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Alkylidenecyclobutanes. Part III.¹ The Addition of Hydrogen Bromide to Diphenylmethylenecyclobutane

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Addition of hydrogen bromide to alkylidenecyclobutanes produces 2,2-dialkylcyclopentyl bromides. The reactions of the products and related compounds are described and the natures of the ionic intermediates are discussed.

RING expansion to derivatives of cyclopentane sometimes accompanies reactions of diphenylcyclobutylmethanol (I) and diphenylmethylenecyclobutane (II). It has been suggested 1 that kinetically controlled reactions, such as the dehydration of (I) in which the covalency of the exocyclic carbon is changing from 4 to 3 take place without rearrangement, and that those, such as peracid oxidation of (II), which would otherwise involve a covalency change from 3 to 4, are accompanied by rearrangement. The addition of bromine to (II)²

¹ Part II, S. H. Graham and A. J. S. Williams, J. Chem. Soc. (C), 1966, 655.
 ² S. H. Graham and A. J. S. Williams, J. Chem. Soc., 1959,

4066.

constitutes an exception to the rule, which is reasonably explained by the partial delocalisation of positive charge on to bromine: this is possible only if no rearrangement occurs.³ The structure of the hydrogen bromide adduct⁴ of (II) has not been established though there is evidence⁵ that the analogous adduct from isopropylidenecyclobutane is the bromide (III). The lack of chemical reactivity 2,4 of the hydrobromide from (II) argues against an unrearranged structure, though the infrared spectrum ($\nu_{C-\rm H}~2981$ and 2890 cm $^{-1})$

³ Cf. K. H. Baggaley, W. H. Evans, D. A. Jonas, and D. H. Jones, *Tetrahedron*, 1968, 24, 3445.
 ⁴ N. Kizhner, J. Russ. Phys. Chem. Soc., 1910, 42, 1228.
 ⁵ N. Kizhner, J. Russ. Phys. Chem. Soc., 1908, 40, 999.

was suggestive of a cyclobutane rather than a cyclopentane derivative. 6



We have now examined the ¹H n.m.r. spectrum of this hydrobromide: the presence of a triplet (1H, J 4 c./sec.) at τ 4.95 excludes addition without rearrangement and is consistent with structure (IV), though the coupling to be expected between 1-H and the vicinal protons is hard to predict.⁷ The hydrobromide from isopropylidenecyclobutane was confirmed as having structure (III) since its ¹H n.m.r. spectrum included both a singlet (6H) at τ 8.96 and a triplet (1H, J 8 c./sec.) at τ 6.08, and the hydrobromide (V) from methylphenylmethylenecyclobutane also had a singlet (3H) at τ 8.54 and triplet (J 7 c./sec.) at τ 5.5 in its ¹H n.m.r. spectrum: further, since the triplets in the three spectra were identical, the structure $(I\bar{V})$ for the adduct from (II) is confirmed. It may be deduced that both (III) and (IV) each populate substantially only one conformation, which must be an envelope⁸ in which C-1 is out of the plane of the other four carbon atoms and ⁶ S. E. Wiberley, S. C. Bunce, and W. H. Bauer, Analyt. Chem., 1960, 32, 217

⁷ S. C. Lewis and G. H. Whitham, J. Chem. Soc. (C), 1967, 274.

the C-Br bond is axial. In this conformation the C(1)-H bond subtends almost equal dihedral angles with both of the C(5)-H bonds. The pseudo-rotation normally associated with cyclopentane rings ⁸ must be absent, presumably because this particular conformation, in which the repulsions between phenyl and bromine are minimised, represents an energy trough. Confirmation of structure (IV) was obtained by dehydrobromination to a mixture of olefins; osmic acid oxidation of this mixture gave the diol (VI) together with small quantities of the diol (VII) and 1,3-dibenzoylpropane. The formation of the two latter compounds is discussed below and is interesting as showing that even under conditions normally regarded as conducive to bimolecular reaction some ionic elimination still takes place. The structure of diol (VI) is based on its further oxidation to 2,2-diphenylglutaric acid.

The formation of (IV) from (II) might be expected to involve the 2,2-diphenylcyclopentyl ion (VIII) as an intermediate: further rearrangement of this ion to the 1.2-diphenylcyclopentyl ion (IX) would be energetically favoured and might well be expected to be rapid. The absence from the reaction product of any substance, e.g., 1,2-diphenylcyclopentene (X), for which the ion (IX) might have been the precursor, is striking and shows that capture of (VIII) by nucleophile must be extremely rapid. Equally striking is the fact that (VIII) is entirely captured by bromide ion even in the presence of acetic acid. A small amount of acetate (too little for isolation) did accompany (III), but even crude samples of (IV) were free of acetate. A little acetate also accompanied the chloride which was formed from (II) by the action of hydrogen chloride in acetic acid [the ¹H n.m.r. spectrum of the chloride showed it to be (XI)]. A model experiment showed that the acetate of 2,2-diphenylcyclopentanol (XIII) was converted into 1,2-diphenylcyclopentene under the conditions of the reaction but, as already pointed out, none of this substance accompanied the halides. Benzhydrylcyclobutanol (XII) is similarly converted into (IV), both (I) and (XII) may first be dehydrated to (II), but 2,2-diphenylcyclopentanol (XIII), under precisely the same conditions, gives only the olefin (X). The ionisation of (IV) itself gives a mixture of (X) and (XIV). The bromide (IV) is unreactive; it solvolysed in buffered formic acid to give (X), and reacted only partially in boiling acetic acid. The exclusive formation of (X) in formic acid might well be the result of acid-catalysed secondary rearrangements, and attempts were made to solvolyse (IV) in a variety of aprotic media. It did not react with dimethyl sulphoxide-lithium chloridecalcium carbonate,⁹ or with tetrahydrofuran-lithium perchlorate-calcium carbonate,10 but did react slowly

⁸ E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, 'Conformational Analysis,' Interscience, New York, 1966, p. 200.

