816. *The Oxidation of Diphenylmethylenecyclobutane.*

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A practicable route for the conversion of cyclobutanecarboxylic acid to cyclobutanone has been devised. Oxidation of diphenylmethylenecyclobutane by electrophilic reagents, such as peracids and chromic acid, involves rearrangement. Rearrangement also accompanies attack by ozone, confirming the electrophilic nature of the process, but oxidation by potassium permanganate or osmium tetroxide proceeds without rearrangement. Addition of hydrogen bromide or of bromine also probably occurs without rearrangement.
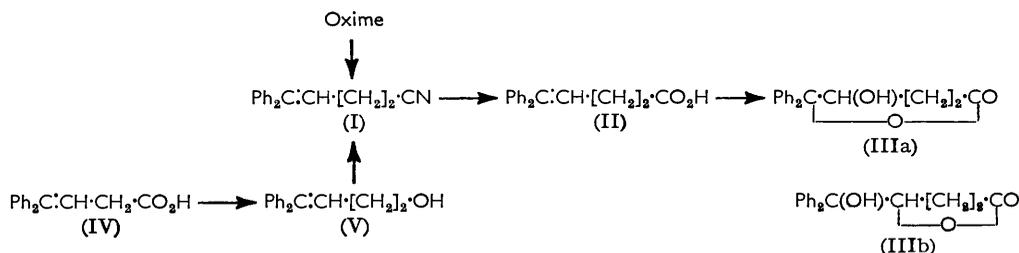
WHILE there are satisfactory methods for the preparation of cyclobutanone, in particular the reaction of keten with diazomethane,[1] these could not be extended to the preparation of alkylcyclobutanones. Degradation of alkylcyclobutanecarboxylic acids seemed to offer a possible route to the substituted ketone.

Whilst methylenecyclobutane can be oxidised to cyclobutanone[2] the oxidation of diphenylmethylenecyclobutane with performic acid, and with other oxidising agents, has been found to proceed differently.

Kishner[3] claims to have oxidised diphenylmethylenecyclobutane to benzophenone by chromic acid. We have found that it is oxidised in good yield to 2,2-diphenylcyclopentanone by chromium trioxide in acetic acid, and that diphenylcyclobutylmethanol is oxidised to the same ketone by chromic acid in aqueous sulphuric acid. The structure of the olefin has therefore been confirmed by converting it by osmium tetroxide into a diol which was then oxidised by lead tetra-acetate to a mixture of benzophenone and cyclobutanone.

Oxidation of the olefin with performic or peracetic acid gave a high yield of 2,2-diphenylcyclopentanone.[4] This part of our work was carried before the report by Easton and Nelson[4] was available to us. Consequently we degraded this ketone to confirm its structure, and report our results here.

The oxime of the ketone was converted by phosphorus pentachloride into an unsaturated nitrile (I) which was hydrolysed to an acid that took up one mol. of hydrogen on catalytic hydrogenation. Attempts to confirm the structure of the acid as 5,5-diphenylpent-4-enoic (II) acid by further oxidation were only partially successful. With aqueous alkaline potassium permanganate it gave benzophenone in good yield, but oxalic acid in place of succinic acid. The use of a limited quantity of permanganate led to some benzophenone, together with a lactone, $C_{17}H_{16}O_3$. The same lactone (IIIa or b) was produced by oxidation with performic acid and subsequent hydrolysis. Oxidation of the acid with chromic acid did, however, yield, in addition to benzophenone, a solid mixture in which succinic acid was detected by paper chromatography.

Oxime
↓

$Ph_2C:CH \cdot [CH_2]_2 \cdot CN$ ⟶ $Ph_2C:CH \cdot [CH_2]_2 \cdot CO_2H$ ⟶ $Ph_2C \cdot CH(OH) \cdot [CH_2]_2 \cdot CO$
(I)   (II) |——O——|
                                                 (IIIa)
↑

$Ph_2C:CH \cdot CH_2 \cdot CO_2H$ ⟶ $Ph_2C:CH \cdot [CH_2]_2 \cdot OH$ $Ph_2C(OH) \cdot CH \cdot [CH_2]_2 \cdot CO$
(IV)   (V) |——O——|
                                                                     (IIIb)

[1] Kaarsemaker and Coops, *Rec. Trav. chim.*, 1951, 1039.
[2] Roberts and Sauer, *J. Amer. Chem. Soc.*, 1949, **71**, 3925.
[3] Kishner, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1228.
[4] Cf. Easton and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 640.

The structure of the nitrile was therefore established by synthesis. 4,4-Diphenylbut-3-enoic acid (IV) was prepared from benzophenone and diethyl succinate, and reduced to the alcohol (V) which was converted into the bromide and thence into the nitrile identical with that obtained from the ketoxime.

