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# **383.** *Studies in Molecular Rearrangement. Part VI.* Syntheses and Oxotropic Rearrangements in the* cyclo*Pentenyl Series.*

By E. A. Braude and W. F. Forbes.

1-Chloro*cyclo*pentene has been converted into *cyclo*pent-1-enyl-lithium. The latter reacts with carbon dioxide to give *cyclo*pent-1-enecarboxylic acid and di*cyclo*pent-1-enyl ketone, and with benzaldehyde, acraldehyde, and crotonaldehyde to give the expected *cyclo*pent-1-enylcarbinols (I, V, and VII). In the presence of acids, *cyclo*pentenylphenylcarbinol undergoes the usual oxotropic rearrangement to 2-benzylidene*cyclo*pentanol (II) which is dehydrated to 2-benzylidene*cyclo*pentene (III) and oxidised to 2-benzylidene*cyclo*pentanone (IV). *cyclo*Pentenylvinylcarbinol similarly rearranges to 2-allylidene*cyclo*pentanol (VI), whereas *cyclo*pentenylpropenylcarbinol rearranges to 4-*cyclo*pent-1′-enylbut-3-en-2-ol (VIII) which is converted by oxidation with manganese dioxide into 4-*cyclo*pent-1′-enylbut-3-en-2-one (IX).

The opposite directions of migration of the hydroxyl group in the vinyl- and propenyl-carbinols correspond with the observations previously made (Part V, *J.*, 1950, 2014) in the case of the *cyclo*hexenyl analogues. The results are discussed in relation to earlier work by Kon, Linstead, and their collaborators on similar prototropic systems.

In a previous paper (Part V, *loc. cit.*; cf. Braude, Coles, and Timmons, *Nature*, 1950, **166**, 58) the synthesis and oxotropic rearrangements of some *cyclo*hex-1-enylcarbinols were described. This work is being extended to substituted *cyclo*hexenyl as well as to lower- and higher-membered *cyclo*alkenyl homologues and the present communication deals with the *cyclo*pentenyl derivatives.

The synthetic method employed depends on the formation of *cyclo*pent-1-enyl-lithium from 1-chloro*cyclo*pentene. The latter was first obtained by Favorskii and Shostakovsky (*J. Gen. Chem. U.S.S.R.*, 1936, **6**, 720), but our experience concerning its preparation and properties is not entirely in accord with their results. Whereas the conversion of *cyclo*hexanone (Part V, *loc. cit.*) and of *cyclo*heptanone (Braude and Forbes, unpublished) into the 1-chloro*cyclo*olefin by means of phosphorus pentachloride proceeds smoothly, the corresponding reaction of *cyclo*pentanone is attended by considerable polymerisation and yields a mixture of 1 : 1-dichloro*cyclo*pentane, the desired 1-chloro*cyclo*pentene, and its 3-chloro-isomer. The behaviour of *cyclo*pentanone thus resembles that of alicyclic ketones, which also generally give mixtures

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* Part V, *J.*, 1950, 2014.

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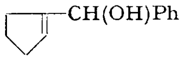
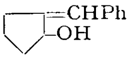
(Favorskii, *J. pr. Chem.*, 1913, **88**, 641). The reaction of ketones with phosphorus pentachloride in all probability involves an addition to the carbonyl group to form an intermediate of the type $R_2CCl{\cdot}O{\cdot}PCl_4$ (Favorskii, *loc. cit.*; cf. Atherton, Clark, and Todd, *Rec. Trav. chim.*, 1950, **69**, 295), followed by elimination either of $POCl_3$ to give the 1 : 1-dichloro-derivative or of $HO{\cdot}PCl_4$ to give the chloro-olefin, and the course of the elimination may well be conditioned by the steric strain in the chloro*cyclo*olefin. 1-Chloro*cyclo*pentene, which is the most highly strained member of the series, is also the least readily formed and even when pure is much less stable than 1-chloro*cyclo*hexene; it is decomposed by water at room temperature and regenerates *cyclo*pentanone when warmed with aqueous alcoholic silver nitrate, a reaction which also proves its structure. The ready hydrolysis of 1-chloro*cyclo*pentene contrasts with that of acyclic and higher-membered cyclic 1-chloro-olefins which requires considerably more drastic conditions (cf. Finch and Marple, U.S.P. 2,354,512; *Chem. Abs.*, **1944**, **38**, 6302; Wichterle, Procházka, and Hofman, *Coll. Czech. Chem. Comm.*, 1948, **13**, 300; Cope and Schmitz, *J. Amer. Chem. Soc.*, 1950, **72**, 3056).

The conversion of 1-chloro*cyclo*pentene into *cyclo*pentenyl-lithium by reaction with lithium in ether takes place rather less readily than the formation of *cyclo*hexenyl-lithium (Part V, *loc. cit.*) (see Experimental). The lower reactivity of 1-chloro*cyclo*pentene towards lithium may be genuine, or it may be only apparent and arise from the greater difficulty of purification. Treatment of the solution of *cyclo*pentenyl-lithium with solid carbon dioxide afforded a mixture of *cyclo*pent-1-enecarboxylic acid and di*cyclo*pent-1-enyl ketone. The ketone was characterised by a 2 : 4-dinitrophenylhydrazone and exhibits the expected ultra-violet light absorption (see Table); its structure was confirmed by catalytic hydrogenation to di*cyclo*pentyl ketone. The formation of ketone as well as of carboxylic acid in the reaction with solid carbon dioxide has also been observed with *cyclo*hexenyl- (Part V, *loc. cit.*), propenyl- (Braude and Coles, *J.*, 1951, in the press), and *iso*butenyl-lithium (Part III, Braude and Timmons, *J.*, 1950, 2000); the proportion of acid to ketone is greater the larger the excess of carbon dioxide employed, but the combined yields of acid and ketone are only *ca.* 20%—considerably lower than the yields of condensation products with other carbonyl compounds (cf. below).