<sup>200.
&</sup>lt;sup>9</sup> A. C. Cope, P. E. Burton, and M. L. Casper, *J. Amer. Chem. Soc.*, 1962, 84, 4861.
¹⁰ S. Winstein, S. Smith, and D. Darwish, *J. Amer. Chem. Soc.*,

¹⁰ S. Winstein, S. Smith, and D. Darwish, *J. Amer. Chem. Soc.*, 1959, **81**, 5511.

in boiling dimethylformamide–lithium bromide–calcium carbonate.¹¹ The resulting mixture of olefins could not be separated, and was oxidised with osmic acid to a mixture of 1,3-dibenzoylpropane and the diol (VII) (in the ratio of 8:1). The structure assigned to the diol is based on its further oxidation to 4-benzoyl-4-phenyl-butyric acid; a sample of this acid and its isomer, 2-phenyl-4-benzoylbutyric acid were synthesised for comparison, the latter by a novel procedure from benzyl cyanide and β -dimethylaminopropiophenone. The direct formation of diketone by osmic acid oxidation of (X) is atypical (1,2-diphenylcyclohexene is oxidised to diol¹²) and is ascribed to steric strains in the osmate ester from (X) due to eclipsing interactions.

The ion (VIII), postulated as an intermediate in the conversion of (II) into (IV), might have been expected to be formed also from the alcohol (XIII) in strong acid. The formation of (X) from (XIII) by the action of hydrogen bromide, rather than conversion into (IV), would be explicable if loss of water from the conjugate acid of (XIII) were to involve phenyl participation to give directly either the ion (IX) or a non-classical ion. The same would be true of the solvolysis of (IV) under non-equilibrating conditions, for the products isolated were both the result of phenyl migration. It has been suggested that phenyl participation is involved in the ionisation of the tosylate of (XIII).13 Since collapse of a diazonium ion into a carbonium ion is an energetically favourable process, the deamination of the amine (XV) was studied in the hope that it might provide a model for the behaviour of ion (VIII), other than when generated by rearrangement. Deamination of (XV) gave a single olefin as the principal product (64% yield), and very small amounts of unidentified alcohol and ester, as well as a little of a nitrogen-containing solid. The olefin was assigned structure (XVI) since it could be oxidised to the diol (VI). No dibenzoylpropane was obtained from this oxidation and so none of the olefin (X) had been formed in the deamination. While clearly no phenyl participation had occurred, the reaction could not have involved the ion (VIII): the complete absence of any rearrangement products (even those involving hydride shift) is more characteristic of an E2 rather than an ionic reaction.¹⁴ If the diazonium ion can readily populate a conformation similar to that proposed above for (IV), then the geometry of the system is certainly suited to concerted elimination; but even so, the almost complete absence of more than traces of alcohol and ester argues considerable difficulty in generating ion (VIII) under what might have seemed to be optimum conditions.

This lack of reactivity in 2,2-diphenylcyclopentyl compounds is in line with the very rapid attack of nucleophile on the ion (VIII) when this is generated by rearrangement. The concept of an extremely short life for ion (VIII), if taken to extremes, would be

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equivalent to saying that nucleophile attack on the diphenylcyclobutylmethyl ion is concerted with the rearrangement process, and it does not seem at present to be meaningful to argue about the distinction. It was not possible to examine the structure of the ion formed by protonation of (II) in sulphuric acid (by recording its ultraviolet spectrum) since sulphonation was rapid, but attempts were made to react the ion (XVIII), formed by protonation of the diamine (XVII), with nucleophile. The green colour of this ion left no doubt as to its structure but we were unsuccessful in finding conditions for reaction with an electron donor, other than proton abstraction.



The conversion of benzhydrylcyclobutanol (XII) into (IV) by hydrogen bromide in acetic acid, as described above, must be contrasted with its oxalic acid catalysed dehydration, which gives (X) as the sole product. Under similar conditions the isomeric alcohol (I) is dehydrated to (II), which is not isomerised to (X) by oxalic acid,² and the dehydration of (XII) must then be regarded as involving a phenyl shift followed by ring expansion as shown in the reaction scheme. Both hydrogen bromide and oxalic acid would be expected to produce the same benzhydrylcyclobutyl ion, and the ability of this ion to react in two ways, by phenyl shift leading ultimately to (X), or by hydride shift or proton loss leading ultimately to (IV), is worth noting.

EXPERIMENTAL

2,2-Disubstituted Cyclopentyl Halides.—These compounds were prepared by treating the appropriate alcohol or olefin with hydrogen bromide in acetic acid (approx. 20% w/v, 12 ml. per g.) or with hydrogen chloride in acetic acid (approx. 14% w/v, 15 ml. per g.). The reactions were exothermic and after keeping for a variable period at room temperature the resulting purple solution was poured into water, extracted with ether, and worked up in the usual way.

(i) 2,2,-Diphenylcyclopentyl bromide (IV). A petroleum solution of the crude bromide (1 g.), obtained from the alcohol (I) or the olefin (II) after 5 days, was chromatographed on alumina (30 g.) to give the bromide (IV),

¹³ R. A. Sneen, R. W. Jenkins, and F. L. Riddle, *J. Amer. Chem. Soc.*, 1962, **84**, 1598.

¹⁴ Cf. M. C. Whiting, Chem. in Britain, 1966, 2, 484.

¹¹ N. K. Kornblum and R. K. Blackwood, J. Amer. Chem. Soc., 1956, **78**, 4037.

¹² P. Tomboulian, J. Org. Chem., 1961, 26, 2652.

