250. *Physical Properties and Chemical Constitution. Part III.* cyclo*Pentane,* cyclo*Hexane,* cyclo*Heptane, and some Derivatives. The Multiplanar Structure of the Methyl*cyclo*hexane Ring.*

By ARTHUR I. VOGEL.

The surface tensions and densities over a range of temperatures, and the refractive indices for the C, D, F, and G lines at 20° have been measured for pure *cyclo*pentane, methyl*cyclo*pentane, *cyclo*hexane, methyl*cyclo*hexane, *cyclo*heptane, and the related ketones, alcohols, and unsaturated hydrocarbons, together with a number of methylene compounds. The parachors, molecular refractivities, dispersions, and molecular refraction coefficients have been evaluated. Several forms of methyl*cyclo*hexane have been isolated; this provides evidence for the multiplanar structure of the simple *cyclo*hexane ring.

IN continuation of the work described in Parts I and II (J., 1934, 333, 1758), the above physical properties have been measured for the compounds enumerated. The comparison of the observed with the theoretical values must await new data now being obtained, for there is some uncertainty in the values for the structural and atomic parachors and possibly in those for the refractivities. For example, for CH_2, C, and H respectively the recorded parachors are: 39·0, 4·8, and 17·1 (Sugden, J., 1924, **125**, 1180); 40·0, 9·2, and 15·4 (Mumford and Phillips, J., 1929, 2112); 40·3, 11·5, and 14·4 (Vogel, Part II, *loc. cit.*).

The method adopted for the preparation of the pure hydrocarbons consisted in reducing the pure ketone to the secondary alcohol by means of sodium and moist ether, dehydrating the alcohol with phosphoric oxide, and reducing the resultant unsaturated hydrocarbon with Adams's platinum catalyst and hydrogen. The constitutions of the unsaturated hydrocarbons from *cyclo*pentanol, methyl*cyclo*pentanol, and *cyclo*hexanol thus prepared are unambiguous, but, contrary to the statement of Harries and Tank (*Ber.*, 1908, **41**, 1709), *cyclo*heptanol yielded a mixture of *cyclo*heptene and a methyl*cyclo*hexene (see Experimental). Pure *cyclo*heptane was ultimately prepared according to the scheme:

$$cyclo\text{Heptanol} \xrightarrow{PBr_3} cyclo\text{heptyl bromide} \xrightarrow{\text{alc. KOH}} cyclo\text{heptene} \xrightarrow{Pt, H_2} cyclo\text{heptane}$$

The dehydration with phosphoric oxide of 2-, 3-, and 4-methyl*cyclo*hexanols gave largely two methyl*cyclo*hexenes, almost identical products being obtained from the 3- and the

4-methyl compound. These two differed from 1-methyl-Δ^1-*cyclo*hexene produced by the facile dehydration of 1-methyl*cyclo*hexanol with a little iodine. It would therefore appear that 2-methyl*cyclo*hexanol yields chiefly the Δ^2-compound, but 3- and 4-methyl*cyclo*hexanols yield largely the Δ^3-compound. There is some uncertainty in the literature concerning the pure Δ^2-compound, but the physical properties (density and refractive index) of the pure Δ^1-compound (compare Wallach, *Annalen*, 1908, **359**, 298; v. Auwers, *ibid.*, 1915, **410**, 300; Nametkin and Jarzew, *Ber.*, 1923, **56**, 1803) and of the Δ^3-hydrocarbon (Nametkin and Brussov, *ibid.*, p. 1807) appear to be well established. The ready isomerisation of the methyl*cyclo*hexenes in the presence of the various dehydrating agents employed by other workers doubtless accounts for the diverse boiling points, densities, and refractive indices recorded (v. Auwers, *loc. cit.*). It would seem that, if appreciable isomerisation occurred in the presence of phosphoric oxide, then the same mixture should be obtained in every dehydration with this reagent; this, however, was not the case. Experiments are in progress with a view to prepare the pure unsaturated hydrocarbons by the method used for *cyclo*heptene, and also to establish their constitution and homogeneity by ozonolysis and other means.

