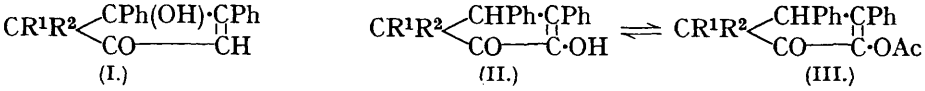
181. *Anionotropic and Prototropic Changes in Cyclic Systems. Part I. Hydroxy*cyclo*pentenones.*

By Harold Burton, Charles W. Shoppee, and Christopher L. Wilson.

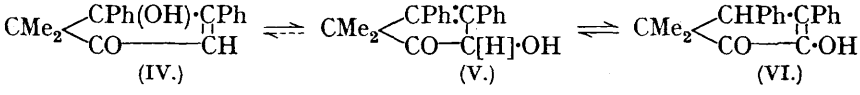
Japp and his collaborators have shown (J., 1885, **47**, 33; 1887, **51**, 425; 1897, **71**, 130; 1899, **75**, 1017; 1901, **79**, 1024; 1903, **83**, 279; 1904, **85**, 1473; 1905, **87**, 673) that benzil condenses with the simpler aliphatic ketones to give 4-hydroxy-3 : 4-diphenyl-Δ^2-*cyclo*-pentenones ("anhydroacetonebenzils") (I). The properties of these cyclic compounds have been further studied by Gray (J., 1909, **95**, 2131, 2138), who emphasised the extreme difficulty of proving directly the presence of the *tert.*-hydroxyl group by acylation. Acetylation proceeds only when R^1 and R^2 are groups other than hydrogen, and the acetyl derivatives formed exhibit an interesting change when hydrolysed. Gray proved conclusively that hydrolysis does not regenerate the parent hydroxy*cyclo*pentenone, but gives

an isomeride (II) which has the properties of an α-hydroxy-ketone and yields the corresponding acetate (III), from which (II) can be regenerated by hydrolysis.



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

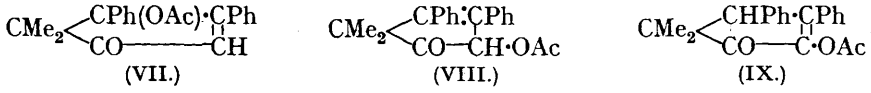
We have investigated the changes involved in the conversion of (I) into (II), using 4-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^2-*cyclo*pentenone (IV) as our initial material and assuming the following working hypothesis: the mechanism consists of two consecutive tautomeric changes, the first anionotropic and the second prototropic in character. Structure (IV) contains both the molecular conditions necessary for three-carbon anionotropy, namely, the group $\cdot\dot{C}_\alpha(OH)\cdot\dot{C}\dot{:}\dot{C}\cdot$, and a suitable activating group (Ph attached to C_α); hence under the conditions which have been laid down by one of us (Burton, J., 1928, 1650) conversion into the tautomeride (V) is to be anticipated. Structure (V), however, contains a three-carbon prototropic system; there is present the group $\cdot\dot{C}\dot{:}\dot{C}\cdot\dot{C}_\alpha[H]\cdot$, and a powerful activating group, namely, CO attached to C_α. Under suitable conditions (see Ingold and Shoppee, J., 1929, 1199), prototropic interconversion of (V) and its isomeride (VI) is to be expected.



(IV.) (V.) (VI.)

Actually the anionotropic change (IV ⟶ V) relates not to the hydroxy-compound (IV), which is static under all the conditions so far investigated, but to its acetate. This is normal, since it has been shown (Burton, *loc. cit.*) that the facility of anionotropic change depends, amongst other things, on the stability of the mobile anion as indicated by the strengths of the corresponding acids (AcOH > HOH). The above mechanism is, in fact, closely analogous to the change occurring in the transformation of αγ-diarylallyl alcohols (acetates) into aryl β-arylethyl ketones (Burton and Ingold, J., 1928, 904; compare Shoppee, J., 1928, 2567).

We have accumulated a considerable amount of evidence supporting this suggested mechanism by investigating 4-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^2-*cyclo*pentenone ("ββ-dimethylanhydroacetonebenzil") (IV) and its derivatives. First, during an attempted catalytic reduction of 4-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^2-*cyclo*pentenone in acetic acid solution, we have isolated an *acetate* which must have the constitution (VII), since it regenerates the parent hydroxy-compound on hydrolysis and, when boiled with acetic anhydride, passes into the acetate, m. p. 137°, described by Gray (*loc. cit.*). To the latter acetate Gray assigned structure (VII), but it must now be formulated as (VIII).

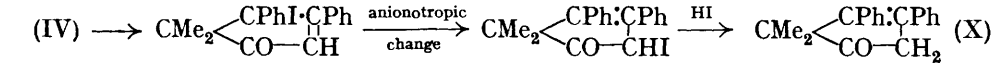


(VII.) (VIII.) (IX.)

Unfortunately, we were unable to prepare (VII) by any known method of acetylation, including the use of keten. The acetate (VIII), when treated with alcoholic potassium hydroxide (Gray, *loc. cit.*), undergoes prototropic conversion into the isomeride (IX), which is hydrolysed readily to 2-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^2-*cyclo*pentenone (VI). We have attempted to isolate the intermediate acetate (IX) by using dry 1·45*N*-sodium ethoxide at 85° as the catalyst for promoting the prototropic change (VIII) ⟶ (IX), but here again hydrolysis supervened. Attempted formation of 2-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^3-*cyclo*pentenone (V) by hydrolysis of the acetate (VIII) with concentrated hydrochloric acid in acetone again led to the isolation of 2-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^2-*cyclo*pentenone, which has been characterised in the tautomeric diketonic form by preparation of a 2 : 4-*dinitrophenylosazone*.

We also endeavoured to establish the position of the acetyl groups in the acetates (VIII) and (IX) by catalytic reduction, since addition of two atoms of hydrogen to either

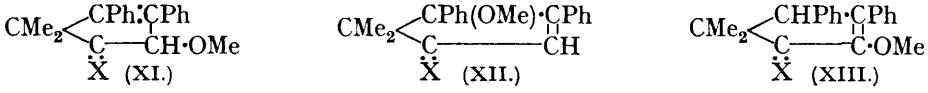
structure should give the same saturated acetate. In both cases absorption of hydrogen in presence of Adams's catalyst is slow and ceases only when five molecules are consumed; the acetyl groups are eliminated and 3(or 4)-*cyclo*hexyl-4(or 3)-phenyl-5 : 5-dimethyl-*cyclo*pentanone, characterised as its 2 : 4-*dinitrophenylhydrazone*, is obtained from either acetate. Similar reduction of 4-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^2-*cyclo*pentenone gave a non-homogeneous product containing none of the above *cyclo*pentanone. The close similarity in the behaviour of the acetates (VIII) and (IX) indicates that their acetoxy-groups are similarly oriented. Reduction of 4-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^2-*cyclo*pentenone with hydriodic acid, or with zinc dust and acetic acid, gives 3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^3-cyclo*pentenone* (X), characterised by the formation of a *benzylidene* derivative, a result which conforms with those of Japp and his collaborators. The generality with which the Δ^2-unsaturated linking migrates to the Δ^3-position is undoubtedly due to the following changes:



3 : 4-Diphenyl-5 : 5-dimethyl-Δ^3-*cyclo*pentenone is fairly resistant to further reduction, but the use of phosphorus and hydriodic acid or the Clemmensen method gives a mixture of 1 : 2-*diphenyl*-3 : 3-*dimethyl*cyclo*pentane* and 3 : 4-diphenyl-5 : 5-dimethyl*cyclo*pentanone. The latter furnishes a *semicarbazone*, m. p. 224°, isomeric with the *semicarbazone*, m. p. 230°, of the 3 : 4-diphenyl-5 : 5-dimethyl*cyclo*pentanone obtained by reduction of 2-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^2-*cyclo*pentenone with phosphorus and hydriodic acid. In view of the different methods of preparation of these *cyclo*pentanones, the semicarbazones may be stereoisomerides.

