951. *Alkenylation with Lithium Alkenyls. Part XIV.** *Syntheses in the* cyclo*Octene Series.*

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R. P. Houghton, and E. S. Waight.

The direct metallation of 1-chloro- and 1-bromo-*cyclo*octene by lithium, the reactions of the lithium alkenyl with aldehydes and ketones, and various reactions of the resulting alcohols are described. The results are generally similar to those observed with the smaller ring systems, except that the double bond shows a greater degree of stability in the endocyclic position.

In earlier papers, a variety of syntheses based on lithium alkenyls of the five-, six-, and seven-membered *cyclo*alkene series have been described.[1-4] This and the following paper deal with derivatives of the " medium-sized " *cyclo*octene and *cyclo*decene ring systems.

The preparation of 1-chloro- and 1-bromo-*cyclo*octene from the 1 : 2-dihalogeno*cyclo*octanes has been described by Kohler *et al.*[5] The action of chlorine on *cis*-*cyclo*octene in chloroform without special precautions gives a mixture of di- and tri-chloro*cyclo*octanes

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* Part XIII, *J.*, 1956, 3333.

[1] Braude and Forbes, *J.*, 1951, 1755.

[2] Braude and Coles, *J.*, 1950, 2014.

[3] Braude, Bruun, Weedon, and Woods, *J.*, 1952, 1414, 1419; Ginsburg, *J.*, 1954, 2361; Braude and Evans, *J.*, 1955, 3334.

[4] Braude, Forbes, and Evans, *J.*, 1953, 2202.

[5] Kohler, Tishler, Potter, and Thompson, *J. Amer. Chem. Soc.*, 1939, **61**, 1057.

(presumably by allylic substitution before addition, as has also been observed with *cyclo*hexene [6]) but, on exclusion of oxygen, 1 : 2-dichloro*cyclo*octane is the principal product; the reaction with bromine appears much less susceptible to catalytic influences, probably because addition is more rapid. The Hofmann elimination reaction of the 1 : 2-halogeno*cyclo*octanes by Kohler's method [5] afforded good yields of the 1-halogeno*cyclo*octenes. Although this method of synthesis could lead to the *trans-cyclo*octene derivatives (*trans*-addition to the *cis*-ring, followed by *trans*-elimination of hydrogen halide), the properties of these 1-halogeno*cyclo*octenes leave no doubt that they are the *cis*-ring isomers; in the eight-membered series, only the parent hydrocarbon has as yet been obtained [7] in the *trans*-configuration.

An alternative preparation of 1-chloro*cyclo*octene, by the action of phosphorus pentachloride on *cyclo*octanone, has been reported by Domnin.[8] This is the method preferred for the lower homologues and it has been suggested [1] that it involves elimination of $HO{\cdot}PCl_4$ from an intermediate of the type $\rangle CCl{\cdot}O{\cdot}PCl_4$, which can readily undergo *trans*-1 : 2-elimination leading to the *cis*-1-chloro*cyclo*alkene. We have confirmed that the products obtained by Kohler's and Domnin's procedures are identical, though the success of the latter method is very dependent on the purity of the *cyclo*octanone; low-melting ketone, of about 80% purity (based on gas–liquid chromatographic analysis), gives a product from which no pure 1-chloro*cyclo*octene can be isolated, and which cannot be successfully used for reactions involving conversion into *cyclo*octenyl-lithium.

The metallation of 1-bromo*cyclo*octene by lithium and the carboxylation of the resulting lithium alkenyl has already been effected by Cope, Burg, and Fenton.[9] *cyclo*Oct-1-enyl lithium from 1-chloro*cyclo*octene is formed less readily, but with an ease comparable to that of the lower homologues, and the same *cyclo*oct-1-enecarboxylic acid is obtained in each case and in nearly identical yield.

The lithium alkenyl prepared from 1-chloro- or 1-bromo-*cyclo*octene also reacts in the normal manner with aldehydes and ketones, to give alcohols in 25—65% yields. 1-Hydroxymethyl*cyclo*octene (I; R = H) (from formaldehyde) and 1-1′-hydroxyethyl*cyclo*octene (I; R = Me) (from acetaldehyde) were characterised as 3 : 5-dinitrobenzoates, and the hydroxyethyl compound was oxidised by chromic oxide in pyridine to 1-acetyl*cyclo*octene. The latter showed normal ultraviolet light absorption ($\lambda_{max.}$ 2360 Å, ε 11,500; cf. 1-acetyl*cyclo*hexene [10]) and on catalytic hydrogenation furnished acetyl*cyclo*octane.

With benzaldehyde the lithium alkenyl gave α-(*cyclo*oct-1-enyl)benzyl alcohol (II), the structure of which was confirmed by oxidation to the known [11] *cyclo*oct-1-enyl phenyl ketone. On treatment with dilute acid, the alcohol (II) underwent oxotropic rearrangement to 2-benzylidene*cyclo*octanol (III), but the intensity of light absorption at 2500 Å, which rose to a constant value (ε 8000), was lower than that expected for complete conversion; further, the material obtained on oxidation of this product showed maxima (at 2500 and 2830 Å) which suggested the presence of the two ketones derived from (II) and (III). Pure 2-benzylidene*cyclo*octanone (IV), showing the expected high-intensity absorption maxima, was prepared by condensation of benzaldehyde with *cyclo*octanone in the presence of boiling aqueous potassium hydroxide; under milder conditions the intermediate aldol could be isolated, and was readily converted into the unsaturated ketone by treatment with naphthalenesulphonic acid. Reduction of this ketone with lithium aluminium hydride gave pure 2-benzylidene*cyclo*octanol (III), and when this was treated with dilute acid it gave the same equilibrium mixture as that obtained from the isomer (II). Dehydration of 2-benzylidene*cyclo*octanol with naphthalenesulphonic acid

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[6] Bloomfield, *J.*, 1944, 114.

[7] Ziegler and Wilms, *Annalen*, 1950, **567**, 1; Cope, Pike, and Spencer, *J. Amer. Chem. Soc.*, 1953, **75**, 3212.

