455. *Anionotropic Systems. Part II.* Syntheses and Rearrangements in the* cyclo*Heptenyl Series.*

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In continuation of earlier work, the study of anionotropic rearrangements in *cyclo*olefinic systems has been extended to the *cyclo*heptenyl series.

Four *cyclo*hept-1-enylcarbinols containing different unsaturated side-chains have been synthesised by the reaction of *cyclo*hept-1-enyl-lithium (the constitution of which is proved by carboxylation) with benzaldehyde, acraldehyde, crotonaldehyde, and sorbaldehyde. The acid-catalysed isomerisations of the carbinols are described. It is found that the rearrangements of the vinyl and the propenyl derivatives take opposite courses, in agreement with the observations previously made in the *cyclo*pentenyl and *cyclo*hexenyl series.

IN earlier papers (Braude and Coles, *J.*, 1950, 2014; Braude and Forbes, 1951, 1755; Braude, Bruun, Toogood, and Weedon, 1952, 1414, 1419), investigations on the anionotropic rearrangements of *cyclo*pentenyl- and *cyclo*hexenyl-carbinols were described. These studies have now been extended to the seven-membered series, both for their synthetic interest in providing routes to a variety of *cyclo*heptenyl derivatives (cf. *Nature*, 1951, **168**, 874; *J.*, 1953, 2208) and for kinetic studies, which will be reported later, on the relation between ring size and reactivity in *cyclo*olefinic systems.

As previously, the method of direct alkenylation proved highly convenient. Conversion of 1-chloro*cyclo*heptene, obtained in good yield from *cyclo*heptanone with phosphorus pentachloride (cf. Favorskii and Domnin, *J. Gen. Chem. U.S.S.R.*, 1936, **6**, 727), into *cyclo*heptenyl-lithium presented no difficulty. The rate of metalation of the carefully purified chloro*cyclo*heptene is somewhat slower than that of the six-membered analogue (Braude and Coles, *loc. cit.*) but overall yields of up to 60% were obtained in the addition reactions described below. The constitution of the lithium alkenyl was established by carboxylation which gave the known *cyclo*hepten-1-enylcarboxylic acid (Dele, Schorlemmer, and Spiegel, *J.*, 1881, 541; Willstätter, *Annalen*, 1901, **317**, 237) as well as di*cyclo*heptenyl ketone (I) which was characterised by a 2 : 4-dinitrophenylhydrazone and converted into di*cyclo*heptyl ketone by catalytic hydrogenation. On treatment with formic and phosphoric acids, di*cyclo*heptenyl ketone underwent cyclisation to the tricyclic ketone (II) (cf. Braude and Coles, *J.*, 1952, 1430).

Reaction of *cyclo*heptenyl-lithium with benzaldehyde, acraldehyde, crotonaldehyde, and sorbaldehyde afforded the secondary alcohols (III, VI, and XII; $n = 1$) and (XII; $n = 2$), all liquids at room temperature. Their structures are confirmed by the ultraviolet light absorptions and by the reactions described below. The alcohol (XII; $n = 1$) was also hydrogenated catalytically to 1-*cyclo*heptylbutan-1-ol.

With Brady's reagent, (III) undergoes oxidation to *cyclo*heptenyl phenyl ketone, which is isolated as the 2 : 4-dinitrophenylhydrazone in about 50% yield. The ease of this interesting reaction appears to be markedly greater in the present case than in those previously described (Braude and Forbes, *J.*, 1951, 1762).

Anionotropic rearrangements of the alcohols (III), (VI), and (XII) to the fully conjugated isomers were effected in practically quantitative yields by treatment with dilute hydrochloric acid in aqueous dioxan or acetone at room temperature. α-*cyclo*Hept-1′-enylbenzyl alcohol (III) gave 2-benzylidene*cyclo*heptanol (IV), which exhibits ultraviolet light absorption typical of a styryl derivative. It was oxidised, most conveniently with chromium trioxide in pyridine (Poos, Arth, Beyler, and Sarett, *J. Amer. Chem. Soc.*, 1953, **75**, 422), to 2-benzylidene*cyclo*heptanone (V). The latter was also prepared directly from *cyclo*heptanone by condensation with benzaldehyde, and could be converted into (IV) by reduction with lithium aluminium hydride.

