

383. *Studies in Molecular Rearrangement. Part VI.* Syntheses and Oxotropic Rearrangements in the cyclopentenyl Series.*

By E. A. BRAUDE and W. F. FORBES.

1-Chlorocyclopentene has been converted into cyclopent-1-enyl-lithium. The latter reacts with carbon dioxide to give cyclopent-1-enecarboxylic acid and dicyclopent-1-enyl ketone, and with benzaldehyde, acetaldehyde, and crotonaldehyde to give the expected cyclopent-1-enylcarbinols (I, V, and VII). In the presence of acids, cyclopentenylphenylcarbinol undergoes the usual oxotropic rearrangement to 2-benzylidenecyclopentanol (II) which is dehydrated to 2-benzylidenecyclopentene (III) and oxidised to 2-benzylidenecyclopentanone (IV). cyclopentenylvinylcarbinol similarly rearranges to 2-allylidenecyclopentanol (VI), whereas cyclopentenylpropenylcarbinol rearranges to 4-cyclopent-1'-enylbut-3-en-2-ol (VIII) which is converted by oxidation with manganese dioxide into 4-cyclopent-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 cyclohexenyl 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 cyclohex-1-enylcarbinols were described. This work is being extended to substituted cyclohexenyl as well as to lower- and higher-membered cycloalkenyl homologues and the present communication deals with the cyclopentenyl derivatives.

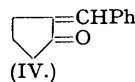
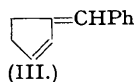
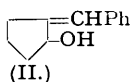
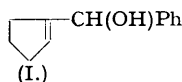
The synthetic method employed depends on the formation of cyclopent-1-enyl-lithium from 1-chlorocyclopentene. The latter was first obtained by Favorskii and Shostakovskiy (*J. Gen. Chem. U.S.S.R.*, 1936, **6**, 720), but our experience concerning its preparation and properties is not entirely in accord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

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

(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 chlorocycloolefin. 1-Chlorocyclopentene, 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-chlorocyclohexene; it is decomposed by water at room temperature and regenerates cyclopentanone when warmed with aqueous alcoholic silver nitrate, a reaction which also proves its structure. The ready hydrolysis of 1-chlorocyclopentene 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).

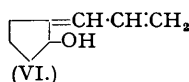
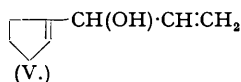
The conversion of 1-chlorocyclopentene into cyclopentenyl-lithium by reaction with lithium in ether takes place rather less readily than the formation of cyclohexenyl-lithium (Part V, *loc. cit.*) (see Experimental). The lower reactivity of 1-chlorocyclopentene towards lithium may be genuine, or it may be only apparent and arise from the greater difficulty of purification. Treatment of the solution of cyclopentenyl-lithium with solid carbon dioxide afforded a mixture of cyclopent-1-enecarboxylic acid and dicyclopent-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 dicyclopentyl ketone. The formation of ketone as well as of carboxylic acid in the reaction with solid carbon dioxide has also been observed with cyclohexenyl- (Part V, *loc. cit.*), propenyl- (Braude and Coles, *J.*, 1951, in the press), and isobutenyl-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).

cyclopentenyl-lithium and benzaldehyde afforded, in 30% yield, cyclopentenylphenylcarbinol (I), the structure of which was confirmed by catalytic hydrogenation to cyclopentylphenylcarbinol and oxidation of the latter to cyclopentyl phenyl ketone. In the presence of hydrochloric acid in aqueous acetone, cyclopentenylphenylcarbinol undergoes the usual oxotropic rearrangement and is quantitatively converted into the solid, conjugated isomer, 2-benzylidenecyclopentanol (II) which was characterised by a *p*-nitrobenzoate and its light absorption (see Table). Distillation of (II) from potassium hydrogen sulphate afforded



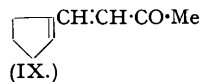
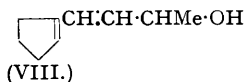
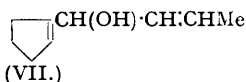
2-benzylidenecyclopentene (III), and Oppenauer oxidation gave 2-benzylidenecyclopentanone (IV), characterised by a 2:4-dinitrophenylhydrazone. This derivative is also formed, though in low yield, when 2-benzylidenecyclopentanol is heated for a short time with Brady's reagent, a reaction found to be general 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).

