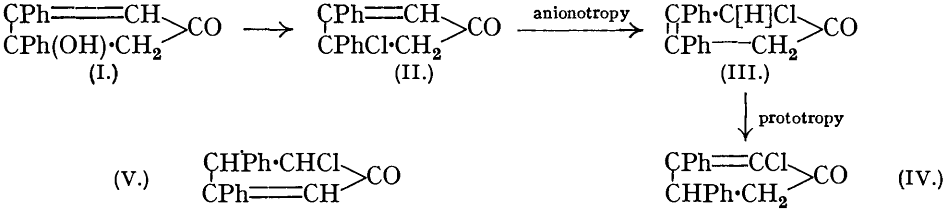
300. *Anionotropic and Prototropic Changes in Cyclic Systems. Part VII. The Structure of the Chlorodiphenyl*cyclo*pentenone obtained by the Action of Hydrogen Chloride on Anhydroacetonebenzil.*

By Harold Burton and Charles W. Shoppee.

Further evidence is presented in support of the view previously put forward (J., 1934, 201) that 2-chloro-3 : 4-diphenyl-Δ^2-*cyclo*pentenone (IV) is formed by the action of ethyl-alcoholic hydrogen chloride on anhydroacetonebenzil (I). The chloride, m. p. 142° (corr.), obtained by Allen and Rudoff (*Canadian J. Res.*, 1937, *B*, **15**, 321) from " 2-hydroxy-3 : 4-diphenyl-Δ^2-*cyclo*pentenone " and phosphoryl chloride and considered by them to be (IV), is shown to be related to the 2 : 3-diphenyl*cyclo*pentenone recently investigated (Burton and Shoppee, this vol., p. 567). The relationship is established by a study of various reduction products, including the diphenyl*cyclo*pentylamines (as acetyl derivatives) obtained from the appropriate oximes.

IN Part III (J., 1934, 201) we suggested that the chloride, m. p. 129° (now referred to as Japp's chloride), originally obtained by Japp and Burton (J., 1887, **51**, 428) from anhydroacetonebenzil (I) and ethyl-alcoholic hydrogen chloride, had the structure (IV) and was formed as a result of the following changes : *



$$\underset{\text{(I.)}}{\begin{array}{l}\text{CPh}{=\!=\!=}\text{CH}\\ \text{CPh(OH)}{\cdot}\text{CH}_2\end{array}\!\!>\!\text{CO}} \longrightarrow \underset{\text{(II.)}}{\begin{array}{l}\text{CPh}{=\!=}\text{CH}\\ \text{CPhCl}{\cdot}\text{CH}_2\end{array}\!\!>\!\text{CO}} \xrightarrow{\text{anionotropy}} \underset{\text{(III.)}}{\begin{array}{l}\text{CPh}{\cdot}\text{C[H]Cl}\\ \text{CPh}{-\!-}\text{CH}_2\end{array}\!\!>\!\text{CO}}$$

$$\big\downarrow \text{prototropy}$$

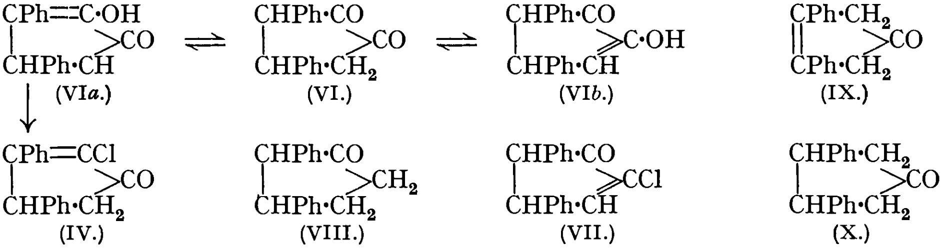
$$\text{(V.)}\quad \begin{array}{l}\text{CHPh}{\cdot}\text{CHCl}\\ \text{CPh}{=\!=\!=}\text{CH}\end{array}\!\!>\!\text{CO} \qquad\qquad \begin{array}{l}\text{CPh}{=\!=}\text{CCl}\\ \text{CHPh}{\cdot}\text{CH}_2\end{array}\!\!>\!\text{CO}\quad\text{(IV.)}$$

We considered the possibility that Japp's chloride might possess the alternative structure (V), which could arise by a prototropic change involving one of the hydrogen atoms of the methylene group of (III), but rejected this and decided in favour of (IV) for the following reasons : (i) the conversion of (II) into Japp's chloride by acids (since not only anionotropy, but also prototropy is capable of catalysis by acidic reagents), (ii) the relatively great stability of the chlorine atom, and (iii) the production of desylacetic acid,

$$\text{COPh}{\cdot}\text{CHPh}{\cdot}\text{CH}_2{\cdot}\text{CO}_2\text{H},$$

in 88% yield † by oxidation with permanganate in acetone at 15°.