The rearrangement of 1-*cyclo*hept-1′-enylallyl alcohol (VI) gave exclusively 2-allyl-

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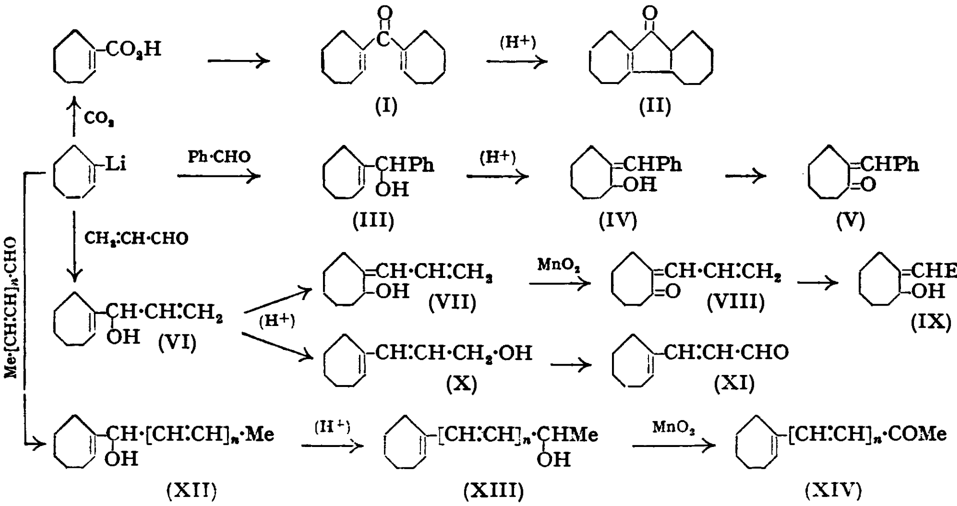
* Part I, *J.*, 1953, 419.

idene*cyclo*heptanol (VII). Complete absence of the alternative isomerisation product (X) was proved by oxidation with manganese dioxide which gave 2-allylidene*cyclo*heptanone (VIII) but no trace of the aldehyde (XI), as shown by a negative Schiff's test. The structures of (VII) and (VIII) were confirmed by their ultra-violet light absorptions (see Table) and by catalytic hydrogenation to 2-*n*-propyl*cyclo*heptanol and 2-*n*-propyl*cyclo*heptanone. The latter was identified by the 2 : 4-dinitrophenylhydrazone which was identical with the derivative of an authentic sample of the ketone obtained by ring-expansion of *cyclo*hexanone with diazo-*n*-butane (cf. Adamson and Kenner, *J.*, 1939, 181; Cook, Raphael, and Scott, *J.*, 1951, 695). The course of the hydrogenation of 2-allylidene*cyclo*heptanone was not completely selective, however, and the main product was admixed with an isomer. This was probably 2-propylidene*cyclo*heptanol (IX); its infra-red light absorption resembled that of 2-propyl*cyclo*heptanol, but showed additional peaks at 1615 and 860 cm.^{-1} which can be ascribed to $C{=}C$ stretching and C–H bending vibrations of a trialkylated ethylenic group.

In contrast to (VI), the higher homologue, 1-*cyclo*hept-1′-enylbut-2-en-1-ol (XII; $n = 1$), undergoes rearrangement with migration of the hydroxyl group in the opposite direction to give 4-*cyclo*hept-1′-enylbut-3-en-2-ol (XIII; $n = 1$). The structure of the rearrangement product was proved by oxidation with manganese dioxide to the corresponding diene ketone (XIV; $n = 1$) which had previously been prepared by a different route by Heilbron, Jones, Toogood, and Weedon (*J.*, 1949, 1827) and was identified by the 2 : 4-dinitrophenylhydrazone. The latter was also obtained directly from (XIII; $n = 1$) by treatment with Brady's reagent. The opposite directions of rearrangement of the vinylcarbinol (VI) and the propenylcarbinol (XII; $n = 1$) correspond to the observations previously made in the *cyclo*pentenyl and *cyclo*hexenyl series (Braude and Coles, 1950; Braude and Forbes, 1951, *locc. cit.*) and no change in behaviour with increasing ring-size is expected or found.



The rearrangement of 1-*cyclo*hept-1′-enylhexa-2 : 4-dien-1-ol (XII; $n = 2$) gave an isomer, the ultra-violet light absorption of which shows that all three ethylenic bonds have become conjugated (see Table). The structure of the product was not rigidly established, but by analogy with the corresponding *cyclo*hexenyl derivatives (Braude, Brunn, Weedon, and Woods, 1952, *loc. cit.*), the direction of migration is again almost certainly along the side-chain to give (XIII; $n = 2$). Direct treatment of (XIII; $n = 2$) with Brady's reagent gave a 15% yield of the 2 : 4-dinitrophenylhydrazone of the corresponding triene ketone (XIV; $n = 2$).

