259. *Alkenylation employing Lithium Alkenyls. Part VI.* The Synthesis and Spectral Properties of Some 6 : 6-Dimethyl*cyclo*hexenyl Derivatives.*

By E. A. Braude, T. Bruun, B. C. L. Weedon, and R. J. Woods.

The method of direct alkenylation has been applied to the synthesis of 6 : 6-dimethyl*cyclo*hexenyl derivatives. 1-Chloro-6 : 6-dimethyl*cyclo*hexene, prepared from 2 : 2-dimethyl*cyclo*hexanone, has been converted into 6 : 6-dimethyl*cyclo*hexenyl-lithium, which with benzaldehyde and benzophenone affords the carbinols (I; R = H and Ph). Under mild acidic conditions, the phenylcarbinol (I; R = H) undergoes rearrangement to the isomer (II; R = H), while the diphenylcarbinol (I; R = Ph) undergoes dehydration to the hydrocarbon (III; R = Ph).

Reaction of the lithium alkenyl with crotonaldehyde and sorbaldehyde, followed by rearrangement, similarly yields the diene and triene carbinols (V; *n* = 1 and 2) which are selectively oxidised to the ethylenic ketones (VI; *n* = 1 and 2).

The ultra-violet light-absorption properties of the various conjugated derivatives are recorded and discussed, and provide further striking evidence for the steric effects previously noted for *gem*-dimethyl substituents.

In two previous papers (Part IV, Braude and Coles, *J.*, 1950, 2014; Braude, Bruun, Weedon, and Woods, *J.*, 1952, 2818) the formation and some synthetic applications of *cyclo*hexenyl-lithium were described. An extension of this work to methylated *cyclo*hexene derivatives was of interest in connection with studies on steric inhibition of resonance in isocyclic systems (cf. *J.*, 1949, 1818), and also in connection with the synthesis of polyenes related to vitamin A (cf. preceding paper). The present communication deals with the preparation and properties of some 6 : 6-dimethyl*cyclo*hexenyl derivatives.

6 : 6-Dimethyl*cyclo*hexenyl-lithium was readily obtained by the action of lithium on 1-chloro-6 : 6-dimethyl*cyclo*hexene. The chloro-compound, together with 1 : 1-dichloro-2 : 2-dimethyl*cyclo*hexane, was prepared by treating 2 : 2-dimethyl*cyclo*hexanone with phosphorus pentachloride. The formation of a mixture of mono- and di-chloro-derivatives was encountered previously with *cyclo*pentanone (Braude and Forbes, *J.*, 1951, 1755), whereas *cyclo*hexanone under similar conditions yielded mainly chloro*cyclo*hexene (Part IV, *loc. cit.*). The by-product in the present instance was obtained as a crystalline solid which was conveniently dehydrochlorinated to the chloro-olefin by means of sodamide in liquid ammonia.

With benzaldehyde, dimethyl*cyclo*hexenyl-lithium affords the crystalline phenylcarbinol (I; R = H) in over 60% yield, and benzophenone similarly gives the diphenylcarbinol (I; R = Ph). On treatment with 0·1M-hydrochloric acid at room temperature, the

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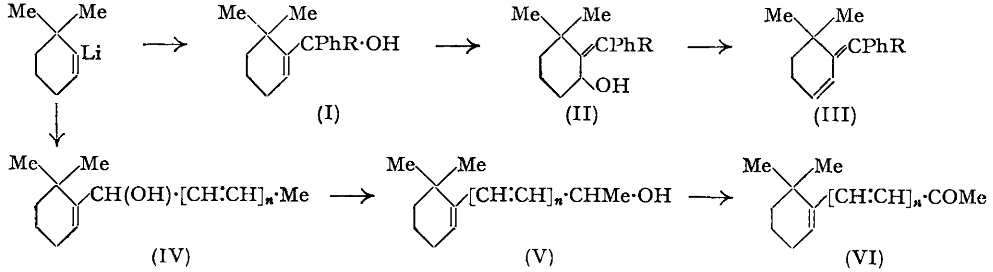
* Part V, *J.*, 1951, 2078.