In contrast with the behaviour of diphenylmethylenecyclobutane, methylenecyclobutane is oxidised by performic acid to a hydroxyformate,[2] and diphenylmethylenecyclohexane [5] is oxidised by peracetic acid to an epoxide.

The diol which we obtained by oxidation of diphenylmethylenecyclobutane with osmium tetroxide was dehydrated to diphenylcyclopentanone by warming it at 40° with formic acid, but it was unaffected by acetic acid at the same temperature.

Oxidation of the olefin with potassium permanganate took a different course. In strongly alkaline conditions [6] it gave the same diol as was obtained from osmium tetroxide and thus provides a satisfactory method of proceeding from cyclobutanecarboxylic acid to cyclobutanone. In the absence of added alkali oxidation, in aqueous acetone or aqueous dioxan, rapidly gave benzophenone and oxalic acid, but with the purely aqueous reagent the olefin was recovered largely unchanged. Control experiments showed that 2,2-diphenylcyclopentanone is stable to permanganate under the same conditions.

Diphenylmethylenecyclobutane reacted with almost exactly one mol. of ozone with the production of benzophenone, diphenylcyclopentanone, and 1,3-dibenzoylpropane. We believe that these products result from reaction with ozone and not from autoxidation by molecular oxygen.[7] Further, diphenylmethylenecyclobutane is unaffected by hydrogen peroxide in the absence of added acid, and so none of the products can have resulted from attack on unchanged olefin by peroxide produced during the hydrolysis of an ozonide. The formation of rearrangement products during the ozonolysis agrees with the view that the initial attack of ozone is electrophilic.[8]

In view of the ready oxidative rearrangement of diphenylmethylenecyclobutane the products obtained by other addition reactions were also investigated. Kishner [3] reported the addition of bromine and of hydrogen bromide and stated that the monobromide was unreactive. The same bromide could be prepared from cyclobutyldiphenylmethanol and hydrobromic acid. We repeated the preparation of the bromide from cyclobutyldiphenylmethanol, and confirm that it does not readily release free bromide ion: for example, 48 hours' boiling with potassium hydroxide in aqueous dioxan produced only traces of bromide ion. This stability is rather unexpected for a diphenylmethyl bromide, but on the other hand our other results agree better, though in rather negative fashion, with an unrearranged structure. We have attempted to synthesise those isomeric bromides which could result from rearrangement, and have been unable to do so. Attempts to prepare 2,2-diphenylcyclopentyl bromide from 2,2-diphenylcyclopentanol produced 1,2-diphenylcyclopentene, and this hydrocarbon gave only tar when treated with hydrogen bromide.

The infrared absorption spectrum of the bromide was of no assistance in resolving this point. Derfer, Pickett, and Boord [9] report that all monoalkylcyclobutanes show a band between 909 and 917 cm.$^{-1}$, although this band is absent from the spectrum of methylenecyclobutane.[10] This criterion ceases to be of value when aryl substituents are present: the spectrum of 1,2-diphenylcyclopentene, for example, has a band at 918 cm.$^{-1}$. The bromide does show a weak absorption at this point but no significance can be attached to it.

Dehydration of 2,2-diphenylcyclopentanol under the conditions used for cyclobutyl-diphenylmethanol also gives 1,2-diphenylcyclopentene, whose structure has been proved

[5] Lyle, Martin, and Fielding, *ibid.*, 1953, **75**, 4089.
[6] Lapworth and Mottram, *J.*, 1925, **127**, 1628.
[7] Cf. Traubs and Schollner, *Chem. Ber.*, 1958, **91**, 2282.
[8] Wibaut *et al.*, *Rec. Trav. chim.*, 1951, **70**, 1005; 1952, **71**, 761.
[9] Derfer, Pickett, and Boord, *J. Amer. Chem. Soc.*, 1949, **71**, 2482.
[10] Marrison, *J.*, 1951, 1614.

by ozonolysis in excellent yield, to 1,3-dibenzoylpropane, and by hydrogenation to the known 1,2-diphenylcyclopentane.[11]

The addition of bromine to diphenylmethylenecyclobutane was also investigated. In carbon disulphide solution this rapidly gave a nicely crystalline product which, however, was unstable. Our material melted, with decomposition, between 80° and 84°; Kishner[3] reported a value of 91°.