*cyclo*Pentenyl-lithium and benzaldehyde afforded, in 30% yield, *cyclo*pentenylphenylcarbinol (I), the structure of which was confirmed by catalytic hydrogenation to *cyclo*pentylphenylcarbinol and oxidation of the latter to *cyclo*pentyl phenyl ketone. In the presence of hydrochloric acid in aqueous acetone, *cyclo*pentenylphenylcarbinol undergoes the usual oxotropic rearrangement and is quantitatively converted into the solid, conjugated isomer, 2-benzylidene*cyclo*pentanol (II) which was characterised by a *p*-nitrobenzoate and its light absorption (see Table). Distillation of (II) from potassium hydrogen sulphate afforded 2-benzylidene*cyclo*pentene (III), and Oppenauer oxidation gave 2-benzylidene*cyclo*pentanone (IV), characterised by a 2 : 4-dinitrophenylhydrazone. This derivative is also formed, though in low yield, when 2-benzylidene*cyclo*pentanol is heated for a short time with Brady's reagent, a reaction found to be general for certain types of primary and secondary α-ethylenic alcohols and analogous in some respects to osazone formation from α-keto-alcohols (Braude and Forbes, succeeding paper).



(I.)



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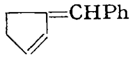

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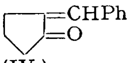
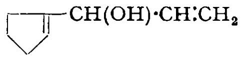


(IV.)

*cyclo*Pentenyl-lithium with acraldehyde and crotonaldehyde afforded, in 30—60% yields, *cyclo*pentenylvinylcarbinol (V) and *cyclo*pentenylpropenylcarbinol (VII), respectively. The structure of the latter was confirmed by catalytic hydrogenation to 4-*cyclo*pentylbutan-2-ol. In the presence of dilute acids the *cyclo*pentenylcarbinols undergo oxotropic rearrangement, but, as in the case of the *cyclo*hexenyl analogues (Part V, *loc. cit.*) and presumably for the same reasons, rearrangement proceeds in opposite directions in the two cases. With the vinylcarbinol, the hydroxyl group migrates into the ring, giving exclusively 2-allylidene*cyclo*pentanol (VI), the structure of which was proved by catalytic hydrogenation to 2-propyl*cyclo*pentanol and oxidation of the latter to the known 2-propyl*cyclo*pentanone. With the propenylcarbinol, on the other hand, the hydroxyl group migrates along the side-chain, giving exclusively



(V.)

(VI.)

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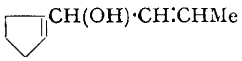
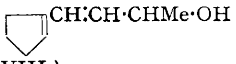
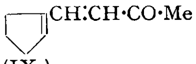
4-*cyclo*pent-1′-enylbut-3-en-2-ol (VIII). The structure of (VIII) was proved by oxidation with manganese dioxide in light petroleum (Ball, Goodwin, and Morton, *Biochem. J.*, 1948, **42**, 516; Wendler, Slates, and Tishler, *J. Amer. Chem. Soc.*, 1949, **71**, 3267; we are indebted to Dr. B. C. L. Weedon for communicating unpublished results concerning the application of this



(VII.)



(VIII.)



(IX.)

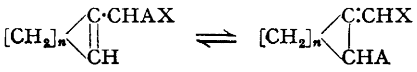
method to the oxidation of secondary ethylenic alcohols) to the ketone (IX) which has recently been synthesised by a different route (Heilbron, Jones, Toogood, and Weedon, *J.*, 1949, 1827). Both the rearranged carbinols exhibited the expected ultra-violet light absorption (see Table). As previously noted in some cases (Heilbron *et al.*, *loc. cit.*), the maxima of the five-membered ring derivatives generally lie at slightly longer wave-lengths than those of the six-membered ring analogues.

*Ultra-violet light absorption properties of* cyclo*pentenyl and* cyclo*pentylidene derivatives and their six-membered ring analogues in ethanol.*

| | *cyclo*Pentenyl series.[1] | | *cyclo*Hexenyl series.[2] | |
|---|---|---|---|---|
| | $\lambda_{\text{max.}}$, A. | $\epsilon_{\text{max.}}$ | $\lambda_{\text{max.}}$, A. | $\epsilon_{\text{max.}}$ |
| *cyclo*Alk-1-enecarboxylic acid | 2110 | 9,300 | 2120 | 11,000 |
| Di*cyclo*alk-1-enyl ketone | 2470 | 11,500 | 2420 | 14,800 |
| | 3300 | 55 | 3190 | 90 |
| 2-Benzylidene*cyclo*alkanol | 2560 | 19,100 | 2430 | 14,200 |
| 2-Benzylidene*cyclo*alkene | 2280 | 8,400 | 2230 | 7,700 |
| | 2880 | 20,300 | 2810 | 18,700 |
| 2-Allylidene*cyclo*alkanol | 2395 | 23,600 | 2330 | 27,000 |
| 4-*cyclo*Alk-1′-enylbut-3-en-2-ol | 2360 | 21,000 | 2350 | 23,000 |
| 4-*cyclo*Alk-1′-enylbut-3-en-2-one[3] | 2810 | 21,000 | 2810 | 20,000 |

[1] This paper. [2] Part IV (*loc. cit.*). [3] Heilbron *et al.* (*loc. cit.*).