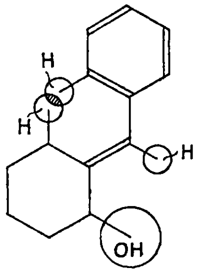
phenylcarbinol is converted smoothly into the conjugated isomer (II; R = H), while the diphenylcarbinol undergoes simultaneous rearrangement and dehydration, yielding only the diene (III; R = Ph). Rearrangement and partial dehydration was also observed in the case of the *cyclo*hexenyl analogue (Part IV, *loc. cit.*), but the occurrence of complete dehydration under such mild conditions is remarkable; it is undoubtedly promoted by the severe steric interference (cf. below) associated with the carbinol (II; R = Ph) which is considerably lessened in the diene (III; R = Ph). The diene (III; R = H) was obtained from the phenylcarbinol (I; R = H) by distillation from potassium hydrogen sulphate.

Reaction of the lithium alkenyl with crotonaldehyde gave a 60% yield of the propenylcarbinol (IV; *n* = 1) which, like the *cyclo*hexenyl analogue (Part IV, *loc. cit.*), rearranges, with migration of the hydroxyl group exclusively in the side chain, to the diene carbinol (V; *n* = 1). The constitution of the latter was established by oxidation with acetone and aluminium *tert.*-butoxide or, in superior yield, with manganese dioxide (cf. Weedon and Woods, *J.*, 1951, 2687; Braude and Forbes, *loc. cit.*), to the known diene ketone (VI; *n* = 1) (Heilbron, Jones, Toogood, and Weedon, *J.*, 1949, 2028). From a corresponding reaction with sorbaldehyde, the rearranged triene carbinol (V; *n* = 2) was obtained directly, the initial product (IV; *n* = 2) evidently having undergone isomerisation during isolation. Oxidation of the triene carbinol by the Oppenauer method and separation of the products by chromatography and treatment with the Girard T reagent yielded the triene ketone (VI; *n* = 2).

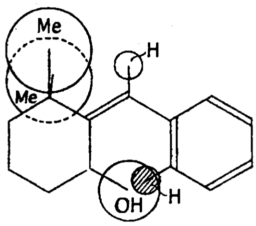


The ultra-violet light absorption of some of the compounds described above and of their *cyclo*hexenyl or *cyclo*hexylidene analogues are collected in the Table. The wave-length locations of the bands due to the conjugated chromophores are almost identical in the *gem*-dimethyl and in the unsubstituted series, but the intensities are much lower in the former, the ratio (*r*) of extinction coefficients ranging from 0·71 to 0·42. Analogous observations have previously been made in a number of similar cases (Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *J.*, 1949, 1890; Braude and Jones, *J. Amer. Chem. Soc.*, 1950, **72**, 1041) and it has been shown that the hypochromic effects can be ascribed to steric inhibition of resonance resulting from the obstruction by the *gem*-dimethyl groups of a coplanar *trans*-arrangement of the conjugated chromophore. A more detailed interpretation of the present results is given in the sequel.

