413. *Alkenylation by Use of Lithium Alkenyls. Part IV. The Condensation of* cyclo*Hexenyl-lithium with Aldehydes and Ketones, and Some Reactions of the Resulting Carbinols.* (*Studies in Molecular Rearrangement. Part V.*)

By E. A. BRAUDE and J. A. COLES.

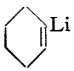
1-Chloro*cyclo*hexene, when highly purified, reacts readily with lithium in ether to give *cyclo*hexenyl-lithium (I), carboxylation of which affords *cyclo*hexene-1-carboxylic acid (II) and di*cyclo*hex-1-enyl ketone (III). Condensation of *cyclo*hexenyl-lithium with benzaldehyde, benzophenone, acraldehyde, or crotonaldehyde furnishes the expected carbinols, the constitution of which is proved by catalytic hydrogenation, in 40—60% yields.

On treatment with dilute acids, *cyclo*hexenylphenyl- and *cyclo*hexenyldiphenyl-carbinol (IV) undergo oxotropic rearrangement to the *cyclo*hexylidene derivatives (V). The latter are dehydrated to the corresponding semicyclic dienes (VI), which are dehydrogenated to diphenyl- and triphenyl-methane, respectively. *cyclo*Hexenylvinylcarbinol (VIII; R = H) similarly undergoes rearrangement to the *cyclo*hexylidene derivative (IX; R = H), the constitution of which is proved by conversion into 2-*n*-propyl*cyclo*hexanone. *cyclo*Hexenylpropenylcarbinol (VIII; R = Me), unlike its lower homologue, undergoes rearrangement with migration of the hydroxyl group into the side chain, to give the isomeric carbinol (X; R = Me) which is converted by Oppenauer oxidation into the ketone (XI), a known lower homologue of β-ionone.

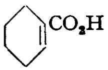
THIS paper describes, in part, the preparation and some reactions of *cyclo*hexenyl-lithium. The scope of synthetic applications of lithium alkenyls is thus extended to cyclic derivatives.

Preparation and Carboxylation of cyclo*Hexenyl-lithium.*—In the preparation of acyclic lithium alkenyls (Parts I—III, preceding papers), the easily accessible alkenyl bromides can be employed. In the *iso*cyclic series, the chlorides are much more readily prepared and fortunately proved very suitable for the purpose in hand. 1-Chloro*cyclo*hexene, when highly purified by fractionation, reacts smoothly with metallic lithium in ether, and the good yields of condensation products obtained with carbonyl compounds (see below) show that the chloride is converted into *cyclo*hexenyl-lithium to the extent of 60% or more. In contrast to the behaviour of *iso*butenyl bromide (Part I), metalation of *cyclo*hexenyl chloride with lithium is not accompanied by a coupling reaction, and no di*cyclo*hexenyl is formed. *cyclo*Hexenyl chloride did not react appreciably with magnesium, or with sodium in ether, even in the presence of benzophenone, which was recovered unchanged.

An ethereal solution of *cyclo*hexenyl-lithium with excess of solid carbon dioxide afforded a mixture of the expected carboxylic acid, *cyclo*hexene-1-carboxylic acid (II), and the expected ketone, di(*cyclo*hex-1-enyl) ketone (III). The acid was identified by its melting point and as the amide. The ketone was characterised by the 2 : 4-dinitrophenylhydrazone, but, like other



(I.)



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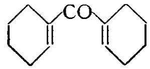
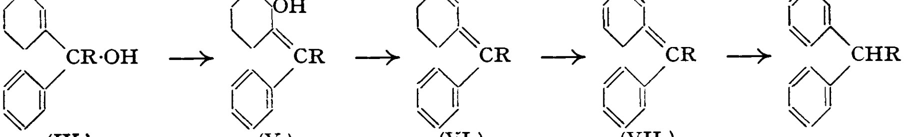


(III.)

dialkenyl ketones (cf. Part III), it did not form a semicarbazone. The ketone readily absorbed two moles of hydrogen in the presence of platinum oxide to give di*cyclo*hexyl ketone. The structures of the acid (II) and of the ketone (III) were also confirmed by their ultra-violet light absorption properties (see Table) characteristic of an αβ-ethylenic acid and of a di-αβ-unsaturated ketone, respectively. No indication was obtained of the formation of any unconjugated isomers, and the lithium metalation of the halide is thus not accompanied by any migration of the ethylenic double bond.