In each of the three oxotropic systems described above, as in the case of the *cyclo*hexenyl analogues (Part V, *loc. cit.*), the conversion of the unconjugated into the conjugated isomer is practically complete and no measurable equilibria are set up. Rearrangement of the *cyclo*alkenylvinyl- and *cyclo*alkenylphenyl-carbinols involves the formation of a *cyclo*alkylidene group (as in II) and these results are of interest in relation to those obtained by Linstead, Kon, and their collaborators in their studies on related prototropic systems (for summaries and references, see Bennett, *Ann. Reports*, 1929, **26**, 117; Baker and Bennett, *ibid.*, 1931, **28**, 105; Kon, *ibid.*, 1932, **29**, 136). In contrast to the behaviour of the oxotropic systems described above, the alkali-catalysed prototropic rearrangements of *cyclo*alkenylacetic acids and some of their derivatives to the *cyclo*alkylidene isomers are measurably reversible, and the position of the equilibrium is intimately dependent on the size of the ring system and the nature of the conjugating group.



(X.) (XI.)

(A = H or OH)

In these systems the equilibrium might be expected to lie far to the side of the *cyclo*alkylidene compounds (XI), for two reasons. First, the *cyclo*alkenyl group should involve rather larger ring-strain than does the *cyclo*alkylidene group. Bennett's discussion of this point (*loc. cit.*) requires some revision because it is now thought that the preferred angle between the two single valency bonds attached to an ethylenic carbon atom is not the tetrahedral value (109·5°), but more nearly 120° (cf. Penney, *Proc. Roy. Soc.*, 1937, **158**, 306; Coulson, *Proc. Roy. Soc., Edinburgh*, 1941, **61**, *A*, 115). An inspection of models shows that the *cyclo*alkenyl ⟶ *cyclo*alkylidene rearrangement will be accompanied by a decrease in ring-strain of about 10° in the five-membered and rather less in the six-membered series, and it can be estimated from bending force constant data that a valency deflection of this magnitude should represent an energy difference of at least 10 kcals./mole (cf. Guy, *J. Chim. physique*, 1949, **46**, 467). If this value possesses quantitative significance, and if, as might be expected, accompanying entropy changes are small, this would correspond to an equilibrium constant of about 10, *i.e.*, 90% conversion into (XI), at ordinary temperatures. Secondly, the isomer (XI) will be stabilised by the additional

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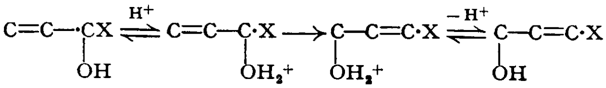
resonance energy of the $C{:}CHX$ group. The extent of this stabilisation will be somewhat dependent on X, but should be of the same order for $X = CH{:}CH_2$, Ph, COR, and $CO_2R$. Its actual magnitude is rather uncertain, values ranging from 7 to only 1 kcal./mole having, for instance, been advocated for the styryl system (Pauling and Sherman, *J. Chem. Physics*, 1933, **1**, 606; Kistiakowsky *et al.*, *J. Amer. Chem. Soc.*, 1936, **58**, 146; Wheland, "The Theory of Resonance," New York, 1944; Dewar, *Trans. Faraday Soc.*, 1946, **42**, 767; Cottrell and Sutton, *J. Chem. Physics*, 1947, **15**, 685; Franklin, *J. Amer. Chem. Soc.*, 1950, **72**, 4278), but a lower limit of 3 kcals./mole seems probable, particularly in view of the fact that essentially complete rearrangement is observed in open-chain oxotropic systems (cf. Braude, *Quart. Reviews*, 1950, **4**, 404) in which ring-strain effects do not come into play.

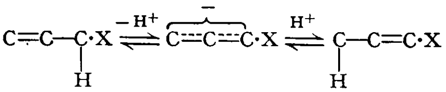
The results obtained with the oxotropic systems are thus in agreement with simple energetic considerations whereas those obtained with the prototropic systems are not. The difference in behaviour cannot be caused solely by the variation of the conjugating group X and must therefore be at least partly, if not mainly, due to the difference in the migrating group. This conclusion is in accord with the view that three-carbon oxotropy and prototropy proceed by quite distinct mechanisms. In acid-catalysed three-carbon oxotropy, the entity actually undergoing rearrangement is the oxonium ion as represented in (*a*) (Braude, *J.*, 1948, 794; *Ann. Reports*, 1949, **46**, 125); the addition of the proton to the hydroxyl group and the position of the equilibrium for the oxonium ions would be expected to be the same as for the neutral structures, *i.e.*, essentially complete rearrangement would still be expected, and is, in fact, observed. In base-catalysed prototropy, on the other hand, the entity actually undergoing rearrangement is the carbanion as represented in (*b*) (cf. Ingold, *Ann. Reports*, 1927, **24**, 106; *J.*, 1948, 22) and the proximity of the fully developed negative charge to the unsaturated groups will have a pronounced effect on the relative stabilities of the two isomeric structures. Whereas in the unconjugated neutral derivatives and in their oxonium ions the resonance interaction between the two unsaturated centres will only be small, the carbanions are mesomeric ions which are subject to charge-resonance and in which the energy differences between the extreme forms are much reduced. There is, in fact, no valid distinction between the unconjugated and the conjugated forms, but a continuous distribution of the excess of electron density which can be expressed in terms of fractional charges on the α- and γ-carbon atoms. The position of equilibrium in prototropy is thus determined, not by the relative stabilities of the neutral isomeric structures (X) and (XI) but by that of the corresponding carbanions and, for this reason, is different from and less one-sided than that observed in oxotropy.