The ultra-violet light absorptions of the *cyclo*heptenyl derivatives show certain significant differences from those of the *cyclo*hexenyl derivatives (Braude and Coles, 1950, *loc. cit.*), *Ultra-violet light absorption of* cyclo*heptenyl derivatives* (*in ethanol*).

	$\lambda_{max.}$, Å	$\varepsilon_{max.}$
*cyclo*Hept-1-enecarboxylic acid	2130	11,200
Di*cyclo*hept-1-enyl ketone (I)	2450 3200	6,000 100
tricyclo[8 : 5 : $0^{3:9}$]Pentadec-1(10)-en-2-one (II)	2420 3020	12,500 100
2-Benzylidene*cyclo*heptanol (IV)	2470	12,100
2-Allylidene*cyclo*heptanol (VII)	2360	22,000
2-Allylidene*cyclo*heptanone (VIII)	2700 2800	15,000 15,000
4-*cyclo*Hept-1′-enylbut-3-en-2-ol (XIII; *n* = 1)	2390	23,500
4-*cyclo*Hept-1′-enylbut-3-en-2-one (XIV; *n* = 1)	2410 2810 2880	4,500 18,000 18,000
6-*cyclo*Hept-1′-enylhexa-3 : 5-dien-2-ol (XIII; *n* = 2)	2290 2700 2800 2880	6,000 12,000 14,500 12,000

but more detailed discussion is deferred until work now in progress on higher-membered *cyclo*alkenyl systems is completed.

EXPERIMENTAL

Analytical data were determined in the microanalytical (Mr. F. H. Oliver) and spectrographic (Mrs. I. A. Boston) laboratories of this Department.

cyclo*Hept-1-enyl-lithium*.—*cyclo*Heptanone (285 ml.) was slowly added to phosphorus pentachloride (500 g.), with stirring and external cooling. After 3 hr., the products were added dropwise to ice-water (4 l.), and the mixture was extracted with ether (1 l.). The ethereal layer was separated, dried ($CaCl_2$), and fractionated through an electrically heated, 8″ Fenske column, giving 1-chloro*cyclo*heptene (235 g., 70%) as a colourless liquid, b. p. 75°/26 mm., n_D^{21} 1·4844 (Found: Cl, 27·2. Calc. for $C_7H_{11}Cl$: Cl, 27·1%). (Favorskii and Domnin, *J. Gen. Chem. U.S.S.R.*, 1936, **6**, 340, give b. p. 58—59°/12 mm.) The chloride is reasonably stable at 0°; it gives no immediate reaction with alcoholic silver nitrate, but a precipitate of silver chloride is formed slowly.

Freshly distilled 1-chloro*cyclo*heptene (65 g., 0·5 mole) in ether (100 ml.) was slowly added to a stirred suspension of finely-cut lithium (6·9 g., 1 g.-atom) in sodium-dried ether (500 ml.) under nitrogen. The mixture was then heated under gentle reflux. Reaction usually set in after 1—2 hr. and was complete after 6—12 hr., almost the whole of the metal being consumed. The solution of *cyclo*hept-1-enyl-lithium has a greenish-grey colour.

cyclo*Hept-1-enecarboxylic Acid and Di*cyclo*hept-1-enyl Ketone*.—Excess of solid carbon dioxide (200 g.) was added to a solution of 1-*cyclo*heptenyl-lithium (from Li, 6·6 g.), with cooling in methanol–solid carbon dioxide. After 6 hr., the solution was acidified with aqueous hydrochloric acid, and the ethereal layer was separated. Extraction with aqueous sodium hydrogen carbonate and working up in the usual way gave *cyclo*hept-1-enecarboxylic acid (2 g., 3%) which, after distillation at 130° (bath)/10^{-5} mm., crystallised from methanol in plates, m. p. 49° (Dele, Schorlemmer, and Spiegel, *J.*, 1881, 541, give m. p. 53—54°), and formed an amide, plates (from aqueous methanol), m. p. 157° (Willstätter, *Annalen*, 1901, **317**, 237, gives m. p. 158—159°). The ethereal layer was dried (Na_2SO_4) and fractionated, giving *di*cyclo*hept-1-enyl ketone* (11 g., 21%), b. p. 116°/2 × 10^{-4} mm., n_D^{21} 1·5230 (Found: C, 82·8; H, 10·4. $C_{15}H_{22}O$ requires C, 82·5; H, 10·2%). Light absorption: see Table. The 2 : 4-*dinitrophenylhydrazone*, after chromatography in benzene–chloroform on alumina, separated from ethyl acetate in prisms, m. p. 200° (Found: C, 63·5; H, 6·7; N, 13·7. $C_{21}H_{26}O_4N_4$ requires C, 63·3; H, 6·5; N, 14·05%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3980 Å, ε 26,800.