Whereas alkyl halides are often equally reactive towards lithium in hydrocarbon solvents and in ether (Gilman, Moore, and Baine, *J. Amer. Chem. Soc.*, 1941, **63**, 2479; Meals, *J. Org. Chem.*, 1944, **9**, 211), *cyclo*hexenyl chloride did not react appreciably with lithium in light petroleum (b. p. 60—80°). In the presence of benzaldehyde, the dehydration product (VI; R = H; see below) of the expected carbinol was obtained in small yield. It has been claimed (Wittig and Harborth, *Ber.*, 1944, **77**, *B*, 306) that *cyclo*hexenyl-lithium is an intermediate in the formation of phenyl*cyclo*hexene from *cyclo*hexenyl chloride and phenyl-lithium, but as has already been pointed out (Part I) evidence in support of this assertion appears to be lacking.

Preparation, Rearrangement, and Dehydration of cyclo*Hexenylphenyl- and* cyclo*Hexenyldiphenyl-carbinol.*—*cyclo*Hexenyl-lithium in ethereal solution condensed smoothly with benzaldehyde to give *cyclo*hexenylphenylcarbinol (IV; R = H), a high-boiling liquid, in 40% yield. The structure of the carbinol is proved by its ultra-violet light absorption properties, which are similar to those of benzyl alcohol, and by its hydrogenation to *cyclo*hexylphenylcarbinol. On treatment with dilute hydrochloric acid in aqueous acetone (IV; R = H) readily underwent the expected oxotropic rearrangement (cf. Braude, Jones, and Stern, *J.*, 1946, 396; Braude and Timmons, Part I) to give 2-benzylidene*cyclo*hexanol (V; R = H), a low-melting solid, which was characterised by the *p*-nitrobenzoate and exhibits ultra-violet light absorption properties typical of styryl derivatives (see Table). On distillation from potassium hydrogen sulphate, the *cyclo*hexanol was dehydrated, though incompletely, to 3-benzylidene*cyclo*hexene (VI; R = H), which exhibits ultra-violet light absorption properties typical of a 1-phenylbutadiene (see Table). Finally, the diene (VI) was dehydrogenated, either by bromination with *N*-bromosuccinimide followed by dehydrobromination with diethylaniline or, in better yield, by heating at 200° with palladised charcoal (Linstead and Thomas, *J.*, 1940, 1127) to diphenylmethane, the hypothetical intermediate triene (VII; R = H) undergoing immediate prototropic rearrangement to the fully benzenoid hydrocarbon. The diene (VI; R = H) was also obtained in low yield (20%) when lithium, *cyclo*hexenyl chloride, and benzaldehyde reacted together in refluxing light petroleum (b. p. 60—80°), the intermediate lithium derivative of the carbinol (IV; R = H) possibly eliminating lithium hydroxide under these conditions.

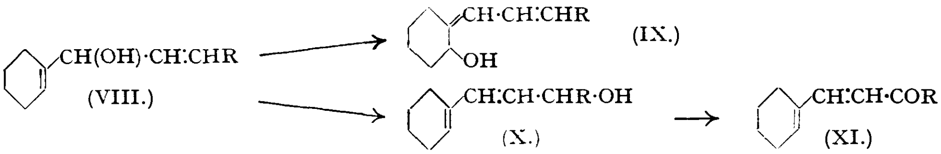


(IV.) (V.) (VI.) (VII.)

In a similar manner, condensation of *cyclo*hexenyl-lithium with benzophenone afforded the solid *cyclo*hexenyldiphenylcarbinol (IV; R = Ph) in 65% yield. Unlike the monophenyl derivative, it could not be hydrogenated over a platinum oxide or a palladium–calcium carbonate catalyst at ordinary pressure, or over a Raney nickel catalyst at 20 atmospheres, presumably owing to " catalyst hindrance " imposed by the additional phenyl group (cf. Linstead *et al.*, *J. Amer. Chem. Soc.*, 1942, **64**, 1985). On treatment with dilute hydrochloric acid in aqueous acetone, the carbinol underwent rapid oxotropic rearrangement to 2-benzhydrylidene*cyclo*hexanol (V; R = Ph) which is readily dehydrated to 3-benzhydrylidene*cyclo*hexene (VI; R = Ph). The *cyclo*hexanol (V; R = Ph), which was characterised as the 3 : 5-dinitrobenzoate, exhibits ultra-violet light absorption similar to 1 : 1-diphenylethylene (see Table) and, on ozonisation, affords benzophenone in good yield. The diene (VI; R = Ph) also exhibits the expected light absorption properties and is smoothly dehydrogenated by palladised charcoal at 200° to triphenylmethane.