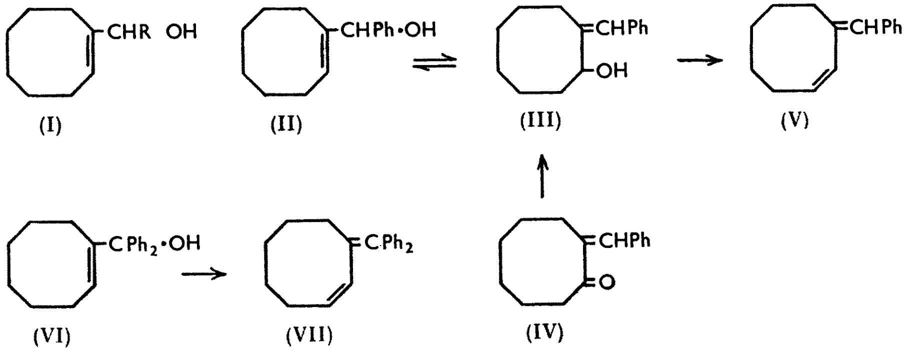
[8] Domnin, *J. Gen. Chem.* (*U.S.S.R.*), 1938, **8**, 851.

[9] Cope, Burg, and Fenton, *J. Amer. Chem. Soc.*, 1952, **74**, 173.

[10] Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *J.*, 1949, 1890.

[11] Cope and Marshall, *J. Amer. Chem. Soc.*, 1953, **75**, 3208.

gave 3-benzylidene*cyclo*octene (V). The incomplete isomerisation of the alcohol (II) indicates that in the *cyclo*octene series, in contrast to the smaller rings, the double bond has considerable stability in the endocyclic position; in this connection it is interesting that Kistiakowsky [12] and Lister,[13] from studies on the hydrogenation and bromination in the series *cyclo*pentene to *cyclo*octene, have concluded that *cyclo*octene is the most stable and least reactive of these *cyclo*olefins.



(I) (II) (III) (V)

(VI) (VII) (IV)

Interaction of *cyclo*octenyl-lithium with benzophenone gave the alcohol (VI) but the acid rearrangement of this was accompanied by dehydration to 3-diphenylmethylene*cyclo*octene (VII).

For the diallylic alcohols (VIII; R = H or Me), which were readily prepared by reaction with acraldehyde and crotonaldehyde respectively, two directions of rearrangement are possible. In the five-, six-, and seven-membered ring series [1,2,4] only one isomer was obtained in each case, though the migration took opposite courses according to whether R was H or Me. In the present investigation 1-*cyclo*oct-1′-enylallyl alcohol (VIII; R = H) gave 2-allylidene*cyclo*octanol (IX), the structure of which was established by oxidation to 2-allylidene*cyclo*octanone and by catalytic hydrogenation to 2-*n*-propyl*cyclo*octanol. The latter was converted into 2-*n*-propyl*cyclo*octanone and an authentic specimen, characterised by a 2 : 4-dinitrophenylhydrazone, was prepared by ring-expansion of *cyclo*heptanone with *N*-*n*-butyl-*N*-nitrosourethane in methanol; the immediate product of this reaction appears to be the unusually stable hemiketal (XI), hydrolysis of which required heating with sulphuric acid. The direction of rearrangement of the alcohol (VIII; R = H) is thus the same as for the analogous compounds with smaller rings. 1-*cyclo*Oct-1′-enylbut-2-en-1-ol (VIII; R = Me) (from which, by oxidation, the corresponding ketone was prepared) on rearrangement gave a mixture of a butenol and a dehydration product. By analogy with the direction of migration in the smaller-ring systems, the butenol is probably (X); this structure is supported by the infrared spectrum, which showed a band at 1363 cm.$^{-1}$ characteristic of a methyl group in a $>$CMe·OH environment, with only a very weak band at 1374 cm.$^{-1}$, the position characteristic of a –CMe= group. The butenol was oxidised by manganese dioxide to (probably) 4-*cyclo*oct-1′-enylbut-3-en-2-one (XII) characterised by a semicarbazone, which exhibited high-intensity ultraviolet light absorption ($\lambda_{max.}$ 2940 and 3030 Å; ε 42,000 and 36,000) typical of a dienone derivative. Dehydration of the mixture gave a conjugated triene, the infrared absorption spectrum of which showed maxima at 895 (vinyl group) and 1377 cm.$^{-1}$ (methyl group); the absorption intensities showed that the vinyl structure (XIII) was present in smaller amount than the isomer (XIV). If the proposed structure (X) for the rearranged alcohol is correct, dehydration is evidently accompanied by further rearrangement.

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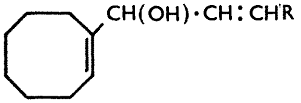
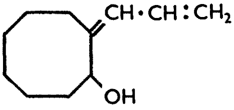
[12] Kistiakowsky, Conn, and Smith, *ibid.*, 1939, **61**, 1868.
[13] Lister, *ibid.*, 1941, **63**, 143.

In the reactions of *cyclo*octenyl-lithium with carbon dioxide and with carbonyl compounds, *cyclo*octene was usually isolated as a by-product. Cross-metallation of the solvent ether is well known [14] with lithium alkyls and with benzylic lithium derivatives, and results in formation of the parent alkane, but hitherto it has not been reported to occur with lithium alkenyls. Investigation has now shown,[15] however, that this appears to be of general occurrence with *cyclo*alkenyl-lithium preparations.



