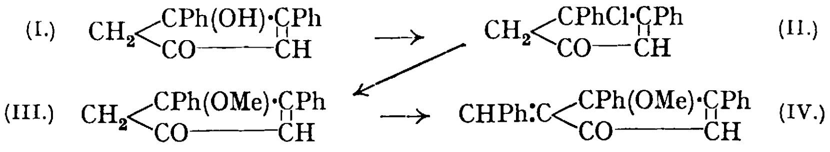
53. *Anionotropic and Prototropic Changes in Cyclic Systems. Part III. The Isomeric Chloro*-3 : 4-*diphenyl*cyclo*pentenones.*

By Harold Burton and Charles W. Shoppee.

In previous papers (J., 1933, 720; preceding paper) we have adduced evidence in support of the hypothesis that the reactions undergone by 4-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl- and -5-benzylidene-Δ^2-*cyclo*pentenones are explicable on the basis of triad anionotropic and prototropic changes. We now deal with the parent compound 4-hydroxy-3 : 4-diphenyl-Δ^2-*cyclo*pentenone (" anhydroacetonebenzil ") (I).

The chemistry of anhydroacetonebenzil is complicated by the presence of the methylene group in the α-position to the keto-group, since the methylene hydrogen atoms can become part of a triad prototropic system [compare, for example, the change (V) ⟶ (VII), which might occur]. We have therefore endeavoured to inter-relate, wherever possible, the compounds of the unsubstituted series with those of the 5-benzylidene series, and to use the latter as reference compounds, since we have shown that their behaviour is precisely analogous to that of the 5 : 5-dimethyl compounds.

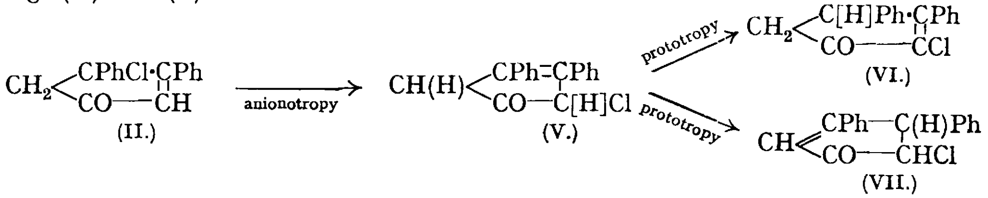
Allen and Spanagel (*J. Amer. Chem. Soc.*, 1932, **54**, 4338), by treatment of (I) with thionyl chloride or acetyl chloride, obtained a chloride which they correctly formulated as (II). We have proved this by identifying the single methyl ether (III), obtained from (II) by the action of methyl alcohol and silver acetate, with that obtained from (I) by direct methylation with methyl iodide and silver oxide, and by showing that the benzylidene derivatives (IV), m. p. 158° and 122°, obtained by condensing (III) with benzaldehyde are identical, each to each, with the methyl ethers prepared from the stereoisomeric 5-benzylideneanhydroacetonebenzils by methylation with methyl iodide and silver oxide.



(I.) $CH_2{<}\begin{matrix}CPh(OH)\cdot CPh\\ CO\text{——}CH\end{matrix}$ ⟶ (II.) $CH_2{<}\begin{matrix}CPhCl\cdot CPh\\ CO\text{——}CH\end{matrix}$

(III.) $CH_2{<}\begin{matrix}CPh(OMe)\cdot CPh\\ CO\text{——}CH\end{matrix}$ ⟶ (IV.) $CHPh{:}C{<}\begin{matrix}CPh(OMe)\cdot CPh\\ CO\text{——}CH\end{matrix}$

In the light of our previous work in the dimethyl series, it was to be anticipated that the chloride (II) would undergo, under the appropriate conditions, the anionotropic change (II) ⟶ (V).