Preparation and Rearrangement of cyclo*Hexenylvinyl- and* cyclo*Hexenylpropenyl-carbinol.*—Condensation of *cyclo*hexenyl-lithium with acraldehyde or crotonaldehyde afforded the expected carbinols (VIII; R = H or Me) in 45% and 60% yields, respectively. Their constitution was confirmed by the lack of high-intensity light absorption in the 2300-A. region and, in the case of *cyclo*hexenylvinylcarbinol, by catalytic hydrogenation to *cyclo*hexylethylcarbinol, followed by oxidation of the latter to *cyclo*hexyl ethyl ketone.

On treatment with dilute acids, the carbinols (VIII) are converted into conjugated isomers which exhibit high-intensity maxima near 2350 A. The oxotropic rearrangement could theoretically give rise to two isomers (IX) and (X), depending on whether the hydroxyl group migrates into the ring or along the side chain. It was shown in Part II that, in the acyclic series, the hydroxyl group in an unsymmetrical dialkenylcarbinol migrates initially to the more highly substituted γ-carbon atom. It would, therefore, be expected that the first rearrangement product of *cyclo*hexenylvinylcarbinol (VIII; R = H) should be (IX; R = H) rather than (X; R = H). This is found to be the case, 2-allylidene*cyclo*hexanol (IX; R = H) being the sole product obtained on rearrangement in aqueous acetone containing hydrochloric acid. The structure of 2-allylidene*cyclo*hexanol was established by catalytic hydrogenation to 2-*n*-propyl*cyclo*hexanol and oxidation of the latter to 2-*n*-propyl*cyclo*hexanone. An authentic sample of the ketone was prepared by treating *cyclo*hexanone with *n*-propyl bromide in the presence of potassium *tert.*-butoxide under conditions recommended by Johnson *et al.* (*J. Amer. Chem. Soc.*, 1948, **70**, 3021; 1949, **71**, 1384) for the Stobbe condensation, and was characterised as the 2 : 4-dinitrophenylhydrazone.



With *cyclo*hexenylpropenylcarbinol (IX; R = Me), both γ-carbon atoms can be regarded as monoalkyl-substituted, but the electron accession at the γ-carbon atom in the ring will be smaller than that at the γ-carbon atom in the side chain, since the hyperconjugative effect of a methyl group is larger than that of any other alkyl group. Moreover, migration into the ring would be expected to be impeded by the strain accompanying the formation of an exocyclic double bond. This factor is evidently not one of predominant influence, since it does not prevent the formation of (IX) rather than (X) from the lower homologue, *cyclo*hexenylvinylcarbinol; but it may contribute in determining the direction of rearrangement in *cyclo*hexenylpropenylcarbinol where the alkyl substitution of the two γ-carbon atoms is more evenly balanced. In agreement with these considerations, *cyclo*hexenylpropenylcarbinol rearranges in aqueous acetone containing hydrochloric acid to 4-*cyclo*hex-1′-enylbut-3-en-2-ol (X; R = Me), the constitution of which was proved by Oppenauer oxidation to 4-*cyclo*hex-1′-enylbut-3-en-2-one (XI; R = Me), a lower homologue of β-ionone recently synthesized by two other routes by Heilbron, Jones, Richardson, and Sondheimer (*J.*, 1949, 737). A considerable proportion of the di-ether of (X; R = Me) is also formed. Self-etherification of this type has also been observed in several other related cases (cf. Heilbron, Jones, and Weedon, *J.*, 1945, 81; Braude, Fawcett, and Newman, *J.*, 1950, 793); further rearrangement in aqueous ethanol instead of aqueous acetone gives only the ethyl ether of (X; R = Me). Kinetic studies of the various rearrangements described in this paper are in progress and will be reported separately.

The ultra-violet light absorption properties of the various derivatives are collected in the Table, together with data for appropriate reference compounds.

The extension of this work to other cyclic lithium alkenyls (particularly *cyclo*pentenyl- and alkylated *cyclo*hexenyl-lithium derivatives) and their application to the synthesis of terpenoid compounds is now under investigation.