*cyclo*Pentene, methyl*cyclo*pentene, *cyclo*hexene, and *cyclo*heptene were readily reduced in alcoholic solution with Adams's platinum catalyst and hydrogen, although the velocity of hydrogenation varied with the compound (cf. Godchot, *Bull. Soc. chim.*, 1934, **1**, 1157). With the methyl*cyclo*hexenes from 2-, 3-, and 4-methyl*cyclo*hexanols, 60—80% reduction occurred in about 30 hours, after which the reaction became extremely slow; to obtain complete reduction it was necessary to remove the alcohol and continue the reduction in the absence of a solvent. Satisfactory reduction of 1-methyl-Δ^1-*cyclo*hexene could only be carried out in the absence of a solvent and was complete after 84 hours.

The most remarkable results were obtained with the methyl*cyclo*hexenes. The same methyl*cyclo*hexane was produced from the Δ^1-compound and from the dehydration products of 3- and 4-methyl*cyclo*hexanols; for the first-named, which was undoubtedly homogeneous, the methyl*cyclo*hexane (*A*) had $d_{4°}^{20·0°}$ 0·7704, $n_C^{20·0°}$ 1·42167, $n_D^{20·0°}$ 1·42410, $n_F^{20·0°}$ 1·42915, $n_{G'}^{20·0°}$ 1·43301. The methyl*cyclo*hexane (*B*) from 2-methyl*cyclo*hexanol had $d_{4°}^{20·0°}$ 0·7679, $n_C^{20·0°}$ 1·42081, $n_D^{20·0°}$ 1·42306, $n_F^{20·0°}$ 1·42839, $n_{G'}^{20·0°}$ 1·43230; upon standing at room temperature for several days, or more rapidly upon warming for a short time at 40—60°, this yielded an apparently stable form (*B'*) with $d_{4°}^{20·0°}$ 0·7694, $n_C^{20·0°}$ 1·42093, $n_D^{20·0°}$ 1·42316, $n_F^{20·0°}$ 1·42846, $n_{G'}^{20·0°}$ 1·43250. The existence of two seemingly stable, (*A*) and (*B'*), and one unstable form (*B*), of the methyl*cyclo*hexane ring provides definite experimental evidence for the multiplanar structure of the ring. The problem as to which of these represents the "chair" or "*Z*," "boat" or "*C*" forms, or mixtures of these two will be discussed when experiments now in progress have been completed. Meanwhile, it is necessary to point out that these physical properties differ considerably from those of ethyl*cyclo*pentane for which Eisenlohr (*Fortschr. Chem. Physik*, 1925, **18**, Heft 9, p. 23) gives b. p. 100·5—101·0°/756 mm., $d_{4°}^{20°}$ 0·7610, $n_\alpha^{20°}$ 1·41612, $n_{He}^{20°}$ 1·41840, $n_\beta^{20°}$ 1·42332, $n_\gamma^{20°}$ 1·42798. Furthermore, Cohen (*Proc. Roy. Acad. Amsterdam*, 1934, **37**, 532), on the basis of geometrical analysis, has suggested two configurations for *cyclo*hexane, one "fixed," represented by the "*Z*" modification, and the other "mobile," having an infinite number of modifications, of which the "*C*" form is one.

Qudrat-i-Khuda's claim (*J. Indian Chem. Soc.*, 1931, **8**, 277; *Nature*, 1935, **136**, 301) that 4-methyl*cyclo*hexane-1-acetic-2-carboxylic acid could be obtained in four forms was not confirmed by Goldschmidt and Gräfinger (*Ber.*, 1935, **68**, 279), and Dey and Linstead (J., 1935, 1063) have shown that his second form of ββ-dimethyl*cyclo*hexanone (*Nature*, 1933, **132**, 210) is in reality 2 : 4 : 4-trimethyl*cyclo*pentanone, a molecular rearrangement having taken place in the Clemmensen reduction of the dimethyldihydroresorcinol. It seems very probable that one of the alleged acetyl*cyclo*hexanes obtained by Zelinsky and Tarassowa (*Annalen*, 1934, **508**, 115) by the action of aluminium chloride or bromide and acetyl chloride upon *cyclo*hexane, followed by catalytic reduction with platinum-black in methyl-alcoholic solution, contains or is a methylacetyl*cyclo*pentane for the following reasons: (i) *cyclo*Hexane when heated with aluminium chloride at 80° passes into methyl*cyclo*pentane (Zelinsky and Turowa-Pollak, *Ber.*, 1932, **65**, 1171). (ii) The physical properties do not differ markedly from those of 1-acetyl-2-methyl*cyclo*pentane, as can be seen from the following table :