With sodium iodide in dry acetone the dibromide gave back a good yield (79%) of diphenylmethylenecyclobutane. As this reaction involves the removal of both bromine atoms in a concerted process [12,13] it is unlikely to be accompanied by rearrangement and may be taken as establishing the structure of the dibromide. In this case, too, we were unable to secure a sample of the isomeric dibromide, 1,2-dibromo-1,2-diphenylcyclopentane. 1,2-Diphenylcyclopentene reacted with bromine in carbon disulphide, but hydrogen bromide was evolved in the cold: only tar resulted.

EXPERIMENTAL

Cyclobutyldiphenylmethanol.—To the cooled Grignard reagent prepared from bromobenzene (425 g.), magnesium (65 g.), and ether (1 l.) was added methyl cyclobutanecarboxylate [14,15] (131 g.) in ether (400 ml.). The reaction was completed by refluxing for 30 min. The product was decomposed with saturated ammonium chloride, and the ether layer washed once with water and dried (Na_2SO_4). After removal of volatile material at 100°/15 mm., the residue solidified and weighed 242 g. (88%). This material was suitable for dehydration to the olefin, but distilled without decomposition at 128°/0·1—0·2 mm. and, recrystallised from light petroleum, had m. p. 54°. Kishner[3] gives b. p. 198°/13 mm., m. p. 54—54·5°.

Diphenylmethylenecyclobutane.—(i) *By pyrolysis of O-cyclobutyldiphenylmethyl S-methyl xanthate.* The alcohol (5 g.) was stirred for 30 min. with ether (12 ml.), carbon tetrachloride (1 ml.), and powdered sodium hydroxide (0·8 g.). After addition of carbon disulphide (1·2 ml.) the mixture was refluxed for 3 hr. Methyl iodide (1·4 ml.) was added and refluxing was continued for 6 hr. Water (5 ml.) was added to dissolve solids, the ether layer was washed and dried (Na_2SO_4), and the solvent removed at reduced pressure. The residue was heated over a flame for 20 min. The product solidified on trituration with methanol. It recrystallised from methanol as plates, m. p. 56—56·5°. Kishner[3] gives m. p. 58°. A portion liquified when mixed with the alcohol.

(ii) *By catalytic dehydration of the alcohol with iodine.* The alcohol (5 g.) was refluxed with iodine (0·1 g.) in benzene (20 ml.) for 12 hr. After being washed with sodium thiosulphate the product was distilled (b. p. 144°/2 mm.). The brown distillate solidified and was treated with charcoal in light petroleum. The pale brown plates (2·75 g.) melted at 57—58°, not depressed on admixture with the product obtained in (i) above.

(iii) *By dehydration of the alcohol with oxalic acid.* The alcohol (30 g.) was heated with oxalic acid dihydrate (120 g.) at 160° for 4 hr. The molten product was allowed to cool with stirring, and then extracted with ether (3 × 100 ml.), the ethereal extract being washed with dilute aqueous sodium hydroxide and water and dried. The distillate (25 g.) boiled at 110—112°/0·2—0·25 mm. and solidified; it was identical with the product obtained in (i) above.

Oxidation of Diphenylmethylenecyclobutane.—(i) *With performic acid.* To the olefin (2·2 g.) in 90% formic acid (6 ml.) was added, with stirring, hydrogen peroxide (1·4 ml.; 100-vol.), the temperature being kept at 40° for 6 hr. The mixture was left to crystallise, giving 2·16 g. of 2,2-diphenylcyclopentanone, m. p. 88—89° (from light petroleum) (Found: C, 86·0; H, 6·8. Calc. for $C_{17}H_{16}O$: C 86·4; H, 6·8%). The infrared spectrum showed a strong carbonyl absorption band at 1739 cm.$^{-1}$, characteristic of cyclopentanones. Easton and Nelson[4] report m. p. 87·5—89·5°. The 2,4-dinitrophenylhydrazone formed yellow-orange plates (from acetic acid or chloroform–light petroleum), m. p. 180—181°; Easton and Nelson[4] report m. p. 182—182·5°.

[11] von Liebig, *Annalen*, 1914, **405**, 207.
[12] Young, Pressman, and Coryell, *J. Amer. Chem. Soc.*, 1939, **61**, 1640.
[13] Winstein, Pressman, and Young, *ibid.*, p. 1645.
[14] Cason and Allen, *J. Org. Chem.*, 1949, **14**, 1036.
[15] Vogel and Jeffery, *J.*, 1948, 1806.

(ii) *With peracetic acid and sulphuric acid.* To the olefin (54 g.) in acetic acid (212 ml.) containing concentrated sulphuric acid (3 ml.) hydrogen peroxide (30 ml.; 100-vol.) was added, dropwise and with stirring, at 40°: the reaction was exothermic. The product (49 g.) crystallised out after 1 hr. and was identical with the product obtained in (i) above.