	$\lambda_{max.}$, A.*	$\varepsilon_{max.}$
*cyclo*Hexene-1-carboxylic acid (I)	2120	11,000
Crotonic acid	2000	10,000 [1]
Di*cyclo*hexenyl ketone (II)	2420 3190	14,800 90
Dipropenyl ketone	2480 3360	16,500 [2] 80
2-Benzylidene*cyclo*hexanol (V; R = H)	2430	14,200
β-Methylstyrene	2460	12,000 [3]
2-Benzhydrylidene*cyclo*hexanol (V; R = Ph)	2400	13,200
1 : 1-Diphenylethylene	2500	11,000 [4]
3-Benzylidene*cyclo*hexene (VI; R = H)	2230 2810	7,700 18,700
1-Phenylbutadiene	2230 2800	12,000 [5] 28,300
3-Benzhydrylidene*cyclo*hexene (VI; R = Ph)	2260 2810	14,800 22,000
2-Allylidene*cyclo*hexanol (IX; R = H)	2330	27,000
Allylidene*cyclo*hexane	2365	8,000 [6]
4-*cyclo*Hex-1-enylbut-3-en-2-ol	2350	23,000
1-Vinyl*cyclo*hexene	2300	8,500 [6]

* Main maxima in ethanol solution.

[1] Mohler and Lohr, *Helv. Chim. Acta*, 1938, **21**, 485 (in water). [2] Braude and Coles, Part V (to be published). [3] Ramart-Lucas and Amagat, *Bull. Soc. chim.*, 1932, **51**, 108. [4] Arends, *Ber.*, 1931, **64**, 1936. [5] Braude, Jones, and Stern, *J.*, 1947, 1087. [6] Booker, Evans, and Gillam, *J.*, 1940, 1453.

EXPERIMENTAL.

(M.p.s were determined on a Kofler block and are corrected.)

cyclo*Hex*-1-*enyl-lithium*.—1-Chloro*cyclo*hexene of high purity is required. Although the chloride has been obtained by several workers (Skita and Ritter, *Ber.*, 1911, **44**, 674; Favorski, *J. Gen. Chem. Russia*, 1936, **6**, 720; Bloomfield, *J.*, 1944, 114; Mousseron, Winternitz, and Jacquier, *Compt. rend.*, 1946, **223**, 36), its preparation does not appear to have been adequately described. *cyclo*Hexanone (250 ml.) was added, during 1—2 hours, to high-grade phosphorus pentachloride (500 g.) contained in a 1-l. flask, the flask being cooled in ice-water and frequently shaken. Next day, the contents of the flask were added drop-wise to water (3 l.) and the mixture was extracted with ether (1 l.). The ethereal solution was dried ($CaCl_2$), the ether removed by distillation, and the product fractionated, to give the chloride as a colourless liquid (180 g., 60%), b. p. 95°/160 mm., n_D^{20} 1·4798. It gives no immediate precipitate with alcoholic silver nitrate, but decomposes slowly when kept at room temperature, and must be refractionated immediately before use.

For the metalation, the freshly-distilled chloride (58 g., 0·5 mol.) was added slowly to a stirred suspension of finely-cut lithium (6·9 g., 1 mol.) in sodium-dried ether (1 l.) under nitrogen. Reaction set in after an induction period of *ca.* $\frac{1}{2}$—1 hour, the solution becoming slightly turbid. A little later, the solution assumed a greenish or bluish colour. Stirring was continued overnight, almost the whole of the metal being consumed. A small amount of unchanged *cyclo*hexenyl chloride (not exceeding 5%) was usually recovered from subsequent condensations.

cyclo*Hexene*-1-*carboxylic Acid* (II) *and Di*(cyclo*hex*-1-*enyl*) *Ketone* (III).—Excess of solid carbon dioxide (300 g.) was added to a solution of *cyclo*hexenyl-lithium (from Li, 6·9 g.) in ether. After being stirred overnight, the solution was acidified with dilute aqueous hydrochloric acid. The ethereal layer was separated and extracted with aqueous sodium carbonate. The alkaline extract was acidified and the *cyclo*hexene-1-carboxylic acid (3 g., 5%) which separated was crystallised from light petroleum (b. p. 60—80°) and then had m. p. 37° (von Auwers and Krullpfeiffer, *Ber.*, 1915, **48**, 1396, give m. p. 38—39°). Light absorption in ethanol: Max. 2120 A., ε = 11,000; inflections 2070 and 2170 A., ε = 8,000 and 10,500, respectively. The amide separated from water in plates, m. p. 136° (Found: C, 66·6; H, 8·8; N, 11·0. Calc. for $C_7H_{11}ON$: C, 67·2; H, 8·8; N, 11·2%) (Einhorn, *Ber.*, 1893, **26**, 457, gives m. p. 127°).