(VIII)



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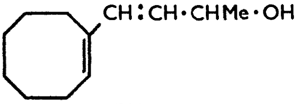

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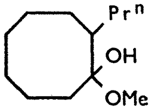

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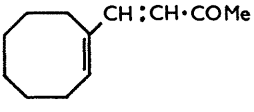

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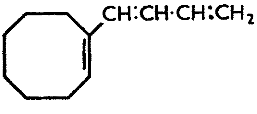
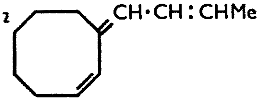


(XIII)



(XIV)

EXPERIMENTAL

Analytical data were determined in the organic microanalytical (Mr. F. H. Oliver, Miss J. Cuckney, and staff) and spectroanalytical (Mr. R. L. Erskine and Mrs. A. I. Boston) laboratories of this Department. The *cyclo*octatetraene was kindly made for us by British Oxygen Research and Development Ltd., by the polymerisation of acetylene under pressure.

cyclo*Octanone and* cyclo*Nonanone*.—(*a*) In accord with directions of Kohler *et al.*,[5] methylnitrosourethane (105 g.) was added to *cyclo*heptanone (56 g.), methanol (52 ml.) and powdered anhydrous sodium carbonate (1 g.). The mixture was kept overnight, filtered, and fractionated, giving: (i) low-boiling products (10 g.), b. p. 75—117°/100 mm.; (ii) impure *cyclo*octanone (25 g.), b. p. 118—127°/100 mm.; (iii) *cyclo*octanone (15 g.), b. p. 128—130°/100 mm., which solidified (m. p. 31°) and formed a 2 : 4-dinitrophenylhydrazone, yellow needles (from ethyl acetate-methanol), m. p. 167°, $\lambda_{\text{max.}}$ 3680 Å (ε 24,000) in $CHCl_3$ (Found: N, 18·3. Calc. for $C_{14}H_{18}O_4N_4$: N, 18·3%) (Brady [16] gives m. p. 163°); (iv) impure *cyclo*nonanone (5 g.), b. p. 131—135°/100 mm. The 2 : 4-*dinitrophenylhydrazone* of *cyclo*nonanone crystallised from ethyl acetate–methanol in yellow needles, m. p. 168°, $\lambda_{\text{max.}}$ 3680 Å (ε 25,000) in $CHCl_3$ (Found: C, 56·2; H, 6·3; N, 17·3. $C_{15}H_{20}O_4N_4$ requires C, 56·2; H, 6·3; N, 17·5%).

2-*Benzylidene*cyclo*nonanone*, prepared from the ketone (4 g.) and benzaldehyde (3·2 g.) in aqueous ethanol–0·1M-potassium hydroxide (20 ml.) at room temperature, had b. p. 90° (bath)/10^{-5} mm., n_D^{23} 1·5792, $\lambda_{\text{max.}}$ 2700 (ε 16,000) and 2800 Å (ε 13,500) in hexane (Found: C, 84·1; H, 9·0. $C_{16}H_{20}O$ requires C, 84·2; H, 8·8%), and formed a red 2 : 4-*dinitrophenylhydrazone* which after chromatography in benzene on alumina and crystallisation from ethyl acetate–methanol had m. p. 158°, $\lambda_{\text{max.}}$ 3940 Å (ε 25,000) in $CHCl_3$ (Found: C, 64·7; H, 6·0; N, 13·7. $C_{22}H_{24}O_4N_4$ requires C, 64·7; H, 5·9; N, 13·7%).

(*b*) Methylnitrosourea (230 g.) was added in small portions during 8 hr. to a stirred solution of potassium hydroxide (130 g.) in water (130 ml.) and methanol (600 ml.) containing *cyclo*heptanone (220 g.), at 5—10° (cooling). The mixture was stirred for 12 hr. at room temperature and then neutralised with acetic acid (35 ml.). The inorganic salts were filtered off and washed with methanol (50 ml.). The filtrate and washings were combined, and most of the methanol was removed by distillation through an 8 in. Dufton column. The residual solution was diluted with water (500 ml.), the aqueous layer extracted with ether (3 × 200 ml.), and the

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[14] Haubein, *Iowa State Coll. J. Sci.*, 1943, **18**, 48; *Chem. Abs.*, 1944, **38**, 716; Ziegler and Gellert, *Annalen*, 1950, **567**, 185; Braude, Chapter 4 in "Progress in Organic Chemistry," J. W. Cook, Ed., Vol. III, Butterworths, London, 1955.

[15] Houghton and Waight, unpublished observations.

[16] Brady, *J.*, 1931, 756.

extract added to the organic layer. The combined organic material was dried ($MgSO_4$) and carefully fractionated through a 2′ Stedman column, giving: (i) low-boiling material (98 g.), b. p. 82—98°/28 mm., n_D^{21} 1·4570—1·4650; (ii) impure *cyclo*octanone (28 g.), b. p. 98—101°/28 mm., m. p. 21—35°; (iii) a series of fractions of *cyclo*octanone (82 g., 32%), b. p. 101°/28 mm., m. p.s 38—41° to 42—43·5° (Kohler *et al.*[5] give m. p. 43·8°). Gas–liquid chromatography of the material of m. p. 42—43·5° showed it to be at least 99% pure.

cyclo*Octene*.—(*a*) *cyclo*Octanone (15·4 g.) was reduced with lithium aluminium hydride (2 g.) in boiling ether (250 ml.), the mixture was treated with water and ice-cold 10% sulphuric acid (150 ml.), and the crude *cyclo*octanol was isolated with ether and dehydrated by distillation from naphthalene-β-sulphonic acid at 180—250°, giving *cis-cyclo*octene (10 g.), b. p. 140°/760 mm., n_D^{21} 1·4690 (Kohler *et al.*[5] give b. p. 144°/773 mm., n_D^{20} 1·4693).

(*b*) *cis-cis-cyclo*Octa-1 : 5-diene (79 g.), kindly supplied by Dr. H. W. B. Reed[17] (Imperial Chemical Industries Limited, Billingham), was hydrogenated in ether (400 ml.) in the presence of 5% palladium–charcoal (0·9 g.). The rapid uptake of gas ceased after 17·8 l. of hydrogen at 18°/804 mm. (calc. for 1 mol., 16·5 l.) had been absorbed. The catalyst was filtered off and the solution was fractionated, giving *cis-cyclo*octene (72 g.), b. p. 88°/141 mm., n_D^{21} 1·4690.

(*c*) *cyclo*Octatetraene (50 g.) in ether (100 ml.) was hydrogenated in the presence of a 1% palladium–calcium carbonate catalyst (1 g.) at room temperature.[18] When the uptake of hydrogen had ceased, the catalyst was filtered off and the solution was fractionated, giving *cis-cyclo*octene (45 g.), b. p. 140°/760 mm., n_D^{21} 1·4690.

