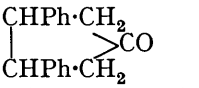
# 128. *Anionotropic and Prototropic Changes in Cyclic Systems. Part VI.* cis- *and* trans-3 : 4-*Diphenyl*cyclo*pentanones. The Structure of the Ketone obtained by Reduction of* 2-*Hydroxy*-3 : 4-*diphenyl*-$\Delta^2$-cyclo*pentenone with Hydriodic Acid.*

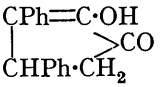
By HAROLD BURTON and CHARLES W. SHOPPEE.

Methods of preparation of *cis*- and *trans*-3 : 4-diphenyl*cyclo*pentanones are given. The " 3 : 4-diphenyl*cyclo*pentanone " of Allen and Rudoff (*Canadian J. Res.*, 1937, *B*, **15**, 321) is proved to be a 2 : 3-*diphenyl*cyclo*pentenone*, since it is reduced to trans-2 : 3-*diphenyl*cyclo*pentanone*. The position of the double linking in the unsaturated ketone could not be established, probably because it is part of an active prototropic system. The ease of prototropic change in *cyclo*pentenones is further investigated.

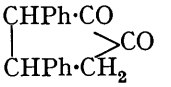
IN connexion with the investigation of a compound considered by us (J., 1934, 201) to be 2-chloro-3 : 4-diphenyl-$\Delta^2$-*cyclo*pentenone, we had prepared two ketones, m. p. 110° and 177°, and from their methods of preparation, analyses, and properties, had concluded that these were the isomeric *cis*- and *trans*-3 : 4-diphenyl*cyclo*pentanones (I*a*, I*b*). We were actually engaged on the synthesis of these ketones from methyl *meso*- and *dl*-$\beta\gamma$-diphenyladipate by means of the Dieckmann reaction when the identical method was published by Weidlich (*Ber.*, 1938, **71**, 1601), who found that the *meso*- and the *dl*-ester gave respectively the *cis*- (m. p. 107°) and the *trans*- (m. p. 177°) ketone.



(I*a*; *cis*.) (I*b*; *trans*.)

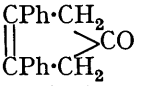


(II.)



(III.)

*trans*-3 : 4-Diphenyl*cyclo*pentanone (I*b*) was actually prepared by von Liebig (*Annalen*, 1914, **405**, 188) by the reduction of 2-hydroxy-3 : 4-diphenyl-$\Delta^2$-*cyclo*pentenone (II), an enolic modification of 3 : 4-diphenyl*cyclo*pentane-1 : 2-dione (III), or of the sulphonic acid formed as an intermediate in the preparation of (II) (*loc. cit.*), with sodium amalgam. We have confirmed the first-named observation, but find that some of the *cis*-isomeride (I*a*) and a small amount of a 3 : 4-*diphenyl*cyclo*pentane*-1 : 2-*diol* are also produced. Von Liebig's conjecture that the ketone (m. p. 175°), that is (I*b*), obtained by him might be 2 : 3-diphenyl*cyclo*pentanone is negatived by the fact that it yields a *dipiperonylidene* derivative. We have also prepared the *cis*-ketone (I*a*) by catalytic reduction of 3 : 4-diphenyl-$\Delta^3$-*cyclo*pentenone (IV) in presence of platinum-black. Reduction proceeds slowly, as might be expected with a compound containing the ·CPh:CPh· group, and it is actually



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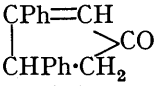

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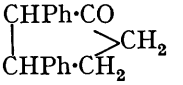


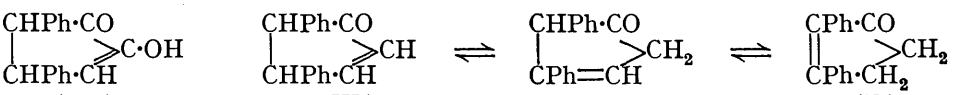
(VI.)

much more convenient to carry out the reduction in presence of Adams's catalyst to cis-3 : 4-*diphenyl*cyclo*pentanol*, which undergoes smooth oxidation by chromic anhydride in 90% acetic acid to the required ketone. If, however, the unsaturated ketone (IV) is reduced by sodium and boiling ethyl alcohol, a mixture of the *cis*- and the *trans*-*cyclo*pentanol is produced; subsequent oxidation gives the ketones, which are readily separated owing to their differing solubilities in methyl alcohol. The *cis*-ketone (I*a*) also yields a *dipiperonylidene* derivative and both (I*a*) and (I*b*) have been further characterised by means of *oximes* and 2 : 4-*dinitrophenylhydrazones*.