cyclopentenyl-lithium with acraldehyde and crotonaldehyde afforded, in 30—60% yields, cyclopentenylvinylcarbinol (V) and cyclopentenylpropenylcarbinol (VII), respectively. The structure of the latter was confirmed by catalytic hydrogenation to 4-cyclopentylbutan-2-ol. In the presence of dilute acids the cyclopentenylcarbinols undergo oxotropic rearrangement, but,



as in the case of the cyclohexenyl 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-2-cyclopentanol (VI), the structure of which was proved by catalytic hydrogenation to 2-propylcyclopentanol and oxidation of the latter to the known 2-propylcyclopentanone. With the propenylcarbinol, on the other hand, the hydroxyl group migrates along the side-chain, giving exclusively

4-cyclopent-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



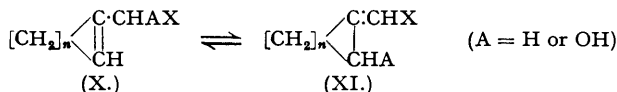
method to the oxidation of secondary ethylenic alcohols) to the ketone (IX) which has recently been synthesised by a different route (Heilbron, Jones, Toogood, and Weedon, *J.*, 1949, 1827). Both the rearranged carbinols exhibited the expected ultra-violet light absorption (see Table). As previously 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 cyclopentenyl and cyclopentylidene derivatives and their six-membered ring analogues in ethanol.

	cycloPentenyl series. ¹		cycloHexenyl series. ²	
	$\lambda_{\text{max.}}$, A.	$\epsilon_{\text{max.}}$	$\lambda_{\text{max.}}$, A.	$\epsilon_{\text{max.}}$
cycloAlk-1-enecarboxylic acid	2110	9,300	2120	11,000
Dicycloalk-1-enyl ketone	2470	11,500	2420	14,800
2-Benzylidenecycloalkanol	3300	55	3190	90
2-Benzylidenecycloalkene	2560	19,100	2430	14,200
2-Allylidenecycloalkanol	2280	8,400	2230	7,700
2-Allylidenecycloalkene	2880	20,300	2810	18,700
2-Allylidenecycloalkanol	2395	23,600	2330	27,000
4-cycloAlk-1'-enylbut-3-en-2-ol	2360	21,000	2350	23,000
4-cycloAlk-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.*).

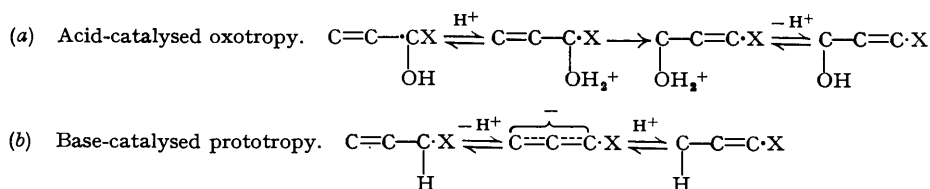
In each of the three oxotropic systems described above, as in the case of the cyclohexenyl analogues (Part V, *loc. cit.*), the conversion of the unconjugated into the conjugated isomer is practically complete and no measurable equilibria are set up. Rearrangement of the cycloalkenylvinyl- and cycloalkenylphenyl-carbinols involves the formation of a cycloalkylidene 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 cycloalkenylacetic acids and some of their derivatives to the cycloalkylidene 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.



In these systems the equilibrium might be expected to lie far to the side of the cycloalkylidene compounds (XI), for two reasons. First, the cycloalkenyl group should involve rather larger ring-strain than does the cycloalkylidene 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 cycloalkenyl \rightarrow cycloalkylidene 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 kcal./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

resonance energy of the C \cdot CHX group. The extent of this stabilisation will be somewhat dependent on X, but should be of the same order for X = CH \cdot CH $_2$, Ph, COR, and CO $_2$ R. 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.