The infrared spectra (3—15 μ) of all three samples were indistinguishable and exhibited $\nu_{max.}$ 3000(w) (=C–H stretching), 2890 (s) and 2820 (s) (⩾C–H stretching), 1645 (w) (C=C stretching), 1460 (s) (⩾C–H bending), 1355 (w), 1246 (w), 982 (w), 890 (m), 752 (s), and 700 (m) cm.$^{-1}$, in excellent agreement with Cope *et al.*[7]

1-*Chloro*cyclo*octene*.—(a) (" *Kohler's chloride.*") Liquid chlorine (13 ml.) was allowed to boil in a stream of nitrogen, and the gas was passed into a solution of *cyclo*octene (22 g.; freshly distilled from sodium) in peroxide-free chloroform (50 ml.) at −60°. Distillation gave 1 : 2-dichloro*cyclo*octane (26·4 g.), b. p. 74°/1 mm., n_D^{24} 1·5055 (Kohler *et al.*[5] give b. p. 130·5°/25 mm., n_D^{20} 1·5061). When chlorine was passed into a solution of *cyclo*octene in commercial chloroform, a mixture, b. p. 86—120°/0·5 mm., n_D^{20} 1·511—1·542, was obtained from which a fraction corresponding to 1 : 2 : 3-*trichloro*cyclo*octane*, b. p. 100—103°/0·5 mm., n_D^{20} 1·5305 (Found: Cl, 48·7. $C_8H_{13}Cl_3$ requires Cl, 49·4%), was isolated.

1 : 2-Dichloro*cyclo*octane (26 g.), benzene (60 ml.), and dimethylamine (30 ml.) were heated in a sealed vessel at 160° for 15 hr. After cooling, dimethylamine hydrochloride (10·3 g.) was filtered off and the filtrate was washed with dilute hydrochloric acid, dried (Na_2SO_4), and distilled, giving *cis*-1-chloro*cyclo*octene (13 g.), b. p. 68°/13 mm., n_D^{21} 1·4923 (Kohler *et al.*[5] give b. p. 77—78°/19 mm., n_D^{20} 1·4928). The infrared spectrum showed $\nu_{max.}$ 3030 (w) (=C–H stretching) 2890 and 2850 (s) (⩾C–H stretching), 1665 (s) (C=C stretching), 1468 (s), 1449 (s) and 1360 (m), (⩾C–H bending), 1220 (m), 1125 (s), 1000 (m), 896 (s), 840 (s), 775 (m), and 739 (m) cm.$^{-1}$.

(b) (" *Domnin's chloride.*") *cyclo*Octanone (26·9 g.), m. p. ≮38°, in light petroleum (30 ml.; b. p. 40—60°) was added during 20 min. to a stirred suspension of phosphorus pentachloride (65 g.) in light petroleum (20 ml.; b. p. 40—60°). The mixture was stirred for 2 hr., then poured into cold water (500 ml.), and the organic material extracted with ether (2 × 100 ml.). The extract was dried ($MgSO_4$) and fractionated through an 8 in. Dufton column, giving 1-chloro*cyclo*octene (13·4 g., 44%), b. p. 82—86°/21 mm., n_D^{20} 1·4918 (Domnin[8] gives b. p. 64—68°/10 mm.). The infrared spectrum was identical with that of " Kohler's chloride."

1-*Bromo*cyclo*octene*.—By following the procedure of Kohler *et al.*,[5] *cyclo*octene (11 g.) was converted into 1-bromo*cyclo*octene (10·5 g.), b. p. 88—90°/15 mm., n_D^{20} 1·5178 (Kohler *et al.*[5] give b. p. 97—98°/23 mm., n_D^{20} 1·5182). The infrared spectrum showed $\nu_{max.}$ 2900 (s) (⩾C–H stretching), 1640 (m) (C=C stretching), 1450 (s) and 1355 (m) (⩾C–H bending), 1212 (s), 1107 (m), 1010 (m), 981 (m), 898 (m), 868 (s), 830 (s), 771 (m), and 730 (m) cm.$^{-1}$.

cyclo*Octene*-1-*carboxylic Acid*.—(*a*) 1-Bromo*cyclo*octene (7·2 g.) in ether (15 ml.) was added to a stirred suspension of finely cut lithium (0·57 g.) in dry ether (100 ml.) under nitrogen. The solution became turbid within 2 min., and after about 5 min. the ether was refluxing. Reaction was complete after 2 hr. and solid carbon dioxide (300 g.) was then added. When the mixture

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[17] Reed, *J.*, 1954, 1931.

[18] Cf. Reppe, Schlichting, Klager, and Toepel, *Annalen*, 1948, **560**, 1; Cope and Estes, *J. Amer. Chem. Soc.*, 1950, **72**, 1128.

had attained room temperature, water (75 ml.) was added and the mixture was acidified with hydrochloric acid. The ether layer was separated and extracted with saturated aqueous sodium hydrogen carbonate. Acidifying this extract with concentrated hydrochloric acid precipitated *cyclo*octene-1-carboxylic acid (0·99 g., 17%); it was recrystallised from water and sublimed at 10^{-4} mm. and then had m. p. 102—103°, $\lambda_{\text{max.}}$ 2150 Å (ε 12,000) in EtOH (Found: C, 69·9; H, 9·3. Calc. for $C_9H_{14}O_2$: C, 70·1; H, 9·2%) (Cope *et al.*[9] give m. p. 101·8—102·6°). The *amide*, prepared by treatment with thionyl chloride followed by ammonia, crystallised from water as plates, m. p. 106° (Found: C, 70·6; H, 10·0; N, 9·0. $C_9H_{15}ON$ requires C, 70·55; H, 9·9; N, 9·1%).

(*b*) 1-Chloro*cyclo*octene (18·5 g.) was added to a stirred suspension of freshly cut lithium (1·8 g.) in ether (350 ml.) under nitrogen. The mixture was stirred and refluxed for 24 hr., assuming an opaque, greenish-grey appearance. Carboxylation as above gave 1-*cyclo*octene-carboxylic acid (3·2 g., 16%), which crystallised from light petroleum (b. p. 40—60°) as plates, m. p. 102°. The ether layer on distillation, gave *cyclo*octene (2·5 g., 19%), b. p. 31°/10 mm., n_{D}^{23} 1·4680 (Found: C, 87·3; H, 13·0. Calc. for C_8H_{14}: C, 87·2; H, 12·8%), which readily decolorised bromine in chloroform and showed an infrared spectrum indistinguishable from that of an authentic specimen.