All the compounds listed in the Table are either products of an oxotropic rearrangement, or are derived from such products, and in those cases where stereoisomerism about a double bond is possible the configuration adopted would therefore be expected to be the less sterically hindered one (Braude and Coles, *J.*, 1951, 2085). 2-Benzylidene*cyclo*hexanol would thus be expected to be obtained in configuration (*a*) with the phenyl group on the far side of the hydroxyl substituent (see figure). The scale diagram (in which covalent bond radii have been used) indicates that even in this configuration some interference occurs between hydrogen atoms of the phenyl and the *cyclo*hexane ring and this is borne out by the light absorption which shows a reduction in intensity and hyperchromic shift when compared with the open-chain analogue, methylstyrylcarbinol ($\lambda_{max.}$ 2510 Å, ε 19 500; Braude, Jones, and Stern, *J.*, 1947, 1087). 6-Benzylidene-2 : 2-dimethyl*cyclo*hexanol, on the other hand, presumably adopts the configuration (*b*) since interference between the phenyl and the methyl groups would be even larger than between the phenyl and the hydroxyl groups; the pronounced decrease in $\varepsilon_{max.}$ signifies that, in configuration (*b*), interference is already considerable and results in an appreciable twisting of the plane of the phenyl ring with respect to that of the ethylenic bond. A similar situation exists in the benzylidene*cyclo*hexenes. The unsubstituted compound, no doubt, is the less hindered, thermodynamically more stable "*trans*"-isomer (*c*) and exhibits absorption similar to that of *trans*-phenylbutadiene ($\lambda_{max.}$ 2800 Å, ε 28 300; Braude, Jones, and Stern, *loc. cit.*). By contrast, the *gem*-dimethyl derivative would be expected to have the *cis*-configuration (*d*) corresponding to that of the carbinol from which it is derived, any tendency for isomerisation to the *trans*-isomer to occur being opposed by the strong interference which would result between the phenyl and the methyl groups. The absorption properties are in agreement with this view and closely resemble those of *cis*-phenylbutadiene ($\lambda_{max.}$ 2700 Å, ε 14 000; Grummitt and Christoph, *J. Amer. Chem. Soc.*, 1951, **73**, 3479).



(*a*)



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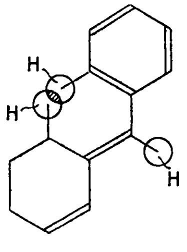
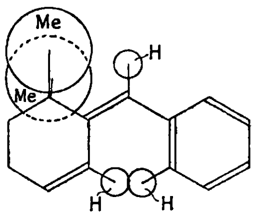
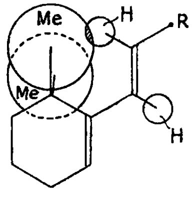


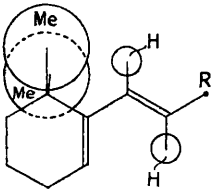
(*c*)



(*d*)



(*e*)



(*f*)

The data for the diphenylmethylene derivatives, in which the possibility of geometrical isomerism does not arise, can be interpreted in an analogous fashion. The absorption of the parent 1 : 1-diphenylethylene ($\lambda_{max.}$ 2500 Å, ε 12 000), unlike that of 1 : 2-diphenylethylene (stilbene), closely resembles that of styrene. The lack of effective conjugation with the second phenyl group may be due to electronic or steric reasons, or both (compare the different spectral relation of Ph·CH=O and $Ph_2C=O$, *Ann. Reports*, 1945, **42**, 108); the essential point for the present purpose is that steric interference resulting in the rotation of *one* phenyl ring with respect to the plane of the double bond in the diphenylethylene grouping $Ph_2C=C$ will have little effect on the spectral properties. Therefore, diphenylmethylene derivatives, in which the coplanarity of neither or of only one phenyl ring is obstructed by substituents should absorb very similarly to the corresponding benzylidene derivatives, and comparison of the data for 2-benzylidene- and 2-diphenylmethylene-*cyclo*hexanol, 2-benzylidene- and 2-diphenylmethylene-*cyclo*hexene, and 3-benzylidene- and 3-diphenylmethylene-4 : 4-dimethyl*cyclo*hexene (see Table) shows that this is indeed the case. Diphenylmethylene derivatives in which the coplanarity of *both* phenyl rings is obstructed by substituents, on the other hand, should show a very large steric effect and it is interesting that 2-diphenylmethylene-3 : 3-dimethyl*cyclo*hexanol (II; R = Ph) is not formed under the usual conditions, the less hindered dehydration product being obtained instead (see above).