(iii) *With peracetic acid.* A solution of the olefin (0·55 g.) in acetic acid (7 ml.) was heated at 50—55° for 5 hr. with a slight excess of hydrogen peroxide. After removal of the solvent *in vacuo* the residue recrystallised from methanol and then from light petroleum; it melted at 87° alone or mixed with diphenylcyclopentanone.

(iv) *With monoperphthalic acid.* The olefin (1·1 g.) was treated in ether with a slight excess (2·5%) of ethereal monoperphthalic acid. The solution was kept at 0° for 3 days. Phthalic acid was then filtered off and washed with dry chloroform. The combined ether and chloroform filtrate was evaporated *in vacuo*, and the residue extracted three times with hot light petroleum (b. p. 60—80°) and filtered off. The residue, phthalic acid, weighed 0·78 g. (theor. 0·88 g.). Evaporation of the light petroleum gave an oil which did not solidify in 4 days at 0°. Distillation (bath 160°/0·1 mm.) gave diphenylcyclopentanone, m. p. 86—88°, after two crystallisations from light petroleum.

(v) *With chromium trioxide in acetic acid.* To a solution of the olefin (0·5 g.) in acetic acid (5 ml.) at 35° chromium trioxide (0·3 g.), dissolved in acetic acid (0·5 ml.), was added. The reaction was exothermic and the vessel was cooled in running water. The solution was heated at 40° for 30 min.; a test portion then rapidly crystallised when stirred into water. The product was isolated by ether-extraction, washing, and drying. Evaporation of ether gave 2,2-diphenylcyclopentanone (150 mg.). The mother-liquors did not contain benzophenone.

(vi) *With ozone.* Through a solution of the olefin (5·5 g., 0·025 mol.) in dry ethyl acetate (100 ml.) at −10° ozone was passed at the rate of 0·007 mol./hr. for 3·6 hr. During this time the iodine liberated in the potassium iodide bubbler by the exit gases was equivalent to 1·5 ml. of 0·5N-sodium thiosulphate. Ozonolysis was continued for a further 15 min. during which iodine equivalent to 2·4 ml. of 0·5N-sodium thiosulphate was liberated. The solvent was removed *in vacuo* and the residual oil refluxed with water (50 ml.) for 15 min. About 15 ml. of water were distilled off but gave only a faint turbidity when treated with 2,4-dinitrophenylhydrazine in 2N-hydrochloric acid. The residual mixture was extracted with ether (25 ml.), and the ethereal layer was washed with water (20 ml.). This aqueous layer also failed to give a positive carbonyl reaction. The ethereal layer was dried (Na_2SO_4). After removal of ether, distillation of the residue gave a fraction (1·65 g.), b. p. 160°/15 mm., which solidified on being seeded with benzophenone and gave a 2,4-dinitrophenylhydrazone (92% yield), m. p. 235—236° (from acetic acid) alone or mixed with benzophenone 2,4-dinitrophenylhydrazone. The residue was then distilled (bath 140°/0·1 mm.), giving 1·35 g. of crystalline material (A) and a residue (B) which also crystallised. After redistillation followed by recrystallisation from light petroleum and then from methanol, material (A) melted at 87° alone or mixed with 2,2-diphenylcyclopentanone. After two recrystallisations from methanol, material (B) melted at 65° alone or mixed with 1,3-dibenzoylpropane.[16]

Repetition of the experiment on the same quantity of olefin dissolved in glacial acetic acid (25 ml.) containing boron trifluoride–ether complex (3 ml.) gave benzophenone (2·1 g.), 2,2-diphenylcyclopentanone (1·32 g.), and 1,3-dibenzoylpropane (0·25 g.).

(vii) *With osmium tetroxide.* To the olefin (0·88 g.) and osmium tetroxide (1 g.) in dry, distilled, " AnalaR " benzene (8 ml.) was added dry, distilled " AnalaR " pyridine (0·63 g.). An exothermic reaction took place and the mixture was kept at room temperature for 48 hr. Black crystals (1·72 g.) were collected and then stirred with methylene chloride (25 ml.), water (100 ml.), potassium hydroxide (1 g.), and mannitol (10 g.) for 3 hr. The aqueous extract was pink. Crystals (0·7 g.) obtained from the methylene chloride were treated in boiling benzene with charcoal (50 mg.). Dilution of the filtrate with light petroleum gave needles, m. p. 144·5—145·5°, of 1-(α-*hydroxy*-αα-*diphenylmethyl*)*cyclobutanol* (Found: C, 80·1; H, 7·1. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%).

This diol was dehydrated to 2,2-diphenylcyclopentanone by 90% formic acid at 40° in 6 hr. but was unchanged in glacial or 90% acetic acid at 55° for 6 hr.

