# 487. *A Synthesis of α-Diketones.*

### By Angela M. Cragg, F. M. Dean, and Graham Winfield.

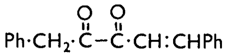
When treated with diethylamine and then aqueous hydrochloric acid, 4 : 5-dibromo-1 : 5-diphenylpent-1-en-3-one gives benzyl styryl diketone, a member of the little-studied class of unsaturated α-diketones. The new compound with hydroxide ion undergoes an internal Michael addition, giving 3 : 4-diphenyl*cyclo*pentane-1 : 2-dione. Both diketones appear to exist entirely as enols, the acetates of which do not show interaction effects such as occur in the infrared spectra of other α-acyloxy-ketones.

Although the reactions of amines with the dibromides of benzylideneacetophenone and related compounds have been extensively explored by Cromwell and his colleagues,[1] it appears that unsaturated dibromides such as that from dibenzylideneacetone have not been studied. From the reaction between diethylamine and the dibromide (I) we were unable to isolate products similar to those obtained in the previous work, but the resulting red gum furnished benzyl styryl diketone (II) in fair yields when hydrolysed by hydrochloric acid. Diketones of this kind are not common although a general method for preparing the related aryl ethers (III; R = aryl) was described[2] in 1902.

Structures (II) or (III; R = H) for the diketone are supported by the yellow colour, the formation of a quinoxaline (IV), and the ultraviolet absorption [$\lambda_{max.}$ 232, 328 mμ (log ε 4·19, 4·50)] of the enol acetate (III; R = Ac) which is close to that [$\lambda_{max.}$ 231, 332 mμ (log ε 4·10, 4·54)] of dibenzylideneacetone. However, the infrared spectrum [$\nu_{max.}$ 1757 (vinyl acetate) and 1653 (dienone C:O)] of this acetate is consistent only if the interaction effects characteristic of saturated α-acyloxy-ketones[3,4] are supposed not to operate. As expected, the diketone is highly enolised: it readily gives a red solution in alkaline media, an intense brown-red ferric reaction in alcohol, and shows marked infrared absorption bands at 3350 (weakly bonded OH), 1620 (hydrogen-bonded αβ : α′β′-diunsaturated C:O), and 1567 cm.$^{-1}$ (olefinic and aromatic systems) but is transparent in the regions (near 1720 and 1680 cm.$^{-1}$) in which the diketonic form would absorb.

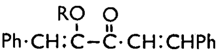
Ph·CHBr·CHBr·CO·CH:CHPh

(I)



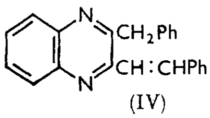
$Ph\cdot CH_2\cdot\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}\cdot CH:CHPh$

(II)

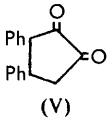


$Ph\cdot CH:\overset{RO}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}\cdot CH:CHPh$

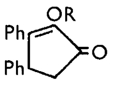
(III)



(IV)



(V)



(VI)

Ph·CO·CHPh·$CH_2$·$CO_2H$

(VII)

Benzyl styryl diketone is rapidly isomerised by warm alkali. Since structure (II) offers opportunity for an internal Michael condensation, the product was considered to be the *cyclo*pentane-1 : 2-dione (V), existing as the enol (VI; R = H), in spite of the facts that it was resistant to alkaline hydrogen peroxide and, unlike other *cyclo*pentane-1 : 2-diones,[5] did not yield a quinoxaline. It was, however, alkali-soluble, and gave an inky-black ferric reaction. Structure (VI; R = H) was established by permanganate oxidation which supplied the acid (VII) with the appropriate spectroscopic properties and identical with an authentic specimen.[6] Moreover, the enol acetate (VI; R = Ac) of the new dione had an ultraviolet absorption spectrum [$\lambda_{max.}$ 285 mμ (log ε 4·3), $\lambda_{min.}$ 236 mμ (log ε 3·5)]

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[1] Cromwell, *J. Amer. Chem. Soc.*, 1940, **62**, 1672, and subsequent papers.
[2] Stoermer and Wehln, *Ber.*, 1902, **35**, 3558.
[3] Grove and Willis, *J.*, 1951, 877.
[4] Jones and Herling, *J. Org. Chem.*, 1954, **19**, 1252.
[5] Dieckmann, *Ber.*, 1902, **35**, 3201.
[6] Thiele and Straus, *Annalen*, 1901, **319**, 164.

almost the same as that [$\lambda_{max.}$ 280 mμ (log ε 4·36), $\lambda_{min.}$ 232 mμ (log ε 3·22)] of 3-phenyl*cyclo*pent-2-en-1-one. It has long been known[5] that *cyclo*pentane-1 : 2-diones are highly enolic, and this tendency, increased by extended conjugation, may account for the unusual chemical properties of the compound. Again the infrared spectrum [$\nu_{max.}$ 3290 (bonded OH) and 1686 cm.$^{-1}$ (hydrogen-bonded *cyclo*pentenone C:O)] favours an enolic structure (VI; R = H), and again the spectrum [$\nu_{max.}$ 1748 (vinyl acetate) and 1701 cm.$^{-1}$ (*cyclo*pentenone C:O)] of the acetate indicates a lack of interaction effects.[8]

## EXPERIMENTAL

Ultraviolet spectra were determined for alcoholic solutions (~$10^{-3}$M) by means of a Unicam S.P. 500 spectrophotometer. Infrared spectra were determined on Nujol mulls by means of a Perkin-Elmer Model 21 double-beam spectrophotometer.