While some of the above work was being carried out, a closely related investigation was published by Allen and Rudoff (*Canadian J. Res.*, 1937, *B*, **15**, 321). These authors state that the hydroxy-ketone (II), or, better, the chloride obtained therefrom by the action of phosphoryl chloride, was reduced by red phosphorus and hydriodic acid to a

3 : 4-diphenyl*cyclo*pentanone, m. p. 92° (corr.), which gave a 2 : 4-dinitrophenylhydrazone, m. p. 228° (corr.), and was dehydrogenated by selenium dioxide in dioxan to the unsaturated ketone (IV). We have prepared this supposed 3 : 4-diphenyl*cyclo*pentanone by the above methods, and we find from analyses of the ketone itself and of its *oxime* and 2 : 4-dinitrophenylhydrazone that it is actually a *diphenyl*cyclo*pentenone* (*A*). We first thought that this ketone might be the unknown 3 : 4-diphenyl-$\Delta^2$-*cyclo*pentenone (V), but we had to abandon this view when we discovered that catalytic reduction (Adams) gave a *diphenyl*cyclo*pentanone*, m. p. 98°, and/or a *diphenyl*cyclo*pentanol*; the latter was readily oxidised by chromic acid to the former. The new saturated ketone thus differs from *cis*- and *trans*-3 : 4-diphenyl*cyclo*pentanone, but since it undergoes Clemmensen reduction to *trans*-1 : 2-diphenyl*cyclo*pentane (Weidlich, *loc. cit.*), it must contain the *cyclo*pentane ring and contiguous phenyl groups. We must, therefore, conclude that the ketone, m. p. 98°, is trans-2 : 3-*diphenyl*cyclo*pentanone* (VI); this has been further characterised by means of its *oxime*, *semicarbazone*, and 2 : 4-*dinitrophenylhydrazone*.

The diphenyl*cyclo*pentenone (*A*) obtained in the reductions with hydriodic acid would then be a 2 : 3-diphenyl*cyclo*pentenone. The production of such a compound from, for example, the hydroxy-ketone (II) may appear surprising, but it must be remembered that the diketone (III) can also react in the alternative enolic modification (VII)—a view originally put forward by von Liebig (*loc. cit.*) in order to explain the production of isomeric benzoates when (II) was benzoylated under alkaline and under acidic conditions. In these circumstances the primary reduction product of (II) [reacting as (VII)] may well



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

be 2 : 3-diphenyl-$\Delta^4$-*cyclo*pentene (VIII), but this, however, contains a prototropic system and may undergo the tautomeric change (VIII) $\rightleftharpoons$ (IX) $\rightleftharpoons$ (X). We have carried out numerous oxidation experiments on the diphenyl*cyclo*pentenone (*A*), but the only identifiable product formed in neutral or acidic media was benzoic acid. On the other hand, alkaline sodium hypobromite gave diphenylmaleic anhydride and (probably) αβ-diphenylglutaric acid but no benzoic acid. The production of the diphenylglutaric acid would appear to involve a reduction (probably at the expense of some of the oxidised material) of the unsaturated ketone to the *cyclo*pentanone and subsequent oxidation of this. The evidence concerning the structure of (*A*) is thus inconclusive, pointing to (X) under strongly alkaline conditions and (IX) or (X) under other conditions. Curiously enough, no evidence has been obtained for structure (VIII), which should give αα′-diphenylsuccinic acid on oxidation. It is probably best to regard the diphenyl*cyclo*pentenone (*A*) as a mixture of interchangeable isomerides. In view of this apparent ease of prototropic changes in the diphenyl*cyclo*pentenone system, we decided to examine the system (IV) $\rightleftharpoons$ (V). In order to do this we attempted the synthesis of (V) by eliminating hydrogen bromide from 2-*bromo*-cis-3 : 4-*diphenyl*cyclo*pentanone*, which, unlike its *trans*-isomeride, was obtained in a crystalline condition. When either bromide was treated with pyridine, even under relatively mild conditions, the sole product was the $\Delta^3$-*cyclo*pentenone (IV), indicating that the prototropic change is again facile.