Allen and Spanagel (*J. Amer. Chem. Soc.*, 1932, **54**, 4338) had previously assigned structure (V) to Japp's chloride, without citing experimental evidence, and on the basis of theoretical reasoning which we were unable to follow. In a recent paper, Allen and Rudoff (*loc. cit.*) admit this reasoning to be no longer valid, but maintain that Japp's chloride is nevertheless correctly represented by (V). The central positive fact upon which Allen and Rudoff based their argument was the production of a new isomeric chloride, m. p. 142° (corr.) (hereafter referred to as Allen's chloride), by the action of phosphoryl chloride on 2-hydroxy-3 : 4-diphenyl-Δ^2-*cyclo*pentenone (VI*a*), an enolic form of 3 : 4-diphenyl*cyclo*pentane-1 : 2-dione (VI). To this new chloride they assigned the structure (IV) by reason of the method of preparation, the unreactivity of the chlorine atom, and the production of desylacetic acid in 60% yield by ozonolysis; they considered therefore that, by exclusion, Japp's chloride must be represented by (V).



$$\underset{\text{(VI}a\text{.)}}{\begin{array}{l}\text{CPh}{=\!=}\text{C}{\cdot}\text{OH}\\ \text{CHPh}{\cdot}\text{CH}\end{array}\!\!>\!\text{CO}} \rightleftharpoons \underset{\text{(VI.)}}{\begin{array}{l}\text{CHPh}{\cdot}\text{CO}\\ \text{CHPh}{\cdot}\text{CH}_2\end{array}\!\!>\!\text{CO}} \rightleftharpoons \underset{\text{(VI}b\text{.)}}{\begin{array}{l}\text{CHPh}{\cdot}\text{CO}\\ \text{CHPh}{\cdot}\text{CH}\end{array}\!\!\geqslant\!\text{C}{\cdot}\text{OH}} \qquad \underset{\text{(IX.)}}{\begin{array}{l}\text{CPh}{\cdot}\text{CH}_2\\ \text{CPh}{\cdot}\text{CH}_2\end{array}\!\!>\!\text{CO}}$$

$$\big\downarrow$$

$$\underset{\text{(IV.)}}{\begin{array}{l}\text{CPh}{=}\text{CCl}\\ \text{CHPh}{\cdot}\text{CH}_2\end{array}\!\!>\!\text{CO}} \qquad \underset{\text{(VIII.)}}{\begin{array}{l}\text{CHPh}{\cdot}\text{CO}\\ \text{CHPh}{\cdot}\text{CH}_2\end{array}\!\!>\!\text{CH}_2} \qquad \underset{\text{(VII.)}}{\begin{array}{l}\text{CHPh}{\cdot}\text{CO}\\ \text{CHPh}{\cdot}\text{CH}\end{array}\!\!\geqslant\!\text{CCl}} \qquad \underset{\text{(X.)}}{\begin{array}{l}\text{CHPh}{\cdot}\text{CH}_2\\ \text{CHPh}{\cdot}\text{CH}_2\end{array}\!\!>\!\text{CO}}$$

Inspection of formula (VI) shows that *two* enolic forms are possible (VI*a*, VI*b*), so that the method of preparation of Allen's chloride furnishes only ambiguous evidence of structure. We have been able to prove that Allen's chloride cannot possess structure (IV), in which the carbonyl group is placed symmetrically with regard to the two phenyl groups. When Allen's chloride, or the hydroxy-ketone (VI*a*, VI*b*) from which it is prepared, is reduced

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* In view of the publication of Allen and Rudoff (*Canadian J. Res.*, 1937, *B*, **15**, 321), who discuss whether, in their proposed change (II) ⟶ (V), " chlorine or hydrogen migrates first," stating that the " sequence of shifts is uncertain," it is necessary to point out that prototropic change is impossible in (II), since the requisite grouping is absent. On the other hand, the system required for anionotropic change is present and complete, *viz.*, ·CPhCl·CPh:CH·, hence the change (II) ⟶ (III) is the only triad change possible.

† Allen and Rudoff (*loc. cit.*, p. 322, footnote) describe this by use of the misleading term " some "; they also give the wrong reference. The correct reference is : Burton and Shoppee, J., 1934, 204.

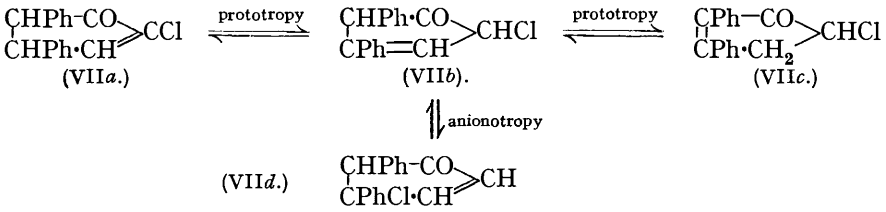
with red phosphorus and hydriodic acid in acetic acid, a 2 : 3-diphenyl*cyclo*pentenone (*A*) is produced (see Burton and Shoppee, this vol., p. 567); this is reduced catalytically (Adams) to *trans*-2 : 3-diphenyl*cyclo*pentanone (VIII). This saturated ketone can also be obtained directly from Allen's chloride by suitable catalytic reduction. Furthermore, the structural relationship of the diphenyl*cyclo*pentenone (*A*) to Allen's chloride is proved by chlorination of (*A*) with sulphuryl chloride in benzene at 15°, whereby the chloride is produced but not in good yield. These observations prove conclusively that the carbonyl group in Allen's chloride must be placed unsymmetrically in relation to the two phenyl groups; the chloride is, in fact, derived from the enolic modification (VI*b*) and can be represented by structure (VII).