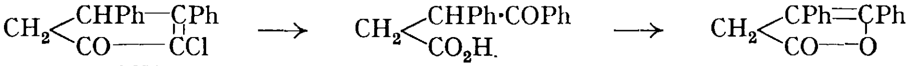
$CH_2{<}\begin{matrix}CPhCl\cdot CPh\\ CO\text{——}CH\end{matrix}$ (II.) $\xrightarrow[\text{anionotropy}]{}$ $CH(H){<}\begin{matrix}CPh{=}CPh\\ CO\text{—}C[H]Cl\end{matrix}$ (V.)

prototropy ⟶ $CH_2{<}\begin{matrix}C[H]Ph\cdot CPh\\ CO\text{——}CCl\end{matrix}$ (VI.)

prototropy ⟶ $CH{\leqslant}\begin{matrix}CPh\text{—}C(H)Ph\\ CO\text{—}CHCl\end{matrix}$ (VII.)

Unlike its 5 : 5-dimethyl derivative, the chloride (II), whilst possessing a potentially ionic chlorine atom, shows no tendency to react in the anionotropic form (V); *e.g.*, it yields the single methyl ether (III), and its most characteristic reaction is the elimination of hydrogen chloride, with subsequent dimerisation of the *cyclo*pentadienone formed.

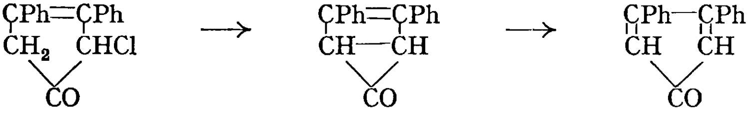
When the chloride (II) is treated with hydrogen chloride in ethereal solution, it passes into an isomeric chloride (compare Allen and Spanagel, *loc. cit.*), previously prepared by Japp and Burton (J., 1887, **51**, 428) from anhydroacetonebenzil by the action of alcoholic hydrogen chloride. The chlorine atom of this chloride is (relatively) very stable, being unaffected by silver acetate in methyl alcohol or acetic acid, or by weak bases such as pyridine. Such properties, taken together with the well-known stability of halogen in the (aliphatic) group C:C·Cl (*e.g.*, ethyl chlorofumarate), suggest that the chloride has the structure (VI), and we proved this in what we consider to be a conclusive manner, by oxidation with potassium permanganate in acetone solution at 15°, whereby an 88% yield of desylacetic acid (VIII) is obtained. The identity of (VIII) was proved by dehydration to βγ-diphenyl-Δ^{β}-butenolactone (IX) (compare Japp and Lander, J., 1897, **71**, 136). This result excludes the alternative formula (VII) for Japp's chloride, which



(VI.) (VIII.) (IX.)

was assigned by Allen and Spanagel on the basis of theoretical reasoning which we are unable to follow. Formula (VII) is inconsistent with the relative unreactivity of the halogen atom, since it is an α-chloro-ketone and as such should react with the above reagents. Formula (VI) is, however, consistent with the formation of the chloride as described by Allen and Spanagel from the isomeride (II), and by Japp and Burton from anhydroacetonebenzil (I), since not only anionotropy but also prototropy is capable of catalysis by acidic reagents.

We are unable to confirm Allen and Spanagel's statement (*loc. cit.*) that Japp's chloride, by treatment with 10% aqueous-alcoholic potassium hydroxide, is converted into the dimeride, $C_{34}H_{24}O_2$, in almost quantitative yield. Under the conditions described by these authors a viscous product results; there is little doubt that the dimeride is first formed, since we have shown that, under the experimental conditions used, the pure dimeride is converted into a similar viscous mass. Since the chloride undoubtedly has the structure (VI) and not (VII), such a conversion cannot be a facile process, for both retrograde prototropic (VI) ⟶ (V) and anionotropic changes (V) ⟶ (II) are necessary for the formation of 3 : 4-diphenyl*cyclo*pentadienone (X) (the precursor of the dimeride) by elimination of hydrogen chloride. It is possible that the prototropic change (VI) ⟶ (V) only might suffice since transannular elimination of hydrogen chloride would give 3 : 4-diphenyl*dicyclo*pentenone (XI), which is the intra-annular valency tautomeride of (X).

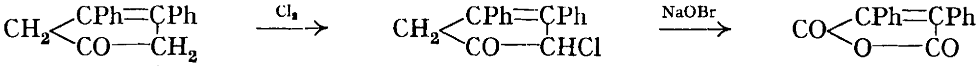


(V.) (XI.) (X.)