Substance.	B. p.	$d_{4^\circ}^{20^\circ}$.	$n_D^{20^\circ}$.	M. p. of semicarbazone.
Acetyl*cyclo*hexane (form *A*)	63°/13 mm.	0·9012	1·4438	150—151°
Acetyl*cyclo*hexane (form *B*)	76—76·5/27 mm.	0·9117	1·4470	171—172
1-Acetyl-2-methyl*cyclo*pentane	59·8—60/15 mm.	0·8983	1·4420	162

(iii) No evidence is presented as to the source or homogeneity of the *cyclo*hexane employed.

Furthermore, Miller and Adams (*J. Amer. Chem. Soc.*, 1936, **58**, 787) were unable to isolate more than one form of 4 : 4-dimethyl*cyclo*hexane-1 : 1-diacetic or -1-carboxylic-1-acetic acid or 4-methyl*cyclo*hexane-1 : 1-diacetic acid in spite of an exhaustive search. It would therefore appear that the author's results supply the first direct experimental evidence for the existence of the simple *cyclo*hexane ring in multiplanar forms. Mention must be made of the fact that the dipole moment of *cyclo*hexa-1 : 4-dione, determined in benzene solution, has been found to be 1·6 D. by Hassel and Naeshagen (*Tids. Kjemi Berg.*, 1930, No. 7) and 1·3 D. by Le Fèvre and Le Fèvre (J., 1935, 1696). According to the calculations of the latter authors, these results indicate that in benzene solution an equilibrium exists between the "*cis-*" and the "*trans-*" strainless form, and that the proportion of the "*cis-*" form is 9—15%. No separation of the two forms was, however, effected. The literature reveals variations in the physical properties of methyl*cyclo*hexane prepared by different methods :

Method.*	B. p.	Density.	Refractive index.
1	101°	$d_{4^\circ}^{20^\circ}$ 0·7693	$n_D^{18^\circ}$ 1·4243
2	103°/760 mm.	$d_{4^\circ}^{18\cdot5^\circ}$ 0·7662	$n_D^{18\cdot5^\circ}$ 1·41705
3	101°/757 mm.	$d_{0^\circ}^{20^\circ}$ 0·7695	$n_D^{20^\circ}$ 1·4230
4	100°/770 mm.	$d_{4^\circ}^{20^\circ}$ 0·7736	$n_\alpha^{20^\circ}$ 1·42365, $n_{He}^{20^\circ}$ 1·42590, $n_\beta^{20^\circ}$ 1·41320, $n_\gamma^{20^\circ}$ 1·43651
5	99·5—100·0°/759 mm.	0·7708	$n_\alpha^{20^\circ}$ 1·42175, $n_{He}^{20^\circ}$ 1·42390, $n_\beta^{20^\circ}$ 1·42931, $n_\gamma^{20^\circ}$ 1·43367
6	100°/770 mm.	0·7725	$n_\alpha^{20^\circ}$ 1·42265, $n_{He}^{20^\circ}$ 1·42500, $n_\beta^{20^\circ}$ 1·43040, $n_\gamma^{20^\circ}$ 1·43470
7	100°/780 mm.	0·7735	$n_\alpha^{20^\circ}$ 1·42355, $n_{He}^{20^\circ}$ 1·42590, $n_\beta^{20^\circ}$ 1·43130, $n_\gamma^{20^\circ}$ 1·43561
8	101·2°	d^{15° 0·77340	$n_\alpha^{15^\circ}$ 1·42305, $n_D^{15^\circ}$ 1·42535, $n_{He}^{15^\circ}$ 1·42550, $n_\beta^{15^\circ}$ 1·43072
		d^{30° 0·76030	$n_\gamma^{15^\circ}$ 1·43510

* (1) From iodo-3-methyl*cyclo*hexane and HI (Zelinsky, *Ber.*, 1897, **30**, 1538). (2) From bromomethyl*cyclo*hexane with zinc dust and HOAc (Knoevenagel, *Annalen*, 1897, **297**, 159). (3) From 3-methyl*cyclo*hexanonehydrazone and solid KOH (Kishner, *Centr.*, 1911, ii, 363). (4) From pure toluene with Pt-black and H_2 in HOAc (Eisenlohr, *loc. cit.*). (5) From *cyclo*hexanone and MeI, etc. (*idem, ibid.*). (6) From *p*-methyl*cyclo*hexanonesemicarbazone and NaOEt (*idem, ibid.*). (7) From *o*-methyl*cyclo*hexanonesemicarbazone and NaOEt (*idem, ibid.*). (8) Source not stated (Timmermans and Martin, *J. Chim. physique*, 1926, **23**, 761).