In the *cyclo*hexenyl derivatives, the structural configurations in question are not stereoisomers about a double bond, but *s-cis-trans* about a conventional single bond possessing some double-bond character (*e, f*). Whereas the barrier to rotation about a double bond is high (cf. Mulliken and Roothaan, *Chem. Reviews*, 1947, **41**, 219), that for a single bond is quite low (*ca.* 2 kcal.; cf. Aston *et al.*, *J. Chem. Physics*, 1946, **14**, 67) and the two planar configurations will be in thermal equilibrium at ordinary temperature, the proportion of each depending on their relative free energies. By analogy with butadiene, the unhindered compounds will exist predominantly in the *s-trans*-configuration which will be more stable than the unhindered *s-cis*-configuration by *ca.* 2 kcal. (Aston *et al., loc. cit.*). The configuration of the *gem*-dimethyl derivatives, in which the *s-trans*-form is hindered, will depend on the relative magnitude of the steric effect, which is also expected to be of the order of 2 kcal. although its exact magnitude is unknown. Two interpretations of the hypochromic effects are therefore possible: the decrease in ε in the *gem*-dimethyl derivatives may be due either (i) to steric hindrance in the predominant *s-trans*-configuration (*e*), or (ii) to a change-over to the *s-cis*-configuration (*f*). We have previously (Braude *et al., loc. cit.*) favoured the former interpretation, but it has since been shown (Barton and Brooks, *J.*, 1951, 261; Turner and Voitle, *J. Amer. Chem. Soc.*, 1951, **73**, 1403) that chromophores with a fixed *s-cis*-configuration generally give rise to bands of considerably reduced intensities, even in the absence of steric hindrance, and the second possibility therefore receives some support. Nevertheless, we consider that, in systems of type (VI) at least, the first interpretation remains the more probable, for the following reason. In our previous discussion, it was inferred that the decrease in intensity, due to steric causes, of a band associated with a multiple chromophore should be coupled with the appearance of a band of shorter wavelength associated with a partial chromophore. In most systems previously studied, the partial-chromophore bands lie outside the observed spectral range, but in the case of the 4-*cyclo*hexenylbut-3-en-2-ones the effect is clearly shown (Braude and Jones, *loc. cit.*), the disappearance of the " dienone " band near 2800 Å being coupled with the appearance of a partial " enone " band near 2200 Å. An even more striking example is provided by the present data for the 6-*cyclo*hexenylhexa-3 : 5-dien-2-ones. The unmethylated ketone exhibits a single band at 3200 Å, associated with the " trienone " chromophore $[C{=}C]_3{\cdot}C{=}O$. In the *gem*-dimethyl derivative the intensity of the " trienone " band is reduced to less than half, but a new set of bands near 2700 Å appears, which is, no doubt, due to the partial " dienone " chromophore of the side chain. The appearance of such a well-defined partial-chromophore band would not be expected if the *gem*-dimethyl derivatives (V) and (VI) adopted the unhindered *s-cis* configuration (*f*).*

Ultra-violet light absorptions for ethanol solutions.

	*cyclo*Hexene series		*gem*-Dimethyl*cyclo*hexene series		
	$\lambda_{max.}$, Å	ϵ	$\lambda_{max.}$, Å	ϵ	r *
2-Benzylidene*cyclo*alkanol (*e.g.*, II; R = H)	2430	14 200 [1]	2370	6700	0·47
3-Benzylidene*cyclo*alkene (*e.g.*, III; R = H)	2810	18 700 [1]	2570	10 000	
			2700	13 000	0·70
			2800	13 000	
2-Diphenylmethylene*cyclo*alkanol	2400	13 200 [1]	—	—	—
3-Diphenylmethylene*cyclo*alkene (*e.g.*, III; R = Ph)	2810	22 000 [1]	2520	15 500	
			2680	15 500	0·71
			2800	15 500	
4-*cyclo*Alkenylbut-3-en-2-ol (*e.g.*, V; *n* = 1)	2350	23 000 [1]	2360	11 000	0·48
4-*cyclo*Alkenylbut-3-en-2-one (*e.g.*, VI; *n* = 1)	2810	20 800 [2]	2810	13 000 [2]	0·62
6-*cyclo*Alkenylhexa-3 : 5-dien-2-ol (*e.g.*, V; *n* = 2)	2700	33 500 [3]	2680	15 000	0·43
			2800	15 000	
6-*cyclo*Alkenylhexa-3 : 5-dien-2-one (*e.g.*, VI; *n* = 2)	3200	37 500 [3]	2680	18 500	
			2800	18 500	
			3260	15 500	0·42 †
			3430	11 500	

* $r = \epsilon$ (*gem*-dimethyl series)/ϵ (unsubstituted series). † Based on 3260-Å band.