Whilst we are unable to distinguish between the foregoing alternatives, the following evidence indicates that it is a prototropic change which is of major importance. Allen and Spanagel found, and we have confirmed their result, that the chloride (VI) is unaffected by boiling pyridine ($K = 2{\cdot}4 \times 10^{-9}$); use of quinoline ($K = 1{\cdot}0 \times 10^{-9}$) at the boiling point slowly causes the chloride to lose hydrogen chloride. With warm piperidine ($K = 1{\cdot}6 \times 10^{-3}$) an almost instantaneous and quantitative elimination of hydrogen chloride occurs, and the use of alcoholic sodium hydroxide undoubtedly causes the same change to occur more rapidly. Since prototropy is catalysed most effectively by basic reagents [*e.g.*, anions in the order of their increasing basicity (compare Ingold and Shoppee, J., 1929, 476; Kon and Linstead, *ibid.*, p. 1269)], we infer that the initial stage in the production of the dimeride $C_{34}H_{24}O_2$ from Japp's chloride is a prototropic change, probably (VI) ⟶ (V).

The chloride (VI) is readily characterised as a ketone by the formation of a 2 : 4-dinitrophenylhydrazone, but attempts to demonstrate the presence of a methylene group in the α-position to the carbonyl group by the usual condensation reactions were abortive owing to the reactions, described above, which supervene in the presence of the usual condensing reagents. Use of zinc chloride was fruitless, and the chloride appeared to be unaffected by nitrosyl chloride.

We have prepared the *chloride* (V), which is very unstable, by direct chlorination of 3 : 4-diphenyl-Δ^3-*cyclo*pentenone (XIII) at 110°, and more satisfactorily by the use of sulphuryl chloride at 20°. The chloride possesses a potentially ionic chlorine atom, and reacts with alcoholic silver nitrate and with methyl-alcoholic silver acetate to give silver chloride; in the latter case a viscous gum also resulted from which no crystalline material could be isolated. When oxidised with sodium hypobromite in aqueous suspension at 0°, the chloride gives diphenylmaleic anhydride (XIV), which affords further proof of its constitution.



$$\mathrm{CH_2}{<}\begin{array}{l}\mathrm{CPh{=}CPh}\\ \mathrm{CO{-\!\!-}CH_2}\end{array} \xrightarrow{\mathrm{Cl_2}} \mathrm{CH_2}{<}\begin{array}{l}\mathrm{CPh{=}CPh}\\ \mathrm{CO{-\!\!-}CHCl}\end{array} \xrightarrow{\mathrm{NaOBr}} \mathrm{CO}{<}\begin{array}{l}\mathrm{CPh{=}CPh}\\ \mathrm{O{-\!\!-}CO}\end{array}$$

(XIII.) (V.) (XIV.)

We have also isolated from the reaction product formed by chlorination of (V), a *monochloro-dimeride*, $C_{34}H_{23}O_2Cl$, which can only arise by passage of (V) into the dimeride $C_{34}H_{24}O_2$ by elimination of hydrogen chloride and subsequent chlorination.

In our letter to *Chemistry and Industry* (1932, 981), we said that "we do not accept all the conclusions drawn by Allen and Spanagel (*J. Amer. Chem. Soc.*, 1932, **54**, 4338), since the possibility of either anionotropic or prototropic change is not clearly recognised by them." In a recent paper (*ibid.*, 1933, **55**, 3780), these authors cite Bredereck's observation (*Ber.*, 1932, **65**, 1833) that 2 : 4-dinitrophenylhydrazones exist in yellow and red modifications, and so infer that our evidence (Part I) regarding the isomeric methoxydiphenyldimethyl*cyclo*pentenone-2 : 4-dinitrophenylhydrazones is inconclusive. We were aware of Bredereck's paper, and we wish to state that under his conditions, no isomerism has ever been observed; we regret that we omitted specifically to mention this in Part I.

We presume that Allen and Spanagel's statement that "ββ-dimethylanhydroacetonebenzil (I) does not give an isomeric chloride under the same conditions as the parent substance" refers to an isomeride analogous to Japp's chloride (above); we agree with this view and should like to point out that our criticism does not refer to such an isomeride. There is, however, no doubt that isomeric chlorides are produced from (I) (see Part I) and our original criticism refers mainly to these isomerides.