Oxidation experiments in this series of compounds are not diagnostic of constitution. For instance, addition of hydroxyl groups to 4-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^2-*cyclo*pentenone and 2-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^3-*cyclo*pentenone (as acetate) gives rise to the same intermediate trihydroxy-derivative. Ozonolysis experiments are of little help, since benzoic acid is invariably the main product.

We have been able to prove, in what we consider to be a conclusive manner, the mechanism suggested above by the following observations. When 2-acetoxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^3-*cyclo*pentenone (VIII) is treated with 2 : 4-dinitrophenylhydrazine in methyl alcohol containing sulphuric acid according to the directions of Brady (J., 1931, 756), alcoholysis of the acetoxy-group accompanies hydrazone formation and 2-*methoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^3-cyclo*pentenone*-2 : 4-*dinitrophenylhydrazone* (XI) results. That (XI) has the constitution assigned to it follows from its non-identity with 4-*methoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^2-cyclo*pentenone*-2 : 4-*dinitrophenylhydrazone* (XII) and 2-*methoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^2-cyclo*pentenone*-2 : 4-*dinitrophenylhydrazone* (XIII), which are prepared from the appropriate methyl ethers. Although (XI) and (XII) melt (with decomposition) at the same temperature and show no depression

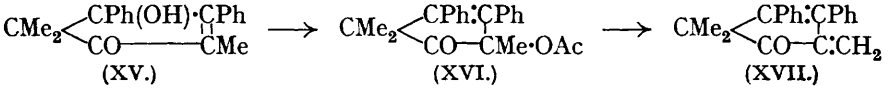


[X = :N·NH·$C_6H_3(NO_2)_2$·]

when mixed, their non-identity is definitely established by their differences in colour and crystalline form and by mixed solubility exaltation. The use of ethyl for methyl alcohol in the above treatment leads to the production of 2-*ethoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^3-cyclo*pentenone*-2 : 4-*dinitrophenylhydrazone* (XI, OMe = OEt), which differs from 2-*ethoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^2-cyclo*pentenone*-2 : 4-*dinitrophenylhydrazone* (XIII, OMe = OEt). Contrary to our statement in *Chem. and Ind.* (1932, **51**, 981), the 2 : 4-dinitrophenylhydrazone (XII, OMe = OEt) of 4-*ethoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^2-cyclo*pentenone* (XIV) is not obtained when this ketone is treated with 2 : 4-dinitrophenylhydrazine in alcoholic-sulphuric or -hydrochloric acid; the resulting *compound*, $C_{25}H_{22}O_5N_4$, is ethoxyl-free and has the composition of a hydroxy-

diphenyldimethyl*cyclo*pentenone-2 : 4-dinitrophenylhydrazone. The compound differs, however, from the 2 : 4-*dinitrophenylhydrazones* of (IV) and (VI), showing that simple hydrolysis, or hydrolysis and subsequent anionotropic and prototropic changes, respectively, do not occur. It is possible that hydrolysis and subsequent anionotropic change take place, in which case the compound is the 2 : 4-dinitrophenylhydrazone of the hitherto unknown (V). We find that the parent ether (XIV), which is prepared under conditions which render a change of structure very improbable, is actually hydrolysed by alcoholic acid, yielding an ethoxyl-free substance of indefinite melting point, but no (IV). The analogous 4-*methoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^2-cyclo*pentenone* is quite stable to hydrolytic agents. We hoped that it might be possible to effect a (partial) prototropic conversion of (XI) into (XIII) by alcoholic potash, in spite of the fact that (XI) contains two prototropic systems, ·N:C·CH and ·C:N·NH·, in addition to that (·CPh:CPh·CH·) essential for the change; this could not be realised.

We also investigated 4-hydroxy-3 : 4-diphenyl-2 : 5 : 5-trimethyl-Δ^2-*cyclo*pentenone (XV) (Japp and Meldrum) (J., 1901, **79**, 1039), which contains an anionotropic but no prototropic system. Treatment of (XV) with acetic anhydride and sulphuric acid gave 3 : 4-*diphenyl*-5 : 5-*dimethyl*-2-*methylene*-Δ^3-cyclo*pentenone* (XVII), which can only result by loss of acetic acid from the intermediate tertiary acetate (XVI); the presence of the extracyclic methylene group was proved by ozonolysis, whereby formaldehyde was formed.

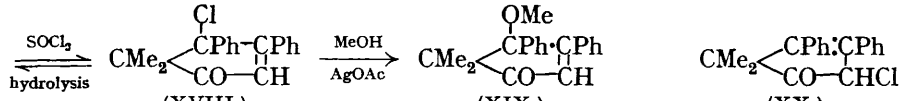


(XV.) (XVI.) (XVII.)

A similar compound was also prepared (but not definitely characterised) by Gray (*loc. cit.*) from 4-hydroxy-3 : 4-diphenyl-5-benzylidene-2-methyl-Δ^2-*cyclo*pentenone.

Whilst we were preparing an account of the above work for publication, Allen and Spanagel (*J. Amer. Chem. Soc.*, 1932, **54**, 4338) described an investigation on the chlorides derived from 4-hydroxy-3 : 4-diphenyl*cyclo*pentenone (I, $R^1=R^2=H$) and its 5 : 5-dimethyl derivative (IV). We do not agree entirely with their conclusions regarding the compounds of either series, but we shall now deal only with the latter; we propose to discuss the former in a subsequent paper.

Treatment of (IV) with thionyl (or acetyl) chloride gives, according to Allen and Spanagel, a chloride, m. p. 133°, which is formulated as (XVIII), and which on refluxing with a very dilute solution of potassium hydroxide in alcohol for ten minutes regenerates (IV) as an insoluble solid, the identity of which is proved by mixed melting point and solubilities; potassium and silver acetates in alcohol led to the same result. Furthermore, (XVIII) and silver acetate in boiling absolute methyl alcohol gave a methoxy-compound, m. p. 144°, formulated as (XIX), whilst silver acetate and glacial acetic acid furnished the acetate, m. p. 137°, described by Gray (*loc. cit.*), and formulated as the 4-acetoxy-derivative (VII).

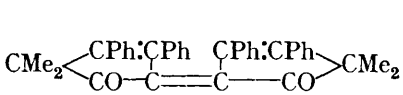


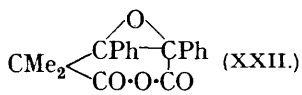
(XVIII.) (XIX.) (XX.)