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recovery 90%, m.p. 94° (lit., 2,4 94-95°) after recrystallisation from methanol, ν_{max} 2981 and 2890 cm.⁻¹. The ¹H n.m.r spectrum showed absorptions at τ 2.84 (10H, m), 4.95 (1H, t, J 4 c./sec., 1-H), 7.2-7.4 (2H, m), and 7.6-7.82 (4H, m). On irradiation at τ 7.75 the triplet at 4.9 collapsed to a singlet.

The alcohol (XII) (1 g.) gave a product which was separated by chromatography on alumina in petroleum into a minor olefinic component (0.09 g.), which was not investigated, and the bromide (IV), m.p. and mixed m.p. 94°

(ii) 2,2-Diphenylcyclopentyl chloride (XI). The olefin (II) (1 g.) gave, after 36 hr., a brown crystalline solid (1.07 g.), ν_{max} (CCl₄) 1740w and 1240 cm.⁻¹. Chromatography of a petroleum solution on alumina (20 g.) gave 2,2-diphenylcyclopentyl chloride (XI) (0.93 g.), needles from ethanol, m.p. 105°, $\nu_{max.}$ 2976 and 2880 cm. $^{-1}.~$ The ¹H n.m.r. spectrum showed absorptions at $\tau 2.87$ (10H, m), 5.06 (1H, t, J 5 c./sec., 1-H), 7.2-7.6 (2H, m), and 7.7-8·2 (4H, m) (Found: C, 79·5; H, 6·6; Cl, 13·8. C17H17Cl requires C, 79.5; H, 6.7; Cl, 13.8%). Continued elution of the alumina with benzene yielded no product and elution with ether yielded only tar.

(iii) 2,2-Dimethylcyclopentyl bromide (III). (a) With aqueous hydrobromic acid. The reaction between cyclobutyldimethylmethanol¹⁵ (4 g.) and 48% hydrobromic acid (20 ml.) was incomplete after stirring at room temperature for 12 hr. (cf. Ford and Kwart $^{16}),\,\nu_{\rm max}$ (CCl₄) 3600— 3300 cm.⁻¹. This product contained two minor impurities (ca. 5%) (g.l.c. on butanediol succinate at 87°), one of which was removed by chromatography in petroleum (b.p. $30-50^{\circ}$) on alumina (40 g.), since the infrared absorption at 3600 cm.⁻¹ disappeared, giving the bromide (III), b.p. 74-76°/40 mm., n²⁰ 1.4792 (lit., ¹⁶ 157-164°/ 760 mm., $n_{\rm p}^{20}$ 1.4792).

(b) With hydrogen bromide in acetic acid. After reacting for 36 hr., cyclobutyldimethylmethanol (5 g.) gave a liquid (6.8 g.), which on fractional distillation gave impure bromide (3.6 g.), b.p. 76—78°/40 mm., n^{20} 1.4712, $v_{\text{max.}}$ (CCl₄) 1740 cm.⁻¹, but no absorption at 3600 cm.⁻¹ (g.l.c. on butanediol succinate showed two impurities, ca. 5%). The bromide (1.7 g.) in ether (20 ml.) was stirred with lithium aluminium hydride (0.2 g.) at room temperature for 0.5 hr. Chromatography on alumina in petroleum (b.p. 30-50°) gave the bromide (III), $n^{15\cdot 5}$ 1.4818, having one minor impurity (g.l.c.), The infrared spectrum and the gas-liquid chromatogram were identical with those of the bromide prepared in (a) above: the gas-liquid chromatogram of a mixture of the two preparations was also identical (Found: C, 47.7; H, 7.35; Br, 44.9. Calc. for C₇H₁₃Br: C, 47.4; H, 7.4; Br, 45.1%). The ¹H n.m.r. spectrum included absorptions at τ 8.96 (6H, s) and at 6.08 (1H, t, J 8 c./sec., 1-H)

(iv) 2-Methyl-2-phenylcyclopentyl bromide (V). After reacting for 40 hr., methylphenylcyclobutylmethanol¹⁷ (prepared by the action of methylmagnesium bromide on benzoylcyclobutane 18) (4.5 g.) gave a neutral fraction (5.7 g.), b.p. 70-74°/0.05 mm., n¹⁴ 1.5658. The infrared spectrum of this distillate (4.55 g.) showed a weak absorption at 1740 cm.⁻¹ and the absence of alcohol, whilst gasliquid chromatography on butanediol succinate at 198°

¹⁵ N. Kizhner, J. Russ. Chem. Soc., 1905, 37, 511.

¹⁶ J. A. Ford and H. Kwart, J. Org. Chem., 1959, 24, 2060.
 ¹⁷ T. A. Favorskaya and I. P. Yakovlev, J. Gen. Chem. (U.S.S.R.), 1952, 22, 122.

¹⁸ W. H. Perkin and W. Sinclair, J. Chem. Soc., 1892, 61, 36.

showed two impurities (ca. 5%) to be present. This distillate (4.5 g.) in ether (50 ml.) was stirred with lithium aluminium hydride (0.1 g.) at room temp. for 0.5 hr. Chromatography of a solution of this product (4.25 g.) in petroleum (b.p. 30-50°) gave 2-methyl-2-phenylcyclopentyl bromide (V) (4.18 g.), b.p. $72^{\circ}/0.05$ mm., n^{20} 1.5649, which still contained two impurities (ca. 5%) (g.l.c.): infrared spectrum showed no absorptions due to OH and acetate (Found: C, 61.9; H, 6.4; Br, 31.8. $C_{12}H_{15}Br$ requires C, 60.2; H, 6.3; Br, 33.4%). The ¹H n.m.r. spectrum included absorptions at τ 8.54 (3H, s), 5.5 (1H, t, J 8 c./sec., 1H), and 2.56-2.72 (5H, m).