1-*Hydroxymethyl*cyclo*octene.*—Gaseous formaldehyde, generated by heating paraformaldehyde (1·5 g.) at 180—200°, was passed into a stirred solution of lithium alkenyl (from 1-bromo*cyclo*octene, 8·6 g.) in ether under nitrogen at 0°. The solution was kept overnight at room temperature, saturated aqueous ammonium chloride (50 ml.) was added at 0°, and the ether layer was separated, dried (Na_2SO_4), and fractionated, giving 1-*hydroxymethyl*cyclo*octene* (1·6 g., 25%), b. p. 104—105°/9 mm., n_{D}^{22} 1·4975 (Found: C, 77·4; H, 11·6. $C_9H_{16}O$ requires C, 77·1; H, 11·5%). The 3 : 5-*dinitrobenzoate* crystallised from light petroleum (b. p. 40—60°) in prisms, m. p. 97—98° (Found: C, 57·3; H, 5·5; N, 8·7. $C_{16}H_{18}O_6N_2$ requires C, 57·5; H, 5·4; N, 8·4%).

1-1′-*Hydroxyethyl*cyclo*octene.*—Acetaldehyde (2·4 g.) in ether (20 ml.) was added dropwise during 10 min. to a solution of *cyclo*octenyl-lithium (from 1-chloro*cyclo*octene, 7·7 g.) in ether (200 ml.). After this had been stirred for 1 hr. at room temperature, saturated aqueous ammonium chloride (100 ml.) was added at 0° and the ether layer was separated, dried ($MgSO_4$), and fractionated, giving: (i) *cyclo*octene (1·14 g., 19%), b. p. 41—42°/16 mm., n_{D}^{22} 1·4685; (ii) 1-1′-*hydroxyethyl*cyclo*octene* (4·57 g., 55%), b. p. 72—79°/0·9 mm., n_{D}^{21} 1·4978 (Found: C, 77·5; H, 11·7. $C_{10}H_{18}O$ requires C, 77·9; H, 11·8%), whose 3 : 5-*dinitrobenzoate* crystallised from light petroleum (b. p. 40—60°) in plates, m. p. 53—54° (Found: C, 58·8; H, 6·0; N, 8·1. $C_{17}H_{20}O_6N_2$ requires C, 58·6; H, 5·8; N, 8·0%).

1-*Acetyl*cyclo*octene.*—A solution of the foregoing alcohol (3·14 g.) in pyridine (30 ml.) was added to chromium trioxide (3·5 g.) in pyridine (35 ml.) at 0° and the mixture was then kept at room temperature for 3 hr. The dark brown solution was carefully diluted with water (150 ml.) and then extracted with ether (3 × 50 ml.). The ether extracts were dried (Na_2SO_4) and distilled, giving the crude ketone (2·8 g.), b. p. 100°/11 mm., n_{D}^{21} 1·4991; this was converted into the *semicarbazone* (1·53 g., 40%) which after crystallisation from ethanol and sublimation at 10^{-4} mm. had m. p. 191—192°, $\lambda_{\text{max.}}$ 2650 Å (ε 20,500) in EtOH (Found: C, 63·2; H, 9·2; N, 20·3. $C_{11}H_{19}ON_3$ requires C, 63·1; H, 9·15; N, 20·1%). Steam-distillation of the semicarbazone with twice its weight of phthalic anhydride regenerated almost quantitatively pure 1-*acetyl*cyclo*octene*, b. p. 62—64°/0·5 mm., n_{D}^{20} 1·4998, $\lambda_{\text{max.}}$ 2360 Å (ε 11,400) in EtOH (Found: C, 78·2; H, 10·6. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). The infrared spectrum showed $\nu_{\text{max.}}$ 1667 (s) (C=O stretching) and 1637 cm.$^{-1}$ (m) (C=C stretching). The ketone formed a red 2 : 4-*dinitrophenylhydrazone* which after chromatography in benzene on alumina and crystallisation from ethyl acetate had m. p. 165°, $\lambda_{\text{max.}}$ 3850 Å (ε 26,000) in $CHCl_3$ (Found: C, 57·7; H, 6·1; N, 16·7. $C_{16}H_{20}O_4N_4$ requires C, 57·8; H, 6·1; N, 16·9%).

The ketone (0·57 g.) was hydrogenated in ethanol (20 ml.) over 5% palladium–charcoal (0·1 g.), to give acetyl*cyclo*octane (0·51 g., 88%), b. p. 81—83°/2 mm., n_{D}^{22} 1·4762. The infrared spectrum showed $\nu_{\text{max.}}$ 1706 cm.$^{-1}$ (s) (C=O stretching). The semicarbazone after crystallisation from aqueous ethanol and sublimation at 10^{-4} mm. had m. p. 180—181° (lit.,[19] 180—181°) (Found: C, 62·5; H, 10·1; N, 19·6. Calc. for $C_{11}H_{21}ON_3$: C, 62·5; H, 10·0; N, 19·9%).

α-(cyclo*Oct*-1-*enyl*)*benzyl Alcohol.*—Freshly distilled benzaldehyde (6·4 g.) in ether (30 ml.) was added dropwise to a solution of *cyclo*octenyl-lithium (from 1-chloro*cyclo*octene, 8·7 g.) at

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[19] Ruzicka and Boekenoogen, *Helv. Chim. Acta*, 1931, **14**, 1319.

such a rate that the ether refluxed gently. Stirring was continued for 2 hr. at room temperature. Saturated aqueous ammonium chloride (300 ml.) was then added at 0°, and the ether layer was separated, dried ($MgSO_4$), and distilled, giving (i) *cyclo*octene (1·47 g., 22%), b. p. 32—38°/12 mm., n_D^{20} 1·4755, and (ii) α-(cyclo*oct*-1-*enyl*)*benzyl alcohol* (6·7 g., 51%), b. p. 111—112°/0·01 mm., n_D^{21} 1·5545, which solidified at 0° and then had m. p. 25—29° (Found: C, 83·5; H, 9·45. $C_{15}H_{20}O$ requires C, 83·3; H, 9·3%). The light absorption in ethanol ($\lambda_{max.}$ 2470 Å; ε 2100) showed that the product probably contained a small amount of ketone, but was free from rearranged alcohol.