It would be expected from the reasoning on p. 721 that some, if not all, of the product of interaction of (IV) and thionyl chloride would be the chloride (XX), which is an α-chloro-ketone. Allen and Spanagel have probably considered such a structure (cf. *loc. cit.*, p. 4339) for the chloride (XVIII) and rejected it on grounds which we are unable to follow. All our (independent) attempts * to prepare the chloride, m. p. 133°, have resulted in the isolation of two well-defined isomerides, one of which is obviously identical with that described by Allen and Spanagel, whilst the other melts at 127°. Attempts to regenerate (IV) from the higher-melting chloride by treatment with dilute alcoholic potash were uniformly unsuccessful; the solid separating during the reaction was potassium

* We wish to emphasise that all the experiments relating to Allen and Spanagel's work have been independently repeated by each of the authors and have always given the same results.

chloride. With silver acetate and alcohol, the product was an oil containing ethoxyl. The use of potassium hydroxide in aqueous acetone gave (VI) as the sole product. With silver acetate in methyl alcohol, the chloride, m. p. 133°, yielded a mixture of isomeric methoxy-compounds; we could not effect a clean separation of this mixture, although we did once isolate 4-methoxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^2-*cyclo*pentenone, m. p. 148°, and a different fraction, m. p. 144°, almost certainly consisting of 2-methoxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^3-*cyclo*pentenone. Unfortunately, we had no means of establishing the identity of the fraction, m. p. 144°, with Allen and Spanagel's methoxy-compound, although this is probable. Silver acetate and acetic acid convert the chloride, m. p. 133°, into a mixture of acetates consisting chiefly of that described by Gray, to which must be assigned constitution (VIII). A small amount of (VI) was also produced. Repetition of these experiments with the lower-melting chloride gave identical results, indicating that the two chlorides possess structures (XVIII) and (XX) and react through the common ion $CMe_2 \cdot \overset{\oplus}{C}Ph \cdot CPh \cdot CH \cdot CO$. We decided, therefore, to establish the constitution of one of these chlorides by an unambiguous method. This we were able to do, since chlorination of 3 : 4-diphenyl-5 : 5-dimethyl-Δ^3-*cyclo*pentenone (X) gave us the *chloride* (XX), m. p. 127°. We infer that Allen and Spanagel's chloride is (XVIII) as suggested by them. Attempted anionotropic conversion of (XVIII) into (XX) by heating in benzonitrile or acetic anhydride gave a *compound* (XXI), $C_{38}H_{32}O_2$, formed by loss of two molecules of hydrogen chloride from two molecules of the chloride (XX), and yielding by oxidation with potassium permanganate in acetone the anhydride (XXII) of αβ-oxido-

(XXI.) 


(XXII.)

αβ-diphenyl-γγ-dimethylglutaric acid. The production of (XXI) constitutes further support for the view, expressed above, that the chlorides (XVIII, XX) form a mobile anionotropic system.

Experimental.

Derivatives of ββ-*Dimethylanhydroacetonebenzil.*

4-*Hydroxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^2-cyclo*pentenone* (**ββ-*Dimethylanhydroacetonebenzil*) (IV).**—COMePr$^\beta$ (50 g.) [p-*nitrophenylhydrazone*, golden-brown plates from MeOH, m. p. 103·5° (Found: N, 19·4. $C_{11}H_{15}O_2N_3$ requires N, 19·0%)] was condensed with benzil (67 g.) under the conditions indicated by Japp and Meldrum (J., 1901, **79**, 1038) at a temp. not less than 30°; the product, recryst. from EtOH, had m. p. 181° (yield, 50—52 g.) [2 : 4-*dinitrophenylhydrazone*, red prisms from AcOEt–EtOH, m. p. 217—218° (Found: C, 65·4; H, 4·8; N, 12·0. $C_{25}H_{22}O_5N_4$ requires C, 65·5; H, 4·8; N, 12·2%)]. ββ-Dimethylanhydroacetonebenzil is not acylated by AcCl or *p*-nitrobenzoyl chloride and C_5H_5N at 100°, by Ac_2O and C_5H_5N at 100° or the b. p., or by treatment with gaseous keten ("Organic Syntheses," IV, 39) in Ac_2O or ether. Attempted acetylation by treatment of the sodium compound, formed by boiling with "molecular" Na in xylene, with slightly less than the theo. quantity of AcCl was also unsuccessful.

2-Acetoxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^3-*cyclo*pentenone (VIII) is readily prepared from ββ-dimethylanhydroacetonebenzil by Gray's method (*loc. cit.*, p. 2137), or by boiling with Ac_2O for 20 hr. The acetate is unaffected by treatment with Zn and boiling AcOH for 4 hr., and with 3% Na–Hg in boiling EtOH, in the presence of AcOH.

Treatment with 2 : 4-dinitrophenylhydrazine sulphate in EtOH gives **2-*ethoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^3-cyclo*pentenone*-2 : 4-*dinitrophenylhydrazone***, orange laminæ from EtOH or C_6H_6–ligroin (b. p. 80—100°), m. p. 182° (decomp.) (Found: C, 66·25, 66·6; H, 5·3, 5·3; N, 11·55; OEt, 9·8. $C_{27}H_{26}O_5N_4$ requires C, 66·7; H, 5·4; N, 11·5; OEt, 9·3%). Substitution of MeOH for EtOH in the foregoing affords **2-*methoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^3-cyclo*pentenone*-2 : 4-*dinitrophenylhydrazone*** (XI), orange laminæ from MeOH, m. p. 196° (decomp.) (Found: C, 66·1; H, 5·2; N, 11·7; OMe, 6·3. $C_{26}H_{24}O_5N_4$ requires C, 66·1; H, 5·1; N, 11·9; OMe, 6·6%). The methoxy-hydrazone (0·3 g.), suspended in hot MeOH (30 c.c.), was heated

for 10 min. with MeOH–KOH (3 c.c. of a solution of 0·3 g. KOH in 12 c.c. MeOH); the clear solution obtained by dilution was acidified, and the ppt. recrystallised several times from AcOEt; the *substance*, m. p. 204°, formed yellow needles (Found: C, 71·4; H, 4·8; N, 13·0; OMe, 7·1. $C_{26}H_{22}O_3N_4$ requires C, 71·3; H, 5·05; N, 12·8; OMe, 7·1%). More drastic treatment of the methoxy-hydrazone with 1·45*N*-NaOMe for 6 hr. on the steam-bath gave a neutral *substance*, separating from AcOEt in yellow prisms, m. p. 207° (decomp.), and depressing the m. p. of the substance $C_{26}H_{22}O_3N_4$ to 188° (Found: C, 64·5; H, 5·3; OMe, 12·3. $C_{27}H_{28}O_6N_4$ requires C, 64·3; H, 5·6; OMe, 12·3%).

Oxidation of the Acetate, m. p. 137°.—(i) A solution of CrO_3 (3 g.) in AcOH (100 c.c.) was added dropwise to the acetate (2 g.) suspended in AcOH (10 c.c.). The mixture was stirred and kept at 10° during the addition and over-night; after dilution and neutralisation with solid Na_2CO_3, the solution was repeatedly extracted with Et_2O. The aq. solution was evaporated to small bulk on the steam-bath, acidified, and extracted with Et_2O. This extract was roughly dried ($CaCl_2$), evaporated, and kept at 40° in vac. to remove AcOH. A partial separation of the residual mixed acids was obtained by treatment with hot H_2O; the more sol. part, further purified, was identified as BzOH, and the less sol. part as αβ-oxido-αβ-diphenyl-γγ-dimethylglutaric acid (Found: C, 69·9; H, 5·65. Calc. for $C_{19}H_{18}O_5$: C, 69·9; H, 5·6%), which, cryst. from Et_2O–ligroin, or C_6H_6, decomposed at 174° to give the anhydride, m. p. 160°, after two crystns. from Et_2O [Found: C, 73·8; H, 5·2; *M* (Rast), 307, 316. Calc. for $C_{19}H_{16}O_4$: C, 74·0; H, 5·2%; *M*, 308]. These two compounds were obtained by Japp and Michie (J., 1903, **83**, 306) by oxidation of ββ-dimethylanhydroacetonebenzil. The original ethereal extract, after drying (K_2CO_3) and evaporation, gave a solid which, twice recryst. from MeOH, had m. p. 124°; it is probably 2-*hydroxy*-3 : 4-*oxido*-3 : 4-*diphenyl*-5 : 5-*dimethyl*cyclo*pentanone* [Found: C, 76·4; H, 6·0; *M* (Rast), 296, 280. $C_{19}H_{18}O_3$ requires C, 77·5; H, 6·1%; *M*, 294]; it gave a semicarbazone, m. p. 159—160°, after crystn. from MeOH.