(viii) *With potassium permanganate in the absence of added alkali.* Dioxan was purified by refluxing it with sodium for 6 hr., then distilling it, refluxing it with potassium permanganate and sodium hydroxide for 4 hr., and distilling it from this mixture.

[16] Milone and Venturatto, *Gazzetta*, 1936, **66**, 808.

To the olefin (5·6 g.) in this dioxan (25 ml.) and water (6 ml.) potassium permanganate (8 g.) was added in portions. An exothermic reaction took place. Manganese dioxide was filtered off and washed with water. The filtrate was diluted with water and extracted twice with ether. White crystals were extracted from the manganese dioxide with ether. The combined ethereal solution was washed with a little water and dried (Na_2SO_4). Removal of ether gave an oil (4·86 g.) which partly solidified. Distillation gave no clearly defined fractions. A forerun (2·70 g.) boiling below 116°/0·4 mm. was collected. Further distillation gave unchanged olefin (2·16 g.), b. p. 118°/0·4 mm.

The forerun failed to solidify after being kept in the refrigerator for 3 days, but with 2,4-dinitrophenylhydrazine hydrochloride gave benzophenone 2,4-dinitrophenylhydrazone.

The combined aqueous solutions (*ca.* 130 ml.) were filtered to remove traces of manganese dioxide, neutralised with hydrochloric acid, and distilled. Only a turbidity was obtained from this distillate and 2,4-dinitrophenylhydrazine in 2N-hydrochloric acid. The residual aqueous solution from the distillation was passed through a column of Zeocarb 225; evaporation then gave oxalic acid dihydrate, m. p. and mixed m. p. 97—99° (from water).

The dioxan could be replaced by acetone (purified by Conant's method [17]). Unchanged olefin and benzophenone dinitrophenylhydrazone were again isolated but no oxalic acid.

The olefin failed to react with aqueous potassium permanganate at room temperature.

(ix) *With potassium permanganate in the presence of added alkali.* To the olefin (2·2 g.) in purified dioxan (60 ml.) potassium permanganate (3·4 g.) and sodium hydroxide (2·4 g.) in water (100 ml.) were added portionwise with stirring. The mixture did not react at 15° but rapidly deposited manganese dioxide at 40°. The reaction was exothermic and was complete within 20 min. The mixture was filtered and the filtrate extracted with ether (2 × 100 ml.); the manganese dioxide was also stirred with ether. The combined ethereal extracts were washed with water (20 ml.) and dried (Na_2SO_4). Removal of solvents gave 1-(α-hydroxy-αα-diphenylmethyl)cyclobutan-1-ol (1·6 g., 62·6%), m. p. 144·5—145·5° (from benzene–light petroleum), undepressed on admixture with the diol obtained in (vii) above.

Attempted Oxidation of 2,2-Diphenylcyclopentanon with Potassium Permanganate.—The ketone (1 g.) dioxan (purified as above; 5 ml.), water (1 ml.), and potassium permanganate (0·75 g.) were warmed at 50—60° for 15 min. Only the ketone (0·87 g.) was recovered.

Oxidation of 1-(α-Hydroxy-αα-diphenylmethyl)cyclobutan-1-ol with Lead Tetra-acetate.—The diol (350 mg.) in dry methylene chloride (4 ml.) was oxidised with recrystallised lead tetraacetate (670 mg.) contained in a sintered-glass thimble above the solution. When extraction of the reagent was complete, refluxing was continued for 1 hr. and the mixture then left overnight, boiled with ethanol (30 ml.) and 2,4-dinitrophenylhydrazine (500 mg., 92%), treated with concentrated hydrochloric acid (1 ml.), refluxed for 1 hr., and cooled in ice (7 hr.). The resulting solids were collected and dissolved in chloroform, washed with water, and dried (Na_2SO_4). Evaporation gave 680 mg. (88%) of mixed dinitrophenylhydrazones.

The mixture of dinitrophenylhydrazones (240 mg.), dissolved in chloroform, was separated by chromatography on bentonite–kieselguhr (20 g.).[18] The first component, eluted with chloroform, was benzophenone 2,4-dinitrophenylhydrazone (125 mg.), m. p. and mixed m. p. 237—238°. The second, eluted with chloroform–ethanol (19 : 1), was cyclobutanone 2,4-dinitrophenylhydrazone (90 mg.), m. p. and mixed m. p. 145° after softening at 143° (Roberts *et al.*[2] give m. p. 146—146·5°). Preliminary experiments on the separation of synthetic mixtures of cyclobutanone dinitrophenylhydrazone and dinitrophenylhydrazine showed that the former is best eluted with chloroform–ethanol (19 : 1): use of chloroform–ethanol (7 : 3) results in the elution of the reagent ahead of the derivative.