We have not criticised Allen and Spanagel's proposed mechanism for the production of the dimeric compound—in fact, we had arrived at the same conclusion. We cannot, however, hold with the view that Japp's chloride is formed by addition of hydrogen chloride to 3 : 4-diphenyl*cyclo*pentadienone.

EXPERIMENTAL.

4-*Chloro*-3 : 4-*diphenyl*-Δ^2-cyclo*pentenone* (II).—This was prepared from anhydroacetonebenzil and acetyl chloride (Allen and Spanagel, *loc. cit.*); the reaction was incomplete, and the product contained the dimeride, $C_{34}H_{24}O_2$. We were unable to obtain either the yield or the m. p. (121°) of the chloride given by Allen and Spanagel; our best preparations had m. p. 116—117° after repeated crystallisation from di-*n*-butyl ether (Found : Cl, 11·5. Calc. for $C_{17}H_{13}OCl$: Cl, 13·2%). Use of thionyl chloride gave some chloride, but the initial material was largely unchanged. When refluxed with glacial acetic acid and silver acetate, the chloride passed into the dimeride, $C_{34}H_{24}O_2$, m. p. 205° (gas evolution).

4-*Methoxy*-3 : 4-*diphenyl*-Δ^2-cyclo*pentenone* (III).—(a) The chloride (II), when refluxed for ½ hour with absolute methyl alcohol and an equal weight of silver acetate, gave a 60% yield of the methyl ether, m. p. 123·5° after crystallisation from methyl alcohol (Found : C, 81·8; H, 6·1; OMe, 11·8. Calc. for $C_{18}H_{16}O_2$: C, 81·7; H, 6·1; OMe, 11·7%).

(b) Anhydroacetonebenzil (5 g.), silver oxide (20 g.), powdered sodium hydroxide (0·2 g.), and methyl iodide (50 c.c.) were heated under reflux for a week. After removal of the excess of methyl iodide, the product was extracted with hot acetone (5 × 20 c.c.), and the combined filtered extracts evaporated. The product crystallised when rubbed with methyl alcohol, and after several crystallisations from this solvent had m. p. 123·5°, mixed m. p. with preparation (a) 123·5° (Found: C, 81·6; H, 6·0; OMe, 11·5, 11·8. Calc. for $C_{18}H_{16}O_2$: C, 81·7; H, 6·1; OMe, 11·7%).

In order further to confirm the identity of the methyl ethers prepared by methods (a) and (b) we attempted to prepare the dibromo-derivative described by Allen and Spanagel. Treatment of either preparation with an excess of bromine in chloroform solution at 15° for 48 hours yielded a *compound*, $C_{17}H_{10}OBr_4$, which, after repeated crystallisation from methyl alcohol, formed buff prisms, m. p. 145° to a red liquid [Found: (a) C, 37·6; H, 1·9; Br, 57·4; OMe, 0: (b) Br, 57·8; OMe, 0. $C_{17}H_{10}OBr_4$ requires C, 37·1; H, 1·8; Br, 58·2%).

Condensation of the Methoxy-compound (III) *with Benzaldehyde.*—By following Allen and Spanagel's directions, there was obtained a low-melting product, from which, by crystallisation from ethyl acetate, 4-methoxy-3 : 4-diphenyl-5-benzylidene-Δ^2-*cyclo*pentenone, m. p. 158°, was obtained; it was shown by mixed m. p. to be identical with the specimen previously prepared (Burton and Shoppee, preceding paper) by methylation of 4-hydroxy-3 : 4-diphenyl-5-benzylidene-Δ^2-*cyclo*pentenone, m. p. 232°, with methyl iodide and activated silver oxide. The ethyl acetate mother-liquors by evaporation, and fractional crystallisation of the product from methyl alcohol, yielded a further quantity of the above benzylidene derivative, m. p. 158°, together with the stereoisomeric 4-methoxy-3 : 4-diphenyl-5-benzylidene-Δ^2-*cyclo*pentenone, m. p. 122°, identical with the specimen prepared by us from the stereoisomeric 4-hydroxy-3 : 4-diphenyl-5-benzylidene-Δ^2-*cyclo*pentenone, m. p. 213·5°.