(ii) The acetate (2 g.) in AcOH (60 c.c.) was ozonised for 16 hr.; after solution in Et_2O and reduction of the ozonides with Zn, the liquid was extracted with 2*N*-Na_2CO_3. The aq. solution was acidified and extracted with Et_2O, and the dried ($CaCl_2$) extract evaporated, first on the steam-bath and then in vac. at 40°. During the latter operation, a volatile solid passed over and was identified as BzOH; the residue also consisted of BzOH only. The ethereal solution, after drying (K_2CO_3) and evaporation, gave an oil which crystallised on keeping, affording a *substance*, m. p. 132°, crystallising in prisms from MeOH or EtOH [Found: C, 69·2; H, 5·9; *M* (Rast), 217, 234. $C_{11}H_{12}O_3$ requires C, 68·8; H, 6·3%; *M*, 192]. The substance was insol. in cold 2*N*-KOH, and crystallised unchanged from Ac_2O; it depressed the m. p. of the acetate of m. p. 137°.

Use of H_2O_2 under various conditions was ineffective, the acetate, m. p. 137°, being recovered unaltered and unaccompanied by other substances.

2-*Hydroxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ²-cyclo*pentenone* (3 : 4-*Diphenyl*-5 : 5-*dimethyl*-cyclo*pentane*-1 : 2-*dione*) (VI).—This compound can be obtained by hydrolysis of the acetate, m. p. 137°, with EtOH–KOH (Gray, *loc. cit.*), or with acetone–HCl; it is most readily prepared by use of hot 1·45*N*-NaOEt. Isolated by pouring into ice-water, acidification and filtration, and cryst. from EtOH, it forms needles, m. p. 158°; it gives a violet-brown colour with $FeCl_3$. It yields with some difficulty a 2 : 4-*dinitrophenylhydrazone*, dark red needles from AcOEt, m. p. 194—195° (Found: N, 11·5. $C_{25}H_{22}O_5N_4$ requires N, 12·2%); by extended treatment with excess of 2 : 4-dinitrophenylhydrazine sulphate it yields the 2 : 4-*dinitrophenylosazone*, scarlet prisms from xylene or AcOEt, m. p. 243° (Found: C, 58·6; H, 4·1. $C_{31}H_{26}O_8N_8$ requires C, 58·3; H, 4·1%). A quinoxaline could not be obtained. The high m. p. (244° decomp.) of the phenylhydrazone described by Gray (*loc. cit.*) suggests that the substance is an osazone; the analytical figures recorded by Gray (C, 81·9; H, 7·0) are not distinctive, since $C_{25}H_{24}ON_2$ requires C, 81·5; H, 6·6%, and $C_{31}H_{30}N_4$ requires C, 81·2; H, 6·6%.

2-*Acetoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ²-cyclo*pentenone* (IX).—(i) Acetylation of the α-ketol, m. p. 158°, with Ac_2O and a trace of H_2SO_4 at 15° (cf. Gray, *loc. cit.*) gives the acetate, m. p. 92°, after crystn. from EtOH.

(ii) The same acetate is obtained by treating a solution of the α-ketol in Ac_2O or Et_2O with keten.

The acetate is easily hydrolysed to regenerate the parent α-ketol, and when treated with excess of 2 : 4-dinitrophenylhydrazine sulphate affords the 2 : 4-dinitrophenylosazone, m. p. 243°.

2-*Methoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ²-cyclo*pentenone*.—The α-ketol was methylated with NaOMe and MeI (cf. Gray, *loc. cit.*); the methoxy-compound had m. p. 88°, and by treatment with 2 : 4-dinitrophenylhydrazine sulphate in MeOH gave the 2 : 4-*dinitrophenylhydrazone*

(XIII), brick-red needles from AcOEt, m. p. 234° (Found: C, 66·1; H, 5·1; N, 12·0; OMe, 6·8. $C_{26}H_{24}O_5N_4$ requires C, 66·1; H, 5·1; N, 11·9; OMe, 6·6%).

2-Ethoxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^2*-cyclopentenone* was prepared in a similar way by means of NaOEt and EtI; it separated from EtOH in colourless prisms, m. p. 70·5—71° (Found: C, 82·3; H, 7·2; OEt, 14·5. $C_{21}H_{22}O_2$ requires C, 82·4; H, 7·2; OEt, 14·7%). With 2 : 4-dinitrophenylhydrazine sulphate it yielded the 2 : 4-*dinitrophenylhydrazone*, scarlet needles from xylene, m. p. 205° (Found: C, 67·0; H, 5·4; N, 11·7; OEt, 9·0. $C_{27}H_{26}O_5N_4$ requires C, 66·66; H, 5·4; N, 11·5; OEt, 9·3%).

Both the foregoing α-alkoxy-ketones by extended treatment with boiling 50% H_2SO_4 regenerate the parent α-ketol, m. p. 158°.

3 : 4-Diphenyl-5 : 5-dimethylcyclopentanone.—The α-ketol, m. p. 156°, was boiled for 2 hr. with HI aq. (*d* 1·78) and red P; the ppt. produced by pouring into H_2O was filtered off and extracted with hot EtOH, from which the ketone crystallised on cooling and dilution; recryst. from EtOH, it formed fine prismatic needles, m. p. 153°; the *semicarbazone* separated in needles from EtOH, m. p. 230° (decomp.) (Found: C, 74·7; H, 7·2. $C_{20}H_{23}ON_3$ requires C, 74·7; H, 7·2%); the 2 : 4-*dinitrophenylhydrazone* formed orange needles from AcOEt–EtOH, m. p. 229° (Found: C, 67·6; H, 5·5; N, 12·5. $C_{25}H_{24}O_4N_4$ requires C, 67·6; H, 5·45; N, 12·6%). The same ketone is obtained when the α-ketol acetate, m. p. 92°, is boiled with HI aq. (*d* 1·95) for a few min.

3 : 4-Diphenyl-5 : 5-dimethyl-Δ^3*-cyclopentenone* (X).—(i) ββ-Dimethylanhydroacetonebenzil (3 g.) in boiling AcOH (50 c.c.) was treated with Zn dust (6 g.) during 4 hr. The cooled product was decanted from Zn and $(AcO)_2Zn$ into H_2O, the residue washed with AcOH, which was added to the aq. mixture, and the pptd. oil extracted with Et_2O. The extract, after washing with 2*N*-NaOH, drying ($CaCl_2$), and evaporation, gave an oil (2·7 g.) which solidified and, twice cryst. from ligroin (b. p. 60—80°), formed colourless rhombic prisms, m. p. 95—96° (Found: C, 86·5, 86·6; H, 7·0, 7·0. $C_{19}H_{18}O$ requires C, 86·9; H, 6·9%).

(ii) ββ-Dimethylanhydroacetonebenzil (0·5 g.) was boiled with HI aq. (*d* 1·95; 5 c.c.) for 5 min., and the mixture cooled and extracted with Et_2O. The extract was washed with H_2SO_3 and 2*N*-Na_2CO_3, dried (K_2CO_3), and evaporated. The oil (0·4 g.) solidified readily and, cryst. twice from ligroin, yielded prisms, m. p. 96° [Found: C, 87·2; H, 7·3; *M* (Rast), 262, 269. $C_{19}H_{18}O$ requires *M*, 262].

(iii) The acetate, m. p. 137°, was boiled (0·5 g.) for a few min. with HI aq. (*d* 1·95; 5 c.c.), and the cooled solution extracted with Et_2O; the extract was washed with H_2SO_3 and 2*N*-Na_2CO_3, dried (K_2CO_3), and evaporated. The product crystallised at once and was identified as 3 : 4-*diphenyl-5 : 5-dimethyl-*Δ^3*-cyclopentenone*, m. p. 96° (yield, 0·4 g.). This is the best method of prepn.

