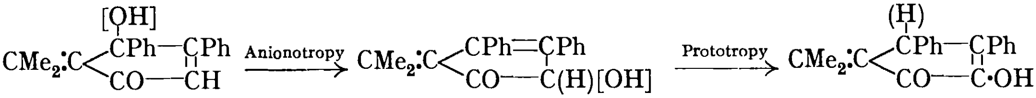
54. *Anionotropic and Prototropic Changes in Cyclic Systems. Part IV. Hydroxy*-3 : 4-*diphenyl*-5-iso*propylidene*cyclo*pentenones.*

By Harold Burton and Charles W. Shoppee.

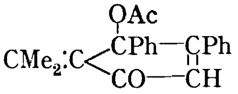
Japp and Knox (J., 1905, **87**, 673) obtained, by condensation of mesityl oxide and benzil in the presence of alkali, 4-hydroxy-3 : 4-diphenyl-5-*iso*propylidene-Δ^2-*cyclo*pentenone (I). This substance, whilst unaffected by treatment with boiling acetic anhydride alone, in the presence of a trace of sulphuric acid affords an acetyl derivative, which, by alkaline hydrolysis, neither regenerates (I) nor affords a hydroxy-ketone of the keto-enol type (Gray, J., 1909, **95**, 2138), thereby appearing to differ from other 5 : 5-substituted *cyclo*pentenones recently examined (Burton, Shoppee, and Wilson, J., 1933, 720; Burton and Shoppee, preceding papers). We are able to show that the transformations undergone by the compounds of the *iso*propylidene series are fundamentally identical with those displayed by the 5 : 5-dimethyl and 5-benzylidene compounds, by the isolation of all three alcohols required by the scheme : I ⟶ II ⟶ III.



$$\mathrm{CMe_2{:}C}<\begin{array}{l}\mathrm{\overset{[OH]}{C}Ph{-}CPh}\\ \mathrm{CO{-}CH}\end{array}\xrightarrow{\text{Anionotropy}}\mathrm{CMe_2{:}C}<\begin{array}{l}\mathrm{CPh{=}CPh}\\ \mathrm{CO{-}C(H)[OH]}\end{array}\xrightarrow{\text{Prototropy}}\mathrm{CMe_2{:}C}<\begin{array}{l}\mathrm{CPh{-}\overset{(H)}{C}Ph}\\ \mathrm{CO{-}C{\cdot}OH}\end{array}$$

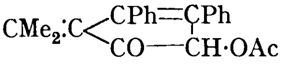
(I.) (II.) (III.)

The acetyl derivative given by (I) has the constitution (V), and is formed by anionotropic change from the hypothetical acetate (IV) of (I). All attempts to isolate (IV) failed, apparently because conditions sufficiently vigorous to cause acetylation also cause anionotropy; under all conditions leading to acetylation, (V) is the sole product. Reduction of (V) with hydriodic acid yields 3 : 4-diphenyl-5-*iso*propylidene-Δ^3-*cyclo*pentenone



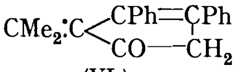
$$\mathrm{CMe_2{:}C}<\begin{array}{l}\mathrm{\overset{OAc}{C}Ph{-}CPh}\\ \mathrm{CO{-}CH}\end{array}$$

(IV.)



$$\mathrm{CMe_2{:}C}<\begin{array}{l}\mathrm{CPh{=}CPh}\\ \mathrm{CO{-}CH{\cdot}OAc}\end{array}$$

(V.)



$$\mathrm{CMe_2{:}C}<\begin{array}{l}\mathrm{CPh{=}CPh}\\ \mathrm{CO{-}CH_2}\end{array}$$

(VI.)