(*a*) Acid-catalysed oxotropy.



$$C{=}C{-}\underset{OH}{C}X \overset{H^+}{\rightleftharpoons} C{=}C{-}\underset{OH_2^+}{C}{\cdot}X \longrightarrow \underset{OH_2^+}{C}{-}C{=}C{\cdot}X \overset{-H^+}{\rightleftharpoons} \underset{OH}{C}{-}C{=}C{\cdot}X$$

(*b*) Base-catalysed prototropy.



$$C{=}C{-}\underset{H}{C}{\cdot}X \overset{-H^+}{\rightleftharpoons} \overset{-}{C{=}C{=}C}{\cdot}X \overset{H^+}{\rightleftharpoons} \underset{H}{C}{-}C{=}C{\cdot}X$$

One difficulty, or apparent difficulty, which arises from the foregoing discussion is that, although it has been deduced that a five- and a six-membered *cyclo*alkylidene group is thermodynamically more stable than a *cyclo*alkenyl group, yet it has been shown that *cyclo*pentenyl- and *cyclo*hexenyl-propenylcarbinol, unlike the corresponding vinylcarbinols, rearrange under mild acid conditions to give the conjugated *cyclo*alkenyl derivatives (*e.g.*, VIII) rather than the *cyclo*alkylidene isomers. However, as has already been pointed out (Part V, *loc. cit.*), the initial direction of rearrangement will be determined, not by the relative stabilities of the respective products, but by the relative rates of the two possible modes of rearrangement as conditioned by the activating influence of substituents. Since oxotropy requires electron-accession at the reaction centre, the activating influence will increase in the sequence $CH_2{=}CH{-} < R{\cdot}CH_2{\cdot}CH{=}CH{-} < CH_3{\cdot}CH{=}CH{-}$, thus accounting for the observed directions of rearrangement. It has been shown (Nazarov and Fisher, *Bull. Acad. Sci. U.S.S.R.*, *Cl. Sci. Chim.*, 1945, 631; 1948, 311, 427; Braude and Timmons, Part II, *J.*, 1950, 2007) that, in acyclic, unsymmetrically substituted dialkenylcarbinols, the initial three-carbon oxotropy is followed by a much slower, five-carbon oxotropy which leads to an equilibrium mixture of the two conjugated isomers. It would therefore be expected that the *cyclo*alkenylbutenols (*e.g.*, VIII) will undergo a slow five-carbon oxotropy to give the isomeric *cyclo*alkylidene derivatives, but we have so far been unable to establish suitable conditions for this change because of the

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ease of dehydration and decomposition of the *cyclo*alkenylbutenols at higher acid concentrations. Conversely, it would be expected that hydroxy*cyclo*alkylidene compounds will *not* undergo rearrangement to the isomeric *cyclo*alkenylbutenols, but again we have so far been unable to establish conditions to demonstrate this because the hydroxy*cyclo*alkylidene compounds readily undergo self-etherification at high acid concentrations. A more exhaustive discussion of mobilities and equilibria in these oxotropic systems will be presented later in conjunction with quantitative kinetic data.

## EXPERIMENTAL.

(M. p.s are uncorrected.)

1-*Chloro*cyclo*pentene*.—The preparation of this compound from *cyclo*pentanone in 80% yield has been claimed by Favorskii and Shostakovsky (*J. Gen. Chem. U.S.S.R.*, 1936, **6**, 720), but we have not been successful in duplicating this result. After many trials, the following procedure was adopted. *cyclo*Pentanone (180 ml.) was added to high-grade phosphorus pentachloride (440 g.) at 0°, the reaction mixture being rapidly stirred. The mixture was then added dropwise to ice-cold water (3 l.), and the dark lower layer formed was separated and again added dropwise to ice-cold water (3 l.). This process was repeated 2—3 times until the lower layer no longer fumed strongly in air. The product was dried ($CaCl_2$) and rapidly fractionated through a 10-inch Dufton column at atmospheric pressure. In a typical run, the following fractions were obtained: (i) b. p. 103—110° (15 ml.), (ii) b. p. 111—116° (65 ml.), (iii) b. p. 117—138° (50 ml.), (iv) b. p. 139—143° (10 ml.). (The use of a more efficient column resulted in extensive decomposition.) Fraction (i) consisted mainly of 3-chloro*cyclo*pentene, which is very unstable (Kraemer and Spilker, *Ber.*, 1896, **29**, 554; Noeldechen, *ibid.*, 1900, **33**, 3348) and rapidly reacts with aqueous-alcoholic silver nitrate solution as would be expected for an allylic chloride. Fraction (ii) consisted mainly of 1-chloro*cyclo*pentene which on refractionation was obtained as a colourless, faintly smelling liquid, b. p. 113°/760 mm., $n_D^{22}$ 1·4666 (Found: C, 58·4; H, 6·6; Cl, 35·4. Calc. for $C_5H_7Cl$: C, 58·8; H, 6·85; Cl, 34·8%) (Favorskii and Shostakovsky, *loc. cit.*, give b. p. 113°/760 mm.). It gives no immediate reaction with aqueous-alcoholic silver nitrate solution, with bromine in carbon tetrachloride solution, or with 2 : 4-dinitrophenylhydrazine in alcoholic sulphuric acid solution, but gives a pale yellow colour with tetranitromethane. It reacts slowly with water at room temperature, more rapidly with dilute acids and dilute alkalis, and decomposes even on being kept at 0°. When 1-chloro*cyclo*pentene is warmed with an equivalent amount of silver nitrate in 50% aqueous ethanol, the quantitative amount of silver chloride is rapidly precipitated and *cyclo*pentanone, identified as the 2 : 4-dinitrophenylhydrazone, m. p. 145°, is formed. Fraction (iv) consisted mainly of 1 : 1-dichloro*cyclo*pentane, which after refractionation had b. p. 143°/760 mm., $n_D^{21}$ 1·4701 (Found: Cl, 50·8. Calc. for $C_5H_8Cl_2$: Cl, 51·0%). Treatment of dichloro*cyclo*pentane with aqueous-ethanolic potassium hydroxide under various conditions afforded mixtures of 1- and 3-chloro*cyclo*pentene and unchanged starting material.