*Di*cyclo*heptyl Ketone*.—The ketone (2 g.) in ethanol (40 ml.) in the presence of platinic oxide absorbed 220 ml. of hydrogen at 17°/750 mm. (Calc., 220 ml.), giving *di*cyclo*heptyl ketone*, b. p. 110°/5 × 10^{-3} mm., n_D^{21} 1·5030 (Found: C, 81·5; H, 11·5. $C_{15}H_{26}O$ requires C, 81·0; H, 11·8%). The 2 : 4-*dinitrophenylhydrazone*, after chromatography in benzene–chloroform on alumina, separated from ethyl acetate in orange needles, m. p. 95° (Found: N, 13·55. $C_{21}H_{30}O_4N_4$ requires N, 13·9%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3700 Å, ε 24,000.

tricyclo[8 : 5 : $0^{3:9}$]*Pentadec-1(10)-en-2-one* (II).—Di*cyclo*heptenyl ketone (7 g.) was cautiously added to a mixture of phosphoric acid (2 g.) and formic acid (8 g.) at 0°. Next day, the mixture was heated at 90° for 6 hr., then cooled, diluted with ice-water (200 ml.), and extracted with ether. The ethereal layer was washed with aqueous sodium carbonate and water, dried (Na_2SO_4), and fractionated, giving the tricyclo-*ketone* (5 g.) as a colourless liquid, b. p. 200° (bath)/10^{-5} mm., which solidified and crystallised from light petroleum (b. p. 40—60°) in colourless plates,

m. p. 43° (Found : C, 82·1; H, 10·1. $C_{15}H_{22}O$ requires C, 82·5; H, 10·2%). Light absorption : see Table. The 2 : 4-*dinitrophenylhydrazone*, after chromatography in benzene–chloroform on alumina, crystallised from ethyl acetate in fine orange-red needles, m. p. 171° (Found : N, 13·7. $C_{21}H_{26}O_4N_4$ requires N, 14·05%). Light absorption in $CHCl_3$: Max. at 3980 Å, ε 29,500.

α-cyclo*Hept-1′-enylbenzyl Alcohol* (III).—Freshly distilled benzaldehyde (40 g.) in ether (50 ml.) was added dropwise to a stirred solution of *cyclo*hept-1-enyl-lithium (from Li, 5·2 g.). After 12 hr., saturated aqueous ammonium chloride (500 ml.) was added and the ethereal layer was separated, dried (Na_2SO_4–K_2CO_3), and fractionated from a trace of potassium carbonate, giving α-cyclo*hept-1′-enylbenzyl alcohol* (37 g., 48%) as a colourless liquid, b. p. 94°/2 × 10^{-3} mm., n_D^{24} 1·5429 (Found : C, 83·2; H, 9·1. $C_{14}H_{18}O$ requires C, 83·1; H, 9·0%). Light absorption in EtOH : $\lambda_{max.}$ 2470 Å, ε 2000.

When α-*cyclo*hept-1′-enylbenzyl alcohol (2 g.) was warmed with 2 : 4-dinitrophenylhydrazine (2·6 g.), concentrated sulphuric acid (6 ml.), ethanol (40 ml.), and water (10 ml.) for 5 min. on the water-bath, cyclo*heptenyl phenyl ketone* 2 : 4-*dinitrophenylhydrazone* (1·9 g., 50%) was gradually precipitated. After chromatography on alumina in benzene–chloroform, it crystallised from ethyl acetate in red needles (1·5 g.), m. p. 131° (Found : C, 63·0; H, 5·6; N, 14·6. $C_{20}H_{20}O_4N_4$ requires C, 63·1; H, 5·3; N, 14·7%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3900 Å, ε 30,600. The yield of hydrazone is considerably higher than observed in other cases (Braude and Forbes, *J.*, 1951, 1762). The m. p. was not depressed on admixture with a specimen prepared from the ketone (Braude and Forbes, following paper).