The ethereal solution was evaporated to give *di*(cyclo*hex*-1-*enyl*) *ketone*, which separated from light petroleum (b. p. 60—80°) in stout, colourless prisms, m. p. 50° (Found: C, 82·3; H, 9·8. $C_{13}H_{18}O$ requires C, 82·2; H, 9·5%). Light absorption: see Table. The 2 : 4-*dinitrophenylhydrazone* was chromatographed on alumina from benzene–chloroform and, after crystallisation from methanol, had m. p. 159° (transition at 147°) (Found: C, 61·0; H, 6·0; N, 15·3. $C_{19}H_{22}O_4N_4$ requires C, 61·6; H, 6·0; N, 15·1%). Light absorption in chloroform: Max. 2560 (ε = 15,500) and 3880 A. (ε = 30,600). No semicarbazone was obtained under the usual conditions.

Hydrogenation of the ketone (3·7 g.) in ethyl acetate (50 ml.) in the presence of platinic oxide resulted in the uptake of 900 ml. of hydrogen at 17°/766 mm. (Calc., 950 ml.), giving di*cyclo*hexyl ketone (3 g.), b. p. 103°/0·3 mm., n_D^{20} 1·4891. The oxime, crystallised from ethanol, had m. p. 164° (Gauerka and Marvel, *J. Amer. Chem. Soc.*, 1928, **50**, 1180, give 158—160°) and the semicarbazone, crystallised from aqueous alcohol, had m. p. 195—196° (Danilow and Venus-Danilowa, *Ber.*, 1929, **62**, 2660, give m. p. 195°).

cyclo*Hexenylphenylcarbinol* (IV; R = H).—Freshly distilled benzaldehyde (53 g., 0·5 mol.) in ether (50 ml.) was added during 1 hour to a solution of *cyclo*hexenyl-lithium (from Li, 6·9 g.) in ether at 0°. After the mixture had been stirred overnight, saturated aqueous ammonium chloride (550 ml.) was added. The ethereal layer was separated, dried (Na_2SO_4–K_2CO_3), and worked up in the usual manner to give cyclo*hexenylphenylcarbinol* (36 g., 40%), b. p. 116°/2 × 10^{-4} mm., n_D^{18} 1·5589 (Found : C, 83·2; H, 8·8. $C_{13}H_{16}O$ requires C, 83·0 ; H, 8·5%). Light absorption in ethanol : Max. 2450 A., ε = 1,700.

Hydrogenation of the carbinol (3·4 g.) in ethyl acetate (50 ml.) in the presence of platinic oxide resulted in the uptake of 420 ml. of hydrogen at 18°/768 mm. (Calc., 450 ml.) to give *cyclo*hexylphenylcarbinol (3 g.), b. p. 128°/2 mm., which solidified when kept and crystallised from pentane in colourless prisms, m. p. 38—40° (Sabatier and Mailhe, *Compt. rend.*, 1904, **139**, 345, give m. p. 41°).

2-*Benzylidene*cyclo*hexanol* (V; R = H).—A solution of *cyclo*hexenylphenylcarbinol (4 g.) in 60% aqueous acetone (100 ml.) containing hydrochloric acid (0·1M.) was kept for 18 hours at room temperature. After neutralisation with aqueous potassium carbonate solution, the acetone was distilled off through a column, and the residue extracted with ether. Fractionation of the ethereal extract afforded 2-*benzylidene*cyclo*hexanol* (3·5 g.), b. p. 110°/10^{-3} mm., which solidified when kept and crystallised from aqueous methanol in colourless needles, m. p. 62° (Found : C, 82·9; H, 8·8. $C_{13}H_{16}O$ requires C, 83·0; H, 8·5%). Light absorption in ethanol: see Table. The p-*nitrobenzoate* crystallised from light petroleum (b. p. 60—80°) and had m. p. 124° (Found : N, 4·3. $C_{20}H_{19}O_4N$ requires N, 4·2%).

3-*Benzylidene*cyclo*hexene* (VI; R = H).—(*a*) The above carbinol was distilled from potassium hydrogen sulphate in a high vacuum. The product was again distilled from potassium hydrogen sulphate, to give 3-*benzylidene*cyclo*hexene*, b. p. 81°/10^{-4} mm., n_D^{21} 1·6190 (Found : C, 91·5; H, 8·5. $C_{13}H_{14}$ requires C, 91·7; H, 8·3%). Light absorption : see Table.