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 *cycloalkylidene* group is thermodynamically more stable than a *cycloalkenyl* group, yet it has been shown that *cyclopentenyl*- and *cyclohexenyl*-propenylcarbinol, unlike the corresponding vinylcarbinols, rearrange under mild acid conditions to give the conjugated *cycloalkenyl* derivatives (*e.g.*, VIII) rather than the *cycloalkylidene* 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 $_2$ ·CH=CH $^-$ < CH $_3$ ·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 *cycloalkenyl*butenols (*e.g.*, VIII) will undergo a slow five-carbon oxotropy to give the isomeric *cycloalkylidene* derivatives, but we have so far been unable to establish suitable conditions for this change because of the

ease of dehydration and decomposition of the *cycloalkenyl*butenols at higher acid concentrations. Conversely, it would be expected that hydroxycycloalkylidene compounds will *not* undergo rearrangement to the isomeric *cycloalkenyl*butenols, but again we have so far been unable to establish conditions to demonstrate this because the hydroxycycloalkylidene 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-Chlorocyclopentene.—The preparation of this compound from *cyclopentanone* 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. *cyclopentanone* (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 (CaCl₂) 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-chlorocyclopentene, 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-chlorocyclopentene which on refractionation was obtained as a colourless, faintly smelling liquid, b. p. 113°/760 mm., n_D^{25} 1.4666 (Found: C, 58.4; H, 6.6; Cl, 35.4. Calc. for C₅H₉Cl: 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-chlorocyclopentene is warmed with an equivalent amount of silver nitrate in 50% aqueous ethanol, the quantitative amount of silver chloride is rapidly precipitated and *cyclopentanone*, identified as the 2:4-dinitrophenylhydrazone, m. p. 145°, is formed. Fraction (iv) consisted mainly of 1:1-dichlorocyclopentane, which after refractionation had b. p. 143°/760 mm., n_D^{25} 1.4701 (Found: Cl, 50.8. Calc. for C₅H₈Cl₂: Cl, 51.0%). Treatment of dichlorocyclopentane with aqueous-ethanolic potassium hydroxide under various conditions afforded mixtures of 1- and 3-chlorocyclopentene and unchanged starting material.

1-cyclopentenyl-lithium.—Freshly distilled 1-chlorocyclopentene (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.

cyclopent-1-enecarboxylic acid and Dicyclopent-1-enyl Ketone.—Solid carbon dioxide (200 g.) was added to an ethereal solution of *cyclopentenyl-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 *cyclopent-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 ($\epsilon = 9300$) and 2130 ($\epsilon = 9100$), inflection at 2060 Å. ($\epsilon = 5200$). 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 *dicyclopent-1-enyl ketone* (4 g., 8%), which separated from pentane in rods, m. p. 59° (Found: C, 81.1; H, 8.7. C₁₁H₁₄O 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. C₁₇H₁₈O₄N₄ requires C, 59.7; H, 5.3; N, 16.4%). Light absorption in chloroform: Max. at 3880 Å. ($\epsilon = 32,000$).

Repetition of the above experiment with a larger excess of solid carbon dioxide (600 g.) gave a higher yield of *cyclopent-1-enecarboxylic acid* (5.0 g., 13%) and a lower yield of *dicyclopent-1-enyl ketone* (0.4 g., 0.7%).

Hydrogenation of *dicyclopentenyl ketone* (1 g.) in absolute ethanol in the presence of platinum oxide resulted in the uptake of 330 ml. of hydrogen at 18°/768 mm. (Calc., 290 ml.), giving *dicyclopentyl 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°). *Dicyclopentyl 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. C₁₇H₂₂O₄N₄ requires N, 16.2%).

cyclopentenyphenylcarbinol.—Freshly distilled benzaldehyde (32 g.) in ether (50 ml.) was added during 1 hour to an ethereal solution of *cyclopenteny*-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 ($\text{Na}_2\text{SO}_4\text{-K}_2\text{CO}_3$), and fractionated from a trace of potassium carbonate, giving *cyclopentenyphenylcarbinol* (*a-cyclopent-1'-enylbenzyl alcohol*) (16 g., 30%) which distilled as a colourless liquid, b. p. $93^\circ/5.5 \times 10^{-4}$ mm., n_D^{20} 1.5650 (Found: C, 82.5; H, 8.2. $\text{C}_{12}\text{H}_{14}\text{O}$ requires C, 82.7; H, 8.1%). Light absorption in ethanol: Max. at 2510 ($\epsilon = 5900$); inflection at 2570 Å. ($\epsilon = 5600$). 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 *cyclopentenyphenylcarbinol*.

cyclopentenyphenylcarbinol and *cyclopentenyphenyl Ketone*.—Hydrogenation of *cyclopentenyphenylcarbinol* (2.5 g.) in absolute ethanol (30 ml.) in the presence of platinum oxide resulted in the uptake of 390 ml. of hydrogen at $19^\circ/770$ mm. (Calc.: 350 ml.) to give *cyclopentenyphenylcarbinol* (2 g.), b. p. $76^\circ/0.1$ mm., n_D^{20} 1.5414 (Edwards and Reid, *J. Amer. Chem. Soc.*, 1930, **52**, 3235, give b. p. 129—131°/5 mm.).