cyclo*Oct-1-enyl Phenyl Ketone*.—The above alcohol (1·32 g.) in dry benzene (15 ml.) was added to the complex prepared from chromium trioxide (1·5 g.) and pyridine (15 ml.), and the mixture was shaken for 12 hr. at room temperature. The solid was filtered off and washed with benzene (20 ml.). The filtrate and washings were combined and passed through a short alumina column (Spence H). The column was eluted with benzene (50 ml.), to give the ketone (1·16 g., 89%) b. p. 128—132°/0·8 mm., n_D^{23} 1·5604 (Cope and Marshall [11] give b. p. 94°/0·06 mm., n_D^{25} 1·5630); the infrared spectrum showed $\nu_{max.}$ 1641 cm.$^{-1}$ (s) (C=O stretching); the light absorption max. in EtOH was at 2450 Å (ε 11,800). The ketone formed a red 2 : 4-dinitrophenylhydrazone which crystallised from methanol–ethyl acetate in two forms, m. p. 135—138° and m. p. 160—161° (Cope and Marshall [11] give m. p. 161—162°).

Oxotropic Rearrangement of α-(cyclo*Oct*-1-*enyl*)*benzyl Alcohol*.—A solution of the alcohol (1·67 g.) in a 0·1M-solution of hydrogen chloride in 80% aqueous acetone (40 ml.) was kept for 18 hr. at room temperature, then neutralised with saturated aqueous sodium hydrogen carbonate, and the acetone was removed under reduced pressure. The organic material was extracted with ether (2 × 10 ml.), and the extract was dried ($MgSO_4$) and distilled, giving a product (1·34 g., 80%), b. p. 130—132°/0·5 mm., n_D^{23} 1·5554, $\lambda_{max.}$ 2500 Å (ε 5500) in EtOH. Re-treatment of the product (0·79 g.) for a further 85 hr. gave material (0·56 g., 71%), b. p. 128—135°/0·5 mm., n_D^{22} 1·5655, $\lambda_{max.}$ 2500 Å (ε 8000) in EtOH.

A mixture of the rearrangement products (0·83 g.) in dry benzene (15 ml.) was added to the complex prepared from chromium trioxide (1·0 g.) and pyridine (10 ml.) in benzene (10 ml.), and shaken for 12 hr. at room temperature, to yield a product (0·69 g., 84%), b. p. 133—138°/0·9 mm., n_D^{21} 1·5668, $\lambda_{max.}$ 2500 and 2830 Å (ε 12,500 and 6,850 respectively) in EtOH, indicating the presence of the two corresponding ketones.

2-*Benzylidene*cyclo*octanone*.—(*a*) A mixture of *cyclo*octanone (14·0 g.), benzaldehyde (7·5 g.), potassium hydroxide (2·5 g.), and water (65 ml.) was refluxed for 3½ hr., then cooled, acidified with acetic acid (3·5 ml.) in water (100 ml.), and extracted with ether (2 × 50 ml.). The extract was dried ($MgSO_4$) and distilled, giving 2-*benzylidene*cyclo*octanone* (8·37 g., 35%), b. p. 145—150°/0·8 mm., n_D^{22} 1·5780, which solidified when cooled in ice, and after recrystallisation from hexane had m. p. 76—77°, $\lambda_{max.}$ 2760 Å (ε 11,600) in *cyclo*hexane, $\lambda_{max.}$ 2850 Å (ε 15,800) in EtOH (Found: C, 84·3; H, 8·5. $C_{15}H_{18}O$ requires C, 84·1; H, 8·5%). The 2 : 4-*dinitrophenylhydrazone*, after chromatography in benzene on alumina and crystallisation from ethyl acetate–methanol, had m. p. 181—182°, $\lambda_{max.}$ 3900 Å (ε 25,000) in $CHCl_3$ (Found: C, 63·8; H, 5·9; N, 13·7. $C_{21}H_{22}O_4N_4$ requires C, 63·9; H, 5·6; N, 14·2%).

(*b*) Benzaldehyde (3·0 g.) in 50% aqueous ethanol (30 ml.) was added with vigorous stirring to *cyclo*octanone (15·1 g.) in 50% aqueous ethanol–0·1M-potassium hydroxide (200 ml.). After 4 hr., water (300 ml.) was added and the solution was extracted with ether. The ether extract was dried (Na_2SO_4) and distilled, giving some unchanged benzaldehyde and *cyclo*octanone, followed by a fraction (1·6 g.), b. p. 142°/0·3 mm., which was redistilled to give 2-(α-*hydroxybenzyl*)cyclo*octanone*, b. p. 80°/10^{-5} mm., n_D^{20} 1·5480 [Found: C, 77·4; H, 8·5; active hydrogen (Zerewitinoff), 0·43. $C_{15}H_{20}O_2$ requires C, 77·6; H, 8·7; 1H, 0·43%].

The hydroxy-ketone (1·1 g.) was heated with naphthalene-β-sulphonic acid (50 mg.) at 70°/10^{-4} mm. 2-Benzylidene*cyclo*octanone (0·6 g.) sublimed and after crystallisation from light petroleum (b. p. 40—60°) had m. p. 76—77°.

2-*Benzylidene*cyclo*octanol*.—Lithium aluminium hydride (0·15 g.) in ether (50 ml.) was added dropwise during 10 min. to 2-benzylidene*cyclo*octanone (2·0 g.) in ether (30 ml.) at 0°. After a further 10 minutes' stirring at 0°, saturated aqueous ammonium chloride (100 ml.) was added. The ether layer was separated, dried ($MgSO_4$), and distilled, giving the *alcohol* (1·80 g., 89%), b. p. 140—143°/0·5 mm., n_D^{24} 1·5770, $\lambda_{max.}$ 2500 Å (ε 12,500) in EtOH (Found: C, 83·15; H, 9·25. $C_{15}H_{20}O$ requires C, 83·3; H, 9·3%). Distillation of the alcohol (0·71 g.) from naphthalene-β-sulphonic acid (0·5 g.) gave 3-*benzylidene*cyclo*octene* (0·45 g., 68%), b. p. 60° (bath)/10^{-5} mm., n_D^{21} 1·5962, $\lambda_{max.}$ 2260, 2510, 2700, and 2800 Å (ε 9000, 10,000, 14,000, and 14,000 respectively) in EtOH (Found: C, 90·0; H, 9·2. $C_{15}H_{18}$ requires C, 90·85; H, 9·15%).