[1] Part IV, *loc. cit.* [2] Heilbron *et al.*, *J.*, 1949, 737, 2028; Braude *et al.*, *ibid.*, p. 1890.

[3] Preceding paper.

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* *Added in Proof.*—Further evidence has now accumulated in support of this view. Oroshnik, Karmas, and Mebane (*J. Amer. Chem. Soc.*, 1952, **74**, 295) have shown that the abnormal spectral properties of vitamin A and its derivatives also receive a satisfactory interpretation on the basis of steric interference in the *s-trans*-configuration and the concomitant appearance of "partial chromophore" bands. Furthermore, the *X*-ray diffraction analysis of crystalline β-ionylidenecrotonic acid (MacGillavry, Kreuger, and Eichhorn, *Proc. K. Ned. Akad. Wet.*, 1951, *B*, **54**, 449) also indicates an *s-trans*-configuration of the bond joining the substituted *cyclo*hexene ring and the unsaturated side-chain. We are indebted to Professor C. H. MacGillavry, Amsterdam, for an advance copy of her paper.

The steric effects manifested by the spectral data are also reflected in the reduced ease of oxotropic rearrangement in the *gem*-dimethyl*cyclo*hexenyl compared with the *cyclo*hexenyl series. Kinetic measurements, details of which will be reported later, show that the rates of rearrangement of the carbinols (I; R = H) and (IV; $n = 1$) are smaller by factors of about 2 than those of the unsubstituted analogues under identical conditions. These differences are larger than are to be expected from the small electronic influences of the *gem*-dimethyl groups and are undoubtedly to be ascribed, at least in part, to the reduced resonance stabilisation which accompanies the rearrangement in the substituted series.

EXPERIMENTAL

(M. p.s. are uncorrected.)

1-*Chloro*-6 : 6-*dimethyl*cyclo*hexene and* 1 : 1-*Dichloro*-2 : 2-*dimethyl*cyclo*hexane*.—2 : 2-Dimethyl*cyclo*hexanone (103 g.) was added dropwise with stirring and cooling (ice-bath) to phosphorus pentachloride (206 g.). Stirring was continued for 1 hour at 20° and the mixture was then added to ice and water (*ca.* 1 l.) and steam-distilled. Isolation of the product from the distillate with ether gave an oil (126 g.), n_D^{20} 1·4800, which was fractionally distilled through a 10″ Dufton column, equipped with an efficient reflux head, and gave (i) 1-*chloro*-6 : 6-*dimethyl*cyclo*hexene* (56 g.), b. p. 52°/10 mm., n_D^{23} 1·4731—1·4739 (Found: C, 66·8; H, 9·1; Cl, 24·5. $C_8H_{13}Cl$ requires C, 66·45; H, 9·05; Cl, 24·5%), and (ii) an oil (55 g.), b. p. *ca.* 80°/10 mm., which solidified on cooling. Recrystallisation of the solid from aqueous alcohol gave 1 : 1-*dichloro*-2 : 2-*dimethyl*cyclo*hexane* (26·5 g.), m. p. 123° (Found: C, 53·1; H, 8·25; Cl, 39·3. $C_8H_{14}Cl_2$ requires C, 53·05; H, 7·8; Cl, 39·15%).

To a solution of the above dichloride (13·3 g.) in a mixture of liquid ammonia (75 ml.) and ether (50 ml.), a solution of sodamide (prepared from 1·85 g. of sodium according to Vaughn, Vogt, and Nieuwland, *J. Amer. Chem. Soc.*, 1934, **56**, 2120) in liquid ammonia (50 ml.) was added slowly. The mixture was stirred for 3 hours, ammonium chloride (5 g.) was then added to decompose the excess of sodamide, and the solvents were evaporated. Isolation of the product with ether and distillation gave (i) 1-chloro-6 : 6-dimethyl*cyclo*hexene (6·3 g.), b. p. 58—60°/14 mm., n_D^{21} 1·4770—1·4781 (Found: C, 67·05; H, 8·75; Cl, 24·65. Calc. for $C_8H_{13}Cl$: C, 66·45; H, 9·05; Cl, 24·5%), and (ii) unchanged dichloride (1·1 g.).