Oxidation of Cyclobutyldiphenylmethanol with Chromic Acid.—The alcohol (1 g.) reacted very vigorously with chromium trioxide (0·7 g.), water (1·5 ml.), and concentrated sulphuric acid (0·75 ml.) to give, after extraction with ether and the usual working up, 2,2-diphenylcyclopentanone (70%).

2,2-Diphenylcyclopentanone Oxime.—To the ketone (8·2 g.) in ethanol (120 ml.) sodium hydroxide (6 g.) and hydroxylamine hydrochloride (5 g.) were added in concentrated aqueous solution. After 6 hours' refluxing alcohol (70 ml.) was distilled off and the cooled residue stirred into dilute hydrochloric acid. Recrystallisation of the resulting solid from methanol

[17] Conant, *J. Amer. Chem. Soc.*, 1924, **46**, 245.
[18] Cf. Elvidge and Whalley, *Chem. and Ind.*, 1955, 589.

(*ca.* 40 ml./g.) gave the *oxime* (7 g., 80%) as needles, m. p. 172° (Found: C, 81·4; H, 6·6; N, 6·0. $C_{17}H_{17}ON$ requires C, 81·2; H, 6·8; N, 5·6%).

The oxime (8 g.) in dry ether (250 ml.) was treated with phosphorus pentachloride (11 g.) and kept overnight at room temperature. After removal of ether the residue was boiled with water, then cooled, and the product collected (6·3 g., 85%). Recrystallisation from methanol gave elongated plates, m. p. 68°, not depressed on admixture with 4-cyano-1,1-diphenylbut-1-ene (see below).

5,5-Diphenylpent-4-enoic Acid.—The nitrile (5 g.) was refluxed for 10 hr. with potassium hydroxide (10 g.) in ethanol (70 ml.) and water (15 ml.). Ethanol was distilled off, water (100 ml.) was added, and the mixture extracted with ether. Acidification of the aqueous layer gave 5,5-*diphenylpent-4-enoic acid* (4·5 g. crude), m. p. 82—83° (plates, from light petroleum) (Found: C, 80·8; H, 6·1. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%).

Oxidation of 5,5-Diphenylpent-4-enoic Acid with Alkaline Potassium Permanganate.—(i) To the acid (2·5 g.) in aqueous potassium hydroxide (0·8 g. in 20 ml.) potassium permanganate (14 g.) in water (200 ml.) was added dropwise with stirring at 40°. Manganese dioxide was filtered off and then stirred with ether. The aqueous filtrate was also extracted with ether. The combined ether extracts contained 1·1 g. (60%) of benzophenone, m. p. and mixed m. p. 45—47° (from light petroleum) (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 238°).

A little hydrogen peroxide was added to the aqueous layer to remove potassium permanganate, and the solution was heated on the steam-bath to decompose hydrogen peroxide and then passed through a column of Zeocarb 225. Evaporation of the eluate at 45°/15 mm. gave 1·3 g. of oxalic acid dihydrate, m. p. and mixed m. p. 100° (from aqueous methanol).

(ii) The acid (1 g.) was treated with water (10 ml.) and potassium hydroxide (0·32 g.). To this solution was added potassium permanganate (1·68 g.) in water (60 ml.) at 40°. Manganese dioxide was precipitated at once and the colour of potassium permanganate was discharged after warming for 5 min. The mixture was worked up as above. The solvent layer contained benzophenone isolated as its 2,4-dinitrophenylhydrazone (250 mg.), m. p. 237°. On passing the aqueous layer through Zeocarb 225 the eluate was found to contain 4,5-*dihydroxy-5,5-diphenylvaleric γ-* or *δ-lactone* which, recrystallised from methanol, then benzene–light petroleum, had m. p. 174° (Found: C, 76·1; H, 5·8. $C_{17}H_{16}O_3$ requires 76·1; H, 6·0%). A further quantity of lactone was obtained by stirring the extruded resin with ether.

γδ-Dihydroxy-δδ-diphenylvaleronitrile.—4-Cyano-1,1-diphenylbut-1-ene (1·17 g.) was stirred at 40° for 2 hr. with 90% formic acid (5 ml.) containing a slight excess of hydrogen peroxide (0·6 ml.; 100-vol.). The resulting crystals were recrystallised from methanol and then from benzene, giving fine needles of 4,5-*dihydroxy-5,5-diphenylvaleronitrile*, m. p. 154—155° (Found: C, 76·3; H, 6·5; N, 4·9. $C_{17}H_{17}O_2N$ requires C, 76·4; H, 6·4; N, 5·2%).