In marked contrast to these results, Japp's chloride is reduced by red phosphorus and hydriodic acid in acetic acid to 3 : 4-diphenyl-Δ^3-*cyclo*pentenone (IX), which results from the first-formed Δ^2-isomeride (Burton and Shoppee, *loc. cit.*). Catalytic reduction of (IX) then gives *cis*-3 : 4-diphenyl*cyclo*pentanone (X), which is also obtained directly from Japp's chloride by catalytic reduction. Furthermore, the presence of the $\cdot CO\cdot CH_2\cdot$ group in Japp's chloride is indicated by the formation of a *piperonylidene* derivative when the condensation with piperonal is effected with hydrogen chloride in acetic acid; under the same conditions, Allen's chloride yields an unidentified *compound*, which cannot be the piperonylidene derivative because of its lack of colour and high oxygen content. The above facts clearly exclude the possibility of obtaining the symmetrically constituted diphenyl*cyclo*pentenone (IX) from Allen's chloride as stated by Allen and Rudoff (*loc. cit.*).

These authors (*loc. cit.*) also state that by ozonolysis of their chloride in ethyl acetate solution they obtained desylacetic acid in 60% yield. We have made several independent repetitions of this oxidative fission, even using ten times the scale employed by Allen and Rudoff, but we have never been able to detect any desylacetic acid, although this acid is a highly characteristic substance and readily isolated. The sole, identifiable ozonolysis product of the chloride is benzoic acid, which is also produced as the only identifiable product when oxidation is effected with permanganate in 90% acetone at − 15° in the presence of magnesium sulphate. Hydrogen peroxide in acetone in the presence of ferrous ions is without action, and chromic anhydride in 90% acetic acid at 43° affords only benzoic acid, although much chloride is unattacked.

In regard to the oxidation of Japp's chloride, we have confirmed our previous statement (J., 1934, 204) that potassium permanganate in acetone at 15° gives a nearly quantitative yield of desylacetic acid; we have endeavoured to meet the criticism of Allen and Rudoff (*loc. cit.*, p. 322, footnote) that the use of an alkaline reagent is unreliable owing to the possible catalysis of αβ–βγ changes, by performing the oxidation in the presence of magnesium sulphate. We must emphasise, however, that none of the possible products of retrograde αβ–βγ changes [(III), (V), or even (II)] can yield desylacetic acid by oxidation.

Although we consider that we have proved beyond all doubt that Allen's chloride cannot be (IV), there is some doubt as to its precise structure; since the structure (VII) contains a prototropic system, the chloride may conceivably be represented by any of the four formulæ (VII *a*, *b*, *c*, and *d*) :



$$\begin{matrix}\text{CHPh-CO}\\ \text{CHPh}\cdot\text{CH}\end{matrix}\!\!>\!\text{CCl} \xrightleftharpoons{\text{prototropy}} \begin{matrix}\text{CHPh}\cdot\text{CO}\\ \text{CPh}{=}\text{CH}\end{matrix}\!\!>\!\text{CHCl} \xrightleftharpoons{\text{prototropy}} \begin{matrix}\text{CPh}-\text{CO}\\ \text{CPh}\cdot\text{CH}_2\end{matrix}\!\!>\!\text{CHCl}$$

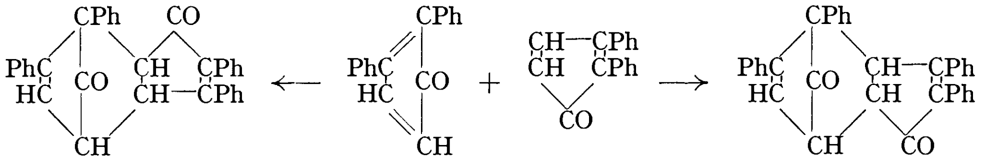
(VII*a*.) (VII*b*). (VII*c*.)

anionotropy

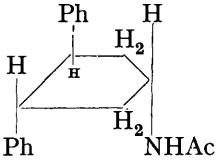
$$\begin{matrix}\text{CHPh-CO}\\ \text{CPhCl}\cdot\text{CH}\end{matrix}\!\!>\!\text{CH}$$

(VII*d*.)

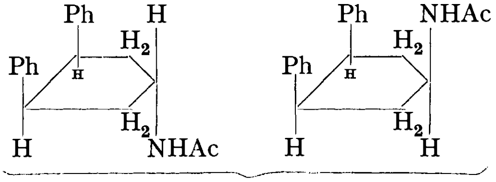
Of these, the two stereoisomerides represented by (*a*) are alone consistent with the unreactivity of the chlorine atom, reported by Allen and confirmed by us. On the other hand, (*c*), (*d*), and probably (*b*), but not (*a*), can yield dimeric substances directly by elimination of hydrogen chloride with subsequent Diels–Alder addition to the diphenyl*cyclo*pentadienone so formed :



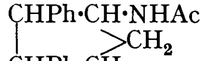
Oxidation of (*a*) should afford αα′-diphenylsuccinic but not benzoic acid, whereas (*b*), (*c*), and (*d*) would probably yield benzoic acid. It is probably best to regard Allen's chloride as a mixture of interchangeable isomerides; in this respect the chloride thus resembles the diphenyl*cyclo*pentenone (*A*) (this vol., p. 567). Further supporting evidence relating to the orientation of the carbonyl group in Japp's and Allen's chlorides has been obtained by a study of the diphenyl*cyclo*pentylamines obtained by reduction of the various ketoximes. For convenience the acetyl derivatives of the bases were actually isolated. There are three symmetrical 1-*acetamido*-3 : 4-*diphenyl*cyclo*pentanes*; the trans-*derivative* (XI) has m. p. 119°, and the cis-*compounds* (XII, XIII) have m. p. 128° and 134°, although it is not known which isomeride corresponds to which configuration.