The ketone does not react with semicarbazide and but slowly with hydroxylamine; it affords an oily phenylhydrazone, but gives a 2 : 4-*dinitrophenylhydrazone*, which separates from AcOEt–EtOH in scarlet needles, m. p. 246° (decomp.) (Found: C, 67·6; H, 5·3; N, 12·4. $C_{25}H_{22}O_4N_4$ requires C, 67·9; H, 5·0; N, 12·7%). The ketone is unaffected by treatment with NOCl in ligroin at 15° and evolves HBr with Br in hot AcOH.

A solution of the ketone (0·5 g.) and benzaldehyde (0·25 g.) in EtOH (3 c.c.) was refluxed for ½ hr. with NaOEt (from 0·05 g. Na in 2 c.c. EtOH); the *benzylidene* derivative separated on cooling and, recryst. from EtOH, formed yellow needles, m. p. 160—161° (Found: C, 89·1; H, 6·3. $C_{26}H_{22}O$ requires C, 89·1; H, 6·3%).

The ketone resists reduction by HI aq. (*d* 1·7) and red P for 1·5 hr.; longer treatment (15 hr.) yielded an oily product giving a sticky semicarbazone. Satisfactory reduction was obtained by Clemmensen's method; after 2 hr., the product was isolated by extraction with Et_2O as a colourless oil. An alc. solution of the oil was treated with semicarbazide acetate for 24 hr., the liquid partly diluted, and the ppt. filtered off. The *semicarbazone*, colourless needles from MeOH, m. p. 224° (Found: C, 74·7; H, 7·2. $C_{20}H_{23}ON_3$ requires C, 74·6; H, 7·2%), is isomeric with 3 : 4-diphenyl-5 : 5-dimethyl*cyclo*pentanonesemicarbazone, m. p. 230°, already described (mixed m. p. 208—210°), and is probably derived from the stereoisomeric 3 : 4-diphenyl-5 : 5-dimethyl*cyclo*pentanone. The aq.-alc. filtrate was evaporated, and the residual oil, after dissolution in Et_2O, drying, and evaporation, distilled at 10 mm.; 3 : 4-*diphenyl-5 : 5-dimethyl*cyclo*pentane* was then obtained as a colourless, high-boiling oil (Found: C, 91·3; H, 8·1. $C_{19}H_{22}$ requires C, 91·2; H, 8·8%).

Catalytic Reduction of ββ-Dimethylanhydroacetonebenzil.—(i) ββ-Dimethylanhydroacetonebenzil (5 g.) in AcOH (50 c.c.) was shaken with Pt-black at 60° in H at atm. press. Absorption was slow and incomplete after many hours; when a stationary state was reached, the liquid

was filtered from Pt, and the least sol. substance (ββ-dimethylanhydroacetonebenzil) removed by fractional pptn. with H_2O. From the residue, two substances were isolated by fractional crystn. from ligroin; the less sol. was **4-*acetoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ²-cyclo*pentenone***, which separated from ligroin (b. p. 100—120°) in well-formed prisms, m. p. 128—129° (Found : C, 78·5; H, 6·6. $C_{21}H_{20}O_2$ requires C, 78·7; H, 6·3%); the more sol. substance, long needles from ligroin (b. p. 60—80°), m. p. 120·5°, appears to be a *dihydro*-derivative of ββ-dimethylanhydroacetonebenzil (Found : C, 85·5; H, 7·3. $C_{19}H_{20}O$ requires C, 86·4; H, 7·6%).

(ii) ββ-Dimethylanhydroacetonebenzil (1·0 g.), dissolved in 96% EtOH (40 c.c.), was shaken with Adams's catalyst (0·2 g.) in H at 15° and atm. press. Absorption was very slow (182 c.c. in 16 hr.; $2H_2 = 176$ c.c.) and then ceased; a repetition confirmed these observations. The product, after filtration from Pt, was treated with semicarbazide acetate for 24 hr., but no semicarbazone formation occurred; the oil, recovered by dilution and extraction with Et_2O, was divided into two parts. One part, treated with 2 : 4-dinitrophenylhydrazine sulphate, afforded a 2 : 4-dinitrophenylhydrazone, m. p. 119° (indefinite) (after several crystns. from AcOEt–EtOH), which seems to be a mixture (yield, about 8%). The other part was treated with 3 : 5-dinitrobenzoyl chloride in C_5H_5N at 100° for 6 hr.; the product, whose homogeneity was doubtful, could not be crystallised satisfactorily, and separated from AcOEt–EtOH, first as an opalescence, and finally as a powder, m. p. 80—100° (indefinite) (yield, about 25%).

The acetate, m. p. 128°, was heated for 0·5 hr. with aq.-alc. KOH, and the mixture cooled, diluted, and filtered; the ppt., cryst. from EtOH, had m. p. 181°, and was identical in every way [mixed m. p. (181°), cryst. form] with ββ-dimethylanhydroacetonebenzil.

Conversion of the Acetate, m. p. 128°, *into the Acetate, m. p.* 137°.—(*a*) A solution of the acetate, m. p. 128°, in Ac_2O was boiled for 6 hr.; after removal of Ac_2O in vac. over KOH, the product, a yellow gum which could not be crystallised, was hydrolysed with 5% alc. KOH; the ppt. obtained by dilution and acidification was insufficient for complete purification and had m. p. 140—150°, but gave the dark brown colour with $FeCl_3$ characteristic of 2-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ²-*cyclo*pentenone, which is known to be the product of hydrolysis of the acetate, m. p. 137°.

(*b*) The acetate, m. p. 128°, with Ac_2O containing a trace of H_2SO_4 was heated to boiling and allowed to cool, the conditions leading to the direct production of the acetate, m. p. 137°, from ββ-dimethylanhydroacetonebenzil, being reproduced. After destruction of Ac_2O with cold 2*N*-Na_2CO_3, the product was extracted with Et_2O, dried (K_2CO_3), and evaporated. The oil solidified on rubbing, and, after draining, was repeatedly crystallised from ligroin (b. p. 60—80°) and finally from EtOH; the substance had m. p. 135—136° and was identical with the acetate, m. p. 137° (mixed m. p. 136—137°).

Catalytic Reduction of the Acetate, m. p. 137°.—Pt-black and H in AcOH or EtOH at 15—60° and pressures up to 3 atm., and colloidal Pd and H under similar conditions, were ineffective; reduction occurs, however, with Adams's catalyst. The acetate (0·5 g.), suspended in 96% EtOH (20 c.c.) at 15°, was shaken with Adams's catalyst (0·1 g.) in H at atm. press.; steady absorption of H occurred during 4 hr. (184 c.c.: $5H_2 = 175$ c.c.). A second expt. yielded similar results. The reduction product, 3(or 4)-*cyclo*hexyl-4(or 3)-phenyl-5 : 5-dimethyl*cyclo*pentanone, was a thick oil, and was characterised by the preparation of the 2 : 4-*dinitrophenylhydrazone*, which formed orange laminæ from EtOH, m. p. 194° [Found : C, 66·75; H, 6·7; *M* (Rast), 407, 411. $C_{25}H_{30}O_4N_4$ requires C, 66·7; H, 6·7%; *M*, 450]. Since β-acetyl-2 : 4-dinitrophenylhydrazine is described as melting at 193—194° (Purgotti, *Gazzetta*, 1894, **24**, i, 561), and 196—197°, 197—198° (Curtius and Dedichen, *J. pr. Chem.*, 1894, **50**, 262; Curtius and Meyer, *ibid.*, 1907, **76**, 382), a specimen of this substance was prepared; it had m. p. 198—200°, and differed sharply in its physical character from the foregoing hydrazone, whose m. p. it depressed. A blank expt. in which the acetate, m. p. 137°, in 96% EtOH was shaken with the previously reduced catalyst in N for 24 hr. showed that no alcoholysis of the acetyl group occurs under the conditions used.