A solution of *cyclopentenyphenylcarbinol* (1.5 g.) in dioxan (30 ml.) was oxidised with potassium dichromate (0.86 g.) in 2N-sulphuric acid (30 ml.) at 0° to *cyclopentenyphenyl ketone* (1 g.), b. p. $88^\circ/8 \times 10^{-4}$ mm., n_D^{20} 1.5435 (Found: C, 82.4; H, 8.1. $\text{C}_{12}\text{H}_{14}\text{O}$ requires C, 82.7; H, 8.1%). Light absorption in hexane: Max. at 2380, 2680, 2800, and 3300 Å.; $\epsilon = 11,800, 800, 800$, 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. $\text{C}_{18}\text{H}_{18}\text{O}_4\text{N}_4$ requires C, 61.0; H, 5.1; N, 15.8%). Light absorption in ethanol: Max. at 3690 Å., $\epsilon = 24,800$. [Added 13.3.51]. *cyclopentenyphenyl 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-Benzylidenecyclopentanol.—A solution of *cyclopentenyphenylcarbinol* (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-benzylidenecyclopentanol* (3.5 g.), b. p. $91^\circ/3 \times 10^{-4}$ mm., which solidified when kept and crystallised from pentane in colourless plates, m. p. 86° (Found: C, 82.4; H, 8.2. $\text{C}_{12}\text{H}_{14}\text{O}$ requires C, 82.7; H, 8.1%). Light absorption in ethanol: Max. at 2510 and 2560 Å.; $\epsilon = 19,100$ and 19,100 respectively; inflection at 2640 Å., $\epsilon = 16,400$. The *p-nitrobenzoate* crystallised from light petroleum (b. p. $60\text{--}80^\circ$) in colourless plates, m. p. 71° (Found: C, 70.4; H, 5.5; N, 4.5. $\text{C}_{15}\text{H}_{11}\text{O}_4\text{N}$ requires C, 70.6; H, 5.3; N, 4.3%). Light absorption in ethanol: Max. at 2510 and 2570 Å.; $\epsilon = 30,700$ and 34,900 respectively; inflection at 2640 Å.; $\epsilon = 27,500$.

When a solution of *2-benzylidenecyclopentanol* (0.5 g.) was warmed with a solution of 2:4-dinitrophenylhydrazine in concentrated sulphuric acid and methanol, the 2:4-dinitrophenylhydrazone of *2-benzylidenecyclopentanone* 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-Benzylidenecyclopentanone.—*2-Benzylidenecyclopentanol* (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-benzylidenecyclopentanone* (1.3 g.), b. p. $120^\circ/8 \times 10^{-4}$ mm., which solidified on storage and crystallised from aqueous methanol in plates, m. p. 48° (Found: C, 92.3; H, 7.8. $\text{C}_{12}\text{H}_{12}$ requires C, 92.3; H, 7.7%). Light absorption in ethanol: see Table.

2-Benzylidenecyclopentanone.—(a) *2-Benzylidenecyclopentanol* (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-benzylidenecyclopentanone* (1.5 g.), which crystallised from light petroleum (b. p. $40\text{--}60^\circ$) 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. $\text{C}_{18}\text{H}_{18}\text{O}_4\text{N}_4$ requires C, 61.4; H, 4.6; N, 15.9%). Light absorption in ethanol: Max. at 3880 Å.; $\epsilon = 30,100$.