1-Benzhydrylcyclobutanol (XII).- Benzhydryl-lithium was prepared from freshly distilled benzhydryl chloride 19 (22 g.; m.p. 20°²⁰) in tetrahydrofuran (50 ml.) and finely cut lithium (2.2 g.) suspended in tetrahydrofuran²¹ (25 ml.). Ethylene dibromide (1 ml.) was added and the mixture then stirred at room temperature in an atmosphere of nitrogen for 48 hr. Cyclobutanone 22 (5 g.) in tetrahydrofuran (15 ml.) was added dropwise and the mixture then warmed at 40° for 0.5 hr. The solution was decanted from lithium and evaporated in vacuo. Addition of water, extraction with ether, and drying (Na2SO4) gave a solid (22 g.) which was separated by chromatography on alumina (50 g. per g.) into diphenylmethane (4 g.), by elution with petroleum, and, by elution with ether, 1-benzhydrylcyclobutanol (XII) (9.1 g., 54%), m.p. 100-101°, after recrystallisation from petroleum (Found: C, 85.9; H, 7.6. C17H18O requires C, 85.7; H, 7.6%).

Dehydration of 1-Benzhydrylcyclobutanol (XII).-The alcohol (XII) (1.6 g.) was dehydrated with oxalic acid as previously described ² for the alcohol (I). A solution of the product in petroleum was chromatographed on alumina (40 g.) to give 1,2-diphenylcyclopentene (X) (1.3 g., 88%), m.p. and mixed m.p. 58-59° (lit., 262.5-63°).

Dehydrobromination of the Bromide (IV).-The bromide (2 g.), absolute ethanol (12 ml.), and potassium hydroxide (1.8 g.) were refluxed for 26 hr. Extraction with ether, washing with water, and drying (MgSO₄) gave a mixture of olefins (1.46 g.; theor. yield of $C_{17}H_{16}$, 1.46 g.), free of bromide (t.l.c.) and of alcohol (infrared spectrum). Tar was removed by chromatography on alumina (40 g.) and elution with petroleum (b.p. 60-80°) gave an oil (A) (1.24 g.), b.p. 140° (bath)/1 mm. (Found: C, 92.6; H, 7.4. Calc. for C₁₇H₁₆: C, 92.7; H, 7.3%).

The oil A (0.44 g.) in benzene (6 ml.) was oxidised with osmium tetroxide (0.5 g) and pyridine (0.42 g) in benzene (5 ml.) for 48 hr. Methylene chloride (25 ml.), mannitol (5 g.), potassium hydroxide (0.5 g.), and water (50 ml.) were then added and the mixture stirred for 3 hr. The organic layer was washed successively with dilute acetic acid, dilute sodium hydroxide, and water, and dried (MgSO₄). The resulting dark brown, viscous oil $[v_{max}]$ (CCl₄) 3600 and 1690 cm.⁻¹] was chromatographed on alumina (25 g.). The petroleum eluate (0.015 g.) was rejected. Benzene eluted 1,3-dibenzoylpropane (0.06 g.), m.p. and mixed m.p. 66° (plates, from petroleum), ether the diol (VII) (0.02 g.), m.p. and mixed m.p. 102°, after removal of tar by recrystallisation from petroleum, and finally chloroform-acetone (7:3) eluted a very tarry solid

¹⁹ M. J. Boeseken, Rec. Trav. chim., 1903, 22, 313.

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 A. M. Ward, J. Chem. Soc., 1927, 2288.
 C. Tamborski, G. J. Moore, and E. Soloski, Chem. and Ind., 1962, 696.

²² Sj. Kaarsemaker and J. Coops, Rec. Trav. chim., 1951, 70, 1037.

(0.23 g.), which was recrystallised from benzene-petroleum with difficulty (charcoal had little effect) to give 3,3-diphenylcyclopentane-cis-1,2-diol (VI) (0.22 g.), m.p. 101- 101.5° , which depressed the melting point of the diol (VII) (Found: C, 79.8; H, 7.3. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%).

Oxidation of the Diol (VI).—A mixture of the diol (0.21 g.) and sodium metaperiodate 23 (0.2 g.) in ethanol (10 ml.) and n-sulphuric acid (10 ml.) was warmed to 40°. After 5 min., sodium metaperiodate (0.2 g.) was added, the mixture was kept at room temperature for 1 hr., then poured into water and extracted with ether $(2 \times 50 \text{ ml.})$. The ethereal extract was washed with 2N-sodium carbonate and water, and dried (Na₂SO₄). Evaporation of ether gave an oil (0.2 g.) to which was added acetic acid (distilled from chromium trioxide, 4 ml.) and 1 ml. of a solution of sodium dichromate dihydrate (5 g.) and conc. sulphuric acid (3.75 g.) diluted to 25 ml. After heating at 100° for 1 hr., the solvent was evaporated in vacuo, and the residue partitioned between ether (25 ml.) and 2Nsodium hydroxide $(2 \times 5 \text{ ml.})$; only traces (0.04 g.) passed into the ether. The acidic fraction (0.13 g.), recrystallised from benzene-petroleum, then chloroform-petroleum, gave 2,2-diphenylglutaric acid, m.p. 194-195° (lit., 195-197°,24 193-194°, 25 193-195°, 26 183° 27), which on heating at 100° for 0.5 hr. with acetic anhydride (1 ml.), evaporation of solvent in vacuo, followed by sublimation $(160^{\circ}/0.05)$ mm.) was converted into the anhydride, m.p. 142-143° (lit., 142-143°,24 138-139° 26)

The mixture of olefins (A) (0.27 g.) also gave 2,2-diphenylglutaric acid (0.14 g.) on oxidation with osmium tetroxide (0.01 g.) and sodium metaperiodate (0.6 g.) in dioxan (6 ml.) and water (2 ml.), followed by heating in acetic acid (6 ml.) at 50° for 3.5 hr. with the sodium dichromatesulphuric acid reagent (2.4 ml.); the neutral fraction (0.1 g.)showed carbonyl stretching frequencies at 1750 and 1690 with a shoulder at 1710 cm.⁻¹.