2-*Benzylidene*cyclo*heptanol* (IV).—The above alcohol (16 g.) was dissolved in a 0·1M-solution of hydrogen chloride in 80% aqueous acetone (400 ml.). After 3 days at room temperature, the solution was neutralised with potassium carbonate and most of the acetone was distilled off through a column. The remaining solution was extracted with ether, and the ethereal layer was dried (K_2CO_3–Na_2SO_4) and fractionated, giving 2-*benzylidene*cyclo*heptanol* (15 g.), b. p. 102°/5 × 10^{-4} mm., n_D^{20} 1·5653 (Found : C, 82·8; H, 8·9. $C_{14}H_{18}O$ requires C, 83·1; H, 9·0%). Light absorption : see Table. The p-*nitrobenzoate* crystallised from light petroleum (b. p. 40—60°)–methanol in needles, m. p. 185° (Found : N, 3·9. $C_{21}H_{21}O_4N$ requires N, 4·0%).

2-*Benzylidene*cyclo*heptanone* (V).—(*a*) A mixture of *cyclo*heptanone (5·6 g.), benzaldehyde (5·3 g.), methanol (20 ml.), and 10N-NaOH (2 ml.) was kept for 15 hr. at 20°. After dilution with water (100 ml.), the products were isolated with ether and distilled. A mixture (4 g.), b. p. 125°/10^{-2} mm., n_D^{19} 1·5560—1·5660 was obtained, consisting of 2-benzylidene*cyclo*heptanone and 2-α-hydroxybenzyl*cyclo*heptanone. Refractionation from a trace of naphthalene-2-sulphonic acid gave pure 2-*benzylidene*cyclo*heptanone* (3·6 g.), n_D^{20} 1·5868, which crystallised from pentane in plates, m. p. 37·5° (Found : C, 83·8; H, 8·2. $C_{14}H_{16}O$ requires C, 84·0; H, 8·0%). Light absorption : Max. at 2700, 2810, and 2900 Å; ε 13,500, 14,500, and 14,000 in EtOH; 2710 and 2800 Å, ε 15,000 in *n*-hexane. The solution in ethanol is unstable, probably because of the formation of 2-α-ethoxybenzyl*cyclo*heptanone. The 2 : 4-*dinitrophenylhydrazone* was chromatographed on alumina in benzene–chloroform, and crystallised from ethyl acetate–methanol in red needles, m. p. 158° (Found : C, 62·8; H, 5·6; N, 14·65. $C_{20}H_{20}O_4N_4$ requires C, 63·1; H, 5·3; N, 14·7%). Light absorption in $CHCl_3$: Max. at 3780 Å; ε 25,000.

(*b*) 2-Benzylidene*cyclo*heptanol (1·2 g.) in dry pyridine (15 ml.) was added to chromium trioxide (1·5 g.) and pyridine (15 ml.). The mixture was kept for 12 hr. at 20° and then added to water (200 ml.) and extracted with ether. The ethereal extracts were washed with 2N-hydrochloric acid and water, dried (Na_2SO_4), and then fractionated, giving 2-benzylidene*cyclo*heptanone (1 g.), b. p. 117—118°/10^{-2} mm., m. p. 37° (from pentane) undepressed on admixture with the authentic specimen described above. It formed a 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 158°.

Reduction of the ketone (0·4 g.) with lithium aluminium hydride (0·7 g.) in ether at 20° reconverted it into the 2-benzylidene*cyclo*heptanol (0·3 g.), b. p. 80° (bath-temp.)/10^{-5} mm., n_D^{23} 1·5775, $\lambda_{max.}$ 2480 Å, ε 12,300, which gave no precipitate on treatment with Brady's reagent.

1-cyclo*Hept-1′-enylallyl Alcohol* (VI).—Freshly distilled acraldehyde (35 g.) in ether (50 ml.) was added dropwise to a stirred, ethereal solution of *cyclo*hept-1-enyl-lithium (from Li, 6·9 g.) at 0°. After a further 3 hr.' stirring at room temperature, saturated aqueous ammonium chloride was added and the products were worked up as described above, giving the *allyl alcohol* (35 g., 46%), b. p. 63°/0·5 mm., n_D^{20} 1·4990 (Found : C, 79·0; H, 10·6. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). Light absorption in EtOH : ε <750 between 2200 and 3000 Å.

2-*Allylidene*cyclo*heptanol* (VII).—The above alcohol (8 g.) was dissolved in a 0·05M-solution of hydrogen chloride in 60% aqueous acetone (200 ml.). After 14 hr. at room temperature, the products were worked up as described above, giving 2-*allylidene*cyclo*heptanol* (7 g.), b. p.