Catalytic Reduction of the Acetate (IX), *m. p.* 92°.—The acetate (0·66 g.), dissolved in EtOH (dry : 25 c.c.), was shaken with Adams's catalyst (0·1 g.) in H at atm. press. The absorption was slower than in the case of the isomeric acetate, m. p. 137°; 131 c.c. H_2 ($3H_2 = 135$ c.c.) were taken up in 2·5 hr., absorption ceasing after 72 hr. (227 c.c. H_2; $5H_2 = 225$ c.c.). The reduction product by treatment with 2 : 4-dinitrophenylhydrazine sulphate gave 3(or 4)-*cyclo*hexyl-4(or 3)-phenyl-5 : 5-dimethyl*cyclo*pentanone-2 : 4-dinitrophenylhydrazone, orange laminæ from EtOH, m. p. 194·5° (Found : C, 66·65; H, 6·6. $C_{25}H_{30}O_4N_4$ requires C, 66·7; H, 6·6%), which was identical with the prepn. described above; a mixture containing equal quantities of each specimen had m. p. 194—194·5°; after solidification, the mixture had m. p. 194·2° on remelting.

4-*Ethoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^2-cyclo*pentenone*.—ββ-Dimethylanhydroacetonebenzil (2·75 g.) was heated for 140 hr. with EtI (30 c.c.), " activated " Ag_2O (11 g.) prepared by means of NaOH, and a trace of powdered NaOH; excess of EtI was removed, the residue extracted with boiling acetone (5 × 20 c.c.), and the combined extracts evaporated. On treatment with warm ligroin (b. p. 40—60°) partial crystn. occurred, giving unaltered ββ-dimethylanhydroacetonebenzil (0·4 g.), which was filtered off and washed with cold ligroin. The ligroin washings and solution were combined and evaporated, and the resulting gum rubbed with a little MeOH; crystn. occurred at once, and the solid was filtered off. **4-*Ethoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^2-cyclo*pentenone*** (1·5 g.) separates from MeOH in rosettes of needles, m. p. 80—80·5° (Found: C, 82·3; H, 7·3; OEt, 14·4. $C_{21}H_{22}O_2$ requires C, 82·4; H, 7·2; OEt, 14·7%), and depresses the m. p. of 2-ethoxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^2-*cyclo*pentenone. When treated with 2 : 4-dinitrophenylhydrazine sulphate in EtOH, it rapidly gives a *compound*, $C_{25}H_{22}O_5N_4$, orange needles from AcOEt or plates from amyl alcohol, m. p. 204° (decomp.), which does not contain OEt (Found: C, 65·6, 65·6, 65·4; H, 4·9, 4·9, 4·7; N, 12·2. $C_{25}H_{22}O_5N_4$ requires C, 65·5; H, 4·8; N, 12·2%). The same substance is formed when a solution of 2 : 4-dinitrophenylhydrazine in EtOH containing 2 drops of conc. HCl at 50° is used; under these conditions, but omitting the hydrazine, the ethoxy-compound, m. p. 80°, decomposes to yield a substance (or substances), m. p. 70—90°, giving a negative result in the Zeisel estimation. The ethoxy-compound becomes sticky on keeping, even in vac. over KOH. Attempts to regenerate ββ-dimethylanhydroacetonebenzil from the ethoxy-compound with boiling 50% H_2SO_4, or HCl–AcOH at 130—135°, led to deep-seated decomp.

4-*Methoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^2-cyclo*pentenone*.—The foregoing procedure was followed, with MeI (30 c.c.) in place of EtI, but boiling was continued for 10 days; after removal of MeI, the mixture was extracted with boiling acetone (5 × 20 c.c.), and the combined extracts concentrated. Unchanged material which separated was removed, and the filtrate completely evaporated; the residue was extracted twice with hot ligroin (b. p. 60—80°), and the combined extracts concentrated; the cryst. product then obtained, recryst. two or three times from MeOH, formed stout colourless prisms of ***4-methoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^2-cyclo*pentenone***, m. p. 148° (Found: C, 82·05; H, 6·85. $C_{20}H_{20}O_2$ requires C, 82·2; H, 6·9%). A 2 : 4-dinitrophenylhydrazone was obtained with difficulty on account of the tendency of the methoxy-compound to separate from MeOH; but by keeping a MeOH solution of 2 : 4-dinitrophenylhydrazine sulphate, into which a hot MeOH solution of the methoxy-compound had been filtered, at 50° for 15 hr., the ***2 : 4-dinitrophenylhydrazone*** (XII), m. p. 196° (decomp.), was obtained (Found: C, 65·9; H, 5·1; N, 11·7; OMe, 6·8. $C_{26}H_{24}O_5N_4$ requires C, 66·1; H, 5·1; N, 11·9; OMe, 6·6%). A mixture of the hydrazone with the 2 : 4-dinitrophenylhydrazone of 2-methoxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^3-*cyclo*pentenone [m. p. 196° (decomp.)] exhibits little or no depression of the m. p.; nevertheless the hydrazones are isomeric and not identical. The 4-methoxy-hydrazone crystallises from AcOEt in orange-brown rosettes, whereas the 2-methoxy-hydrazone forms bright yellow prisms; moreover, the hydrazones have different solubilities and mixed solubilities. The following figures relate to solubility in the same sample of abs. MeOH at 36°:

4-Methoxyhydrazone.	2-Methoxyhydrazone.	Mixture.
0·00053 g./c.c.	0·00095 g./c.c.	0·00117 g./c.c.

The above ether is unaffected by extended treatment with MeOH–conc. H_2SO_4 at 50° (reproduction of conditions of hydrazone formation).

Derivatives of αββ-Trimethylanhydroacetonebenzil.

Ethyl iso*Propyl Ketone*.—Interaction of *iso*butyramide and EtMgBr gave a poor yield of a product distilling completely below 110°. The ketone was readily prepared from *iso*butyryl chloride (75 g.) and $ZnEt_2$ (50 g.), the fraction of b. p. 114—115° (50 g.) being collected (cf. Michael, *J. Amer. Chem. Soc.*, 1919, **41**, 417). The p-***nitrophenylhydrazone*** forms golden-brown prisms from EtOH, m. p. 133·5° (Found: C, 61·3; H, 7·2. $C_{12}H_{17}O_2N_3$ requires C, 61·3; H, 7·3%); the ***2 : 4-dinitrophenylhydrazone*** separates from EtOH in orange laminæ, m. p. 109—109·5° (Found: C, 51·5; H, 5·75. $C_{12}H_{16}O_4N_4$ requires C, 51·4; H, 5·75%).

4-*Hydroxy*-3 : 4-*diphenyl*-2 : 5 : 5-*trimethyl*-Δ^2-cyclo*pentenone* (αββ-*Trimethylanhydroacetonebenzil*) (XV).—$COEtPr^{\beta}$ (48 g.) was condensed with benzil (80 g.) under the conditions described by Japp and Meldrum (J., 1901, **79**, 1039); having been kept for 12 weeks, the mixture was heated under reflux on the steam-bath for 24 hr. and poured into H_2O and the ppt. filtered off.