It is possible that a *partial* explanation of the differences is to be found in the preponderance of one or other of the multiplanar forms.

EXPERIMENTAL.

Details of the preparation of the various pure compounds are given below. All operations were conducted in Pyrex vessels, and the final distillations were carried out in all-Pyrex apparatus fitted with interchangeable ground-glass joints. Middle constant-boiling fractions were separately collected for the physical measurements, and kept in Pyrex test-tubes which had been thoroughly cleaned with chromic acid mixture, washed with distilled water, and dried at 120°.

The refractive indices and dispersions at 20·0° and also the surface tensions and densities over a range of temperatures were measured as described in Part II (*loc. cit.*); for a temperature of *ca.* 41° redistilled methylene chloride was used. Three surface-tension apparatus, *A*, *B*, and *C*, were employed, the constants of which, when determined with pure benzene, were 1·8725, 2·3449, and 2·4827, respectively.

In the tabulated results, t is the temperature, h the observed difference in height (in mm.) in the two arms of the U-tube, H the corrected value, $d_{4^\circ}^{t^\circ}$ the density (calculated from the observed densities by assuming a linear variation with temperature), γ the surface tension (dynes/cm.) computed from the equation $\gamma = KHd$, P the parachor, M the molecular weight, and $Mn_D^{20\cdot0^\circ}$ the molecular refraction coefficient. The parachor was calculated in the usual way, allowance for the density of the vapour being made when the temperature of measurement was within 60° of the b. p.; the density of the vapour was evaluated by Sugden's method (J., 1925, **127**, 1540). The number in parenthesis following the value of $\gamma_{20°}$ is the temperature coefficient of the surface tension. All measurements of the refractive indices were carried out at 20·0° ± 0·05°. The following abbreviations are employed: $d_{4°}^{20°}$ for $d_{4°}^{20·0°}$; $Mn_D^{20°}$ for $Mn_D^{20·0°}$; R_C, R_D, R_F, $R_{G'}$, for $[R_L]_C$, $[R_L]_D$, $[R_L]_F$, and $[R_L]_{G'}$ respectively.

Assistance in the preparations and measurements marked with an asterisk was given by Mr. R. J. Tudor, M.Sc., A.I.C. The new values for the surface tensions, densities, and parachors for some of the various ketones replace those previously published (Vogel, J., 1928, 2029; Vogel and Oommen, J., 1930, 770; Vogel, J., 1931, 1801); greater care was taken with the purification, and the final distillation was conducted in an all-Pyrex glass apparatus. Godchot (collected results in *Bull. Soc. chim.*, 1934, **1**, 1153) determined, *inter alia*, $d_{13·5°}^{13·5°}$, $n_{Hg\text{-}\alpha}^{13·5°}$, $n_D^{13·5°}$, $\gamma_{13·5°}$ for a number of unsaturated and saturated alicyclic hydrocarbons, but did not give full details of the purity of the starting materials; his parachor was computed from one determination at 13·5°.

* cyclo*Pentanone*.—This was prepared from adipic acid, m. p. 151—152° (Vogel, J., 1929, 727), and purified through the semicarbazone, m. p. 206° (*ex* alcohol), from which the ketone was regenerated in this and the following cases with oxalic acid. M = 84·11; b. p. 129°/756 mm.; n_C 1·43452, n_D 1·43680, n_F 1·44243, $n_{G'}$ 1·44652; R_C 23·20, R_D 23·31, R_F 23·56, $R_{G'}$ 23·75; $R_{G'-C}$ 0·55, R_{F-C} 0·36; $Mn_D^{20°}$ 120·85. Densities determined: $d_{4°}^{20°}$ 0·9450, $d_{4°}^{64·4°}$ 0·9075, $d_{4°}^{87·4°}$ 0·8857.