Solvolytic Reactions of the Bromide (IV).-(i) With formic acid. The bromide (0.4 g.), 98% formic acid (25 ml.), and sodium acetate (0.15 g) were heated to reflux for 50 min.; on more prolonged heating the mixture darkened. After evaporation of solvent in vacuo the residue was dissolved in ether, which was then washed with 2N-sodium hydroxide and water, and dried (Na₂SO₄). Evaporation of ether gave an oil (0.24 g) which was refluxed in ether with lithium aluminium hydride (0.4 g.) for 2 hr. After the usual working-up, the product (0.22 g.) contained no bromide (t.l.c.) and was chromatographed in petroleum on alumina (25 g.) to give 1,2-diphenylcyclopentene (X) (0.15 g.), m.p. and mixed m.p. 59-60°.

(ii) With acetic acid. The bromide (0.4 g.) was refluxed for 2 hr. in acetic acid (5 ml.), then worked up in the usual way to give, after chromatography on alumina in petroleum, impure 1,2-diphenylcyclopentene (0.05 g.), m.p. and mixed m.p. $45-55^{\circ}$ and the bromide (IV) (0.17 g.).

(iii) With dimethyl sulphoxide.9 Lithium chloride (1 g.) was dissolved in dimethyl sulphoxide (20 ml.) by heating to 40° . Calcium carbonate (0.1 g.) and the bromide (0.4 g.) were added; after the mixture had been kept at room temperature for 2 days the bromide (0.37 g.) was recovered.

(iv) With lithium perchlorate in tetrahydrofuran.¹⁰ Lithium perchlorate (2 g.) was dissolved in cold tetrahydro-

²⁴ D. H. Hey and B. H. Chase, J. Chem. Soc., 1952, 553.

furan (purified by distillation from sodium) (25 ml.). Calcium carbonate (0.3 g.) and the bromide (0.4 g.) in tetrahydrofuran (2 ml.) were added and the mixture was kept at room temperature for 36 hr. Removal of solvent *in vacuo* and the usual working-up gave the bromide (0.4 g.), m.p. and mixed m.p. 93° .

Quantitative recovery of the bromide was also obtained after the reaction had been carried out at reflux temperature for 4 hr. When the reaction was continued at reflux for 5 days the recovery of bromide was almost quantitative, although thin-layer chromatography indicated the presence of a trace of olefin.

(v) With lithium bromide in dimethylformamide.¹¹ The bromide (5.05 g.) was refluxed in dimethylformamide (130 ml.) containing calcium carbonate (3.3 g.) and lithium bromide (22.6 g.) for 6 hr. Most of the solvent was removed in vacuo, the residue treated with water (250 ml.) and extracted with ether (2 \times 125 ml.). The ethereal extract was washed twice with water and dried (MgSO₄). Removal of ether gave a solid B (3.64 g.; theor. yield of $C_{17}H_{16}$, 3.7 g.) which contained none of the bromide (t.l.c.). The use of lithium chloride and dimethylformamide at 100° gave less complete reaction.

This solid was separated from tar by chromatography on alumina (20 g.) and elution with petroleum (b.p. 60- 80°); recovery 91%. To this eluate (0.88 g.) in benzene (9 ml.), at 0°, was added osmium tetroxide (1 g.) in benzene (7 ml.), and then pyridine (0.64 ml.) in benzene (2 ml.). Oxidation was complete (t.l.c.) after keeping at room temperature for 40 hr. The mixture was then stirred with methylene chloride (25 ml.), water (100 ml.), potassium hydroxide (1 g.), and mannitol (10 g.) for 3 hr. The organic layer was washed successively with 2n-acetic acid, 2nsodium hydroxide, and water, and dried (Na₂SO₄). Evaporation of solvent gave a black solid which was chromatographed on alumina (50 g.); the petroleum eluate (0.04 g.)was rejected. Benzene, followed by ether, eluted 1,3-dibenzoylpropane (0.45 g.), m.p. and mixed m.p. 66°, and then methanol eluted a black solid (0.58 g.), purified with difficulty by recrystallisation from benzene-petroleum (charcoal), to give 2,3-diphenylcyclopentane-cis-1,2-diol (VII) (0.06 g.), m.p. 102° (Found: C, 80.3; H, 7.1. C₁₇H₁₈O₂ requires C, 80.3; H, 7.1%).

An attempt was made to separate the mixture of olefins comprising the solid B (3.64 g.) by chromatography on alumina (65 g.). Elution with petroleum $(3 \times 30 \text{ ml.})$ gave fraction C (2.06 g.), m.p. 40-62°, fraction D (1.24 g.), m.p. 50-62°, raised to 65-68° on recrystallisation from methanol, λ_{max} (hexane) 255 m μ (ϵ 9640), λ_{min} 230 m μ (ϵ 4540) [for 1,2-diphenylcyclopentene [λ_{max} 270 m μ (ϵ 10,220), λ_{min} 247 m μ (ϵ 6030)], and fraction E (0.14 g.), m.p. 56—68°, each fraction being recrystallised from methanol with poor recovery.