Twice recryst. from EtOH, the substance formed colourless prisms (4 g.), m. p. 131°, and reacted slowly to yield the **2 : 4-*dinitrophenylhydrazone***, m. p. 184—185° (decomp.), red needles from AcOEt–EtOH (Found : C, 66·1; H, 5·1. $C_{26}H_{24}O_5N_4$ requires C, 66·1; H, 5·1%). αββ-Trimethylanhydroacetonebenzil could not be acetylated by treatment with keten in Ac_2O or Et_2O, or with hot Ac_2O.

3 : 4-*Diphenyl*-5 : 5-*dimethyl*-2-*methylene*-Δ³-cyclo*pentenone* (XVII).—A solution of αββ-trimethylanhydroacetonebenzil (2·5 g.) in Ac_2O (25 c.c.) containing 5 drops of H_2SO_4 deposited, slowly at 15° and rapidly on boiling, a red solid (1·0 g.) which, recryst. from hot toluene, gave **3 : 4-*diphenyl*-5 : 5-*dimethyl*-2-*methylene*-Δ³-cyclo*pentenone*** in orange-red plates, m. p. above 290° (Found : C, 88·3; H, 6·4. $C_{20}H_{18}O$ requires C, 87·6; H, 6·6%). A further small quantity was obtained by decomp. of the Ac_2O mother-liquor with H_2O. The substance is unaffected by hot 2*N*-NaOH. Dissolution in $CHCl_3$ and ozonolysis at 0°, followed by decomp. of the ozonide with hot H_2O, gave H·CHO (resorcinol test), benzoic acid, and an aldehydic (ketonic) substance (*p*-nitrophenylhydrazone, m. p. 117—118°), the amount of which was insufficient for purification.

4-*Chloro*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ²-cyclo*pentenone* (XVIII) ***and*** **2-*Chloro*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ³-cyclo*pentenone*** (XX).—ββ-Dimethylanhydroacetonebenzil (3 g.) was heated on the steam-bath for ½ hr. with $SOCl_2$ (10 c.c.) (cf. Allen and Spanagel, *loc. cit.*), the product poured into H_2O and extracted with Et_2O, and the roughly dried ($CaCl_2$) extract allowed to evaporate. The resulting solid was treated with warm ligroin (b. p. 40—60°) and repeatedly crystallised from *n*-Bu_2O, 4-chloro-3 : 4-diphenyl-5 : 5-dimethyl-Δ²-*cyclo*pentenone (0·6 g.), m. p. 133°, being obtained (Found : Cl, 11·8. Calc. for $C_{19}H_{17}OCl$: Cl, 12·0%). This chloride crystallises unchanged from MeOH or EtOH in magnificent prisms, m. p. 133°, mixed m. p. 133° (cf. Allen and Spanagel, *loc. cit.*); it is unaltered by 7 days' standing in cold H_2O; it slowly gives a **2 : 4-*dinitrophenylhydrazone***, m. p. 197° (decomp.), which forms scarlet needles from AcOEt (Found : C, 63·1; H, 4·5; N, 11·4. $C_{25}H_{21}O_4N_4Cl$ requires C, 63·0; H, 4·4; N, 11·7%).

The *n*-Bu_2O mother-liquors and the ligroin washings were mixed and evaporated, giving a gummy solid, readily sol. in *n*-Bu_2O; crystn. from ligroin (b. p. 60—80°) yielded two products, separable in part by hand picking : (*a*) m. p. 128°, faintly pink felted needles, consisted mainly of 4-chloro-3 : 4-diphenyl-5 : 5-dimethyl-Δ²-*cyclo*pentenone (mixed m. p.; Found : Cl, 11·5%); (*b*) m. p. 122°, colourless star-shaped aggregates, depressed the m. p. of the 4-chloro-compound to below 100°, and consisted mainly of **2-*chloro*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ³-cyclo*pentenone*** (Found : C, 76·8; H, 5·8; Cl, 12·5. $C_{19}H_{17}OCl$ requires C, 76·9; H, 5·7; Cl, 12·0%), the m. p. of which is raised to 126—127° by crystn. from *n*-Bu_2O or ligroin (b. p. 60—80°) (Found : C, 77·0; H, 5·75; Cl, 12·2%). The same two chlorides may be isolated by fractional crystn. of the foregoing gummy solid from ligroin (b. p. 60—80°), in which the 2-chloride is the more sol.

Reactions of **4-*Chloro*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ²-cyclo*pentenone***.—(i) ***With alcoholic potassium hydroxide.*** The chloride (0·3 g.; 0·001 mol.) was refluxed for 10 min. with 8·5 c.c. (0·003 mol. KOH) of 2% alc. KOH. The solution became faintly green and then colourless and a white solid was pptd., consisting of KCl uncontaminated by any org. substance. The filtrate was diluted largely, and twice extracted with Et_2O; the extract, washed with ice-cold 5% KOH aq., dried ($CaCl_2$), and evaporated, gave an oil (0·20 g.) which solidified completely on rubbing with EtOH, and was identified as unchanged 4-chloro-3 : 4-diphenyl-5 : 5-dimethyl-Δ²-*cyclo*pentenone (Found : C, 77·4; H, 5·9; Cl, 11·7%). The aq. alkaline liquor, by treatment with CO_2, Et_2O extraction, and drying and evaporation of the extract, gave traces of 2-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ²-*cyclo*pentenone (brown-violet colour with $FeCl_3$). Use of an excess of 0·5% alc. KOH yielded the same results; in another expt. the product still contained Cl after 5 hrs.' refluxing, and no trace of ββ-dimethylanhydroacetonebenzil could be isolated (cf. Allen and Spanagel, *loc. cit.*).

(ii) ***With aqueous potassium hydroxide.*** The chloride was heated for ½ hr. on the steam-bath with 2*N*-KOH in aq.-acetone solution, the same colour changes being observed. After removal of acetone by evaporation, the cooled solution was extracted with Et_2O, the aq. liquid treated with CO_2, and the ppt. extracted with Et_2O. After drying and evaporation, the second ethereal extract gave a good yield of 2-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ²-*cyclo*pentenone, identified by m. p. 158°, mixed m. p. 158°, and by the characteristic colour reaction with $FeCl_3$.

(iii) ***With acetic acid and silver acetate.*** The chloride (0·5 g.), AcOAg (1·0 g.), and A.R. AcOH (5 c.c.) were refluxed for 10 min. and the solution was filtered from AgCl and excess of AcOAg and diluted. The solid obtained, m. p. 120—130°, cryst. from EtOH, gave 2-acetoxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ³-*cyclo*pentenone (0·3 g.); mixed m. p. 137°. The filtrate, combined with the alc. mother-liquor, was extracted with Et_2O and the product obtained

by evaporating the dried extract was crystallised fractionally from ligroin (b. p. 40—60°); only the foregoing acetate, m. p. 137°, could be isolated, but it was accompanied by traces of oily matter. Repetitions yielded similar results.

(iv) *With methyl alcohol and silver acetate.* The chloride (0·6 g.), AcOAg (0·6 g.), and abs. MeOH (5 c.c.) were refluxed for ¼ hr., and the filtered solution diluted. The product (0·5 g.) crystallised well from MeOH but did not appear to be homogeneous, since it melted at 122° to a turbid liquid which cleared at *ca.* 135° (cf. Allen and Spanagel, *loc. cit.*). In a second expt. the MeOH filtrate was cooled; the greater part of the product then separated, m. p. 125—135°; the material pptd. from the MeOH mother-liquors by addition of H_2O was small in amount, and, after crystn. from MeOH, had m. p. 125—135°. The product is a mixture of isomeric ***methoxy*-3 : 4-*diphenyl*-5 : 5-*dimethyl*cyclo*pentenones*** (Found : C, 82·2; H, 6·75; OMe, 10·8. $C_{20}H_{20}O_2$ requires C, 82·2; H, 6·9; OMe, 10·6%); recrystn. from ligroin, MeOH, AcOEt, Ac_2O and other solvents did not alter the m. p., but on one occasion when ligroin (b. p. 60—80°) was used a largely complete separation on a small scale was effected, giving (*a*) a fraction, m. p. 144—145°, which, mixed with 4-methoxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^2-*cyclo*pentenone, melted at 144°; and (*b*) a fraction, m. p. 141—142°, which depressed the m. p. of the last-named 4-methoxy-compound to 118°, and probably consisted of 2-methoxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^3-*cyclo*pentenone.