We have found, however, that the 3 : 4-diphenyl-$\Delta^3$-*cyclo*pentenone (IV) can react in its isomeric modification (V), since ozonolysis invariably gives some desylacetic acid ($COPh{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$), which can only arise from (V). It may be noted that the

(XI.) (XII.)

dimethyl homologues, (XI) and (XII), of (IV) and (V) exist as separate individuals and that Japp and Maitland (J., **1904**, **85**, 1484) observed the change (XII $\longrightarrow$ XI) in the presence of alcoholic hydrogen chloride.

We are at a loss to account for Allen and Rudoff's assertion that their "3 : 4-diphenyl-

*cyclo*pentanone " could be dehydrogenated to (IV); under their experimental conditions we have never been able to obtain (IV) or, for that matter, any other identifiable product.

The production of the diphenyl*cyclo*pentenone (*A*) from the chloride obtained by Allen and Rudoff (*loc. cit.*) from (II) and phosphoryl chloride must, we think, be considered fairly conclusive evidence against the structure, *viz.*, 2-chloro-3 : 4-diphenyl-$\Delta^2$-*cyclo*pentenone (II, with OH = Cl), assigned by these authors to the chloride. We hope to present further evidence on this point in another communication.

## Experimental.

*Reduction of* 2-*Hydroxy*-3 : 4-*diphenyl*-$\Delta^2$-cyclo*pentenone* (II) *with Sodium Amalgam. Formation of* cis- *and* trans-3 : 4-*Diphenyl*cyclo*pentanone* (I*a*) (I*b*).—A solution of the hydroxy-ketone (II) (7·5 g.) in hot aqueous potassium hydroxide was cooled to 40° and treated with 1 kg. of 3% sodium amalgam with stirring for 18 hours. After filtration, the clear liquid was extracted thrice with ether and the combined extracts were dried with potassium carbonate and evaporated, furnishing a colourless oil, which crystallised when kept; after drainage on porcelain, and two crystallisations from methyl alcohol, 3 : 4-*diphenyl*cyclo*pentane*-1 : 2-*diol* formed colourless plates, m. p. 114° [Found : C, 80·0; H, 7·1; *M* (Rast), 279. $C_{17}H_{18}O_2$ requires C, 80·0; H, 7·1%; *M*, 254].

The solid residue from the foregoing filtration was extracted repeatedly with ether, and the combined extracts dried with potassium carbonate and partially evaporated; a solid which then separated was filtered off, and the filtrate (F) was worked up as described later. After the solid had been washed with a little ether and twice crystallised from methyl alcohol, *trans*-3 : 4-diphenyl*cyclo*pentanone separated in long colourless needles, m. p. 177° (cf. Weidlich, *loc. cit.*) [Found : C, 86·2; H, 6·7; *M* (Rast), 247. Calc. for $C_{17}H_{16}O$ : C, 86·4; H, 6·8%; *M*, 236]. The 2 : 4-*dinitrophenylhydrazone*, rapidly formed by Brady's method (J., 1931, 756), crystallised from chloroform–methyl alcohol in orange-yellow rosettes, m. p. 170° (Found : C, 66·7; H, 4·7; N, 13·6. $C_{23}H_{20}O_4N_4$ requires C, 66·35; H, 4·85; N, 13·5%). The *oxime*, recrystallised from methyl alcohol, formed colourless plates which contained methyl alcohol, m. p. (indefinite) 109—113°; the crystals effloresced on keeping and then had m. p. 121·5° [Found : C, 80·9; H, 6·6; N, 5·9; *M* (Rast), 233. $C_{17}H_{17}ON$ requires C, 81·3; H, 6·8; N, 5·6%; *M*, 251]. The *dipiperonylidene* derivative was obtained by heating the ketone (0·23 g.) with piperonal (0·3 g.) in alcohol (10 c.c.) containing potassium hydroxide (0·3 g.) on the steam-bath; the clear yellow solution deposited crystals in a few minutes, and after 48 hours these were filtered off and recrystallised from ethyl alcohol, separating in yellow needles, m. p. 220° [Found : C, 79·2; H, 4·8; *M* (Rast), 560. $C_{33}H_{24}O_5$ requires C, 79·2; H, 4·8%; *M*, 500].