Oxotropic Rearrangement of 2-*Benzylidene*cyclo*octanol*.—A solution of the alcohol (0·59 g.) in a 0·1M-solution of hydrogen chloride in 80% aqueous acetone (20 ml.) was kept for 63 hr. at room temperature. Isolation in the usual way gave a product (0·39 g., 66%), b. p. 138°/0·9 mm., n_D^{23} 1·5710, $\lambda_{max.}$ 2510 Å (ε 8200) in EtOH. The infrared spectrum was almost indistinguishable from that of the material obtained by oxotropic rearrangement of α-(*cyclo*oct-1-enyl)-benzyl alcohol.

α-(cyclo*Oct*-1-*enyl*)*diphenylmethanol*.—Benzophenone (4·5 g.) in ether (40 ml.) was added to the lithium alkenyl (from 1-bromo*cyclo*octene, 4·7 g.) in ether at room temperature. Next day, saturated aqueous ammonium chloride (50 ml.) was added, and the ether layer was separated, dried (Na_2SO_4–K_2CO_3), and distilled, giving the *alcohol* (4·0 g., 55%), b. p. 80—90° (bath)/10^{-5} mm., n_D^{22} 1·5925 (Found: C, 86·3; H, 8·3. $C_{21}H_{24}O$ requires C, 86·25; H, 8·3%).

A solution of the alcohol (3·3 g.) in 80% aqueous acetone–0·1M-hydrogen chloride (100 ml.) was kept for 3 days at room temperature. The mixture was neutralised with potassium carbonate and worked up by the procedure previously described, yielding a product (2·5 g.), b. p. 70—80° (bath)/10^{-5} mm., n_D^{21} 1·607—1·615 (Found: C, 89·9; H, 8·1%), which was redistilled from naphthalene-β-sulphonic acid (50 mg.) to give 3-*diphenylmethylene*cyclo*octene*, b. p. 100° (bath)/10^{-3} mm., n_D^{20} 1·6192, $\lambda_{max.}$ 2260, 2510, 2560, and 2670 Å (ε 21,500, 10,000, 11,500, and 11,500, respectively) in EtOH (Found: C, 91·8; H, 8·1. $C_{21}H_{22}$ requires C, 91·9; H, 8·1%).

1-cyclo*Oct*-1′-*enylallyl alcohol*.—Freshly distilled acraldehyde (4·4 ml.) in ether (15 ml.) was added to 1-*cyclo*octenyl-lithium (from 1-bromo*cyclo*octene, 12·9 g.) in ether at 0°. After 1·5 hr. at room temperature, saturated aqueous ammonium chloride (50 ml.) was added at 0° and the ether layer was separated, dried (Na_2SO_4–K_2CO_3), and distilled, giving the *alcohol* (7·0 g., 62%), b. p. 72—74°/0·15 mm., n_D^{22} 1·5080, ε < 1000 between 2000 and 3000 Å (Found: C, 79·4; H, 11·1. $C_{11}H_{18}O$ requires C, 79·5; H, 10·9%).

2-*Allylidene*cyclo*octanol*.—A solution of the foregoing alcohol (7·5 g.) in 80% aqueous acetone–0·05M-hydrogen chloride (200 ml.) was kept for 15 hr. at room temperature and then neutralised with potassium carbonate. The acetone was distilled off through a column, and the product was isolated by ether-extraction, giving the *alcohol* (5·1 g.), b. p. 80—82°/0·5 mm., n_D^{24} 1·5335, $\lambda_{max.}$ 2380 Å (ε 22,000) in EtOH (Found: C, 79·6; H, 11·0. $C_{11}H_{18}O$ requires C, 79·5; H, 10·9%).

2-*Allylidene*cyclo*octanone*.—The foregoing alcohol (1·5 g.) in pyridine (20 ml.) was added to chromium trioxide (2·0 g.) in pyridine (20 ml.) at 0°. The mixture was kept overnight at room temperature and diluted with water (200 ml.), and the product, which gave no colour with Schiff's reagent, was isolated by ether-extraction and distilled, giving the *ketone* (1·1 g.), b. p. 76—78°/0·5 mm., n_D^{18} 1·5508, $\lambda_{max.}$ 2800 Å (ε 16,000) in EtOH (Found: C, 80·5; H, 9·9. $C_{11}H_{16}O$ requires C, 80·4; H, 9·8%). The 2 : 4-*dinitrophenylhydrazone*, after chromatography in benzene on alumina and crystallisation from ethyl acetate–methanol, had m. p. 225°, $\lambda_{max.}$ 3930 Å (ε 32,000) in $CHCl_3$ (Found: C, 59·3; H, 6·1; N, 16·1. $C_{17}H_{20}O_4N_4$ requires C, 59·3; H, 5·85; N, 16·3%).

2-n-*Propyl*cyclo*octanol*.—2-Allylidene*cyclo*octanol (1·63 g.) was hydrogenated in methanol (25 ml.) over platinic oxide (25 mg.). The uptake of hydrogen ceased when 490 ml. at 20°/782 mm. (calc. for 2 mol., 468 ml.) had been absorbed. The catalyst was filtered off and the solution distilled, giving the *alcohol* (0·5 g.), b. p. 70—72°/0·5 mm., n_D^{20} 1·4770 (Found: C, 78·0; H, 12·9. $C_{11}H_{22}O$ requires C, 77·6; H, 13·0%). The 3 : 5-*dinitrobenzoate* crystallised from light petroleum (b. p. 60—80°) and had m. p. 78—79° (Found: C, 59·6; H, 7·0; N, 7·7. $C_{18}H_{24}O_6N_2$ requires C, 59·3; H, 6·6; N, 7·7%).

