The keto-acid (I) (15 g.) was boiled with amalgamated zinc (45 g.; B.D.H. grade), hydrochloric acid (230 ml.), water (15 ml.), and sulphur-free xylene (100 ml.) for 30 hr., then worked up as usual. The product was extracted with hot benzene. The soluble fraction crystallised from benzene–light petroleum (b. p. 50—70°), to give *γ-2-xanthenylbutyric acid*, m. p. 143—144° (11 g.) (Found: C, 76·1; H, 6·2. $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0%). The benzene-insoluble fraction (2 g.) proved to be the unchanged keto-acid.

The *methyl ester* of the product was prepared by diazomethane in 95% yield, and had m. p. 49—50° [from light petroleum (b. p. 30—50°)] (Found: C, 75·6; H, 6·4. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%).

1′,2′,3′,4′-Tetrahydro-4′-oxo-2,3-benzoxanthen (VII).—A stirred suspension of γ-2-xanthenylbutyric acid (IV; R = H) (2·7 g., 1 mol.) in thiophen-free benzene (25 ml.) was cooled in an ice-bath, then treated portionwise with phosphorus pentachloride (2·3 g., 1·1 mol.), kept at room temperature for 30 min., cooled in ice again, and treated portionwise during 30 min. with a solution of anhydrous stannic chloride (5·2 g., 2·4 ml.) in thiophen-free benzene (8 ml.). Stirring was continued for 1·5 hr. at 5—10°, and the mixture then worked up as usual. The product was extracted with sodium carbonate and filtered off (1·5 g., 59%). It crystallised from ethanol to give *1′,2′,3′,4′-tetrahydro-4′-oxo-2,3-benzoxanthen*, m. p. 163—164° (Found: C, 81·3; H, 5·7. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%). Its *2,4-dinitrophenylhydrazone*, red crystals from dioxan,

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[8] Bellamy, *op. cit.*, p. 153.

had m. p. >360° (Found: C, 64·2; H, 4·4; N, 13·1. $C_{23}H_{18}N_4O_5$ requires C, 64·2; H, 4·2; N, 13·0%).

1′,2′,3′,4′-*Tetrahydro*-4′-*hydroxy*-2,3-*benzoxanthen* (VIII).—A suspension of powdered lithium aluminium hydride (0·4 g.) in dry ether (25 ml.) was refluxed for 15 min., then treated dropwise with a solution of 1′,2′,3′,4′-tetrahydro-4′-oxo-2,3-benzoxanthen (VII) (0·4 g.) in dry benzene (25 ml.). Refluxing was continued for further 3 hr., and the mixture then left overnight at room temperature. The *product* crystallised from benzene–light petroleum (b. p. 50—70°), then from aqueous methanol in pale yellow needles, m. p. 149—150° (Found: C, 80·7; H, 6·2. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%).

1′,2′,3′,4′-*Tetrahydro*-2,3-*benzoxanthen* (X).—The cyclic ketone (VII) (0·5 g.) was reduced by Martin's modification of Clemmensen's method in boiling benzene for 30 hr. 1′,2′,3′,4′-*Tetrahydro*-2,3-*benzoxanthen* (0·4 g., 85%) had m. p. 125—127° (from ethanol). Purification was best effected by sublimation at 230—240° in carbon dioxide or at 200°/20 mm.; the material then had m. p. 133° (Found: C, 86·1; H, 6·8. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8%).

1′,2′-*Dihydro*-2,3-*benzoxanthen*-3′,4′-*dicarboxylic Anhydride* (VI).—To a stirred ice-cold suspension of potassium ethoxide [from potassium (2 g., 1·15 g.-atom) and ethanol (2·5 g., 1·15 mol.)] in dry ether (100 ml.), freshly distilled diethyl oxalate (13·0 g., 1·8 mol.) was added in one lot. After 30 min., methyl γ-2-xanthenylbutyrate (13·0 g., 1 mol.) in dry ether (50 ml.) was added during a further 30 min. The mixture was left for 18 hr. at room temperature with frequent stirring, then poured on ice and dilute sulphuric acid, left for 2 hr., and finally extracted with ether. Removal of the solvent gave the oxalyl derivative (V) as a dark orange-red oil. The crude derivative was heated with 70% sulphuric acid (v/v) (100 ml.) on a boiling-water bath for 1 hr. with stirring, then poured on ice and left overnight. The product was extracted with 10% sodium hydrogen carbonate solution (300 ml.) and filtered off (2·8 g., 20%). Acidification of the carbonate solution gave resinous acids. The anhydride was dissolved in hot 10% sodium hydroxide solution (charcoal), and the mixture was filtered, cooled, and acidified. The precipitated dibasic acid (2·8 g.) was refluxed with acetyl chloride (50 ml.) for 1 hr., the excess of reagent was removed under reduced pressure, then the residue (2·5 g.) was crystallised from acetic acid–acetic anhydride (3 : 1), to give 1′,2′-*dihydro*-2,3-*benzoxanthen*-3′,4′-*dicarboxylic anhydride* in orange-yellow needles, m. p. 242—243° (Found: C, 75·1; H, 4·0. $C_{19}H_{12}O_4$ requires C, 75·0; H, 4·0%).

2,3-*Benzoxanthen*-3′,4′-*dicarboxylic Anhydride* (IX).—1′,2′-Dihydro-2,3-benzoxanthen-3′,4′-dicarboxylic anhydride (0·5 g.) was heated with 40% palladised charcoal (0·1 g.) in a bath of boiling α-methylnaphthalene for 1 hr. The product (0·35 g.) was extracted with hot acetic anhydride, and crystallised from the same solvent to give dark yellow 2,3-*benzoxanthen*-3′,4′-*dicarboxylic anhydride*, m. p. 228—230° (Found: C, 75·2; H, 3·5. $C_{19}H_{10}O_4$ requires C, 75·5; H, 3·3%).

Dehydrogenation of this anhydride was also effected by heating it above its m. p. until gas evolution stopped. The same product was obtained but in a less pure form.

2,3-*Benzoxanthone* (XIV).—(i) A mixture of 1′,2′,3′,4′-tetrahydro-2,3-benzoxanthen (X) (0·1 g.) and 40% palladised charcoal (0·02 g.) was heated in a bath of boiling α-methylnaphthalene for 3 hr. Unchanged starting material that sublimed was separated, and the solid residue extracted with benzene to give 2,3-benzoxanthen (0·03 g., 31%). This was dissolved in 1 : 3 aqueous acetone (20 ml.), and directly oxidised with potassium permanganate (0·05 g., 2 mol.) at room temperature. After 30 min., the mixture was warmed at 50° for a few minutes, then worked up as usual. The product (0·03 g.), m. p. 198—201°, crystallised from acetic acid to give 2,3-benzoxanthone [5] as greenish-yellow needles, m. p. and mixed m. p. 201—202°. It gave a red-violet colour with concentrated sulphuric acid. (ii) 2,3-Benzoxanthen-3′,4′-dicarboxylic acid (XII) (0·3 g.) was added portionwise to copper-bronze (0·3 g.) in boiling quinoline (5 ml.). The mixture was refluxed for 4 hr., then worked up as usual. The product (0·14 g.) was oxidised with potassium permanganate (0·2 g.) in aqueous acetone as above, then crystallised from acetic acid to give dark yellow 2,3-benzoxanthone,[5] m. p. and mixed m. p. 195—197° (red violet colour with concentrated sulphuric acid).

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