The ethereal filtrate (F) (above) and washings were combined and evaporated, and the resulting semi-solid triturated with methyl alcohol; after draining on porcelain, the product was repeatedly crystallised from methyl alcohol, *cis*-3 : 4-diphenyl*cyclo*pentanone being obtained in colourless plates, m. p. 110° (cf. Weidlich, *loc. cit.*) [Found : C, 86·1; H, 6·8; *M* (Rast), 243. Calc. for $C_{17}H_{16}O$ : C, 86·4; H, 6·8%; *M*, 236]; an alternative solvent is ligroin (b. p. 60—80°), from which the ketone separates in long needles. The 2 : 4-*dinitrophenylhydrazone* was readily prepared; twice recrystallised from ethyl acetate–methyl alcohol, it formed yellow needles, m. p. 208° (Found : C, 66·7; H, 4·8; N, 13·8. $C_{23}H_{20}O_4N_4$ requires C, 66·35; H, 4·85; N, 13·5%). The *oxime* separated from dilute methyl alcohol in colourless needles, m. p. 137—138° (Found : C, 81·6; H, 6·9; N, 5·6. $C_{17}H_{17}ON$ requires C, 81·3; H, 6·8; N, 5·6%). The *dipiperonylidene* derivative (prepared similarly to the corresponding *trans*-compound) formed yellow needles from methyl acetate–methyl alcohol, m. p. 240°, unchanged by further crystallisation [Found : C, 79·2; H, 4·9; *M* (Rast), 560. $C_{33}H_{24}O_5$ requires C, 79·2; H, 4·8%; *M*, 500].

*Reduction of* 3 : 4-*Diphenyl*-$\Delta^3$-cyclo*pentenone* (IV).—The ketone (IV) was prepared from anhydroacetonebenzil by the method of Japp and Lander (J., 1897, **71**, 131), and characterised as its 2 : 4-*dinitrophenylhydrazone*, which has been reported to melt at 233° by Allen and Rudoff (*loc. cit.*); several independent preparations, recrystallised from (*a*) chloroform–methyl alcohol, (*b*) xylene, and (*c*) ethyl acetate–ethyl alcohol (the best medium), gave red needles, m. p. 259—260° (decomp.) [Found : C, 66·8; H, 4·3; N, 13·7 (*a*); C, 66·55; H, 4·3; N, 13·5 (*b*); C, 66·6; H, 4·4; N, 13·3 (*c*). $C_{23}H_{18}O_4N_4$ requires C, 66·7; H, 4·4; N, 13·5%].

(a) *With platinum-black.* The ketone (0·6 g.), dissolved in alcohol and shaken with platinum-black in hydrogen, absorbed 50 c.c. in 1½ hours (calc., 57 c.c.). Evaporation, and crystallis-

ation of the resulting solid from methyl alcohol, furnished *cis*-3 : 4-diphenyl*cyclo*pentanone, m. p. 105—106°, which was characterised by formation of the 2 : 4-dinitrophenylhydrazone, m. p. 208°, not depressed by admixture with a genuine specimen [Found : C, 66·45; H, 4·6; N, 13·2%; *M* (Rast), 266], and the dipiperonylidene derivative, m. p. 240°, mixed m. p. 240° [Found : C, 79·3; H, 4·8%; *M* (Rast), 513].

(b) *With platinum oxide.* The ketone (11·9 g.), dissolved in 250 c.c. of alcohol and shaken with Adams's catalyst (1 g.) in hydrogen, absorbed 2·1 l. (calc., 2·24 l.) in 10 hours. The blue fluorescent solution was evaporated; the residual oil crystallised at once. Recrystallised from ligroin (b. p. 60—80°), cis-3 : 4-*diphenyl*cyclo*pentanol* formed rosettes of needles, m. p. 85—86° [Found : C, 85·7; H, 7·7; *M* (Rast), 256. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%; *M*, 238].

The carbinol (6·7 g.), dissolved in 200 c.c. of 90% acetic acid, was treated with chromic anhydride (2·1 g.) at room temperature. After standing overnight, the green solution was poured into water and extracted with ether, and the extract washed with 2N-sodium hydroxide and with water, dried with potassium carbonate, and evaporated. The oil crystallised readily and, recrystallised from methyl alcohol, afforded *cis*-3 : 4-diphenyl*cyclo*pentanone (6 g.), m. p. 108—109°.