1-cyclo*Pentenyl-lithium*.—Freshly distilled 1-chloro*cyclo*pentene (31 g.) in ether (100 ml.) was added to a stirred suspension of finely cut lithium (4·1 g.) in sodium-dried ether (700 ml.) under nitrogen. When all the chloride had been added, the flask containing the reaction mixture was warmed (electric heating mantle) until the ether refluxed gently. Reaction set in after 2—6 hours as shown by a change in the appearance of the lithium and the formation of a white turbidity; later the solution assumed a greenish-grey colour. Refluxing was continued for 6—10 hours, until most of the metal had been consumed.

cyclo*Pent*-1-*enecarboxylic acid and Di*cyclo*pent*-1-*enyl Ketone*.—Solid carbon dioxide (200 g.) was added to an ethereal solution of *cyclo*pentenyl-lithium (from Li, 4·1 g.), cooled in solid carbon dioxide–methanol. After being stirred overnight, the solution was acidified with dilute aqueous hydrochloric acid. The ethereal layer was separated and extracted with aqueous sodium carbonate. Acidification of the alkaline extract gave *cyclo*pent-1-enecarboxylic acid (0·35 g., 1%), which crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 122° (Haworth and Perkin, *J.*, 1894, **65**, 101, give m. p. 119—121°; Cook and Linstead, *J.*, 1934, 956, give m. p. 121°). Light absorption in ethanol: Max. at 2110 ($\varepsilon = 9300$) and 2130 ($\varepsilon = 9100$), inflection at 2060 A. ($\varepsilon = 5200$). The amide separated from water in prisms, m. p. 205° (Kenner and Wain, *Ber.*, 1939, **72**, 456, give m. p. 206°). Evaporation of the ethereal solution gave *di*cyclo*pent*-1-*enyl ketone* (4 g., 8%), which separated from pentane in rods, m. p. 59° (Found: C, 81·1; H, 8·7. $C_{11}H_{14}O$ requires C, 81·4; H, 8·7%). Light absorption in ethanol: see Table. The 2 : 4-*dinitrophenylhydrazone* was chromatographed on alumina from benzene–chloroform solution and crystallised from ethanol in red needles, m. p. 163° (Found: C, 60·0; H, 5·6; N, 16·6. $C_{17}H_{18}O_4N_4$ requires C, 59·7; H, 5·3; N, 16·4%). Light absorption in chloroform: Max. at 3880 A. ($\varepsilon = 32{,}000$).

Repetition of the above experiment with a larger excess of solid carbon dioxide (600 g.) gave a higher yield of *cyclo*pent-1-enecarboxylic acid (5·0 g., 13%) and a lower yield of di*cyclo*pent-1-enyl ketone (0·4 g., 0·7%).

Hydrogenation of di*cyclo*pentenyl ketone (1 g.) in absolute ethanol in the presence of platinic oxide resulted in the uptake of 330 ml. of hydrogen at 18°/768 mm. (Calc., 290 ml.), giving di*cyclo*pentyl ketone, identified as the semicarbazone which, crystallised from aqueous ethanol, had m. p. 167° (Nenitzescu and Ciorănescu, *Ber.*, 1936, **69**, 1820, give m. p. 165°). Di*cyclo*pentyl ketone formed a 2 : 4-*dinitrophenylhydrazone* which was chromatographed on alumina from benzene–chloroform solution and crystallised from aqueous ethanol in orange needles, m. p. 103—104° (Found: N, 16·0. $C_{17}H_{22}O_4N_4$ requires N, 16·2%).