(*b*) 1-Chloro*cyclo*hexene (29 g., 0·25 mol.), lithium (3·5 g., 0·5 mol.) and benzaldehyde (27·5 g.) in sodium-dried light petroleum (b. p. 60—80°) (500 ml.) were stirred for 20 hours in an atmosphere of nitrogen. Only 3-benzylidene*cyclo*hexene (8 g., 20%) was obtained.

Diphenylmethane.—(*a*) 3-Benzylidene*cyclo*hexene (1 g.) was refluxed with *N*-bromosuccinimide (4 g.) and benzoyl peroxide (20 mg.) in carbon tetrachloride (70 ml.) for 3 hours, and the resulting dibromide was heated with diethylaniline (5 ml.) for 1 hour at 100°. The impure diphenylmethane (0·3 g.) thus obtained was oxidised with potassium dichromate in sulphuric acid to benzophenone (2 : 4-dinitrophenylhydrazone, m. p. 238—239°, undepressed on admixture with an authentic specimen).

(*b*) 3-Benzylidene*cyclo*hexene (1 g.) was heated with a palladium–charcoal catalyst (0·3 g.; Linstead and Thomas, *J.*, 1940, 1127) at 200° for 22 hours in a slow stream of nitrogen. On ether-extraction, diphenylmethane (0·6 g.) was isolated and converted into benzophenone 2 : 4-dinitrophenylhydrazone, m. p. 238—239°, as above.

cyclo*Hexenyldiphenylcarbinol* (IV; R = Ph).—Benzophenone (91 g.) in ether (200 ml.) was added to *cyclo*hexenyl-lithium (from Li, 6·9 g.) in ether at 0°. After 18 hours' stirring, saturated aqueous ammonium chloride solution (500 ml.) was added and the ethereal layer was separated and dried. On removal of the ether, the residue solidified and, after being washed once with light petroleum (b. p. 60—80°), crystallised from aqueous ethanol to give cyclo*hexenyldiphenylcarbinol* (58 g., 60%) as white prisms, m. p. 154—155° (Found : C, 86·1; H, 7·8. $C_{19}H_{20}O$ requires C, 86·4; H, 7·6%). Light absorption in ethanol : Max. at 2560, 2580, and 2640 A., ε = 420, 450, and 345. A solution of the carbinol in benzene assumes a deep yellow colour on addition of one drop of concentrated sulphuric acid.

The carbinol was not hydrogenated in methanol in the presence of platinic oxide or a palladium–charcoal catalyst at ordinary pressure, or with a Raney nickel catalyst at 20 atmospheres' pressure.

2-*Benzhydrylidene*cyclo*hexanol* (V; R = Ph), 2-*Benzhydrylidene*cyclo*hexene* (VI; R = Ph), *and Triphenylmethane.*—The above carbinol (3 g.) was dissolved in 80% aqueous acetone (100 ml.) containing hydrochloric acid (0·1M.) and the solution set aside for 18 hours at room temperature. The solution was neutralised with aqueous potassium carbonate, the acetone removed by distillation through a column, and the residue extracted with ether. The ether was evaporated off, and the oil which remained was extracted with a little pentane. The insoluble portion of 2-*benzhydrylidene*cyclo*hexanol* crystallised from ethanol in colourless prisms, m. p. 110—111° (Found : C, 86·6; H, 7·7. $C_{19}H_{20}O$ requires C, 86·4; H, 7·6%). Light absorption : see Table. Ozonolysis of the carbinol (2 g.) in carbon tetrachloride (40 ml.) for 18 hours, followed by decomposition of the ozonide with boiling water (100 ml.) and zinc dust (3 g.), gave an oily product which on treatment with phenylhydrazine afforded only benzophenone phenylhydrazone (1·3 g., 62%), m. p. 138—139°, undepressed on admixture with an authentic specimen.

The pentane-soluble portion gave 3-*benzhydrylidene*cyclo*hexene* (1 g.), which crystallised from aqueous ethanol as a pale yellow solid, m. p. 67—68° (Found : C, 92·3; H, 7·4. $C_{19}H_{18}$ requires C, 92·7; H, 7·3%). Light absorption : see Table. The hydrocarbon (0·8 g.) was heated with a palladium–charcoal catalyst (0·25 g.) at 200° for 20 hours, as described above. Extraction with hot light petroleum (b. p. 80—100°) afforded triphenylmethane, m. p. 92·5°, undepressed on admixture with an authentic specimen.

cyclo*Hexenylvinylcarbinol* (VIII; R = H).—Acraldehyde (28 g., 0·5 mol.) in ether (30 ml.) was slowly added to *cyclo*hexenyl-lithium (from Li, 6·9 g.) in ether at 0°. Stirring was continued for 1 hour at room temperature and the products were worked up in the usual manner. After separation of a considerable quantity of solid polymeric material, cyclo*hexenylvinylcarbinol* (26 g., 40%) was obtained as a colourless liquid, b. p. 94°/13 mm., 67°/0·4 mm., n_D^{20} 1·4986 (Found : C, 78·3; H, 10·3. $C_9H_{14}O$ requires C, 78·3; H, 10·2%). Light absorption in ethanol : ε < 200 in the region 2200—4000 A.