*Benzyl Styryl Diketone* (II) or (III; R = H).—The red mixture obtained by heating under reflux in an atmosphere of nitrogen for ¼ hr. 4 : 5-dibromo-1 : 5-diphenylpent-1-en-3-one (I) (5 g.) with diethylamine (40 ml.) was cooled and poured on ice (150 g.). When stirred with concentrated hydrochloric acid, the red pasty mass slowly gave a yellow solid which, after purification from methanol, gave *benzyl styryl diketone* in bright yellow plates (0·95 g.), m. p. 120°, $\lambda_{max.}$ 235, 261, 367 mμ (log ε 4·10, 3·96, 4·40) (Found: C, 81·5; H, 5·7. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%). Essentially the same result was obtained when the starting material was α-bromodibenzylideneacetone. The *acetate* (III; R = Ac) (prepared by acetic anhydride and sodium acetate) crystallised from methanol in pale yellow prisms, m. p. 113°, devoid of a ferric reaction (Found: C, 78·0; H, 5·6; OAc, 17·6. $C_{17}H_{13}O{\cdot}OAc$ requires C, 78·1; H, 5·5; OAc, 14·7%). 2-*Benzyl*-3-*styrylquinoxaline* (IV), formed by use of *o*-phenylenediamine hydrochloride and sodium acetate in hot alcohol, separated from light petroleum (b. p. 60—80°) in pale yellow prisms, m. p. 142—143° (Found: C, 85·8; H, 5·7; N, 8·6. $C_{23}H_{18}N_2$ requires C, 85·7; H, 5·6; N, 8·7%).

3 : 4-*Diphenyl*cyclo*pentane*-1 : 2-*dione* (V) or (VI; R = H).—The red colour of a solution of benzyl styryl diketone (300 mg.) in alcohol (20 ml.) and 2N-sodium hydroxide (10 ml.) faded at 80° to yellow in 5 min. Liberated from the cooled solution by concentrated hydrochloric acid, the product crystallised from alcohol, giving 3 : 4-*diphenyl*cyclo*pentane*-1 : 2-*dione* in faintly yellow needles (300 mg.), m. p. 173—176°, insoluble in aqueous sodium hydrogen carbonate and having $\lambda_{max.}$ 306 mμ (log ε 4·39) (Found: C, 81·5; H, 5·8. Calc. for $C_{17}H_{14}O_2$: C, 81·6; H, 5·6%). The *acetate* (VI; R = Ac) (formed by acetic anhydride and sodium acetate), when purified from alcohol, formed massive prisms, m. p. 146° (Found: C, 78·0; H, 5·8; OAc, 18·3. $C_{17}H_{13}O{\cdot}OAc$ requires C, 78·1; H, 5·5; OAc, 14·7%).

γ-*Oxo*-βγ-*diphenylbutyric Acid* (VII).—3 : 4-Diphenyl*cyclo*pentane-1 : 2-dione (0·5 g.) in the least volume of acetone was treated slowly with a saturated solution of potassium permanganate in 2N-sulphuric acid until a permanent pink colour developed. On decolorisation with sulphur dioxide and evaporation of the acetone, the solution deposited a white solid which was purified from aqueous alcohol, giving the organic acid in prisms, m. p. 163°, soluble in aqueous sodium hydrogen carbonate (Found: C, 75·4; H, 5·8%; equiv., 261. Calc. for $C_{15}H_{13}O{\cdot}CO_2H$: C, 75·6; H, 5·5%; equiv., 254). This acid was identical (mixed m. p. and infrared techniques) with a specimen prepared by the method of Thiele and Straus;[6] it gave with boiling aniline a pyrrolone,[6] m. p. 198°; its infrared spectrum included bands at 2630 and 1690 ($CO_2H$) and 1672 cm.$^{-1}$ (acetophenone C:O); and its ultraviolet spectrum [$\lambda_{max.}$ 246 mμ (log ε 4·09)] agreed with that of acetophenone.

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[7] Wilds, Beck, Close, Djerassi, Johnson, Johnson, and Shunk, *J. Amer. Chem. Soc.*, 1947, **69**, 1985.

[8] Bellamy and Williams, *J.*, 1957, 861.