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cyclo*Pentenylphenylcarbinol.*—Freshly distilled benzaldehyde (32 g.) in ether (50 ml.) was added during 1 hour to an ethereal solution of *cyclo*pentenyl-lithium (from Li, 4·3 g.) at 0°. After 6 hours' stirring, ice-cold saturated aqueous ammonium chloride (500 ml.) was added. Stirring was continued for 2 hours and the ethereal layer was then separated, dried ($Na_2SO_4$–$K_2CO_3$), and fractionated from a trace of potassium carbonate, giving cyclo*pentenylphenylcarbinol* (α-cyclo*pent*-1′-*enylbenzyl alcohol*) (16 g., 30%) which distilled as a colourless liquid, b. p. 93°/5·5 × $10^{-4}$ mm., $n_D^{19}$ 1·5650 (Found : C, 82·5; H, 8·2. $C_{12}H_{14}O$ requires C, 82·7; H, 8·1%). Light absorption in ethanol : Max. at 2510 (ε = 5900); inflection at 2570 A. (ε = 5600). It is essential in this condensation to remove any unconsumed lithium before adding the benzaldehyde solution, otherwise the product is contaminated with hydrobenzoin which is formed by pinacol reduction of benzaldehyde during the decomposition stage and distils with *cyclo*pentenylphenylcarbinol.

cyclo*Pentylphenylcarbinol and* cyclo*Pentylphenyl Ketone.*—Hydrogenation of *cyclo*pentenylphenylcarbinol (2·5 g.) in absolute ethanol (30 ml.) in the presence of platinic oxide resulted in the uptake of 390 ml. of hydrogen at 19°/770 mm. (Calc.: 350 ml.) to give *cyclo*pentylphenylcarbinol (2 g.), b. p. 76°/0·1 mm., $n_D^{18}$ 1·5414 (Edwards and Reid, *J. Amer. Chem. Soc.*, 1930, **52**, 3235, give b. p. 129—131°/5 mm.).

A solution of *cyclo*pentylphenylcarbinol (1·5 g.) in dioxan (30 ml.) was oxidised with potassium dichromate (0·86 g.) in 2N-sulphuric acid (30 ml.) at 0° to cyclo*pentyl phenyl ketone* (1 g.), b. p. 88°/8 × $10^{-4}$ mm., $n_D^{19}$ 1·5435 (Found : C, 82·4; H, 8·1. $C_{12}H_{14}O$ requires C, 82·7; H, 8·1%). Light absorption in hexane : Max. at 2380, 2680, 2800, and 3300 A.; ε = 11,800, 800, 800, and 20, respectively. The ketone formed a 2 : 4-*dinitrophenylhydrazone* which was chromatographed on alumina from benzene–chloroform solution and crystallised from ethanol in orange plates, m. p. 141° (Found : C, 61·3; H, 5·2; N, 16·0. $C_{18}H_{18}O_4N_4$ requires C, 61·0; H, 5·1; N, 15·8%). Light absorption in ethanol : Max. at 3690 A., ε = 24,800. [*Added* 13.3.51]. *cyclo*Pentyl phenyl ketone has since been described by Nightingale and Maienthal (*J. Amer. Chem. Soc.*, 1950, **72**, 4823) who give b. p. 103—105°/5 mm., $n_D^{20}$ 1·5452; 2 : 4-dinitrophenylhydrazone, m. p. 145°.

2-*Benzylidene*cyclo*pentanol.*—A solution of *cyclo*pentenylphenylcarbinol (4 g.) in 80% aqueous acetone 0·1N-hydrochloric acid (100 ml.) was kept for 18 hours at room temperature. After neutralisation with aqueous potassium carbonate, the acetone was removed by distillation through a column and the residue extracted with ether. Fractionation of the ethereal extract afforded 2-*benzylidene*cyclo*pentanol* (3·5 g.), b. p. 91°/3 × $10^{-4}$ mm., which solidified when kept and crystallised from pentane in colourless plates, m. p. 86° (Found : C, 82·4; H, 8·2. $C_{12}H_{14}O$ requires C, 82·7; H, 8·1%). Light absorption in ethanol : Max. at 2510 and 2560 A.; ε = 19,100 and 19,100 respectively; inflection at 2640 A., ε = 16,400. The p-*nitrobenzoate* crystallised from light petroleum (b. p. 60—80°) in colourless plates, m. p. 71° (Found : C, 70·4; H, 5·5; N, 4·5. $C_{19}H_{17}O_4N$ requires C, 70·6; H, 5·3; N, 4·3%). Light absorption in ethanol : Max. at 2510 and 2570 A.; ε = 30,700 and 34,900 respectively; inflection at 2640 A.; ε = 27,500.

When a solution of 2-benzylidene*cyclo*pentanol (0·5 g.) was warmed with a solution of 2 : 4-dinitrophenylhydrazine in concentrated sulphuric acid and methanol, the 2 : 4-dinitrophenylhydrazone of 2-benzylidene*cyclo*pentanone was gradually precipitated. It was isolated in 20% yield (0·2 g.) and, after crystallisation from ethanol, had m. p. 164°, undepressed on admixture with the authentic specimen described below.

2-*Benzylidene*cyclo*pentene.*—2-Benzylidene*cyclo*pentanol (4 g.) was heated for 30 minutes with potassium hydrogen sulphate (0·4 g.) on the steam-bath. Distillation of the reaction mixture in a high vacuum gave 2-*benzylidene*cyclo*pentene* (1·3 g.), b. p. 120°/8 × $10^{-4}$ mm., which solidified on storage and crystallised from aqueous methanol in plates, m. p. 48° (Found : C, 92·3; H, 7·8. $C_{12}H_{12}$ requires C, 92·3; H, 7·7%). Light absorption in ethanol : see Table.