83°/0·5 mm., n_D^{20} 1·5071 (Found: C, 79·2; H, 10·7. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). Light absorption: see Table. The 3 : 5-*dinitrobenzoate* crystallised from light petroleum (b. p. 60—80°) in plates, m. p. 77° (Found: C, 58·7; H, 5·3; N, 8·2. $C_{17}H_{18}O_6N_2$ requires C, 59·0; H, 5·2; N, 8·1%). Light absorption in EtOH: $\lambda_{max.}$ 2300 Å, ε 43,000; $\lambda_{infl.}$ 2370 Å, ε 42,000.

2-Allylidene*cyclo*heptanol (6·5 g.) in absolute ethanol (50 ml.) in the presence of platinic oxide absorbed 1390 ml. of hydrogen at 21°/768 mm. (Calc., 1400 ml.), giving (*trans* ?-)2-*n*-propyl*cyclo*heptanol (6 g.), b. p. 67°/0·5 mm., n_D^{22} 1·4702. Infra-red light absorption: Max. at 3350—3450 (s), 1460 (s), 1025 (s), and 925 (m) cm.$^{-1}$. It formed a 3 : 5-*dinitrobenzoate*, prisms [from light petroleum (b. p. 60—80°)], m. p. 90—91° (Found: C, 58·0; H, 6·4; N, 8·4. $C_{17}H_{22}O_6N_2$ requires C, 58·3; H, 6·3; N, 8·0%). Light absorption in EtOH: $\lambda_{max.}$ 2280 Å (ε 23,000); $\lambda_{infl.}$ 2370 Å (ε 20,500).

2-*Allylidene*cyclo*heptanone* (VIII).—2-Allylidene*cyclo*heptanol (15 g.), vacuum-dried manganese dioxide (150 g.), and sodium-dried light petroleum (b. p. 40—60°) were shaken under nitrogen for 3 days at room temperature. The mixture was filtered, and the filtrate and washings were fractionated. The product gave no colour with Schiff's reagent and was 2-*allylidene*cyclo*heptanone* (12 g.), b. p. 46°/0·1 mm., n_D^{22} 1·5358 (Found: C, 79·7; H, 9·7. $C_{10}H_{14}O$ requires C, 80·0; H, 9·4%). Light absorption: see Table. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in red, monoclinic needles, m. p. 158—159° (Found: N, 16·95. $C_{16}H_{18}O_4N_4$ requires N, 16·95%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3840 Å, ε 19,000.

In absolute ethanol (70 ml.) in the presence of platinic oxide (200 mg.) the ketone (10·7 g.) absorbed 2400 ml. of hydrogen during 48 hr. at 20°/772 mm. (Calc. for 2 mols., 3400 ml.). Fractionation of the product gave a series of fractions (total, 10 g.) ranging from b. p. 42°/0·1 mm., n_D^{21} 1·4705 (Found: C, 77·8; H, 11·9. Calc. for $C_{10}H_{18}O$: C, 77·9; H, 11·8%), to b. p. 48°/0·1 mm., n_D^{21} 1·4800 (Found: C, 77·7; H, 12·0%), which consisted of mixtures of 2-*n*-propyl*cyclo*heptanone and an isomer, probably 2-propylidene*cyclo*heptanol. The infra-red spectrum of the lowest-boiling fraction was almost identical with that of an authentic sample of the saturated ketone (see below), whereas the infra-red spectrum of the highest-boiling fraction showed maxima at 3350—3450 (s) (O–H stretching), 1616 (w), 1460 (s), 1042 (s) (C–O stretching; cf. Zeiss and Tsutsu, *J. Amer. Chem. Soc.*, 1953, **75**, 897), 999 (s), and 860 (w) cm.$^{-1}$. The spectra of the middle fractions were intermediate in character. The highest-boiling fraction contained 0·48% of active hydrogen (Zerewitinoff) (Calc. for propylidene*cyclo*heptanol, 0·65%). On treatment with 2 : 4-dinitrophenylhydrazine in ethanol–sulphuric acid, each fraction gave 2-*n*-propyl*cyclo*heptanone 2 : 4-dinitrophenylhydrazone (total, 4·9 g., 23%), m. p. 90—92°, undepressed on admixture with the authentic sample described below. The derivative (1 g.) was warmed with chloroform (20 ml.), pyruvic acid (27 ml.), and a solution of hydrogen bromide in acetic acid (2·3N; 2·2 ml.) for 2·5 hr. at 45° with occasional shaking, and the mixture extracted with aqueous sodium hydrogen carbonate (cf. Mattox and Kendall, *J. Amer. Chem. Soc.*, 1948, **70**, 882). The regenerated 2-*n*-propyl*cyclo*heptanone had b. p. 50°/0·5 mm., n_D^{21} 1·4569, and formed a semicarbazone, m. p. 137°, undepressed on admixture with the authentic specimen described below.