(XI.)



(XII, XIII.)



(XIV.)

The results are summarised in the table below; this is not quite complete, since we have been unable to prepare the oxime of Allen's chloride. The *oxime* of Japp's chloride readily affords the *trans*-derivative (XI), whereas the halogen-free ketones from Allen's chloride lead to 1-*acetamido*-2 : 3-*diphenyl*cyclo*pentanes* (as XIV), since these differ from the symmetrically constituted compounds.

Ketone.	M. p. of oxime.	Reducing agent.	Acetyl derivative.	
			M. p.	Structure.
trans-3 : 4-Diphenyl*cyclo*pentanone, m. p. 177° ...	121·5°	Na,EtOH	119°	(XI)
cis-3 : 4-Diphenyl*cyclo*pentanone, m. p. 110°	137—138	Na,EtOH	128, 134	(XII), (XIII)
3 : 4-Diphenyl-Δ^3-*cyclo*pentenone (IX), m. p. 100°	179	Na,EtOH	119	(XI)
Japp's chloride, m. p. 129°	172	H_2,PtO_2	119	(XI)
trans-2 : 3-Diphenyl*cyclo*pentanone (VIII), m. p. 98°	187	Na,EtOH	171, 187	as (XIV)
2 : 3-Diphenyl*cyclo*pentenone, m. p. 89°	257	Na, amyl alcohol	171, 187	as (XIV)
Allen's chloride, m. p. 140°	—	—	—	—

We have also attempted to synthesise 2 : 3-diphenyl*cyclo*pentanone (VIII) by means of the Dieckmann reaction with *methyl γδ-diphenylvalerate*, $CH_2Ph\cdot CHPh\cdot CH_2\cdot CH_2\cdot CO_2Me$; ketonic material was isolated as (?) *semicarbazone*, but, as this did not have the expected composition, it was not investigated further.

EXPERIMENTAL.

(All molecular weights were determined by Rast's method.)

Allen's Chloride (as VII).—(i) Treatment of 2-hydroxy-3 : 4-diphenyl-Δ^2-*cyclo*pentenone (5 g.) with phosphoryl chloride (15 c.c.) according to the directions of Allen and Rudoff (*loc. cit.*) led to some carbonisation and a black product. Some improvement was effected by using a bath at 110° to heat the reaction mixture, and the yield of crystallised chloride, m. p. 139°, from 5 g. of the hydroxy-ketone was increased from 0·9 g. to 2·2 g. by reducing the time of heating from 15 to 10 mins., the amount of tar formed being correspondingly decreased. The viscous, dark red product after decomposition with ice (it is important to stir until all phosphoryl chloride has decomposed, and the oil has solidified) gave a black-brown solid, which, when dry, was extracted with boiling ethyl alcohol (100 c.c.), and then with 50 c.c. of solvent. The two alcoholic extracts were boiled separately with charcoal, filtered, and kept overnight; the crude chloride which separated was repeatedly crystallised from alcohol, or, better, benzene–ligroin (b. p. 60—80°), and was finally obtained as yellow-buff plates, m. p. 140° (Found: C, 75·75, 75·8; H, 5·0, 5·0; Cl, 13·4, 12·9; *M*, 297. Calc. for $C_{17}H_{13}OCl$: C, 76·0; H, 4·9; Cl, 13·2%; *M*, 268·5).

(ii) 2 : 3-Diphenyl*cyclo*pentenone (2 g.) (see Burton and Shoppee, this vol., p. 567), dissolved in dry benzene (2 c.c.), was treated with sulphuryl chloride (1·0 c.c.); a vigorous evolution of hydrogen chloride occurred with slight production of heat. After standing overnight, the mixture was decomposed with ice, the product extracted with benzene, and the extract washed with 2N-sodium carbonate and dried with potassium carbonate. The residue obtained by evaporation gradually crystallised in part; two recrystallisations of the solid from benzene–ligroin (b. p. 60—80°) furnished pale yellow-buff plates, m. p. 140°, mixed m. p. 140° with a specimen of Allen's chloride prepared by method (i) (Found: Cl, 12·5, 13·05%). The 2 : 4-dinitrophenylhydrazone after crystallisation from chloroform–methyl alcohol had m. p. 215° and depressed the m. p. of the 2 : 4-dinitrophenylhydrazone of Japp's chloride to 200° (Found: C, 61·1; H, 3·6; N, 12·8; Cl, 7·5. Calc. for $C_{23}H_{17}O_4N_4Cl$: C, 61·4; H, 3·8; N, 12·5; Cl, 7·9%).