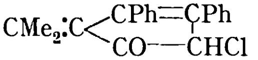
(VI), previously obtained by Japp and Knox (*loc. cit.*) by reduction of (I) with hydriodic acid. Since the ketone gives a *benzylidene* derivative, it must have the constitution (VI), and its production from (I) therefore constitutes a further example of the $\Delta^2 \longrightarrow \Delta^3$-double-bond migration, the explanation of which we have already given (Burton, Shoppee, and Wilson, *loc. cit.*).

When the acetate (V) is treated with alkaline reagents, deep-seated decomposition occurs. Hydrolysis with hydrochloric acid in acetone, however, proceeds smoothly, to give a mixture of a *chloride* and an *alcohol*, in which the former preponderates. The chlorine atom of the chloride is unaffected by metal acetates, but with 3% aqueous-alcoholic potassium hydroxide it is removed to furnish *2-hydroxy-3 : 4-diphenyl-5-*iso*propylidene-Δ^2-*cyclo*pentenone* (III); this substance is a typical keto-enol, and gives a brown-violet colour with ferric chloride.

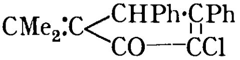
Since the alcohol, the isolation of which is mentioned above, gives no colour with ferric chloride, is isomeric and non-identical with either (I) or (III), and gives acetone by ozonolysis, it must have the constitution (II). We were, however, unable to cause prototropic conversion (II) ⟶ (III) by brief treatment with hot alcoholic sodium ethoxide solution, and lack of material prevented a repetition over a more extended period.

The foregoing chloride might have either of the structures (VII) and (VIII); the former is supported solely by the formation of traces of diphenylmaleic anhydride on oxidation with potassium permanganate.

(VII.)



$$\mathrm{CMe_2{:}C}<\begin{array}{l}\mathrm{CPh{=}CPh}\\ \mathrm{CO{-}CHCl}\end{array}$$



$$\mathrm{CMe_2{:}C}<\begin{array}{l}\mathrm{CHPh{\cdot}CPh}\\ \mathrm{CO{-}CCl}\end{array}$$

(VIII.)

On the other hand the stability of the chlorine atom is inconsistent with formulation as an α-chloro-ketone (VII); formula (VIII) expresses the relative unreactivity of the chlorine atom, and receives some support from the reactions and method of formation of the lower homologue, 2-chloro-3 : 4-diphenyl-Δ^2-*cyclo*pentenone (Burton and Shoppee, preceding paper). Scarcity of material prevented us from reaching a definite conclusion as to the structure of the chloride.

EXPERIMENTAL.

*4-Hydroxy-3 : 4-diphenyl-5-*iso*propylidene-Δ^2-*cyclo*pentenone* (I).—This was prepared as described by Japp and Knox (*loc. cit.*); it was found advantageous to dissolve the dry black semi-solid reaction product in the minimum amount of benzene, filter off the crystalline product, and recrystallise it from benzene; the yield was exceedingly small. A second yellow substance, insoluble in pyridine, and crystallising from nitrobenzene, m. p. 251—252° (decomp.), was also formed (Found : C, 84·2; H, 5·5%).

*2-Acetoxy-3 : 4-diphenyl-5-*iso*propylidene-Δ^3-*cyclo*pentenone* (V).—The dark product obtained by treating (I) with acetic anhydride in the presence of a trace of concentrated sulphuric acid (Japp and Knox, *loc. cit.*) was extracted with hot ligroin (b. p. 60—80°), and the solid which separated repeatedly crystallised from the same solvent. The acetate formed buff needles, m. p. 140—141° (Found: C, 79·1; H, 6·2. Calc. for $C_{22}H_{20}O_3$: C, 79·5; H, 6·05%). We were unable to verify the double m. p. reported by Japp and Knox for this acetate.