$\gamma_{20°}$ = 33·31 (0·11). Apparatus *A*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
23·0°	18·93	18·69	0·9423	32·98	213·9	86·5°	15·91	15·67	0·8865	26·01	214·2
64·1	17·05	16·81	0·9078	28·57	214·2					Mean	214·1

(Wallach, *Annalen*, 1907, **353**, 331, gives b. p. 129°, $d^{20°}$ 0·948, $n_D^{20°}$ 1·4366; v. Auwers, Hinterseber, and Treppmann, *ibid.*, 1915, **410**, 281, give b. p. 130·0—130·4°, $d_{4°}^{17·8°}$ 0·9513, $n_\alpha^{17·8°}$ 1·43535, $n_D^{17·8°}$ 1·43757, $n_\beta^{17·8°}$ 1·44340, $n^{17·8°}$ 1·44820; Vogel, J., 1928, 2030, gives b. p. 129·5°/761·5 mm., $d_{4°}^{16·0°}$ 0·9524, $n_D^{16·0°}$ 1·4383, *P* 214·2.)

* 3-*Methyl*cyclo*pentanone*.—The ketone, b. p. 143—144°, from pure β-methyladipic acid (cf. Part II, *loc. cit.*) was purified through the semicarbazone, m. p. 185—186° (*ex* alcohol); b. p. 144°/770 mm.; M = 98·14; n_C 1·43153, n_D 1·43360, n_F 1·43941, $n_{G'}$ 1·44353; R_C 27·86, R_D 27·97, R_F 28·30, $R_{G'}$ 28·53; $R_{G'-C}$ 0·67, R_{F-C} 0·44; $Mn_D^{20°}$ 140·69. Densities determined: $d_{4°}^{20°}$ 0·9129, $d_{4°}^{62·5°}$ 0·8751, $d_{4°}^{87·5°}$ 0·8524.

$\gamma_{20°}$ = 29·72 (0·10). Apparatus *A*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
21·3°	17·57	17·33	0·9117	29·59	251·1	87·0°	14·77	14·53	0·8529	23·21	251·4
62·2	15·89	15·65	0·8754	25·65	252·3					Mean	251·6

(Wallach, *Annalen*, 1912, **394**, 371, gives b. p. 144—144·5°, $d^{22°}$ 0·913, n_D 1·4329; Vogel, J., 1931, 1800, gives b. p. 143·5—144°/759 mm., $d_{4°}^{17·5°}$ 0·9155, *P* 252·7.)

* cyclo*Hexanone*.—The purest commercial ketone was purified through the semicarbazone, m. p. 165° (*ex* methyl alcohol); b. p. 155°/763·5 mm.; M = 98·14; n_C 1·44737, n_D 1·44977, n_F 1·45563, $n_{G'}$ 1·45995; R_C 27·75, R_D 27·87, R_F 28·19, $R_{G'}$ 28·42; $R_{G'-C}$ 0·67, R_{F-C} 0·44; $Mn_D^{20°}$ 142·28. Densities determined: $d_{4°}^{20°}$ 0·9455, $d_{4°}^{64·6°}$ 0·9077, $d_{4°}^{87·6°}$ 0·8876.

$\gamma_{20°}$ = 35·32 (0·13). Apparatus *A*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
20·7°	20·15	19·91	0·9449	35·23	25·30	86·9°	16·54	16·30	0·8882	27·10	252·1
62·8	17·58	17·34	0·9091	29·52	251·5					Mean	252·2

(Wallach, *Annalen*, 1907, **353**, 331, gives b. p. 155°, $d^{21°}$ 0·947, $n_D^{20°}$ 1·4503: v. Auwers, Hinterseber, and Treppmann, *loc. cit.*, give b. p. 156·6—156·8°, $d_{4°}^{15·3°}$ 0·9503, $n_\alpha^{15·3°}$ 1·45024, $n_D^{15·3°}$ 1·45261, $n_\beta^{15·3°}$ 1·45859, $n_\gamma^{15·3°}$ 1·46370; Vogel, *loc. cit.*, gives b. p. 47°/15 mm., $d_{4°}^{16·9°}$ 0·9488, $n_D^{16·9°}$ 1·4521, *P* 251·4.)