We are able to confirm Allen and Rudoff's statement that the chlorine atom of the chloride is unaffected by silver nitrate and potassium acetate (in aqueous-alcoholic solution), but is removed by sodium hydroxide and piperidine; the chloride was insoluble in piperidine at 15° but dissolved at *ca.* 40° with immediate precipitation of piperidine hydrochloride, but no crystalline product could be isolated. We find that the stability of the chloride to sodium carbonate appears to depend on the conditions. For instance, in 90% dioxan after refluxing for 0·5 hour, the chloride was recovered unaltered; after 5 hours' treatment the product was sticky, but the chloride, m. p. 137°, was the only crystalline substance isolable. In methyl alcohol, however, refluxing for 0·5 hour afforded the monomethoxy-dimeride, m. p. 205° with gas evolution at *ca.* 250°, described by Allen and Rudoff (*loc. cit.*, p. 326), although our value for its molecular weight is just double that recorded by these workers (Found: C, 83·9; H, 5·7; OMe, 6·5%; *M*, 1001). On the other hand, neither silver nor barium carbonate in boiling methyl alcohol reacted with the chloride, which was recovered unaltered in 90% yield, m. p. and mixed m. p. 140°.

We were unable to obtain an oxime of Allen's chloride, despite many attempts; the chloride was recovered unchanged after prolonged treatment with hydroxylamine or its acetate at 15°. With hydroxylamine hydrochloride and sodium acetate (anhydrous) in alcohol for 4 days at 40°, or for shorter times at higher temperatures, the only isolable product was a dimeric chlorine-free *oxime*, which separated from boiling *iso*amyl alcohol in pale buff plates, m. p. 258—259° (decomp.) (Found: C, 82·9; H, 5·15; N, 5·5; *M*, 465. $C_{34}H_{26}O_2N_2$ requires C, 82·6; H, 5·3; N, 5·6%; *M*, 494).

The chloride gives a colourless *compound*, which may be dimeric, when treated for 24 hours with piperonal (2 mols.) in methyl alcohol saturated with hydrogen chloride at 0°; the product, washed with ether, in which it is practically insoluble, and twice crystallised from ethyl acetate–ethyl alcohol, forms colourless rosettes, m. p. 188—189°, with gas evolution at 210—215° (Found: C, 69·05; H, 4·25; Cl, 15·2%; *M*, 377 *). The same compound slowly separates after some days when glacial acetic acid saturated with hydrogen chloride at 10° is used as the medium; recrystallised from acetic acid, it had m. p. 190—191°, with gas evolution at *ca.* 215° (Found: C, 68·0; H, 4·05; Cl, 15·15%; *M*, 210 *).

Reduction of Allen's Chloride with Hydriodic Acid and Phosphorus: Formation of 2 : 3-*Diphenyl*cyclo*pentenone*.—The chloride (0·5 g.), red phosphorus (0·3 g.), 48% hydriodic acid (1 c.c.), and acetic acid (2·5 c.c.) were refluxed for 2 hours, the solution filtered hot into 35 c.c. of water containing a little dissolved sulphur dioxide, and the mixture extracted twice with ether. The combined ethereal extracts were washed with 2N-sodium carbonate and with water, dried with potassium carbonate, and evaporated. Owing to the difficulty previously encountered (Burton and Shoppee, *loc. cit.*) of crystallising the unsaturated ketone, and to its somewhat variable m. p. (83—89°), the product was identified by conversion into its highly characteristic oxime by treatment with hydroxylamine hydrochloride (4 mols.) and sodium acetate in alcohol on the steam-bath. The oxime, crystallised from boiling *iso*amyl alcohol, had m. p. 257° (decomp.), possessed the appropriate crystalline form, and did not depress the m. p. of a genuine specimen.

Catalytic Reduction of Allen's Chloride: Formation of trans-2 : 3-*Diphenyl*cyclo*pentanone* (VIII).—(i) The chloride (1·0 g.) and sodium acetate trihydrate (0·5 g.), dissolved in alcohol (100 c.c.), were shaken with platinum oxide (0·2 g.) in an atmosphere of hydrogen; 250 c.c. of gas were absorbed in 25 mins. (Calc. for $3H_2$: 251 c.c.), and the reaction was then stopped.

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* Molecular weights are unreliable, as the substance slowly decomposes in camphor at 170°.

After filtration from platinum and removal of the solvent in a vacuum, the product was dissolved in ether, washed with water (the washings contained chloride ion) and with 2N-sodium carbonate, dried with potassium carbonate, and evaporated. The resultant oil rapidly crystallised, and afforded *trans*-2 : 3-diphenyl*cyclo*pentanone, m. p. 97—98°, after two crystallisations from ether–ligroin; mixed m. p. with a genuine specimen, 97—98°. (ii) The chloride (10·5 g.), sodium acetate (1·5 g., 3 mols.), and hydroxylamine hydrochloride (0·28 g., 1·1 mol.) dissolved in alcohol (100 c.c.), were shaken with platinum-black (1·0 g.) in an atmosphere of hydrogen; 160 c.c. of gas were absorbed in 5 mins. (Calc. for $2H_2$: 175 c.c.); hydrogen was then slowly taken up until 325 c.c. had been absorbed in 5 hours (Calc. for $3H_2$: 262 c.c.; for $4H_2$: 350 c.c.), whereupon reduction ceased. After filtration from platinum, and dilution with water (500 c.c.), the liquid was made alkaline with sodium hydroxide, and repeatedly extracted with ether. The combined ethereal extracts, after several washings with 2N-acetic acid, were washed with water, dried with potassium carbonate, and evaporated. The resultant oil, dissolved in ether-ligroin, was set aside, and *trans*-2 : 3-diphenyl*cyclo*pentanone separated in colourless prisms, m. p. 97—98°, mixed m. p. 97—98°. Basification of the acetic acid extracts and extraction with ether furnished no basic material.