2-*Benzylidene*cyclo*pentanone.*—(*a*) 2-Benzylidene*cyclo*pentanol (3 g.), aluminium *tert.*-butoxide (8 g.), dry benzene (100 ml.), and acetone (100 ml.) were refluxed together for 30 hours. After cooling, the solution was carefully acidified with hydrochloric acid, and the product was worked up in the usual manner, giving 2-benzylidene*cyclo*pentanone (1·5 g.), which crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 66°, undepressed on admixture with the specimen described below. It formed a 2 : 4-*dinitrophenylhydrazone* which was chromatographed an alumina from benzene–chloroform solution and crystallised from ethanol in red needles, m. p. 164° (Found : C, 61·7; H, 4·9; N, 15·9. $C_{18}H_{16}O_4N_4$ requires C, 61·4; H, 4·6; N, 15·9%). Light absorption in ethanol : Max. at 3880 A.; ε = 30,100.

(*b*) Benzaldehyde (5 g.) in 50% aqueous ethanol (50 ml.) was added dropwise to a vigorously stirred solution of *cyclo*pentanone (25 g.) in 50% aqueous-ethanolic 0·1N-potassium hydroxide (200 ml.). The precipitate of dibenzylidene*cyclo*pentanone was filtered off and the solution was diluted with water and extracted with ether. Fractionation of the ethereal extract afforded 2-benzylidene*cyclo*pentanone (0·5 g.), b. p. 170°/2 × $10^{-4}$ mm., which slowly solidified and crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 66° (Vorländer and Hobohm, *Ber.*, 1896, **29**, 1836, give m. p. 68°).

cyclo*Pentenylvinylcarbinol.*—Acraldehyde (14 g.) in ether (30 ml.) was slowly added to an ethereal solution of *cyclo*pentenyl-lithium (from Li, 3·1 g.) at 0°. Stirring was continued for 3 hours at room temperature, and ice-cold, saturated aqueous ammonium chloride (400 ml.) was then added. After a further 2 hours' stirring, the ethereal layer was separated, dried ($Na_2SO_4$–$K_2CO_3$), and fractionated, giving cyclo*pentenylvinylcarbinol* (1-cyclo*pentenylallyl alcohol*) (13 g., 32%) as a colourless liquid, b. p. 43°/0·5 mm., $n_D^{22}$ 1·4890 (Found : C, 77·1; H, 9·6. $C_8H_{12}O$ requires C, 77·4; H, 9·7%). Light absorption in ethanol : ε < 1000 in the region 2200—4000 A.

2-*Allylidene*cyclo*pentanol.*—*cyclo*Pentenylvinylcarbinol (8 g.) was dissolved in 60% aqueous acetone 0·025M-hydrochloric acid (200 ml.), and the solution was kept for 18 hours at room temperature. The solution was then neutralised with aqueous potassium carbonate, and the acetone removed by distillation

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through a column. The aqueous residue was extracted with ether, and the ethereal extract was dried and fractioned, giving 2-*allylidene*cyclo*pentanol* (6 g.) as a colourless liquid, b. p. 50°/0·4 mm., $n_D^{21}$ 1·5279 (Found : C, 77·1; H, 9·8. $C_8H_{12}O$ requires C, 77·4; H, 9·7%). Light absorption in ethanol: see Table.

2-n-*Propyl*cyclo*pentanol and* 2-n-*Propyl*cyclo*pentanone*.—Hydrogenation of 2-allylidene*cyclo*pentanol (5·1 g.) in absolute ethanol (50 ml.) in the presence of platinic oxide resulted in the uptake of 2100 ml. of hydrogen at 22°/755 mm. (Calc. 2000 ml.), to give 2-*n*-propyl*cyclo*pentanol (4·5 g.), b. p. 87°/30 mm., $n_D^{22}$ 1·4540 (Vavon and Flurer, *Bull. Soc. chim.*, 1929, **45**, 754, give b. p. 79—80°/10 mm., $n_D^{9}$ 1·4600). The 3 : 5-dinitrobenzoate crystallised from light petroleum (b. p. 40—60°) in plates, m. p. 69° [Vavon and Flurer, *loc. cit.*, give m. p. 70—71° for the *cis*(?)-isomer].

2-*n*-Propyl*cyclo*pentanol (2·6 g.) in acetone (30 ml.) was treated with a solution of potassium dichromate (2·5 g.) in 2N-sulphuric acid (100 ml.) at 0°. Isolation of the product in the usual manner gave 2-*n*-propyl*cyclo*pentanone (2·2 g.), b. p. 83°/30 mm., $n_D^{21}$ 1·4410 (Vavon and Flurer, *loc. cit.*, give b. p. 67°/8 mm., $n_D^{7}$ 1·4470). The semicarbazone crystallised from methanol in needles, m. p. 210° (decomp.) [Vavon and Flurer, *loc. cit.*, give m. p. 212—213° (decomp.)]. The 2 : 4-*dinitrophenylhydrazone* was chromatographed on alumina from benzene–chloroform solution and crystallised from ethyl acetate in orange needles, m. p. 150° (Found : N, 18·1. $C_{14}H_{18}O_4N_4$ requires N, 18·3%). Light absorption in chloroform : Max. at 3700 A.; ε = 22,300. The m. p.s of both derivatives were undepressed on admixture with those of an authentic sample of 2-*n*-propyl*cyclo*pentanone, prepared according to Vavon and Flurer (*loc. cit.*) by the condensation of *cyclo*pentanone with propaldehyde to give 2-propylidene-*cyclo*pentanone, followed by catalytic hydrogenation.