Fraction D (0.43 g.), m.p. 65-68°, in benzene (4 ml.) reacted exothermically with osmium tetroxide (0.5 g.)and pyridine (0.16 ml.) in benzene (6 ml.). After 5 days little complex had separated and the mixture was therefore stirred with methylene chloride (25 ml.), potassium hydroxide (0.5 g.), mannitol (5 g.), and water (50 ml.) for 3 hr. The usual working-up and chromatography on alumina (25 g.) gave, by elution with ether, 1,3-dibenzoylpropane

²³ E. L. Jackson, Org. Reactions, 1944, 2, 363.

²⁵ J. J. Trevedi, N. L. Phalnikar, and K. S. Nargund, J. Univ. Bombay, 1942, 10, Pt. 5, 135. ²⁶ F. Salmon-Legagneur, Bull. Soc. chim. France, 1952, 994.

²⁷ F. Salmon-Legagneur, Compt. rend., 1941, 213, 152.

(0.1 g.), m.p. and mixed m.p. 66°, after recrystallisation from petroleum, and then, by elution with methanol, the diol (VII) (0.06 g.), m.p. and mixed m.p. 102°, after recrystallisation from benzene-petrol (charcoal).

Chromatography of a petroleum solution of the residues from the recrystallisation of fraction D on alumina-silver nitrate (9:1; 25 g.) gave, by elution with petroleum $(16 \times 5 \text{ ml.})$, in eluates 2—7, solid (0.2 g.), m.p. 45—58°, and, in eluates 9-16, solid (0.25 g.), m.p. 65-68°. The latter was oxidised with osmium tetroxide and pyridine in benzene as described in the preceding paragraph. The product was separated by chromatography on alumina into 1,3-dibenzoylpropane (0.02 g.) and the diol (VII) (0.2 g).

Oxidation of the Diol (VII).-This diol (0.1 g.) was oxidised with periodic acid, using equivalent quantities of reagents, as described for the diol (VI). The resulting oil was heated at 50° for 1.5 hr. in acetic acid (2 ml.), with the sodium dichromate-sulphuric acid mixture (0.4 ml.), then worked up as above to give a neutral fraction (0.02 g.) which was rejected, and 4-benzoyl-4-phenylbutyric acid (0.08 g.), m.p. and mixed ²⁸ m.p. 130-132°, after recrystallisation from benzene-petroleum. This acid depresses the m.p. of 4-benzoyl-2-phenylbutyric acid.

The procedure of Brown and Garg²⁹ failed to oxidise the keto-aidehyde.

4-Benzoyl-2-phenylbutyric Acid.— β-Dimethylaminopropiophenone hydrochloride 30 (20.1 g.) was added to potassium hydroxide (6.1 g.) in water (20 ml.) followed by benzyl cyanide (11.7 g.) in ethanol (50 ml.). The mixture was heated at 100° for 2 hr., then poured into water and extracted with ether. The ethereal extract was washed successively with 2N-hydrochloric acid, 2N-sodium hydroxide, and water, and dried $(MgSO_4)$. Distillation gave fractions, b.p. 110-120°/17 mm. (5·2 g.) and b.p. 120-200°/0·05 mm. (3 g.); the latter, after chromatography on alumina (70 g.), elution with benzene-petroleum (1:1) followed by recrystallisation from aqueous methanol, or from etherpetroleum (b.p. 30-50°), gave lustrous plates of 4-benzoyl-2-phenylbutyronitrile (2.8 g.), m.p. 44–45°, ν_{max} 2245 and 1680 cm.⁻¹ (Found: C, 81.6; H, 6.0; N, 5.7. C₁₇H₁₅NO requires C, 81.9; H, 6.1; N, 5.6%).

This nitrile (1 g.) was refluxed for 10 hr. with potassium hydroxide (2 g.) in ethanol (30 ml.) and water (5 ml.). After distillation of ethanol, the residue was treated eith water and ether. Acidification of the aqueous layer gave 4-benzoyl-2-phenylbutyric acid (0.85 g.), m.p. 136° (lit.,³¹ 130-131°) (needles, from benzene-petroleum) (Found: C, 76.0; H, 5.9. Calc. for $C_{17}H_{16}O_3$: C, 76.1; H, 6.0%).

Reaction between 1,2-Diphenylcyclopentene (X) and Osmium Tetroxide.—Recrystallised olefin (X) (0.21 g.), m.p. 62°, in benzene (2 ml.) was treated with osmium tetroxide (0.25 g.) and pyridine (0.08 ml.) in benzene (4 ml.) for 5 days. The product was filtered and the residue (0.01 g.) was rejected. The filtrate, after stirring with methylene chloride (25 ml.), potassium hydroxide (0.5 g.), mannitol (5 g.), and water (50 ml.) for 3 hr., then working up in the usual way, gave only 1,3-dibenzoylpropane (0.2 g.), m.p. and mixed m.p. 66°, after recrystallisation from petroleum (charcoal).

2,2-Diphenylcyclopentylamine (XV).-2,2-Diphenylcyclopentanone oxime² (7 g.) in tetrahydrofuran (100 ml.) was added to lithium aluminium hydride (7 g.) in tetrahydro-

28 A. D. Campbell and I. D. R. Stevens, J. Chem. Soc., 1956, 959.

furan (200 ml.) and the mixture was then stirred and refluxed for 8 hr. Most of the solvent was evaporated in vacuo and replaced by ether (200 ml.). 10n-Sodium hydroxide (25 ml.) was added dropwise, the ether was decanted, and the residue extracted thoroughly with ether. The combined ether extracts were extracted with 2N-hydrochloric acid $(2 \times 50 \text{ ml.})$; the ether layer was rejected. The hydrochloric acid extract was heated at 100° for 1.5 hr.,

and a turbidity which appeared was removed by ether extraction. Basification of the hydrochloric acid solution gave 2,2-diphenylcyclopentylamine (XV) (6 g.) as a viscous oil, b.p. 140–148°/0.05 mm., ν_{max} (CCl₄) 3380 and 3310 cm.⁻¹. Some decomposition occurred on distillation, even when the process was carried out rapidly, and hence reliable analytical figures could not be obtained for this compound; N-toluene-p-sulphonyl-2,2-diphenylcyclopentylamine (by reaction with toluene-p-sulphonyl chloride in pyridine at room temp.), m.p. 141-142°, after recrystallisation from benzene-petroleum (Found: C, 73.7; H, 6.0; N, 3.6; S, 8·4. C₂₄H₂₅NO₂S requires C, 73·6; H, 6·4; N, 3·6; S, 8·2%).