*2-Chloro-3 : 4-diphenyl-Δ^2-*cyclo*pentenone* (*Japp's Chloride*) (IV).—The chloride was prepared from anhydroacetonebenzil (Burton and Shoppee, *loc. cit.*, p. 204); it is important that the time of treatment with alcoholic hydrogen chloride should not exceed 24 hours. The *oxime*, obtained in almost quantitative yield by treatment with hydroxylamine acetate in alcohol at 40° for a week, separated from methyl alcohol in colourless cubes, m. p. 172° (Found : C, 71·8; H, 5·0; N, 4·8; Cl, 12·5; *M*, 270. $C_{17}H_{14}ONCl$ requires C, 71·9; H, 4·9; N, 4·9; Cl, 12·5%; *M*, 283·5); treatment with acetyl chloride in pyridine on the steam-bath was ineffective, the unchanged oxime being recovered (Found : C, 71·75; H, 4·9; N, 4·95; Cl, 12·2%). The *piperonylidene* derivative was obtained by condensation of the chloride (1·3 g.) with piperonal (1·5 g.) in glacial acetic acid (10 c.c.) saturated with hydrogen chloride at 10°; after standing for a week at room temperature, the large yellow octahedra of the derivative were filtered off. Recrystallised from ethyl alcohol, the compound formed bright yellow prisms, m. p. 165° (Found : C, 74·7; H, 4·4; Cl, 8·5, 8·7; *M*, 312. $C_{25}H_{17}O_3Cl$ requires C, 74·9; H, 4·3; Cl, 8·8%; *M*, 400). The chloride was recovered unaltered, m. p. 127°, mixed m. p. 127—128°, after treatment with nitrosyl chloride in benzene for 48 hours.

Reduction of Japp's Chloride with Hydriodic Acid and Phosphorus : Formation of 3 : 4-*Diphenyl-Δ^3-*cyclo*pentenone* (IX).—The chloride (2 g.) was reduced as described for Allen's chloride (p. 1412). The resulting ketone, after crystallisation from benzene (from which it separated in solvated form) and then from ethyl alcohol, had m. p. 110°, mixed m. p. 110° with a genuine specimen prepared by the method of Japp and Lander (J., 1897, **71**, 132). The 2 : 4-dinitrophenylhydrazone (see Burton and Shoppee, this vol., p. 569), crystallised from ethyl acetate–ethyl alcohol, had m. p. 260° (decomp.), a mixed m. p. with a genuine specimen showing no depression (Found : C, 66·45; H, 4·3; N, 13·35. Calc. for $C_{23}H_{18}O_4N_4$: C, 66·7; H, 4·4; N, 13·5%).

Catalytic Reduction of Japp's Chloride : Formation of cis-3 : 4-*Diphenyl*cyclo*pentanone* (X).—Use of platinum-black with hydrogen at atmospheric pressure in alcohol was ineffective, the chloride being recovered unchanged, and the product obtained by ultimate evaporation of the alcoholic mother-liquor having m. p. 127—128°.

When the chloride (1 g.), dissolved in alcohol, was shaken with platinum oxide (0·2 g.) in an atmosphere of hydrogen, 250 c.c. (Calc. for $3H_2$: 250 c.c.) were absorbed in 3 hours. The residual oil crystallised, and after draining on porcelain, was twice recrystallised from ligroin (b. p. 40—60°), from which it separated in colourless clusters of needles, m. p. 91°; the compound showed no carbonyl reactivity and appears to be cis-3 : 4-*di*cyclo*hexyl*cyclo*pentanol* (Found : C, 80·8; H, 11·6; *M*, 246. $C_{17}H_{30}O$ requires C, 80·2; H, 12·0%; *M*, 250), reduction of the phenyl groups probably being catalysed by the hydrogen chloride formed during the reduction.

Catalytic reduction under the conditions used above for Allen's chloride gave a solid, which when crystallised from ligroin (b. p. 60—80°) had m. p. 109—110°, raised by recrystallisation to 110°, and was identified as *cis*-3 : 4-diphenyl*cyclo*pentanone by direct comparison, and by mixed m. p.

Oxidation of Allen's Chloride.—(i) *With ozone.* The chloride (0·1 g.) in ethyl acetate (50 c.c.) was treated with ozonised oxygen at 15° for 70 mins. (cf. Allen and Rudoff, *loc. cit.*, p. 326). After removal of the solvent in a vacuum, the ozonide was decomposed by treatment with water containing a little hydrogen peroxide in the presence of ferrous sulphate; the product was extracted with ether, and the extract dried with sodium sulphate, partly evaporated, mixed with an equal volume of acetone, and allowed to evaporate spontaneously. The crystalline residue consisted of benzoic acid only, m. p. 121°, mixed m. p. 121°.