2-n-*Propyl*cyclo*octanone*.—(*a*) The foregoing alcohol (0·3 g.) was oxidised with chromic oxide (0·5 g.) in pyridine (10 ml.), and the product was treated with Brady's reagent, giving 2-*n*-propyl*cyclo*octanone 2 : 4-dinitrophenylhydrazone (0·5 g.) which, after chromatography in benzene on alumina and crystallisation from methanol, had m. p. 133—134°, undepressed on admixture with the specimen described below.

(*b*) *N*-*n*-Butyl-*N*-nitrosourethane [20] (5 g.) was added to a stirred mixture of *cyclo*heptanone

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[20] Wilds and Meader, *J. Org. Chem.*, 1948, **13**, 763; cf. Cook, Raphael, and Scott, *J.*, 1951, 695.

(18·5 ml.), methanol (17 ml.), and sodium carbonate (0·3 g.). After 30 min., a vigorous reaction took place which was controlled by external cooling. More urethane (total 26 g.) was then added in portions during 1 hr. at 20—25°. The mixture was kept overnight and filtered, and the solution was fractionated, giving a product formulated as 1-*methoxy*-2-n-*propyl*cyclo*octan*-1-*ol* (7 g.), b. p. 41°/0·5 mm., n_D^{23} 1·4571 (Found: C, 71·95; H, 11·9. $C_{12}H_{24}O_2$ requires C, 71·95; H, 12·1%).

The hemiketal (2 g.) was heated with acetic acid (20 ml.) and sulphuric acid (2 g.) for 3 hr. at 80°. The solution was kept for 3 days at room temperature, diluted with water, neutralised with sodium carbonate, and extracted with ether. The ether extract was dried (Na_2SO_4) and distilled, giving 2-n-*propyl*cyclo*octanone* (0·7 g.), b. p. 69°/0·1 mm., n_D^{21} 1·4590 (Found: C, 78·5; H, 12·0. $C_{11}H_{20}O$ requires C, 78·5; H, 12·0%). The 2 : 4-*dinitrophenylhydrazone*, obtained by treating either the hemiketal or the ketone with Brady's reagent, was chromatographed in benzene–chloroform on alumina and crystallised from ethyl acetate in fine orange needles, m. p. 132°, $\lambda_{max.}$ 3700 Å (ε 27,000) in $CHCl_3$ (Found: C, 58·5; H, 7·1; N, 16·0. $C_{17}H_{24}O_4N_4$ requires C, 58·6; H, 6·9; N, 16·1%).

1-cyclo*Oct*-1′-*enylbut*-2-*en*-1-*ol*.—Crotonaldehyde (2·4 ml.) in ether (20 ml.) was added dropwise during 10 min. to a solution of *cyclo*octenyl-lithium (from 1-chloro*cyclo*octene, 4·4 g.) in ether (150 ml.). After 2 hours' stirring at room temperature, saturated aqueous ammonium chloride (100 ml.) was added at 0°. The ether layer was separated, dried ($MgSO_4$), and fractionated, giving *cyclo*octene (0·80 g., 24%), b. p. 30—31°/10 mm., n_D^{22} 1·4660, and the *alcohol* (2·51 g., 46%), b. p. 90—94°/0·4 mm., n_D^{22} 1·5075 (Found: C, 80·2; H, 11·3. $C_{12}H_{20}O$ requires C, 79·9; H, 11·2%), ε < 800 between 2000 and 3000 Å in EtOH.

1-cyclo*Oct*-1′-*enylbut*-2-*en*-1-*one*.—The above alcohol (1·21 g.) in dry benzene (10 ml.) was shaken with the complex prepared from chromium trioxide (1·4 g.) and pyridine (15 ml.) in benzene (15 ml.) for 3 hr. at room temperature. Isolation of the organic material as above gave the ketone (0·91 g., 76%), b. p. 105—107°/1·5 mm., n_D^{21} 1·5205, $\lambda_{max.}$ 2450 Å (ε 7100) in EtOH, $\nu_{max.}$ 1660 (s), 1616 (s), and 975 (s) cm.$^{-1}$. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate and had m. p. 233—234°, $\lambda_{max.}$ 3980 Å (ε 27,600) (Found: C, 60·6; H, 6·1; N, 15·4. $C_{18}H_{22}O_4N_4$ requires C, 60·3; H, 6·2; N, 15·6%).

Rearrangement of 1-cyclo*Oct*-1′-*enylbut*-2-*en*-1-*ol*.—A solution of the alcohol (0·99 g.) in a 0·1M-solution of hydrogen chloride in 80% aqueous acetone (25 ml.) was kept for 24 hr. at room temperature. Isolation of the product in the usual way gave an oil (0·50 g.), b. p. 80—100°/0·4 mm., n_D^{21} 1·5321, $\lambda_{max.}$ 2400, 2680, and 2770 Å (ε 16,200, 6320, and 6480 respectively) in EtOH, $\nu_{max.}$ 3356 (m) (O–H stretching), 1374 (w) and 1363 (m) (C–H deformation of $C-CH_3$) and 893 cm.$^{-1}$ (w) (C–H out of plane deformation of $C=CH_2$).

The above mixture (0·32 g.) was distilled from anhydrous potassium hydrogen sulphate (0·1 g.) to give a product (0·14 g., 49%), b. p. 130—150° (bath)/1·5 mm., n_D^{22} 1·5572 $\lambda_{max.}$ 2680 and 2770 Å (ε 26,100 and 26,300 respectively) in EtOH. The infrared spectrum in CCl_4 shows $\nu_{max.}$ 1377 and 895 cm.$^{-1}$ (ε 29 and 54 respectively).

A further portion of the rearrangement product (2·2 g.) was shaken with manganese dioxide (20 g.) in light petroleum (b. p. 40—60°; 200 ml.) for 3 days, and the product was distilled and treated with semicarbazide acetate and aqueous ethanol, giving (probably) 4-cyclo*oct*-1′-*enylbut*-3-*en*-2-*one semicarbazone* (0·55 g.), which after crystallisation from ethanol and sublimation at 10^{-5} mm. had m. p. 181—182°, $\lambda_{max.}$ 2940 and 3030 Å (ε 42,000 and 36,000 respectively) (Found: C, 66·6; H, 9·2; N, 18·0. $C_{13}H_{21}ON_3$ requires C, 66·4; H, 9·0; N, 17·9%).

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