The freshly prepared monochloride gave no immediate precipitate with alcoholic silver nitrate or with a methanolic solution of 2 : 4-dinitrophenylhydrazine sulphate.

(6 : 6-*Dimethyl*cyclo*hexenyl*)*phenylcarbinol* (I; R = H).—6 : 6-Dimethyl*cyclo*hexenyl-lithium was prepared from 1-chloro-6 : 6-dimethyl*cyclo*hexene (43·5 g.; freshly distilled) and lithium (4·2 g.) in ether (600 ml.) by a procedure similar to that described for the preparation of *cyclo*hexenyl-lithium (Braude and Coles, *J.*, 1950, 2014). After removal of a small amount of unchanged lithium, the ethereal solution was cooled to 0°, a solution of benzaldehyde (23·8 g.) in ether (75 ml.) was added dropwise, and the mixture stirred for 18 hours at 20°. Saturated aqueous ammonium chloride (250 ml.) was then added, and the product isolated in the usual manner, giving the *carbinol* (30·7 g., 63%) which crystallised from pentane in needles, m. p. 73·5° (Found: C, 83·6; H, 9·6. $C_{15}H_{20}O$ requires C, 83·3; H, 9·3%). Light absorption in ethanol: maxima, 2580 and 2640 Å; ε, 205 and 160 respectively.

2-*Benzylidene*-3 : 3-*dimethyl*cyclo*hexanol* (II; R = H).—A solution of the preceding carbinol (6·0 g.) in a 0·1M-solution of sulphuric acid in a mixture of water (40 ml.) and acetone (160 ml.) was kept at 20° for 48 hours. The solution was then neutralised by the addition of aqueous sodium hydrogen carbonate solution, the bulk of the acetone was removed by distillation under reduced pressure through a Dufton column, and the product was isolated with ether in the usual manner. Distillation gave a viscous oil (5·4 g.), b. p. 70° (bath-temp.)/10^{-4} mm., n_D^{20} 1·5563, which solidified on cooling of its solution in pentane to 0°. Recrystallisation from the same solvent yielded the *carbinol* (3·1 g.) as prisms, m. p. 58·5° (Found: C, 83·55; H, 9·6. $C_{15}H_{20}O$ requires C, 83·3; H, 9·3%). Light absorption: see Table.

3-*Benzylidene*-4 : 4-*dimethyl*cyclo*hexene*.—A mixture of (6 : 6-dimethyl*cyclo*hexenyl)phenylcarbinol (3·0 g.) and finely powdered potassium hydrogen sulphate (2·0 g.) was heated at 80° for 20 minutes under reduced pressure. The products were distilled at 100° (bath)/10^{-4} mm. The distillate (2·5 g.) was diluted with pentane (3 ml.) and cooled to −30°, the crystalline precipitate of unchanged carbinol (m. p. 72°; 1·1 g.) was filtered off, and the mother-liquors were again distilled, giving the *hydrocarbon* (1·1 g.) as a colourless oil, b. p. 85° (bath)/10^{-4} mm., n_D^{25} 1·5720 (Found: C, 90·2; H, 9·0. $C_{15}H_{18}$ requires C, 90·85; H, 9·15%). Light absorption: see Table.