The degradation was repeated with 1 g. of the chloride dissolved in 50 c.c. of ethyl acetate at 0°, and the ozonide decomposed as described above. The acidified product was extracted twice with ether, and the combined extracts washed with sodium bicarbonate solution. The ethereal extract, dried and evaporated, furnished no residue; the alkaline washings were acidified with 2N-hydrochloric acid and repeatedly extracted with ether, and the extract dried with sodium sulphate and evaporated. The crystalline residue was dissolved in benzene and concentrated; it afforded only benzoic acid, m. p. 120°, mixed m. p. 120—121°. No detectable trace of desylacetic acid was present, although this is much less soluble than benzoic acid in benzene and crystallises in characteristic cubes.

Reduction of the Oxime of Japp's Chloride : Formation of trans-3 : 4-*Diphenyl*cyclo*pentylamine* (as XI).—Use of 3% sodium amalgam and acetic acid in boiling alcohol furnished little basic material, but with platinum oxide (0·5 g.) in acetic acid the oxime (5 g.) absorbed 1500 c.c. of hydrogen in 10 hours (Calc. for $2H_2$: 1560 c.c.). After filtration from platinum into a large volume of water, non-basic material was removed by two extractions with ether; after basification, the aqueous liquor (which contained chloride ion) was repeatedly extracted with ether and the ethereal extracts were combined, dried with potassium carbonate, and evaporated under a column. The residual oil became largely crystalline on cooling, and the solid material was filtered off, washed with ether–ligroin (1 : 1), and crystallised from ether–ligroin (b. p. 40—60°); trans-3 : 4-*diphenyl*cyclo*pentylamine* formed colourless plates, m. p. 119—120°, which absorbed carbon dioxide rapidly (Found: C, 82·5; H, 7·85; N, 5·6. $C_{17}H_{19}N$ requires C, 86·1; H, 8·0; N, 5·9%). The *picrate*, prepared by treating the amine, dissolved in dry ether, with ethereal picric acid, separated from dilute methyl alcohol in yellow prisms, m. p. 232° (decomp. after previous softening), and was photosensitive, darkening on exposure to light (Found: C, 59·7; H, 4·8; N, 11·6, 11·65. $C_{23}H_{22}O_7N_4$ requires C, 59·2; H, 4·75; N, 12·0%). The acetyl derivative was prepared (*a*) directly from the base by means of hot acetic anhydride, and (*b*) from the picrate by treatment with anhydrous sodium acetate in boiling acetic anhydride. After decomposition with water, basification, and extraction with ether, the ethereal extract was washed repeatedly with 2N-sodium hydroxide to remove picric acid [in case (b) only], with water, dried with potassium carbonate, and evaporated. The two specimens were identical and consisted of a single substance, 1-*acetamido*-trans-3 : 4-*diphenyl*cyclo*pentane* (*A*), which, twice crystallised from ether–ligroin (b. p. 40—60°), formed colourless cubes, m. p. 119° (Found: C, 81·5; H, 7·4; N, 5·1. $C_{19}H_{21}ON$ requires C, 81·7; H, 7·55; N, 5·0%), depressed by admixture with the above amine.

Reduction of the Oximes of cis- *and* trans-3 : 4-*Diphenyl*cyclo*pentanone : Formation of* cis- (as XII, XIII) *and* trans-3 : 4-*Diphenyl*cyclo*pentylamines*.—The *trans*-ketoxime, m. p. 121·5° (0·75 g.), was reduced with sodium wire (3 g.) and ethyl alcohol (45 c.c.). A crystalline solid separated on dilution with water; this was filtered off, and dried in a vacuum over potassium hydroxide. Crystallised from aqueous alcohol, *trans*-3 : 4-diphenyl*cyclo*pentylamine formed colourless silky needles, m. p. 119—120°. The picrate separated immediately when ethereal solutions of the base and picric acid were mixed; crystallised from aqueous alcohol, it formed photosensitive, yellow, prismatic needles, m. p. 231° (decomp. with previous softening and sintering) (Found : C, 59·8; H, 4·95; N, 11·7%). The acetyl derivative (*B*) was prepared from the base and acetic anhydride; it separated from ether–ligroin in cubes, m. p. 119°, mixed m. p. with (*A*) 119°, mixed m. p. with (*C*) (below) 119°.

The *cis*-ketoxime, m. p. 137—138° (2 g.), was reduced similarly with sodium wire (8 g.) and ethyl alcohol (120 c.c.); dilution afforded a base which, after drying in a vacuum over potassium hydroxide, was acetylated with acetic anhydride. Fractional crystallisation of the product from benzene–ligroin yielded two isomerides; the less soluble 1-*acetamido*-cis-3 : 4-*diphenyl*cyclo*pentane* had m. p. 133—134° (Found: C, 81·45; H, 7·35; N, 5·0; *M*, 270. $C_{19}H_{21}ON$ requires C, 81·7; H, 7·55; N, 5·0%; *M*, 279), and the more soluble *isomer* had m. p. 128°, unchanged by recrystallisation (Found : C, 81·35; H, 7·4; N, 5·2%; *M*, 292).