2-n-*Propyl*cyclo*heptanone*.—(*a*) *N*-Nitroso-*n*-butylurethane (91 g.), prepared from *n*-butylurethane by the method of Cook, Raphael, and Scott (*J.*, 1951, 695), was added slowly to a stirred mixture of *cyclo*hexanone (53·3 g.), methanol (57 ml.), and sodium carbonate (1 g.) at 20—25°. Next day, the mixture was filtered and the filtrate fractionated, giving 2-n-*propyl*cyclo*heptanone* (40 ml.), b. p. 50°/0·5 mm., n_D^{24} 1·4553 (Found: C, 77·7; H, 11·8. $C_{10}H_{18}O$ requires C, 77·9; H, 11·8%). Infra-red light absorption: Max. at 3340 (m) (C = O stretching overtone), 1700 (s) (C = O stretching), 1460 (s), and 933 (s) cm.$^{-1}$. The *semicarbazone* crystallised from methanol in plates, m. p. 137—138° (Found: N, 19·9. $C_{11}H_{21}ON_3$ requires N, 19·9%). Light absorption in EtOH: $\lambda_{max.}$ 2280 Å, ε 15,400. The 2 : 4-*dinitrophenylhydrazone*, after chromatography on alumina in benzene–chloroform, crystallised from ethyl acetate in red needles, m. p. 90—91° (Found: C, 57·9; H, 6·6; N, 17·1. $C_{16}H_{22}O_4N_4$ requires C, 57·5; H, 6·6; N, 16·8%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3680 Å, ε 25,000.

The ketone was recovered unchanged when an ethanol solution was shaken with platinum oxide in hydrogen at room temperature.

(*b*) The ketone was also obtained, in low yield, by the following method based on unpublished work by Mr. P. H. Gore. Ethyl oxalate (29·6 g.), followed by *cyclo*heptanone (22·4 g.), was added to a solution of sodium ethoxide (from Na, 4·6 g.) in absolute ethanol (46 ml.) at 5°. Most of the ethanol was removed under reduced pressure, benzene (100 ml.) was added, followed by *n*-propyl bromide (36 ml.) and the mixture was then heated under reflux for 36 hr. After washing with water and removal of benzene, the residue was warmed with aqueous sodium hydroxide (5%; 200 ml.). Ether-extraction gave a mixture, b. p. 70—100°/16 mm., which on treatment with Brady's reagent afforded a small yield of 2-*n*-propyl*cyclo*heptanone 2 : 4-dinitrophenylhydrazone, m. p. 90°, undepressed on admixture with the specimen obtained as under (*a*).

1-cyclo*Hept*-1'-*enylbut*-2-*en*-1-*ol* (XII; $n = 1$) *and* -*butan*-1-*ol*.—Crotonaldehyde (35 g.) in ether (50 ml.) was added dropwise to a stirred ethereal solution of *cyclo*heptenyl-lithium (from Li, 6·9 g.). Stirring was continued for 12 hr. at room temperature, and saturated aqueous ammonium chloride solution (500 ml.) was then added. The products were worked up as described above, giving 1-cyclo*hept*-1'-*enylbut*-2-*en*-1-*ol* (50 g., 60%), b. p. 72°/0·5 mm., n_D^{21} 1·5010 (Found: C, 79·4; H, 11·0. $C_{11}H_{18}O$ requires C, 79·5; H, 10·9%). Light absorption in EtOH: $\varepsilon < 800$ between 2200 and 3000 Å.

Hydrogenation of the above alcohol (8·7 g.) in ethanol (60 ml.) in the presence of platinic oxide (uptake, 2400 ml. at 18°/762 mm. Calc., 2500 ml.) gave 1-cyclo*heptylbutan*-1-*ol*, b. p. 130°/25 mm., n_D^{23} 1·4776 (Found: C, 77·4; H, 12·6. $C_{11}H_{22}O$ requires C, 77·6; H, 13·0%). The 3 : 5-*dinitrobenzoate*, after repeated crystallisation from light petroleum (b. p. 60—80°) and methanol, formed fine needles, m. p. 68° (Found: C, 59·4; H, 6·9; N, 7·5. $C_{18}H_{24}O_6N_2$ requires C, 59·3; H, 6·6; N, 7·7%).