* 2-*Methyl*cyclo*hexanone*.—The 2-, 3-, and 4-methyl*cyclo*hexanones were prepared for this research by Messrs. Howards from the chemically pure cresols. The 2-methyl ketone had b. p. 164°/770 mm. and was purified through the semicarbazone, m. p. 196° (*ex* rectified spirit). B. p. 165°/764 mm.; M = 112·17; n_C 1·44527, n_D 1·44766, n_F 1·45340, $n_{G'}$ 1·45759; R_C 32·37, R_D 32·51, R_F 32·87, $R_{G'}$ 33·13; $R_{G'-C}$ 0·76, R_{F-C} 0·50; $Mn_D^{20°}$ 162·13. Densities determined: $d_{4°}^{20°}$ 0·9231, $d_{4°}^{62·5°}$ 0·8896, $d_{4°}^{83·7°}$ 0·8715.

γ_{20° = 32·05 (0·10). Apparatus *B*.

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
22·1°	14·97	14·73	0·9214	31·83	289·1	86·9°	12·58	12·34	0·8689	25·14	289·1
61·6	13·51	13·27	0·8903	27·70	289·1					Mean	289·1

(Wallach, *Annalen*, 1906, **346**, 251, gives b. p. 165°, $d_{4^\circ}^{21\cdot5^\circ}$ 0·923, $n_D^{21\cdot5^\circ}$ 1·4461; Sabatier and Mailhe, *Ann. Chim.*, 1907, **10**, 527, give b. p. 162—163°, $d_{4^\circ}^{13^\circ}$ 0·935, $n_D^{13^\circ}$ 1·454; v. Auwers, Hinterseber, and Treppmann, *loc. cit.*, give b. p. 167°/740 mm., $d_{4^\circ}^{14\cdot6^\circ}$ 0·9300, $n_\alpha^{14\cdot6^\circ}$ 1·44827, $n_D^{14\cdot6^\circ}$ 1·45049, $n_\beta^{14\cdot6^\circ}$ 1·45653, $n_\gamma^{14\cdot6^\circ}$ 1·41635; v. Auwers and Lange, *Annalen*, 1915, **410**, 319, give b. p. 164—165°, $d_{4^\circ}^{20^\circ}$ 0·924, $n_D^{20^\circ}$ 1·4493; Eisenlohr, *loc. cit.*, gives b. p. 165°/757 mm., $d_{4^\circ}^{20^\circ}$ 0·9240, $n_\alpha^{20^\circ}$ 1·44481, $n_{He}^{20^\circ}$ 1·44747, $n_\beta^{20^\circ}$ 1·45332, $n_\gamma^{20^\circ}$ 1·45845; Vogel and Oommen, J., 1930, 774, give b. p. 165°/757 mm., $d_{4^\circ}^{19\cdot4^\circ}$ 0·9255, $n_D^{19\cdot4^\circ}$ 1·4484, *P* 288·2.)

* 3-*Methyl*cyclo*hexanone*.—Howards' product, b. p. 168—169°/770 mm., was purified through the semicarbazone, m. p. 191° (*ex* methyl alcohol). B. p. 169°/762 mm.; *M* = 112·17; n_C 1·44301, n_D 1·44566, n_F 1·45127, $n_{G'}$ 1·45565; R_C 32·48, R_D 32·65, R_F 33·01, $R_{G'}$ 33·29; $R_{G'-C}$ 0·81, R_{F-C} 0·53; $Mn_D^{20^\circ}$ 162·16. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9155, $d_{4^\circ}^{62\cdot2^\circ}$ 0·8815, $d_{4^\circ}^{86\cdot9^\circ}$ 0·8641.

γ_{20° = 31·33 (0·10). Apparatus *B*.