In an attempt to prepare 2-*n*-propyl*cyclo*pentanone by direct alkylation of *cyclo*pentanone by the method of Braude and Coles (*J.*, 1950, 2014), a mixture of *cyclo*pentanone (10 g.) and *n*-propyl bromide (16 g.) was added to a boiling solution of potassium *tert.*-butoxide (from K, 5·6 g.) in *tert.*-butanol. After a further 20 minutes' heating under reflux, the solution was allowed to cool and acidified with ice-cold hydrochloric acid. Isolation of the product in the usual manner gave 5-cyclo*pentylidene*-2-n-*propyl*-cyclo*pentanone* (6 g.), b. p. 70°/0·1 mm., $n_D^{24}$ 1·4890 (Found : C, 81·3; H, 10·6. $C_{13}H_{20}O$ requires C, 81·2; H, 10·5%). Light absorption in ethanol: Max. at 2280 and 3040 A.; ε = 3800 and 200 respectively. The relatively low intensity of the 2280-A. band may be ascribed to steric inhibition of resonance owing to interference between the carbonyl group and the α-hydrogen atom of the *cyclo*pentylidene group (cf. Braude *et al.*, *J.*, 1949, 1890); there was no indication of admixture with the unconjugated isomer, 5-*cyclo*pent-1′-enyl-2-*n*-propyl*cyclo*pentanone, as observed in the case of *cyclo*hexylidene*cyclo*hexanone (cf. Evans and Gillam, *J.*, 1941, 815; Bagchi *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 990).

cyclo*Pentenylpropenylcarbinol*.—Freshly distilled crotonaldehyde (25 g.) in ether (50 ml.) was added dropwise to an ethereal solution of *cyclo*pentenyl-lithium (from Li, 4·3 g.) at 0°. After 6 hours' stirring, ice-cold saturated aqueous ammonium chloride (500 ml.) was added. Stirring was continued for 2 hours and the ethereal layer was then separated, dried ($Na_2SO_4$–$K_2CO_3$) and fractionated, giving cyclo*pentenylpropenylcarbinol* (13·5 g., 32%) as a colourless liquid, b. p. 60°/0·5 mm., $n_D^{21}$ 1·4910 (Found : C, 78·1; H, 10·2. $C_9H_{14}O$ requires C, 78·2; H, 10·2%). Light absorption in ethanol: ε < 1000 in the region 2200—4000 A. The yields obtained in this condensation fluctuated in different experiments under apparently identical conditions, and the value quoted is a minimum; in one run the yield reached 61%.

Hydrogenation of *cyclo*pentenylpropenylcarbinol (1·7 g.) in absolute ethanol (60 ml.) in the presence of platinic oxide resulted in the uptake of 580 ml. of hydrogen at 18°/768 mm. (Calc., 600 ml.) to give *cyclo*pentylpropylcarbinol (1·5 g.), b. p. 100°/20 mm., $n_D^{20}$ 1·4502 (Edwards and Reid, *J. Amer. Chem. Soc.*, 1930, **52**, 3235, give b. p. 115°/52 mm., *n* 1·4510). The 3 : 5-dinitrobenzoate crystallised from carbon tetrachloride in needles, m. p. 83° (Edwards and Reid, *loc. cit.*, give m. p. 85°).

4-cyclo*Pent*-1′-*enylbut*-3-*en*-2-*ol*.—A solution of *cyclo*pentenylpropenylcarbinol (4 g.) in 60% aqueous acetone 0·1M-hydrochloric acid (200 ml.) was kept for 24 hours at room temperature. After neutralisation with aqueous potassium carbonate, most of the acetone was removed by distillation through a column. The aqueous residue was extracted with ether, and the ethereal extract was dried ($Na_2SO_4$) and fractionated, giving 4-cyclo*pent*-1′-*enylbut*-3-*en*-2-*ol* (2 g.), b. p. 68°/0·5 mm., $n_D^{21}$ 1·5178 (Found : C, 77·8; H, 10·1. $C_9H_{14}O$ requires C, 78·2; H, 10·2%). Light absorption in ethanol: see Table.

4-cyclo*Pent*-1′-*enylbut*-3-*en*-2-*one*.—4-*cyclo*Pent-1′-enylbut-3-en-2-ol (2 g.), vacuum-dried manganese dioxide (20 g.), and sodium-dried light petroleum (200 ml.; b. p. 40—60°) were shaken for 12 hours. The solution was filtered and the residue washed with light petroleum (b. p. 40—60°). The solution and washings were combined and fractionated, giving 4-*cyclo*pent-1′-enylbut-3-en-2-one (1 g.), b. p. 64°/0·5 mm., $n_D^{23}$ 1·5409 (Heilbron *et al.*, *J.*, 1949, 1827, give b. p. 85—87°/3 mm., $n_D^{22}$ 1·5442). The ketone formed, in 80% yield, a 2 : 4-dinitrophenylhydrazone which was shown to be homogeneous by chromatography on alumina from benzene–chloroform solution and crystallised from ethyl acetate in deep red prisms, m. p. 214°, undepressed on admixture with the specimen prepared by Heilbron *et al.* (*loc. cit.*).

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