4-cyclo*Hept*-1'-*enylbut*-3-*en*-2-*ol* (XIII; $n = 1$).—The but-2-en-1-ol (XII; $n = 1$) (7 g.) was dissolved in 0·1M-solution of hydrogen chloride in 60% aqueous acetone (200 ml.). After 24 hr. at room temperature, the solution was neutralised with potassium carbonate and worked up in the manner described above, giving 4-cyclo*hept*-1'-*enylbut*-3-*en*-2-*ol* (6 g.), b. p. 87°/0·2 mm., n_D^{20} 1·5293 (Found: C, 79·7; H, 11·0. $C_{11}H_{18}O$ requires C, 79·5; H, 10·9%). Light absorption: see Table.

4-cyclo*Hept*-1'-*enylbut*-3-*en*-2-*one* (XIV; $n = 1$).—The above but-3-enol (2 g.), vacuum-dried manganese dioxide (20 g.), and light petroleum (b. p. 40—60°; 200 ml.) were shaken under nitrogen for 30 hr. at room temperature. After filtration, the solution and washings were fractionated, giving the diene ketone (1·8 g.), b. p. 70°/0·1 mm., n_D^{22} 1·5421. Light absorption: see Table. [Heilbron *et al.*, *J.*, 1949, 1827, give b. p. 76°/0·1 mm., n_D^{24} 1·5400, $\lambda_{max.}$ 2820 Å (ε 16,500).] The ketone formed, in 80% yield, a 2 : 4-dinitrophenylhydrazone which was chromatographed on alumina in benzene–chloroform and crystallised once from ethyl acetate to give red needles, m. p. 187°. After further crystallisation, the m. p. rose to 195° (Found: N, 16·2. Calc. for $C_{17}H_{20}O_4N_4$: N, 16·3%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3060 and 4000 Å, ε 17,000 and 31,000 respectively. The m. p.s of both samples were undepressed on admixture with the authentic specimen, m. p. 188° (*idem, ibid.*).

The 2 : 4-dinitrophenylhydrazone was also formed, though only in 10% yield, on direct treatment of 4-*cyclo*hept-1'-enylbut-3-en-2-ol with Brady's reagent (cf. Braude and Forbes, *J.*, 1951, 1762).

1-cyclo*Hept*-1'-*enylhexa*-2 : 4-*dien*-1-*ol* (XII; $n = 2$).—Freshly prepared sorbaldehyde (41 g.; Kuhn and Hoffer, *Ber.*, 1930, **63**, 2168) in ether (60 ml.) was added dropwise to a stirred ethereal solution of *cyclo*heptenyl-lithium (from Li, 6·9 g.) at 0°. Stirring was continued for 3 hr. at room temperature and excess of saturated aqueous ammonium chloride was then added. Working up as described above gave the *dienol* (53 g., 55%), b. p. 90°/5×10^{-3} mm., n_D^{20} 1·5285 (Found: C, 80·8; H, 10·5. $C_{13}H_{20}O$ requires C, 81·2; H, 10·5%). Light absorption in EtOH: $\lambda_{max.}$ 2280 Å, ε 14,500.

6-cyclo*Hept*-1'-*enylhexa*-3 : 5-*dien*-2-*ol* (XIII; $n = 2$).—The above dienol (3 g.) was dissolved in a 0·001M-solution of hydrogen chloride in 60% aqueous acetone (150 ml.). After 12 hr. at room temperature, the solution was neutralised with potassium carbonate and worked up as described above, giving the *dienol* (2 g.), b. p. 92°/5×10^{-3} mm., n_D^{20} 1·5835 (Found: C, 80·2; H, 10·1. $C_{13}H_{20}O$ requires C, 81·2; H, 10·5%). Light absorption: see Table.

On treatment of the dienol (1 g.) with Brady's reagent as described for 2-benzylidene*cyclo*heptanol, 6-cyclo*hept*-1'-*enylhexa*-3 : 5-*dien*-2-*one* 2 : 4-*dinitrophenylhydrazone* (0·3 g., 15%) was precipitated. After chromatography on alumina in benzene–chloroform, it crystallised from ethyl acetate in dark red prisms, m. p. 230—232° (decomp.) (Found: N, 15·0. $C_{19}H_{22}O_4N_4$ requires N, 15·1%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3050 and 4030 Å, ε 16,000 and 30,000, respectively.

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