The acetate was reduced by boiling with hydriodic acid (*d* 1·95) for 5 minutes; the solid obtained on cooling was dissolved in a large volume of ether, and the ethereal solution washed with sulphurous acid and with 2*N*-sodium carbonate solution, dried (potassium carbonate), and evaporated. The ketone, crystallised twice from benzene, had m. p. 171° (Found: C, 87·4; H, 6·7. Calc. for $C_{20}H_{18}O$: C, 87·6; H, 6·6%); the *benzylidene* derivative, obtained by condensation with benzaldehyde in the presence of alcoholic sodium ethoxide, separated from alcohol as an orange powder, m. p. 234°; the amount was insufficient for complete purification (Found: C, 88·2; H, 6·0. $C_{27}H_{22}O$ requires C, 89·5; H, 6·1%).

Ozonolysis of the acetate in chloroform solution, and decomposition of the ozonide with hot water, gave acetone (iodoform reaction) and unidentified substances.

Alkaline hydrolysis of the acetate invariably led to the formation of dark intractable viscous products.

Acid Hydrolysis of the Acetate (V).—The acetate (2 g.), acetone (22·5 c.c.), and concentrated hydrochloric acid (2·5 c.c.) were refluxed on the steam bath for ½ hour, and the acetone allowed to evaporate. Crystallisation of the product from ligroin (b. p. 100—120°) showed the presence of two substances; the first crop, feathery prisms, had m. p. 172°, and the second crop, which separated in burrs, had m. p. 192°. Fractional crystallisation from ligroin (b. p. 100—120°) ultimately gave as the major product 2-*chloro*-3 : 4-*diphenyl*-5-iso*propylidene*-Δ^2-cyclo*pentenone* (?), m. p. 188° [Found: C, 78·0, 77·7; H, 5·7, 5·6; Cl, 11·3, 11·9; *M* (Rast), 297, 289. $C_{20}H_{17}OCl$ requires C, 77·8; H, 5·55%; *M*, 308·5]; the chloride separated from alcohol in colourless prisms, m. p. unchanged. As the minor product, there was obtained 2-*hydroxy*-3 : 4-*diphenyl*-5-iso*propylidene*-Δ^3-cyclo*pentenone* (II), which crystallised from alcohol in colourless felted needles, m. p. 207° [Found: C, 82·7, 82·7; H, 6·3, 6·3; *M* (Rast), 262, 280, 280, 295. $C_{20}H_{18}O_2$ requires C, 82·7; H, 6·25%; *M*, 290]. The substance gave no colour with ferric chloride, and was recovered unchanged after treatment for ¼ hour with hot 1·45*N*-sodium ethoxide. Ozonolysis in chloroform solution, and decomposition of the ozonide with hot water, gave acetone and unidentified substances.

2-*Hydroxy*-3 : 4-*diphenyl*-5-iso*propylidene*-Δ^2-cyclo*pentenone* (III).—The chloride was heated for ½ hour with 3% aqueous-alcoholic potassium hydroxide; the yellow solution was cooled, diluted, and filtered, and the filtrate acidified. The precipitate was recrystallised several times from glacial acetic acid, from which 2-*hydroxy*-3 : 4-*diphenyl*-5-iso*propylidene*-Δ^2-cyclo*pentenone* separated in colourless needles, m. p. 252° [Found: C, 82·5; H, 6·3; *M* (Rast), 277, 274. $C_{20}H_{18}O_2$ requires C, 82·7; H, 6·25%; *M*, 290]. With alcoholic ferric chloride, the substance gave a brown-violet colour.

Oxidation of the Chloride (VII *or* VIII) *with Potassium Permanganate.*—The procedure given by Burton and Shoppee (this vol., p. 204) was followed. The acid extract gave only benzoic acid, but the quasi-acid fraction yielded a small quantity of diphenylmaleic anhydride, m. p. 149—150°, identified by direct comparison with a genuine specimen. The neutral fraction consisted of the unaltered chloride, m. p. 188° after crystallisation from alcohol.

Non-action of Methyl Alcohol and Silver Acetate on the Chloride (VII *or* VIII).—After refluxing with an equal weight of silver acetate in absolute methyl alcohol for ½ hour, the chloride was unaltered.

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[*Received, December* 12*th*, 1933.]