(c) *With sodium and ethyl alcohol.* A solution of the ketone (10 g.) in 100 c.c. of hot alcohol was poured on sodium wire (20 g.); after solution of all the metal (necessitating the addition of a further 100 c.c. of alcohol), the product was treated with much water and extracted several times with ether, and the combined extracts well washed with water, dried with potassium carbonate, and evaporated. The resulting oil was distilled, the main portion (6·5 g.) passing over as a yellow oil, b. p. 195—197°/2 mm., which would not crystallise and probably consisted of a mixture of stereoisomeric 3 : 4-diphenyl*cyclo*pentanols.

The mixed carbinols (6·2 g.), dissolved in 200 c.c. of 90% acetic acid, were treated with chromic anhydride (2·0 g.) at room temperature; after standing overnight, the product was poured into much water, and the precipitate filtered off. A solution of the dry precipitate in hot methyl alcohol, on cooling, deposited the *trans*-ketone in an almost pure condition; after evaporation of the mother-liquor to one half its bulk, the *cis*-ketone crystallised on cooling. Recrystallisation afforded the ketones in a state of purity, m. p. 177° and 108—109°, respectively.

*Clemmensen Reduction of the* cis- *and* trans-3 : 4-*Diphenyl*cyclo*pentanones*.—(i) The *cis*-ketone (0·75 g.) was heated under reflux with amalgamated zinc wool and hydrochloric acid for 5 hours; the product was taken up in ether, and the ethereal extract washed with much water and with 2N-sodium hydroxide, dried, and evaporated; the residual oil, possessing a faint geranium-like odour, crystallised on cooling in ice, and furnished *cis*-1 : 2-diphenyl*cyclo*pentane, m. p. 47°, after crystallisation from ligroin (b. p. 40—60°).

(ii) Similar procedure with the *trans*-ketone (0·25 g.) afforded *trans*-1 : 2-diphenyl*cyclo*pentane, as an oil with a pronounced odour of geraniums, which crystallised with extreme ease and after recrystallisation from ligroin (b. p. 60—80°) had m. p. 65° (cf. Weidlich, *loc. cit.*).

*Reduction of* 2-*Hydroxy*-3 : 4-*diphenyl*-$\Delta^2$-cyclo*pentenone* (II) *with Hydriodic Acid and Phosphorus. Formation of* 2 : 3-*Diphenyl*cyclo*pentenone* (*A*).—The hydroxy-ketone (II) (2 g.), red phosphorus (1·2 g.), 48% hydriodic acid (4 c.c.), and acetic acid (10 c.c.) were refluxed for 4 hours, the solution filtered hot into 140 c.c. of water containing a little sulphur dioxide, and the mixture extracted thrice with ether (cf. Allen and Rudoff, *loc. cit.*). The combined ethereal extracts were washed twice with 2N-sodium hydroxide (the washings exhibited no turbidity on acidification), with water, dried with potassium carbonate, and evaporated, yielding a colourless oil, which readily solidified on stirring. In contrast with its ready solidification, the product was extremely difficult to crystallise; a dilute solution in aqueous alcohol slowly deposited crystals, m. p. 76—77°, which were unsaturated to permanganate in acetone, but decolorised a solution of bromine in carbon tetrachloride only slowly and with evolution of hydrogen bromide; we found the best medium for crystallisation to be ligroin (b. p. 60—80°) containing a little ether or benzene, the vessel being lagged with cotton wool; crystallised twice in this way, 2 : 3-*diphenyl*cyclo*pentenone* formed nodules, m. p. 83° [Found : C, 86·7, 87·1; H, 6·0, 6·4; *M* (Rast), 247. $C_{17}H_{14}O$ requires C, 87·2; H, 6·0%; *M* 234]. Another preparation (time of reduction, 2 hours) had m. p. 83—84° after two crystallisations (Found : C, 86·7; H, 6·15%), and the highest m. p. observed after repeated crystallisation was 89° with slight previous softening (Found : C, 86·9; H, 6·2%) (Allen and Rudoff, *loc. cit.*, give 92° corr.). The product could be distilled, b. p. 215°/15 mm., and after crystallisation had m. p. 83—84°. The 2 : 4-*dinitrophenylhydrazone* was highly characteristic; although formed