(6 : 6-*Dimethyl*cyclo*hexenyl)diphenylcarbinol* (I; R = Ph).—Benzophenone (6·9 g.) in ether (30 ml.) was added slowly to a solution of 6 : 6-dimethyl*cyclo*hexenyl-lithium (from 6·6 g. of 1-chloro-6 : 6-dimethyl*cyclo*hexene and 0·63 g. of lithium) in ether (120 ml.) at 0° and the whole stirred at 20° for 24 hours. Saturated aqueous ammonium chloride solution (50 ml.) was then added and the ethereal layer was separated and dried. Evaporation of the solvent and distillation of the residue gave (i) unchanged benzophenone (6·0 g.), b. p. 99—107°/0·3 mm., and (ii) the *carbinol* which sublimed at 160° (bath-temp.)/10^{-4} mm., and crystallised from aqueous alcohol in hexagonal prisms (1·51 g., 14%), m. p. 95·5° (Found: C, 86·4; H, 8·25. $C_{21}H_{24}O$ requires C, 86·25; H, 8·25%). Light absorption: maximum, 2580 Å; ε, 290. The yield quoted is based on a single experiment and could no doubt be raised considerably.

3-*Diphenylmethylene*-4 : 4-*dimethyl*cyclo*hexene* (III; R = Ph).—A solution of (6 : 6-dimethyl*cyclo*hexenyl)diphenylcarbinol (800 mg.) in a 0·1M-solution of hydrochloric acid in a mixture of water (6 ml.) and acetone (24 ml.) was kept at 20° for 20 hours. Neutralisation of the mixture, removal of the acetone, and isolation of the product in the usual manner gave the *hydrocarbon* (368 mg.) which crystallised from aqueous ethanol in needles, m. p. 63—64° (Found: C, 91·5; H, 8·15. $C_{21}H_{22}$ requires C, 91·9; H, 8·1%). Light absorption: see Table. On dilution of the mother-liquors from the crystallisation with water and seeding, a further crop of the hydrocarbon (255 mg.), m. p. 58—62°, was obtained.

1-(6 : 6-*Dimethyl*cyclo*hex*-1-*enyl*)*but*-2-*en*-1-*ol* (IV; *n* = 1).—A solution of crotonaldehyde (4·2 g.) in ether (25 ml.) was added slowly at 0° to a solution of 6 : 6-dimethyl*cyclo*hexenyl-lithium (from 11·5 g. of 1-chloro-6 : 6-dimethyl*cyclo*hexene and 1·1 g. of lithium) in ether (200 ml.). The mixture was stirred at 20° for 15 hours, a saturated aqueous ammonium chloride solution (90 ml.) was added, and the product isolated as usual. Distillation gave the *carbinol* (8·6 g., 60%), b. p. 60—65° (bath-temp.)/10^{-3} mm., n_D^{25} 1·4990 (Found: C, 79·7; H, 11·15. $C_{12}H_{20}O$ requires C, 79·9; H, 11·2%). The carbinol exhibited no light absorption with ε >200 in the region 2200—3000 Å.

4-(6 : 6-*Dimethyl*cyclo*hex*-1-*enyl*)*but*-3-*en*-2-*ol* (V; *n* = 1).—A solution of the preceding carbinol (4·3 g.) in a 0·01M-solution of hydrochloric acid in a mixture of water (40 ml.) and acetone (60 ml.) was kept at 20° for 2 hours. The product was isolated in the usual manner and distilled, giving the *carbinol* (3·35 g.), b. p. 60—65° (bath-temp.)/10^{-3} mm., n_D^{22} 1·5045 (Found: C, 80·1; H, 11·2. $C_{12}H_{20}O$ requires C, 79·9; H, 11·2%). Light absorption: see Table.

4-(6 : 6-*Dimethyl*cyclo*hex*-1-*enyl*)*but*-3-*en*-2-*one* (VI; *n* = 1).—(*a*) A mixture of the preceding carbinol (3·6 g.), aluminium *tert.*-butoxide (11·5 g.), acetone (190 ml.), and benzene (290 ml.) was heated under reflux for 48 hours. The mixture was then cooled and poured into dilute sulphuric acid (2·5% w/v; 1500 ml.). Isolation of the product in the usual way gave the crude ketone (3·8 g.) which was treated with an excess of semicarbazide acetate in methanol. The resulting semicarbazone (2·1 g.) had m. p. 186—187° which was raised to 188°, undepressed on admixture of the sample with an authentic specimen, on crystallisation from methanol (Heilbron, Jones, Toogood, and Weedon, *J.*, 1949, 2028, give m. p. 186—187°).