Deamination of 2,2-Diphenylcyclopentylamine (XV).--A solution of this amine (2.33 g.) (not distilled) in 2N-hydrochloric acid (5 ml.) was buffered to pH 4 by the dropwise addition of aqueous sodium acetate and cooled to 0° ; an ice-cold solution of sodium nitrite (0.7 g.) in water (2 ml.) was added dropwise. A turbidity rapidly formed and 10% acetic acid was added to restore the pH. The mixture was kept at room temperature overnight, then ether (25 ml.) and conc. hydrochloric acid (5 ml.) were added. Basification of the hydrochloric acid extract gave no turbidity. The ethereal layer, after washing successively with 2N-sodium hydroxide and water, then drying (Na_2SO_4), gave an oil (1.9 g.) theor. yield of olefin, C₁₇H₁₆, 2.16 g.), v_{max} (CCl₄) 3600 and 1745 cm.⁻¹, both weak absorptions. The oil was extracted with hot petroleum (b.p. 60--80°) to remove tar and the petroleum extract was then chromatographed on alumina (40 g.). Elution with petroleum gave 3,3-diphenylcyclopentene (XVI) (1.38 g.), b.p. 135° (bath)/ 0.05 mm. (Found: C, 92.9; H, 6.9. C₁₇H₁₆ requires C, 92.7; H, 7.3%). Elution with benzene $(7 \times 10 \text{ ml.})$ gave, in eluates 1 and 2, an oil (0.09 g.) having no carbonyl absorption in the infrared, in eluate 3 an oil (0.02 g.), $\nu_{max.}$ (CCl_4) 1720 and 1745 cm.⁻¹, in eluate 4 an oil (0.05 g.), $v_{\text{max.}}$ (CCl₄) 1750 cm.⁻¹, and in eluates 5 and 6 a solid (0.07 g.) which after several recrystallisations from petroleum gave pale yellow crystals, m.p. 129°, showing a broad absorption at 3600-3200 cm.⁻¹ but no carbonyl absorption. This material was presumably 2,2-diphenylcyclopentyl diazohydroxide (Found: C, 76.4; H, 6.9; N, 10.4. $C_{17}H_{18}N_2O$ requires C, 76.7; H, 6.8; N, 10.5%). Elution with ether (30 ml.) gave an oil (0.08 g.), $\nu_{max.}$ (CCl₄) 3600 and 1720 cm.⁻¹, which was reduced with lithium aluminium hydride. Further elution with ether gave an oil (0.02 g.) showing hydroxylic but no carbonyl absorptions. Esterification of each fraction with 3,5-dinitrobenzoyl chloride was unsuccessful.

Oxidation of 3,3-Diphenylcyclopentene (XVI).-The olefin (XVI) (0.44 g.) was oxidised with osmium tetroxide (0.5 g.)and pyridine (0.4 g.) in benzene (9 ml.) and worked up as

29 H. C. Brown and C. P. Garg, J. Amer. Chem. Soc., 1961, 83,

2951.
³⁰ C. E. Maxwell, Org. Synth., Coll. Vol. III, 1955, 305.
³¹ E. C. Horning and A. F. Finelli, J. Amer. Chem. Soc., 1949,

described for fraction D above to give a partly crystalline product (0.5 g.), $\nu_{max.}$ (CCl₄) 3600 cm.⁻¹ but no carbonyl absorption, which was chromatographed on alumina (10 g.). Benzene eluted a brown gum (0.09 g.), ether a gummy white solid (0.25 g.), m.p. 45-55°, and chloroform-acetone (7:3) the diol (VI) (0.04 g.), m.p. and mixed m.p. 100-101°.

The ether eluate was re-chromatographed on alumina (25 g.), and eluted successively with petroleum, benzene, and benzene-ether (1:1); the material (0.07 g.) recovered in this way was rejected. Elution with ether $(20 \times 20 \text{ ml.})$ gave the diol (VI), m.p. and mixed m.p. 100-101° after recrystallisation from petroleum, and also a polymorphic form of this diol, m.p. 110-111°, changing to m.p. 100° on seeding a solution in petroleum with the diol, m.p. 100° (Found: C, 80.3; H, 7.1. Calc. for C₁₇H₁₈O₂: C, 80.3; H, 7.1%). Recrystallisation of the residues from mother-liquors gave needles, m.p. 115°, which gave diol, m.p. 100°, on further recrystallisation.

2,2-Diphenylcyclopentyl Acetate.—The alcohol² (XIII) (1.2 g.) in ether (10 ml.) was added to sodium hydride ³² (0.75 g.) in ether (50 ml.) and the mixture was refluxed for 6 hr. in an atmosphere of nitrogen. Acetyl chloride (1.6 g)was then added and refluxing continued for 3 hr. The usual work-up gave the ester free from alcohol; shorter reaction times or the use of an increased proportion of alcohol led to substantial contamination with starting material at this point. A benzene solution of the product was chromatographed on alumina (40 g.) to give 2,2-diphenylcyclopentyl acetate (0.8 g.), m.p. 75-75.5°, after recrystallisation from petroleum (Found: C, 81.1; H, 7.3. C₁₉H₂₀O₂ requires C, 81.4; H, 7.2%).