rapidly with methyl-alcoholic 2 : 4-dinitrophenylhydrazine sulphate (Brady, *loc. cit.*) as an orange precipitate, it separated from ethyl acetate–ethyl alcohol in dark red needles, m. p. 225° (as described by Allen and Rudoff, who give m. p. 228° corr.) (Found : C, 66·75; H, 4·5; N, 13·0. $C_{23}H_{18}O_4N_4$ requires C, 66·7; H, 4·4; N, 13·5%). The *oxime* was sparingly soluble in boiling alcohol, from which it separated in iridescent plates or needles, decomp. 257—258° after previous darkening and sintering [Found : C, 82·0; H, 6·0; N, 5·6; *M* (Rast) 262, 267. $C_{17}H_{15}ON$ requires C, 81·9; H, 6·0; N, 5·6%; *M*, 249]; the oxime was more soluble in boiling *iso*amyl alcohol, from which it separated in iridescent plates. Attempts to prepare a piperonylidene derivative under alkaline conditions were unsuccessful, the product consisting of an amorphous buff precipitate; use of hydrogen chloride in glacial acetic acid (Ruhemann and Levy, J., 1913, **103**, 551) gave an apparently uncrystallisable orange solid.

Treatment of the ketone with selenium dioxide in dioxan according to the directions of Allen and Rudoff (*loc. cit.*) furnished a little unaltered ketone, isolated as the characteristic 2 : 4-dinitrophenylhydrazone, m. p. 224°, mixed m. p. 224—225°, as the only identifiable product. Repetition on a larger scale yielded traces of two imperfectly crystalline 2 : 4-dinitrophenylhydrazones insufficient for purification : (*a*) bright red and the more soluble in ethyl acetate, m. p. 243—245° (decomp.); (*b*) dark red and less soluble, m. p. 252° (decomp.). No trace could be discovered of the 2 : 4-dinitrophenylhydrazone, m. p. 233°, described by Allen and Rudoff (*loc. cit.*) and considered by them to be that of the $\Delta^3$-*cyclo*pentenone (IV) (see p. 569).

*Reduction of* 2 : 3-*Diphenyl*cyclo*pentenone* (*A*) *with the Clemmensen Reagent. Formation of* trans-1 : 2-*Diphenyl*cyclo*pentane*.—The ketone was heated under reflux with amalgamated zinc wool and hydrochloric acid for 5 hours; the sublimate, which collected in the condenser, was dissolved out with ether. The ethereal solution by evaporation gave *trans*-1 : 2-diphenyl-*cyclo*pentane, m. p. 63° after crystallisation from ligroin (b. p. 40—60°).

*Reduction of* 2 : 3-*Diphenyl*cyclo*pentenone* (*A*) *with Platinum Oxide. Formation of* trans-2 : 3-*Diphenyl*cyclo*pentanone* (VI).—Use of platinum-black and hydrogen with alcohol as solvent was ineffective. The unsaturated ketone (3·6 g.) was therefore shaken with Adams's catalyst (0·6 g.) and hydrogen in alcoholic solution (30 c.c.); when 345 c.c. of hydrogen had been absorbed in 55 mins. (calc. for one double bond, 344 c.c.), the reaction was stopped. After filtration, and removal of the solvent in a vacuum, the residual oil was dissolved in ether, and the solution dried with potassium carbonate, evaporated, and distilled. The whole of the product passed over from 170—180°/0·5 mm., and rapidly crystallised on cooling and scratching. After two recrystallisations from ether–ligroin (b. p. 40—60°) trans-2 : 3-*diphenyl*-cyclo*pentanone* formed colourless prisms, m. p. 98° [Found : C, 86·4, 86·55; H, 7·0, 6·7; *M* (Rast), 228, 256. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8%; *M*, 236]. The 2 : 4-*dinitrophenyl-hydrazone* formed rapidly and crystallised from ligroin (b. p. 80—100°) in orange needles, m. p. 142° (Found : C, 66·5; H, 5·0; N, 13·6. $C_{23}H_{20}O_4N_4$ requires C, 66·35; H, 4·85; N, 13·5%). The *semicarbazone*, twice crystallised from hot methyl alcohol, formed colourless needles, which were photosensitive; m. p. 195—196° (decomp.) (Found : C, 73·5; H, 6·55; N, 14·25. $C_{18}H_{19}ON_3$ requires C, 73·7; H, 6·5; N, 14·3%). The *oxime* separated from alcohol in colourless plates, m. p. 187° (Found : C, 81·3; H, 6·8; N, 5·6. $C_{17}H_{17}ON$ requires C, 81·3; H, 6·8; N, 5·6%). The ketone and piperonal did not yield a piperonylidene derivative in presence of methyl-alcoholic potassium hydroxide or of sodium methoxide; both these agents afforded the same *substance*, which appeared to be the addition product $C_{25}H_{22}O_4$ and crystallised from methyl alcohol in pale lemon-yellow prisms, m. p. 190° [Found : C, 77·45, 77·45, 77·9, 77·8; H, 5·0, 5·05, 5·1, 5·1; *M* (Rast), 400. $C_{25}H_{22}O_4$ requires C, 77·7; H, 5·7%; *M*, 386]. The substance was unaffected by boiling acetic anhydride, or by a boiling mixture of acetic acid and acetic anhydride containing a trace of iodine, but was altered by boiling acetic anhydride containing one drop of sulphuric acid to an amorphous substance.