2-*Chloro*-3 : 4-*diphenyl*-Δ^2-cyclo*pentenone* (VI).—(a) Anhydroacetonebenzil was dissolved in a cold saturated solution of hydrogen chloride in alcohol; after 24 hours, the product was precipitated by much water. After several crystallisations and treatment with charcoal 2-*chloro*-3 : 4-*diphenyl*-Δ^2-cyclo*pentenone* was obtained in colourless prisms, m. p. 128—129° [Found: Cl, 13·6; *M* (Rast), 230, 248. $C_{17}H_{13}OCl$ requires Cl, 13·2%; *M*, 268·5]. By treatment with 2 : 4-dinitrophenylhydrazine sulphate in alcohol, it readily gave the 2 : 4-dinitrophenylhydrazone, m. p. 217° (decomp.), described by Allen and Spanagel (Found: C, 61·2; H, 3·95; Cl, 8·1. Calc. for $C_{23}H_{17}O_4N_4Cl$: C, 61·4; H, 3·8; Cl, 7·9%).

(b) A solution of the chloride (II) in dry ether was saturated with dry hydrogen chloride and kept over-night. The solid obtained by spontaneous evaporation was drained from oil, and consisted of the dimeride, $C_{34}H_{24}O_2$, and some unchanged chloride. The oil partly solidified when rubbed with methyl alcohol, and the solid, after draining, was recrystallised from alcohol. It had m. p. 128° and was identical with preparation (a).

The chloride (VI) is unchanged by treatment with boiling alcoholic silver nitrate, methyl-alcoholic silver acetate, or by boiling pyridine. With boiling quinoline, the solution darkens, and after ¼ hour, by dilution of the product with dry ether, quinoline hydrochloride was isolated; the ether-soluble portion of the product could not be crystallised. By warming with piperidine, the liquid rapidly solidified to a mass of crystals of piperidine hydrochloride, m. p. 237°; after filtration from the hydrochloride, the filtrate was treated with ice-cold 2*N*-hydrochloric acid, and the precipitated solid filtered off. The dry solid, crystallised from benzene several times, had m. p. 205° (gas evolution), and did not depress the m. p. of a genuine specimen of the dimeride, $C_{34}H_{24}O_2$; the yield was nearly quantitative.

Reduction of the Chloride (VI).—Use of zinc dust in boiling glacial acetic acid was only partly effective, the bulk of the chloride being recovered unaltered; a *substance*, $C_{34}H_{25}OCl$, crystallising from benzene in orange-pink rosettes, m. p. 210° (decomp.), was isolated (Found: C, 84·6; H, 5·4; Cl, 6·6. $C_{34}H_{25}OCl$ requires C, 84·3; H, 5·2; Cl, 7·3%).

Oxidation of the Chloride (VI).—(a) *With ozone.* The chloride (1 g.), dissolved in chloroform, was treated with ozonised oxygen for 4 hours. On decomposition of the product, obtained by evaporating the chloroform, with hot water, traces of a volatile aldehydic (ketonic) substance giving a *p*-nitrophenylhydrazone, m. p. 117—118° (crude), were obtained; the bulk of the chloride was recovered unchanged. The acid fraction consisted principally of benzoic acid, and the aqueous solution contained chloride ions.

(b) *With potassium permanganate.* The chloride (1·8 g.), dissolved in A.R. acetone, was treated with powdered potassium permanganate (2·1 g.) at 15°. After 24 hours, the acetone was evaporated, and the manganese oxides dissolved in sulphurous acid. The solution was further acidified with 2*N*-sulphuric acid, and repeatedly extracted with ether. The ethereal extract was washed with sodium bicarbonate solution, and the alkaline washings acidified and extracted with ether. This extract after drying (sodium sulphate) and evaporation gave desylacetic acid (0·9 g.), m. p. 162° after crystallisation from acetone–ether [Found : C, 75·4; H, 5·65; *M* (Rast), 249, 253. Calc. for $C_{16}H_{14}O_3$: C, 75·6; H, 5·55%; *M*, 254]. The acid was completely stable to alkaline permanganate; further to identify it and to exclude desyleneacetic acid (compare Japp and Lander, *loc. cit.*), the acid was dehydrated by heating at 220° in a vacuum, whereby βγ-diphenyl-Δ^{β}-butenolactone, m. p. 151° after crystallisation from benzene, was obtained (compare Klingemann, *Annalen*, 1892, **269**, 134) (Found : C, 81·3; H, 5·3. Calc. for $C_{16}H_{12}O_2$: C, 81·35; H, 5·1%). From the original ethereal extract the chloride (VI) (0·7 g.) was recovered, m. p. 128—129°, mixed m. p. 128—129°.