1-cyclo*Hexylpropan*-1-*ol*.—Hydrogenation of *cyclo*hexenylvinylcarbinol (9·45 g.) in absolute ethanol (60 ml.) in the presence of platinic oxide resulted in the uptake of 3200 ml. of hydrogen at 17°/766 mm. (Calc., 3300 ml.) to give 1-cyclo*hexylpropan*-1-*ol* (8·5 g.), b. p. 88°/16 mm., n_D^{19} 1·4662 (Found : C, 75·6;

H, 12·5. $C_9H_{18}O$ requires C, 76·1; H, 12·7%). The carbinol (5 g.) was oxidised with potassium dichromate in sulphuric acid to *cyclo*hexyl ethyl ketone (3 g.), b. p. 82°/16 mm., n_D^{21} 1·4528 (Colonge and Duroux, *Bull. Soc. chim.*, 1940, **7**, 459, give b. p. 79°/9 mm.). The ketone was identified by the oxime, m. p. 70—72° (Colonge and Duroux give m. p. 72°), and by the semicarbazone, m. p. 154° (Colonge and Duroux give 151°).

2-*Allylidene*cyclo*hexanol* (IX; R = H).—A solution of *cyclo*hexenylvinylcarbinol (10 g.) in 60% aqueous acetone (200 ml.) containing hydrochloric acid (0·025M.), kept for 18 hours at room temperature, gave 2-*allylidene*cyclo*hexanol* (7·5 g.) as a colourless liquid, b. p. 109°/16 mm., n_D^{20} 1·5340, which partly solidified on storage; it had m. p. 41—43° (Found: C, 78·5; H, 10·3. $C_9H_{14}O$ requires C, 78·3; H, 10·3%). Light absorption: see Table.

2-n-*Propyl*cyclo*hexanone*.—(*a*) Hydrogenation of 2-allylidene*cyclo*hexanol (2·45 g.) in ethyl acetate (15 ml.) and ethanol (15 ml.) in the presence of platinic oxide resulted in the uptake of 850 ml. of hydrogen at 18°/771 mm. (Calc., 900 ml.), to give 2-*n*-propyl*cyclo*hexanol, b. p. 88°/16 mm., n_D^{19} 1·4677 (Fujise, *Chem. Zentr.*, 1929, I, 2991, reported b. p. 84°/6 mm., n_D^{25} 1·4604). The alcohol was oxidised by potassium dichromate in sulphuric acid to 2-*n*-propyl*cyclo*hexanone, b. p. 80°/16 mm., n_D^{16} 1·4552 (Vavon and Anziani, *Bull. Soc. chim.*, 1927, **41**, 1642, give b. p. 84°/13 mm., n_D^{13} 1·4558). The ketone gave a semicarbazone, m. p. 118—121°, and a 2 : 4-dinitrophenylhydrazone, m. p. 153—154°, both undepressed on admixture with the authentic specimens described below.

(*b*) *cyclo*Hexanone (6 g.) and *n*-propyl bromide (8 g.) were added, in one lot, to a boiling solution of potassium *tert.*-butoxide (from potassium, 2·8 g.) in *tert.*-butanol. After 20 minutes, the solution was allowed to cool and then acidified with ice-cold hydrochloric acid. Isolation of the product in the usual manner afforded 2-*n*-propyl*cyclo*hexanone (2·5 g., 30%), b. p. 86°/16 mm., n_D^{21} 1·4502. The semicarbazone, crystallised from aqueous ethanol, had m. p. 116—118° (Found: C, 61·6; H, 9·7; N, 21·1. Calc for $C_{10}H_{19}ON_3$: C, 61·0; H, 9·5; N, 21·3%) (Vavon and Anziani, *loc. cit.*, give m. p. 134°; Dice, Loveless, and Cates, *J. Amer. Chem. Soc.*, 1949, **71**, 3546, give m. p. 119—120°). The 2 : 4-*dinitrophenylhydrazone* was chromatographed on alumina from benzene–chloroform and crystallised from ethyl acetate in red plates, m. p. 153—154° (Found: C, 56·4; H, 6·3; N, 17·6. $C_{15}H_{20}O_4N_4$ requires C, 56·3; H, 6·3; N, 17·6%). Light absorption in chloroform: Max. 3680 A., $\varepsilon = 22{,}400$.