The ether–ligroin mother-liquor from the crystallisation of the ketone was evaporated, and the residual oil dissolved in alcohol and treated with semicarbazide acetate for 48 hours; after removal of the semicarbazone, dilution of the alcoholic solution furnished an oil (O).

In a repetition of the hydrogenation, with platinum oxide (0·65 g.), the unsaturated ketone (5·4 g.) in alcohol (50 c.c.) rapidly absorbed hydrogen (520 c.c.; calc. for $H_2$, 517 c.c.), but the product, b. p. 165—180°/0·5 mm., would not solidify. It was dissolved in alcohol and treated with semicarbazide acetate, which removed a quantity of the saturated ketone present; the alcoholic solution by dilution yielded an oil, which was combined with the previous specimen (O); the oil, extracted with ether, dried (potassium carbonate), and distilled, boiled constantly at 160°/0·5 mm., crystallised after some months, and proved to be trans-2 : 3-*diphenyl*-

cyclo*pentanol* (Found : C, 85·4, 85·6; H, 7·65, 7·55. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%). The carbinol (3 g.), dissolved in 90% acetic acid (100 c.c.), was oxidised with chromic anhydride (1·0 g.) at 15°; the product was poured into water and extracted with ether, and the extract washed with 2N-sodium hydroxide and with water, dried with potassium carbonate, and evaporated; *trans*-2 : 3-diphenyl*cyclo*pentanone, m. p. 97—98° after crystallisation from ether–ligroin, was then obtained.

*Clemmensen Reduction of* trans-2 : 3-*Diphenyl*cyclo*pentanone to* trans-1 : 2-*Diphenyl*cyclo*pentane*.—The ketone (2 g.) was refluxed for 5 hours with amalgamated zinc and hydrochloric acid, the product extracted with ether, and the extract, after being washed with 2N-sodium hydroxide and with water, dried, and evaporated, leaving *trans*-1 : 2-diphenyl*cyclo*pentane, m. p. 62° (crude), m. p. 65—66° after crystallisation from ligroin (b. p. 60—80°) [Found : C, 91·8; H, 8·2; *M* (Rast), 219. Calc. for $C_{17}H_{18}$ : C, 91·9; H, 8·1%; *M*, 222].

*Oxidation of* 2 : 3-*Diphenyl*cyclo*pentenone* (*A*).—The ketone was recovered unchanged after treatment with ethereal hydrogen peroxide in the presence of osmium tetroxide at 15° for 12 hours (Criegee, *Annalen*, 1936, **522**, 94), and after boiling for 6 hours in dioxan with potassium chlorate and a trace of osmium tetroxide.

Ozonolysis at 0° in methyl acetate or in chloroform and decomposition of the ozonide by water containing a little hydrogen peroxide and ferrous sulphate gave only benzoic acid; use of warm water alone for fission of the ozonide furnished only benzoic acid. The neutral product in all cases consisted of a mere trace of oil, from which no ketone was recoverable. Similarly, use of potassium permanganate in 90% acetone at — 15°, or of chromium trioxide in 90% acetic acid at 15°, afforded only benzoic acid, unaccompanied by any unaltered ketone. After oxidation by potassium hypobromite by stirring in suspension in aqueous dioxan at 0° to 15° for 48 hours, much ketone was filtered off and recovered unchanged. The filtrate after acidification by passage of sulphur dioxide, and further acidification with 2N-sulphuric acid, was repeatedly extracted with ether. From the combined extracts (E), acid products were removed by washing with sodium bicarbonate solution; acidification of the alkaline liquor, extraction with ether, drying, and evaporation furnished an oil, which solidified when rubed with benzene. After draining, two crystallisations from benzene and recrystallisation from toluene afforded αβ-diphenylglutaric acid, m. p. 207° [Found : C, 71·6; H, 5·7; *M* (by titration), 280; *M* (Rast) 337. Calc. for $C_{17}H_{16}O_4$ : C, 71·8; H, 5·7%; *M*, 284]; the acid was stable to alkaline permanganate.