This nitrile (400 mg.) was refluxed with potassium hydroxide (1 g.) in ethanol (10 ml.) and water (1·5 ml.) until no more ammonia was evolved (4 hr.). Pouring the products into water (30 ml.) and acidifying them with concentrated hydrochloric acid gave the above lactone, m. p. 173°, sparingly soluble in methanol.

Oxidation of 5,5-Diphenylpent-4-enoic Acid with Chromic Acid.—The unsaturated acid (170 mg.) was heated at 40° with chromium trioxide (150 mg.) in acetic acid (3 ml.). The mixture was diluted with water and extracted with ether. The usual working up of the ether layer gave an oil which gave benzophenone 2,4-dinitrophenylhydrazone. The aqueous layer was warmed with ethanol in order to reduce chromic acid, then passed through Zeocarb 225. The colourless eluate was evaporated under reduced pressure leaving a whitish solid which was shown to contain succinic acid by paper chromatography in ammonia–ethanol. An attempt to isolate succinic anhydride by vacuum-sublimation was unsuccessful.

4,4-Diphenylbut-3-en-1-ol.—4,4-Diphenylbut-3-enoic acid [19] (9·4 g.) was esterified by ethereal diazomethane (yield, 8·85 g.; b. p. 128°/0·2 mm.). The ester (8 g.) in ether (50 ml.) was added dropwise, with stirring, to lithium aluminium hydride (1·2 g.) suspended in ether (150 ml.). After 2 hours' refluxing and storage overnight a grey sticky complex had separated. Ethyl acetate (6 ml.) was added, then crushed ice, followed by 2N-sulphuric acid (80 ml.). The ethereal layer was washed with dilute sodium carbonate and water, and dried (Na_2SO_4). Distillation gave the alcohol (4·29 g.), b. p. 138—140°/0·18—0·20 mm. [3,5-*dinitrobenzoate*, m. p. 129—130° (from benzene–light petroleum, then aqueous dioxan, then benzene–light petroleum) (Found: C, 66·0; H, 4·3; N, 6·7. $C_{23}H_{18}O_6N_2$ requires C, 66·0; H, 4·3; N, 6·7%)].

[19] Johnson, Peterson, and Schneider, *J. Amer. Chem. Soc.*, 1947, **69**, 74.

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4-Cyano-1,1-*diphenylbut*-1-*ene.*—Bromine (1·43 g.) was added to triphenyl phosphite (2·77 g.) at 0°. The mixture was kept for 30 min., then stirred with 4,4-diphenylbut-3-en-1-ol (2 g.) for a further 30 min. After 30 minutes' heating at 100° the product was dissolved in chloroform, washed with dilute sodium hydroxide and water, and dried (Na$_2$SO$_4$). The residue remaining after removal of solvent weighed 3·85 g. Distillation gave 4-bromo-1,1-diphenylbut-1-ene (1·26 g.), b. p. 140—148°/0·35 mm., and triphenyl phosphate (1·75 g.), b. p. 160—180°/0·3 mm., m. p. 49° (lit., b. p. 245°/11 mm., m. p. 49°).

This bromide (1·26 g.), ethanol (8 ml.), potassium cyanide (0·33 g.), and water (1 ml.) were refluxed for 24 hr. The solvent was removed *in vacuo*, and the residue was dissolved in ether, washed, dried (Na$_2$SO$_4$), and evaporated. Then recrystallisation from light petroleum (charcoal) gave 4-cyano-1,1-diphenylbut-1-ene (0·26 g.), m. p. 65—66° (Found: C, 87·4; H, 6·5; N, 5·8. C$_{17}$H$_{15}$N requires C, 87·5; H, 6·5; N, 6·0%).

Reaction between Cyclobutyldiphenylmethanol and Hydrogen Bromide.—The alcohol (2 g.) was kept overnight at room temperature with a 22% w/v solution (20 ml.) of hydrogen bromide in acetic acid, and the resulting dark red solution was poured into water. The bromide, recrystallised from methanol, had m. p. 94—95° (1·75 g., 70%); Kishner [3] gives m. p. 94—95°. If the mixture was heated a tar was obtained.