Action of Alkaline Reagents on the Chloride (VI).—(a) Aqueous-alcoholic potassium hydroxide under the conditions given by Allen and Spanagel (*loc. cit.*) yielded only yellow resins, completely and readily soluble in alcohol and benzene. Three experiments were made and in no case were we able to isolate the dimeride, $C_{34}H_{24}O_2$. The pure dimeride under the same conditions gave a similar resinous uncrystallisable product.

(b) The chloride (VI) was treated for 3 hours with boiling 1·45*N*-sodium methoxide; fractional crystallisation of the product yielded only amorphous high-melting brown solids.

2-*Chloro*-3 : 4-*diphenyl*-Δ^3-cyclo*pentenone* (V).—(a) 3 : 4-Diphenyl-Δ^3-*cyclo*pentenone (2·35 g.) (see preceding paper) was treated with chlorine at 115° until the gain in weight was 0·35 g.; the cooled product was dissolved in benzene, and the solid which crystallised filtered off. The benzene filtrate was diluted with ligroin (b. p. 40—60) and cooled to − 8°; the benzene–ligroin mixture was decanted from the solid which separated, the latter washed with ligroin, and recrystallised from benzene–ligroin with cooling. The *chloride* melted at 50° to a turbid liquid which cleared a few degrees higher, and was probably identical with preparation (b). The solid which separated first was crystallised from benzene or di-*n*-butyl ether; it formed colourless needles, m. p. 216° (with gas evolution), and is a *monochloro-dimeride*, $C_{34}H_{23}O_2Cl$ [Found : C, 82·4; H, 4·8; Cl, 6·8; *M* (Rast), 404, 411. $C_{34}H_{23}O_2Cl$ requires C, 81·8; H, 4·6; Cl, 7·1%; *M*, 498].

(b) 3 : 4-Diphenyl-Δ^3-*cyclo*pentenone (5 g.) in benzene (15 c.c.) reacted readily with sulphuryl chloride (2·5 c.c.) at 20°. The liquid was diluted with ligroin (b. p. 40—60°) and cooled to − 8°. The crystalline solid which separated was rapidly drained on porcelain, washed with ligroin, and recrystallised from benzene–ligroin with cooling. 2-*Chloro*-3 : 4-*diphenyl*-Δ^3-cyclo*pentenone* melts at 48° to a turbid liquid, clearing at 52° [Found : C, 76·1; H, 5·1; Cl, 13·4; *M* (Rast), 219, 235. $C_{17}H_{13}OCl$ requires C, 76·0; H, 4·9; Cl, 13·2%; *M*, 268·5]. The chloride rapidly decomposes in air, giving a sticky solid; the chlorine atom reacts readily with metal salts. In some preparations we have isolated from the benzene–ligroin mother-liquor after standing the monochloro-dimeride, m. p. 216° (with gas evolution) (Found : Cl, 8·0%).

Oxidation of the Chloride (V) *with Sodium Hypobromite*.—The procedure described by Japp and Lander (*loc. cit.*, p. 132) was followed; the solution was kept at 0° and stirred mechanically. The acid extract gave only benzoic acid, but the quasi-acid fraction consisted of diphenylmaleic anhydride, m. p. 150° after crystallisation from ligroin (b. p. 100—120°) (Found : C, 76·9; H, 4·2. Calc. for $C_{16}H_{10}O_3$: C, 76·8; H, 4·0%). The neutral fraction was small and viscous, and afforded no identifiable product.

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