The ethereal extracts (E) were washed with 2N-sodium hydroxide, and the washings acidified and extracted with ether; after drying and evaporation, a yellow oil was obtained which readily solidified; twice crystallised from ligroin (b. p. 120—140°), the substance formed yellow needles, m. p. 150°, and was identified as diphenylmaleic anhydride, mixed m. p. 150° with a genuine specimen.

*Bromination of the* cis- *and* trans-3 : 4-*Diphenyl*cyclo*pentanones, and Formation of* 3 : 4-*Diphenyl*-$\Delta^3$-cyclo*pentenone* (IV).—(i) The *cis*-ketone (1·15 g.) was treated in chloroform solution with bromine (0·8 g.); after a short induction period, the bromine disappeared with evolution of hydrogen bromide. Following the removal of solvent in a vacuum, the product was dissolved in ether, washed with water, and dried with sodium sulphate; evaporation left an oil, which solidified on treatment with benzene–ligroin, and two crystallisations from ligroin (b. p. 60—80°) containing a trace of ether furnished 2-*bromo*-cis-3 : 4-*diphenyl*cyclo*pentanone*, m. p. 91° to a turbid liquid, clearing at 98° (Found : Br, 24·45. $C_{17}H_{15}OBr$ requires Br, 25·4%). The bromo-ketone by treatment with boiling pyridine afforded 3 : 4-diphenyl-$\Delta^3$-*cyclo*pentenone, m. p. 110°, mixed m. p. 110°, unaccompanied by any other product. A repetition conducted for 18 hours at 35°, the product being maintained below 10° during working up, yielded the $\Delta^3$-unsaturated ketone, m. p. 110°, and no trace of a $\Delta^2$-isomeride could be discovered.

(ii) The *trans*-ketone (1·15 g.) was subjected to the treatment given above, but the product could not be satisfactorily crystallised and was therefore treated directly with pyridine at 35° for 18 hours; the sole product isolable was the $\Delta^3$-unsaturated ketone.

*Ozonolysis of* 3 : 4-*Diphenyl*-$\Delta^3$-cyclo*pentenone* (IV).—The ketone (2·0 g.), dissolved in methyl acetate (50 c.c.) or in chloroform (50 c.c.), was treated with ozonised oxygen at 0° for 3 hours, and the solvent removed in a vacuum; the ozonide was decomposed by treatment with warm water or by solution in moist ether containing a little acetic acid and addition of zinc dust. In every case (at least six ozonolyses were performed), crystallisation of the acid fraction from benzene afforded desylacetic acid, which separated in small cubes and had m. p. 160—162°, mixed m. p. 160—162°, after a single recrystallisation from benzene. Examin-

ation of the benzene mother-liquor yielded benzoic acid only in each case. The neutral product was a thick yellow oil which was not further investigated.

*Chlorination of* trans-2 : 3-*Diphenyl*cyclo*pentanone*.—Use of sulphuryl chloride in benzene at 15° was ineffective. The ketone (1·18 g.) was therefore maintained at 102° and treated with chlorine until the increase in weight was 0·18 g. On cooling, the product became semi-solid; it separated from benzene–ligroin in yellow crystals, and recrystallisation from the same medium gave 5-*chloro*-trans-2 : 3-*diphenyl*cyclo*pentanone* in yellow cubes, m. p. 137° (Found : C, 75·8; H, 4·7; Cl, 12·3. $C_{17}H_{15}OCl$ requires C, 75·4; H, 5·5; Cl, 13·1%). The chloride was unaffected by pyridine at 35° during 18 hours; when it was refluxed in pyridine solution for 2 hours, hydrogen chloride was eliminated, but only intractable amorphous products were formed.

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