(b) Benzaldehyde (5 g.) in 50% aqueous ethanol (50 ml.) was added dropwise to a vigorously stirred solution of *cyclopentanone* (25 g.) in 50% aqueous-ethanolic 0.1N-potassium hydroxide (200 ml.). The precipitate of dibenzylidenecyclopentanone was filtered off and the solution was diluted with water and extracted with ether. Fractionation of the ethereal extract afforded *2-benzylidenecyclopentanone* (0.5 g.), b. p. $170^\circ/2 \times 10^{-4}$ mm., which slowly solidified and crystallised from light petroleum (b. p. $40\text{--}60^\circ$) in needles, m. p. 66° (Vorländer and Hobohm, *Ber.*, 1896, **29**, 1836, give m. p. 68°).

cyclopentenyvinylcarbinol.—Acraldehyde (14 g.) in ether (30 ml.) was slowly added to an ethereal solution of *cyclopenteny*-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 ($\text{Na}_2\text{SO}_4\text{-K}_2\text{CO}_3$), and fractionated, giving *cyclopentenyvinylcarbinol* (*1-cyclopentenyallyl alcohol*) (13 g., 32%) as a colourless liquid, b. p. $43^\circ/0.5$ mm., n_D^{20} 1.4890 (Found: C, 77.1; H, 9.6. $\text{C}_8\text{H}_{12}\text{O}$ requires C, 77.4; H, 9.7%). Light absorption in ethanol: $\epsilon < 1000$ in the region 2200—4000 Å.

2-Allylidenecyclopentanol.—*cyclopentenyvinylcarbinol* (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

through a column. The aqueous residue was extracted with ether, and the ethereal extract was dried and fractionated, giving 2-allylidene-cyclopentanol (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*-Propylcyclopentanol and 2-*n*-Propylcyclopentanone.—Hydrogenation of 2-allylidene-cyclopentanol (5.1 g.) in absolute ethanol (50 ml.) in the presence of platinum oxide resulted in the uptake of 2100 ml. of hydrogen at 22°/755 mm. (Calc. 2000 ml.), to give 2-*n*-propylcyclopentanol (4.5 g.), b. p. 87°/30 mm., n_D^{23} 1.4540 (Vavon and Flurer, *Bull. Soc. chim.*, 1929, 45, 754, give b. p. 79—80°/10 mm., n_D^{20} 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*-Propylcyclopentanol (2.6 g.) in acetone (30 ml.) was treated with a solution of potassium dichromate (2.5 g.) in 2*N*-sulphuric acid (100 ml.) at 0°. Isolation of the product in the usual manner gave 2-*n*-propylcyclopentanone (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^{19} 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 Å.; $\epsilon = 22,300$. The m. p.s of both derivatives were undepressed on admixture with those of an authentic sample of 2-*n*-propylcyclopentanone, prepared according to Vavon and Flurer (*loc. cit.*) by the condensation of cyclopentanone with propaldehyde to give 2-propylidene-cyclopentanone, followed by catalytic hydrogenation.

In an attempt to prepare 2-*n*-propylcyclopentanone by direct alkylation of cyclopentanone by the method of Braude and Coles (*J.*, 1950, 2014), a mixture of cyclopentanone (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-cyclopentylidene-2-*n*-propylcyclopentanone (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 Å.; $\epsilon = 3800$ and 200 respectively. The relatively low intensity of the 2280-Å. band may be ascribed to steric inhibition of resonance owing to interference between the carbonyl group and the α -hydrogen atom of the cyclopentylidene group (cf. Braude *et al.*, *J.*, 1949, 1890); there was no indication of admixture with the unconjugated isomer, 5-cyclopent-1'-enyl-2-*n*-propylcyclopentanone, as observed in the case of cyclohexylidene-cyclohexanone (cf. Evans and Gillam, *J.*, 1941, 815; Bagchi *et al.*, *J. Amer. Chem. Soc.*, 1949, 71, 990).

cyclopent-1'-enylpropenylcarbinol.—Freshly distilled crotonaldehyde (25 g.) in ether (50 ml.) was added dropwise to an ethereal solution of cyclopentenyl-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 cyclopent-1'-enylpropenylcarbinol (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: $\epsilon < 1000$ in the region 2200—4000 Å. 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 cyclopentenylpropenylcarbinol (1.7 g.) in absolute ethanol (60 ml.) in the presence of platinum oxide resulted in the uptake of 580 ml. of hydrogen at 18°/768 mm. (Calc., 600 ml.) to give cyclopentylpropylcarbinol (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-cyclopent-1'-enylbut-3-en-2-ol.—A solution of cyclopentenylpropenylcarbinol (4 g.) in 60% aqueous acetone 0.1*M*-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-cyclopent-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-cyclopent-1'-enylbut-3-en-2-one.—4-cyclopent-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-cyclopent-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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