(*b*) A solution of the preceding carbinol (2·0 g.) in light petroleum (200 ml.; b. p. 40—60°) was shaken with manganese dioxide (20 g.; cf. Weedon and Woods, *J.*, 1951, 2687) at 20° for 3 hours. The mixture was filtered and the filtrate was evaporated. Distillation of the residue gave the ketone (1·51 g.), b. p. 60° (bath-temp.)/10^{-3} mm., n_D^{20} 1·5111. A portion (0·89 g.) of the ketone was converted into the semicarbazone which crystallised from methanol in plates (0·97 g.), m. p. 187—188°, undepressed on admixture of the sample with an authentic specimen. The 2 : 4-dinitrophenylhydrazone gave a single band on chromatography (benzene–alumina) and crystallised from 1 : 1 ethyl acetate–methanol in red needles, m. p. 157°, undepressed on admixture with an authentic specimen (*idem, loc. cit.*, give m. p. 154—155°).

6-(6 : 6-*Dimethyl*cyclo*hex*-1-*enyl*)*hexa*-3 : 5-*dien*-2-*ol* (V; *n* = 2).—A solution of sorbaldehyde (26 g.) in ether (75 ml.) was added slowly to a solution of 6 : 6-dimethyl*cyclo*hexenyl-lithium (from 51 g. of 1-chloro-6 : 6-dimethyl*cyclo*hexene and 4·9 g. of lithium) in ether (600 ml.) at 0°. The mixture was stirred overnight at 20°, saturated aqueous ammonium chloride (450 ml.) was then added, and the product isolated in the usual manner. Distillation gave the *carbinol* (14·5 g., 26%), b. p. 80° (bath-temp.)/10^{-4} mm., n_D^{23} 1·5316 (Found: C, 81·8; H, 10·65. $C_{14}H_{22}O$ requires C, 81·5; H, 10·75%). Light absorption: see Table. No change in light absorption was observed after treatment of a small portion of the carbinol for 2 hours at 20° with 0·01M-sulphuric acid in 4 : 1 dioxan–water.

6-(6 : 6-*Dimethyl*cyclo*hex*-1-*enyl*)*hexa*-3 : 5-*diene*-2-*one*.—A mixture of the preceding carbinol (6·5 g.), aluminium *tert.*-butoxide (15·6 g.), acetone (250 ml.), and benzene (500 ml.) was heated under reflux for 60 hours. The mixture was cooled and poured into dilute sulphuric acid (700 ml.). The product was isolated in the usual manner and dissolved in light petroleum (b. p. 40—60°; 20 ml.). The solution was poured on to a column of alumina (350 g.; grade IV; Brockmann and Schodder, *Ber.*, **1941**, **74**, 73) and the chromatogram developed with the same solvent. The main yellow band yielded an oil (2·7 g.), n_D^{17} 1·5647, a portion (1·8 g.) of which was treated with Girard T reagent (Girard and Sandulesco, *Helv. Chim. Acta*, **1936**, **19**, 1095). Isolation of the ketonic fraction gave 6-(6 : *6-dimethyl*cyclo*hex-1-enyl)hexa-3 : 5-dien-2-one* as an oil (0·58 g.), b. p. 80° (bath-temp.)/10^{-4} mm., n_D^{21} 1·5680 (Found: C, 82·2; H, 9·8. $C_{14}H_{20}O$ requires C, 82·3; H, 9·85%). Light absorption: See Table.

We thank the Norges Tekniske Högskole for a grant (to T. B.), the Department of Scientific and Industrial Research for a maintenance grant (to R. J. W.), and Glaxo Laboratories, Ltd., for gifts of chemicals. Analyses were carried out in the microanalytical laboratory of this Department (Mr. F. H. Oliver).

Imperial College of Science and Technology,
South Kensington, London, S.W 7.

[*Received, November 30th*, 1951.]