cyclo*Hexenylpropenylcarbinol* (VIII; R = Me).—Freshly distilled crotonaldehyde (35 g., 0·5 mol.) in ether (50 ml.) was added to *cyclo*hexenyl-lithium (from Li, 6·9 g.) in ether at 0°. Stirring was continued for 26 hours and the product was worked up in the usual manner. cyclo*Hexenylpropenylcarbinol* (42 g., 55%) distilled as a colourless liquid, b. p. 88°/0·8 mm., n_D^{19} 1·4998 (Found: C, 78·7; H, 10·7. $C_{10}H_{16}O$ requires C, 79·0; H, 10·5%). Light absorption in ethanol: $\varepsilon < 200$ in the region 2200—4000 A.

Rearrangement of (VIII; R = Me).—A solution of the above carbinol (5 g.) in 60% aqueous acetone (100 ml.) containing hydrochloric acid (0·1M.) was set aside for 24 hours at room temperature. The products were fractionated to give 4-cyclo*hex*-1′-*enylbut*-3-*en*-2-*ol* (3 g.), b. p. 116°/16 mm., n_D^{21} 1·5250 (Found: C, 79·3; H, 10·7. $C_{10}H_{16}O$ requires C, 79·0; H, 10·5%), and the corresponding *ether* (1·5 g.), b. p. 130°/10^{-3} mm., n_D^{18} 1·5312 (Found: C, 83·8; H, 10·6. $C_{20}H_{30}O$ requires C, 83·9; H, 10·5%). The ether produced no effervescence with an ethereal solution of methylmagnesium iodide. Light absorption of the carbinol: see Table. Light absorption of the ether in ethanol: Max. 2320 A., $\varepsilon = 28{,}000$. [*Added*, 3.5.50. Since this paper was submitted, the above alcohol has been described by Chanley and Sobotka (*J. Amer. Chem. Soc.*, 1949, **71**, 4140) who give b. p. 90°/1·5 mm., n_D^{25} 1·5220, $\lambda_{max.}$ 2335 A., ε 24,300.]

Rearrangement of *cyclo*hexenylpropenylcarbinol in 60% aqueous ethanol containing hydrochloric (0·1M.) or acetic acid (0·1M.) resulted in the formation of the corresponding 2-*ethoxy*-4-cyclo*hex*-1′-*enylbut*-3-*ene* (6 g.), b. p. 107°/16 mm., n_D^{20} 1·5012 (Found: C, 79·7; H, 11·2. $C_{12}H_{20}O$ requires C, 80·0; H, 11·1%). Light absorption in ethanol: Max. 2350 A., $\varepsilon = 23{,}000$.

4-cyclo*Hex*-1′-*enylbut*-3-*en*-2-*one* (XI; R = Me).—4-*cyclo*Hex-1′-enylbut-3-en-2-ol (4 g.), aluminium *tert.*-butoxide, dry benzene (200 ml.), and acetone (100 ml.) were refluxed for 30 hours. The product was worked up in the usual manner to give 4-*cyclo*hex-1′-enylbut-3-en-2-one (2 g.), b. p. 65°/0·1 mm., n_D^{17} 1·5401. It formed, in 90% yield, a 2 : 4-dinitrophenylhydrazone which was chromatographed on alumina from benzene–ethyl acetate and crystallised from ethyl acetate in deep-red prisms, m. p. 196—197°, undepressed on admixture with an authentic specimen (Heilbron, Jones, Richardson, and Sondheimer, *J.*, 1949, 737).

Attempted Formation of 1-cyclo*Hexenylsodium*.—1-Chloro*cyclo*hexene (60 g., 0·5 mol.), sodium (23 g., 1 mol.), and benzophenone (46 g.) in ether (100 ml.) were stirred for 18 hours in an atmosphere of nitrogen, the solution being refluxed for part of the time. The solution assumed a deep blue colour owing to the formation of the ketyl, but most of the sodium remained undissolved. The solution was filtered and benzophenone (40 g.) was recovered. 1-Chloro*cyclo*hexene similarly failed to react with magnesium in ether.

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