A solution of this ester (0.25 g.) in 20% w/v hydrogen bromide in acetic acid (5 ml.) was kept for 10 days at room temperature during which time the colour gradually darkened to deep purple. The usual working-up gave a tarry product (0.22 g.) which was chromatographed on alumina (10 g.). Petroleum (3×5 ml.) eluted an olefin fraction (0.1 g.), m.p. 50-58°, containing none of the bromide (IV) (t.l.c. on alumina), which was ozonised as previously described ² to give 1,3-dibenzoylpropane, m.p. and mixed m.p. 66°.

Elution with benzene $(6 \times 5 \text{ ml.})$ gave, in the second eluate only, tar (0.06 g.), $\nu_{max.}$ (CCl₄) 1740 and 1240 cm.⁻¹ $(R_{\rm F} 0.55, {\rm t.l.c.} \text{ on alumina in benzene}).$

Reaction of 2,2-Diphenylcyclopentanol (XIII) with Hydrogen Bromide in Acetic Acid.²—The alcohol (0.2 g.) was allowed to react with the hydrogen bromide reagent (2.9)ml.; 22% w/v) for 26 days at room temperature, the colour of the mixture changing to deep purple with the separation of an oil. Extraction into ether and the usual working up gave a tarry product containing none of the bromide (IV) (t.l.c. on alumina in petroleum). Chromatography of a solution in petroleum on alumina (12 g.) gave 1,2-diphenylcyclopentene (X), m.p. and mixed m.p. 59-61° (softening at 57°), after recrystallisation from methanol.

Bis-(p-dimethylaminophenyl)methylenecyclobutane (XVII). -p-Dimethylaminophenylmagnesium bromide 33 was prepared by refluxing and stirring for 1 hr., in an atmosphere of nitrogen, p-bromodimethylaniline (4 g.), magnesium (0.5 g.), a crystal of iodine, and tetrahydrofuran (20 ml.).

³² J. D. Roberts and V. C. Chambers, J. Amer. Chem. Soc., 1951, 73, 5037.

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The mixture was stirred at room temperature with methoxycarbonylcyclobutane ^{34,35} (1.2 g.) in tetrahydrofuran (5 ml.) for 1 hr., then treated at 0° with saturated ammonium chloride (5 ml.) and filtered. Evaporation of the filtrate in vacuo gave a solid, sparingly soluble in ether but soluble in chloroform. After the usual working-up this product (1.55 g.) showed no absorption at 3600 cm.⁻¹; recrystallised from ethanol, it melted at 137° , recovery 84%. This unsaturated amine (1 g.) was chromatographed on alumina (40 g.) to give, by elution with benzene-petroleum (10:1), a compound (0.01 g.) [t.l.c. on alumina in benzene-petroleum (10:1), R_F 0.45], m.p. 209°, which was rejected, and bis-(p-dimethylaminophenyl)methylenecyclobutane (XVII) (0.98 g.), $R_{\rm F}$ 0.6, m.p. 138° (needles, from ethyl acetateethanol) (lit., 36 136-137°) (Found: C, 82.2; H, 8.6; N, 9.1. Calc. for $C_{21}H_{26}N_2$: C, 82.3; H, 8.6; N, 9.1%).

Cyclobutylmagnesium bromide 37, 38 failed to react with Michler's ketone in ethereal solution (cf. Gilman³⁹).

Hydrogenation of the amine (XVII) (0.552 g.) in ethyl acetate (50 ml.) over 5% Pd-C (0.1 g.) gave (after the uptake of 46.0 ml., theor. 44.7 ml./19.5°/754 mm.) cyclobutylbis-(p-dimethylaminophenyl)methane, m.p. 78-79°, needles, from methanol (Found: C, 81.8; H, 9.2; N, 9.1. $C_{21}H_{28}N_2$ requires C, 81.8; H, 9.2; N, 9.1%). The ¹H n.m.r. spectrum included absorptions at $\tau 2.94 - 3.52$ (8H, two doublets, Ar), 6.35 (1H, d, Ar₂CHCH<), and 7.18(12H, s, NMe₂).

Reactions of the Cyclobutylbis-(p-dimethylaminophenyl)methyl Cation (XVIII).-(i) After dissolving the olefin (XVII) in an excess of 0.1N-hydrochloric acid the pH was adjusted to approx. 7. The solution was kept at room temperature overnight. Basification gave the original olefin, m.p. and mixed m.p. 138°.

(ii) The olefin (0.25 g.) was treated with hydrogen bromide in acetic acid (20% w/v; 5 ml.). The resulting pale yellow solution suffered no visible change on keeping at room temperature overnight. Dilution and basification gave a very tarry product (0.22 g.). Chromatography on alumina (10 g.) and elution with methylene chloride failed to remove tar. Re-chromatography on alumina (10 g.) and elution with benzene-petroleum (10:1) gave the olefin (XVII) (0.03 g.) and a tarry solid (0.13 g.), m.p. 165-170°, which could not be purified by recrystallisation.

(iii) The olefin (0.25 g.) was recovered unchanged after treatment with triethylamine hydrobromide (0.25 g.) in water (0.3 ml.) and dimethylformamide (5 ml.).

(iv) In dimethyl sulphoxide (5 ml.), the olefin (0.2 g.)and NN-dimethylaniline hydrobromide (1.8 g.) gave a green solution, which was kept at room temperature for 3 weeks. The product was a dark brown oil which contained substantially the olefin (XVII) and two minor products [t.l.c. on alumina, benzene-petroleum (9:1)].

(v) The olefin (0.2 g.) in dimethylformamide (5 ml.)behaved similarly when treated with NN-dimethylaniline hydrobromide (1.8 g) and lithium bromide (1 g).

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