(v) *With ethyl alcohol and silver acetate.* The chloride (0·5 g.), AcOAg (0·5 g.), and EtOH (dried with Ca) (5 c.c.) were refluxed for 10 min., and the filtered solution diluted with H_2O, extracted with Et_2O, and separated into neutral and quasi-acid fractions. No quasi-acid matter was obtained, and the neutral fraction was a gum (0·5 g.), which was very sol. in EtOH and contained Cl; no trace of ββ-dimethylanhydroacetonebenzil could be found (cf. Allen and Spanagel, *loc. cit.*). In a second expt., equal wts. of the chloride and AcOAg were refluxed with EtOH (dried with Mg) for 2 hr.; the product was free from Cl and formed a resin-like mass, very sol. in EtOH (Found : OEt, 12·1. $C_{21}H_{22}O_2$ requires OEt, 14·7%); it contained no ββ-dimethyl-anhydroacetonebenzil; acidification of the 5% aq.-KOH used to wash the Et_2O solution of the product gave no 2-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^2-*cyclo*pentenone. Treatment of the product with 2 : 4-dinitrophenylhydrazine sulphate yielded a ***bisdinitrophenylhydrazone***, scarlet needles, m. p. 245°, from AcOEt (Found : C, 58·8; H, 3·9. $C_{31}H_{26}O_8N_8$ requires C, 58·3; H, 4·1%), which appears to be isomeric and not identical with the osazone, m. p. 243°; a second, more sol. *dinitrophenylhydrazone* was also isolated, golden-yellow plates, m. p. 252°, from EtOH (Found : N, 9·8%).

Reactions of 2-*Chloro*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^3-cyclo*pentenone*.—(i) *With aqueous potassium hydroxide.* The chloride, by treatment with 2*N*-KOH and a little acetone on the steam-bath, gave a good yield of 2-hydroxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^2-*cyclo*pentenone, m. p. 158°, which was unaccompanied by any other product.

(ii) *With acetic acid and silver acetate.* The chloride (0·1 g.), AcOAg (0·2 g.), and A.R. AcOH (3 c.c.) were heated under reflux for ¼ hr.; after filtering from AgCl and excess of AcOAg, the liquid was diluted, and the ppt. collected. The product was 2-acetoxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^3-*cyclo*pentenone, m. p. 137° after crystn. from EtOH, mixed m. p. 137°; it appeared to be accompanied by traces of other material, which could not be obtained cryst.

(iii) *With methyl alcohol and silver acetate.* The chloride (0·1 g.) and AcOAg (0·1 g.) were refluxed with abs. MeOH for ½ hr., and the hot solution filtered into H_2O. The ppt., m. p. 115—120°, was crystallised from MeOH; a fortuitous but largely complete separation of the isomeric methoxy-compounds was achieved. The first crop had m. p. 140—141° after softening at 130°, and, recryst., m. p. 142°; it depressed the m. p. (148°) of 4-methoxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^2-*cyclo*pentenone to 122° and consisted of 2-methoxy-3 : 4-diphenyl-5 : 5-dimethyl-Δ^3-*cyclo*-pentenone. The second crop was similar to the first, but the third crop had m. p. 147° after softening at 144°, m. p. 148° after recrystn., and did not depress the m. p. of the pure 4-methoxy-compound.

Synthesis of 2-*Chloro*-3 : 4-*diphenyl*-5 : 5-*dimethyl*-Δ^3-cyclo*pentenone*.—Cl was passed into 3 : 4-diphenyl-5 : 5-dimethyl-Δ^3-*cyclo*pentenone (1·5 g.) at 100° until an increase of wt. of 0·2 g. resulted. The viscous product was dissolved in *n*-Bu_2O, and the solution kept at *ca.* 0°; cryst. material then separated. The first crop, recryst. several times from *n*-Bu_2O, consisted of 2-chloro-3 : 4-diphenyl-5 : 5-dimethyl-Δ^3-*cyclo*pentenone, m. p. 126°; it did not depress the m. p. of a specimen prepared from ββ-dimethylanhydroacetonebenzil as above, and depressed the m. p. (133°) of the 4-chloro-isomeride to 104°. The second crop consisted largely of well-formed rhombs; after repeated crystn. from ligroin (b. p. 60—80°) these had m. p. 121°, and depressed the m. p. of 2-chloro-3 : 4-diphenyl-5 : 5-dimethyl-Δ^3-*cyclo*pentenone. The sub-

stance is probably **3**(or **4**)-*phenyl*-**4**(or **3**)-p-*chlorophenyl*-**5** : **5**-*dimethyl*-Δ^3-cyclo*pentenone* (Found : Cl, 11·8. $C_{19}H_{17}OCl$ requires Cl, 12·0%), since the Cl atom cannot be removed by extended treatment with AcOAg in boiling AcOH (the compound is recovered unaltered), and on ozonolysis gives benzoic and *p*-chlorobenzoic acids.

3 : **4**-*Diphenyl*-**5** : **5**-*dimethyl*-Δ^3-cyclo*pentenonylidene*-**3** : **4**-*diphenyl*-**5** : **5**-*dimethyl*-Δ^3-cyclo*pentenone* (XXI).—When 4-chloro-**3** : 4-diphenyl-**5** : 5-dimethyl-Δ^3-*cyclo*pentenone is heated under reflux with Ac_2O or PhCN for **1**—**2** hr., HCl is eliminated, and a yellow solid separates (yield, almost theo.); the same substance is obtained from the 2-chloro-Δ^3-isomeride. Recryst. from AcOH, the *compound* forms yellow laminæ, which turn red at **240**—**245**° and melt at **300**° [Found : C, 87·6; H, 6·2; *M* (Rast), **503**, **513**. $C_{38}H_{32}O_2$ requires C, 87·7; H, 6·2%; *M*, **520**]. Solutions of the compound in boiling EtOH, AcOH, Ac_2O, or PhCN are red, the colour fading to yellow on cooling. Oxidation with H_2O_2 in the presence of traces of $Fe^{\bullet\bullet}$ was ineffective, but treatment with $KMnO_4$ (equiv. to **3**O) in warm acetone afforded the anhydride of αβ-oxido-αβ-diphenyl-γγ-dimethylglutaric acid, which crystallised from Et_2O in fine rhombic prisms, m. p. 160° (Found : C, 73·9; H, 5·2. Calc. for $C_{19}H_{16}O_4$: C, 74·0; H, 5·2%) (cf. Japp and Michie, *loc. cit.*). The neutral part of the oxidation product, treated with **2** : **4**-dinitrophenylhydrazine sulphate, gave *mesityl oxide* **2** : **4**-*dinitrophenylhydrazone*, scarlet needles from AcOEt, m. p. 201° (Found : C, 51·9; H, 5·1; N, 20·1. $C_{12}H_{14}O_4N_4$ requires C, 51·8; H, 5·1; N, 20·1%); the mesityl oxide was undoubtedly derived from the acetone used as the medium in the oxidation.

One of us (C. W. S.) wishes to acknowledge a grant from the Royal Society.

UNIVERSITY OF LEEDS.
UNIVERSITY COLLEGE, LONDON. [*Received, March 28th*, 1933.]