Reduction of 3 : 4-*Diphenyl*-Δ^3-cyclo*pentenoneoxime : Formation of* trans-3 : 4-*Diphenyl*cyclo*pentylamine* (as XI).—The ketone (2·35 g.), hydroxylamine hydrochloride (0·85 g.), and anhydrous sodium acetate were refluxed in alcohol on the steam-bath for 3 hours. The *oxime* was precipitated by pouring into water, filtered off, and crystallised from aqueous methyl alcohol, from which it separated in pale yellow, felted needles, m. p. 179° (Found: C, 82·0; H, 6·0; N, 5·3; *M*, 246. $C_{17}H_{15}ON$ requires C, 81·9; H, 6·0; N, 5·6%; *M*, 249).

The oxime (2 g.) was reduced with sodium wire (8 g.) and ethyl alcohol (120 c.c.); after dilution with water (500 c.c.) and extraction with ether, basic products were removed from the combined ethereal extracts by 2N-acetic acid. The base from the acidic solution was recrystallised from ether–ligroin; *trans*-3 : 4-diphenyl*cyclo*pentylamine formed long colourless plates, m. p. 117—118° (Found : C, 85·6; H, 7·8; N, 6·2%). The picrate, obtained by mixing ethereal solutions of the base and picric acid, formed yellow plates from aqueous methyl alcohol (1 : 2), m. p. 232° (decomp. after previous darkening and softening) (Found : C, 59·45; H, 4·65; N, 12·3%). The acetyl derivative (*C*) formed prisms, m. p. 119°, after two crystallisations from ether–ligroin, mixed m. p. with (*A*) 119°, mixed m. p. with (*B*) 119° (Found : C, 81·5; H, 7·2; N, 5·3%; *M*, 280).

Reduction of trans-2 : 3-*Diphenyl*cyclo*pentanoneoxime : Formation of* 2 : 3-*Diphenyl*cyclo*pentylamine* (as XIV).—The oxime (2·4 g.) was reduced with sodium wire (9·6 g.) and ethyl alcohol (175 c.c.). The base was extracted as above, and acetylated with boiling acetic anhydride. The dried solid material was dissolved in the minimum amount of boiling benzene, and the crystalline material which separated on cooling was recrystallised four times from ethyl acetate; 1-*acetamido*-2 : 3-*diphenyl*cyclo*pentane* was thus obtained in colourless prismatic needles, m. p. 187° after slight previous sintering (Found : C, 81·8; H, 7·45; N, 5·1; *M*, 297. $C_{19}H_{21}ON$ requires C, 81·7; H, 7·55; N, 5·0%; *M*, 279). The benzene mother-liquors were diluted with ligroin (b. p. 60—80°) and the material which separated was also recrystallised four times from ethyl acetate; the isomeric 1-*acetamido*-2 : 3-*diphenyl*cyclo*pentane* was then obtained in colourless silky needles, m. p. 170—171° with slight previous sintering (Found : C, 81·5; H, 7·35; N, 5·1; *M*, 290. $C_{19}H_{21}ON$ requires C, 81·7; H, 7·55; N, 5·0%; *M*, 279).

Reduction of 2 : 3-*Diphenyl*cyclo*pentenoneoxime*.—The oxime (2·3 g.) in boiling *iso*amyl alcohol (180 c.c.) was treated with sodium (9·2 g.) added in eight portions. When dissolution was complete, the mixture was cooled, acidified with concentrated hydrochloric acid and then steam-distilled to remove all volatile products. The cold acidic solution was filtered from a small amount of resinous material, made alkaline, and the base extracted in the above manner. Fractionation of the solid acetyl derivative as described in the previous paragraph gave the same 1-acetamido-2 : 3-diphenyl*cyclo*pentanes, m. p. and mixed m. p. 186—187° and 170—171°, both after slight previous sintering.

γδ-Diphenyl-Δ^{α}-pentenoic acid was prepared from αβ-diphenylpropaldehyde (36 g.) by the method of Burton and Shoppee (J., 1937, 548). The solid acid, which was accompanied by a liquid fraction probably consisting largely of a geometrical isomeride (see below), yielded an *anilide*, which crystallised from alcohol in colourless needles, m. p. 129—130° (Found : C, 83·9; H, 6·2. $C_{23}H_{21}ON$ requires C, 84·4; H, 6·4%).

*γδ-Diphenyl-*n*-valeric Acid*.—Both solid and liquid γδ-diphenyl-Δ^{α}-pentenoic acids rapidly absorbed the calculated amount of hydrogen in presence of platinic oxide and methyl alcohol. The new acid could not be obtained crystalline; it was characterised as the *anilide*, which formed colourless needles from methyl alcohol, m. p. 111—112° (Found : C, 83·5; H, 6·9. $C_{23}H_{23}ON$ requires C, 83·9; H, 7·0%). Esterification of the saturated acid from each experiment with methyl alcohol containing 5% of concentrated sulphuric acid gave the same *methyl γδ-diphenylvalerate*, b. p. 206—208°/15 mm. (Found : C, 80·2; H, 7·7. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·5%).

An unsuccessful attempt was made to synthesise ethyl γ-hydroxy-γδ-diphenylvalerate from deoxybenzoin and ethyl β-iodopropionate by the Reformatsky reaction.

Treatment of the methyl diphenylvalerate with sodium powder in dry benzene gave semisolid materials which yielded a (?) *semicarbazone*, m. p. 237° (decomp.), when crystallised from acetic acid (Found : C, 67·8, 68·3; H, 7·1, 6·7; N, 11·55, 11·6%).

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