2,2-Diphenylcyclopentanol.—2,2-Diphenylcyclopentanone (10·5 g.) in dry ether (200 ml.) was added, with stirring, to lithium aluminium hydride (6 g.) suspended in ether (150 ml.). After 6 hours' refluxing, ethyl acetate (25 ml.) was added, then ice and 2N-sulphuric acid (300 ml.). The ethereal layer was separated, the aqueous layer was extracted once with ether (100 ml.), and the combined ethereal solutions were washed with 2N-sodium hydroxide and water and dried (Na$_2$SO$_4$). Distillation gave 2,2-*diphenylcyclopentanol* (8·7 g., 82%), b. p. 132°/0·2 mm., m. p. 51—52° [needles, from light petroleum (b. p. 40—60°)] (Found: C, 85·5; H, 7·6. C$_{17}$H$_{18}$O requires C, 85·7; H, 7·6%) [3,5-*dinitrobenzoate*, m. p. 122° (from benzene–light petroleum) (Found: C, 66·8; H, 4·9; N, 6·6. C$_{24}$H$_{20}$O$_6$N$_2$ requires C, 66·7; H, 4·7; N, 6·5%)].

Reaction between 2,2-Diphenylcyclopentanol and Triphenyl Phosphite Dibromide.—Triphenyl phosphite dibromide [20] was prepared from triphenyl phosphite (7·75 g.) and bromine (4 g.) at 0°. The cyclopentanol (6 g.) was added and the mixture heated at 60° for 45 min. Within a few seconds the colour changed to greenish-blue and fumes were evolved. The mixture was cooled, dissolved in chloroform, washed with 2N-sodium hydroxide and water, and dried (Na$_2$SO$_4$). Distillation gave 1,2-*diphenylcyclopentene* (4·28 g., 77·4%), b. p. 114°/0·1 mm., m. p. 62·5—63° (needles, from methanol) (Found: C, 92·7; H, 7·1. C$_{17}$H$_{16}$ requires C, 92·7; H, 7·3%); Weidlich and Meyer-Delius [21] describe it as a liquid. The residue from the distillation was triphenyl phosphate.

After a reaction at room temperature overnight, the product failed to crystallise on trituration with solvents and storage at 0°.

Dehydration of 2,2-Diphenylcyclopentanol.—The alcohol (0·75 g.) was dehydrated by oxalic acid dihydrate (3 g.) at 150—160° for 4 hr. to 1,2-diphenylcyclopentene. The same compound was produced by prolonged refluxing of the alcohol with hydrogen bromide in acetic acid (22% w/v).

Ozonolysis of 1,2-Diphenylcyclopentene.—The cycloalkene (1 g.) in dry ethyl acetate (50 ml.) was treated with ozone (4 × 10^{-3} mole/hr.) at 0°. After the calculated time the contents of the trap bottle containing potassium iodide were titrated, and ozonisation continued for a further 15 min., during which iodine was rapidly liberated by the exit gases. The solvent was then removed *in vacuo* and the residue treated with peracetic acid.[22] This gave 1,3-dibenzoylpropane (1 g. 87%), m. p. and mixed m. p. 65—66°.

Hydrogenation of 1,2-Diphenylcyclopentene.—The cycloalkene (220 mg.) was hydrogenated over Adams catalyst (50 mg.) in ethyl acetate (15 ml.) containing ethanol (1 ml.). Uptake of hydrogen was 24·8 ml. at 21°/758 mm. (one double bond, 24·8 ml.). Removal of solvent and recrystallisation from methanol gave 1,2-diphenylcyclopentane, m. p. 45—46° (lit.,[11] 46°).

1-Bromo-1-(α-*bromo-*αα-*diphenylmethyl*)*cyclobutane.*—Diphenylmethylenecyclobutane (2 g.) in carbon disulphide was treated portionwise with a slight excess of bromine in carbon disulphide (5% v/v) at room temperature. Evaporation, followed by recrystallisation from light

[20] Cf. Landauer and Rydon, *J.*, 1954, 2281.
[21] Weidlich and Meyer-Delius, *Ber.*, 1941, **74**, 1195.
[22] Cf. Henne and Hill, *J. Amer. Chem. Soc.*, 1943, **65**, 752.

petroleum, gave a solid (1·7 g.) melting between 70° and 80° to a green liquid; some hydrogen bromide was evolved during the recrystallisation. On further crystallisation from light petroleum, hydrogen bromide was again evolved, the melting range being 80—84° (decomp.): Kishner [3] reports m. p. 91—92°.

This material (1·7 g.) was refluxed in dry acetone (10 ml.) with sodium iodide (0·7 g.) for 1 hr., then extracted with ether. Extraction with aqueous sodium thiosulphate and then with 2N-sodium hydroxide failed to remove a deep red colour from the ethereal layer. The ethereal solution was washed with water and dried (Na_2SO_4). Evaporation gave black crystals. Distillation (bath 140—150°/0·2 mm.) and one recrystallisation from methanol gave diphenyl-methylenecyclobutane (780 mg., 79%), m. p. and mixed m. p. 56—56·5°.