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
21·3°	14·79	14·55	0·9145	31·20	289·9	85·8°	12·46	12·22	0·8650	25·27	290·8
60·8	13·37	13·13	0·8826	27·17	290·2					Mean	290·3

(Wallach, *Annalen*, 1896, **289**, 339, gives b. p. 169°, d^{21° 0·915, $n_D^{21^\circ}$ 1·4456; Knoevenagel, *ibid.*, 1897, **297**, 155, gives b. p. 169—170°, $d_{4^\circ}^{19\cdot3^\circ}$ 0·9213, $n_D^{19\cdot3^\circ}$ 1·44174; Sabatier and Mailhe, *loc. cit.*, give b. p. 169°/765 mm., $d_{4^\circ}^{14^\circ}$ 0·930, $n_D^{14^\circ}$ 1·454; v. Auwers, Hinterseber, and Treppmann, *loc. cit.*, give b. p. 60—60·2°/15 mm., $d_{4^\circ}^{25\cdot15^\circ}$ 0·9139, $n_\alpha^{25\cdot15^\circ}$ 1·44092, $n_D^{25\cdot15^\circ}$ 1·44313, $n_\beta^{25\cdot15^\circ}$ 1·44914, $n_\gamma^{25\cdot15^\circ}$ 1·45394; Eisenlohr, *loc. cit.*, gives b. p. 170·5°/755 mm., $d_{4^\circ}^{20^\circ}$ 0·9182, $n_\alpha^{20^\circ}$ 1·44270, $n_{He}^{20^\circ}$ 1·44526, $n_\beta^{20^\circ}$ 1·45122, $n_\gamma^{20^\circ}$ 1·45598; Vogel and Oommen, *loc. cit.*, give b. p. 169°/747·5 mm., $d_{4^\circ}^{18\cdot7^\circ}$ 0·9151, $n_D^{18\cdot7^\circ}$ 1·4463, *P* 290·0.)

* 4-*Methyl*cyclo*hexanone*.—Howards' product, b. p. 170—171°/770 mm., was purified through the semicarbazone, m. p. 197° (*ex* methyl alcohol–ethyl alcohol, 1 : 1). B. p. 170°/761 mm.; *M* = 112·17, n_C 1·44290, n_D 1·44506, n_F 1·45081, $n_{G'}$ 1·45509; R_C 32·51, R_D 32·65, R_F 33·01, $R_{G'}$ 33·29; $R_{G'-C}$ 0·78, R_{F-C} 0·50; $Mn_D^{20^\circ}$ 162·10. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9145, $d_{4^\circ}^{60\cdot9^\circ}$ 0·8832, $d_{4^\circ}^{85\cdot9^\circ}$ 0·8269.

γ_{20° = 30·94 (0·09). Apparatus *B*.

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
23·2°	14·57	14·33	0·9120	30·65	289·4	86·1°	12·48	12·24	0·8627	24·76	290·0
60·5	13·37	13·13	0·8835	27·20	289·9					Mean	289·8

(Wallach, *Annalen*, 1905, **346**, 251, gives b. p. 169—171°, $d_{4^\circ}^{20^\circ}$ 0·914, $n_D^{20^\circ}$ 1·4435; Sabatier and Mailhe, *loc. cit.*, give b. p. 169·5°/760 mm., $d_{4^\circ}^{13^\circ}$ 0·9235, $n_D^{13^\circ}$ 1·452; Haller, *Compt. rend.*, 1913, **157**, 743, gives b. p. 170°/760 mm., $d_{4^\circ}^{20^\circ}$ 0·9132, $n_D^{20^\circ}$ 1·4458; v. Auwers, Hinterseber, and Treppmann, *loc. cit.*, give b. p. 55·8—56·4°/10·5 mm., $d_{4^\circ}^{24\cdot4^\circ}$ 0·9119, $n_\alpha^{24\cdot4^\circ}$ 1·44092, $n_D^{24\cdot4^\circ}$ 1·44322, $n_\beta^{24\cdot4^\circ}$ 1·44918, $n_\gamma^{24\cdot4^\circ}$ 1·45413; v. Auwers and Kolligs, *Ber.*, 1922, **55**, 45, give b. p. 169·2°, $d_{4^\circ}^{19\cdot9^\circ}$ 0·91685, $n_\alpha^{19\cdot9^\circ}$ 1·44285, $n_D^{19\cdot9^\circ}$ 1·44509, $n_\beta^{19\cdot9^\circ}$ 1·45110, $n^{19\cdot9^\circ}$ 1·45595; Eisenlohr, *loc. cit.*, gives, *inter alia*, b. p. 171·5°/750 mm., $d_{4^\circ}^{20^\circ}$ 0·9128, $n_\alpha^{20^\circ}$ 1·44099, $n_{He}^{20^\circ}$ 1·44346, $n_\beta^{20^\circ}$ 1·44924, $n_\gamma^{20^\circ}$ 1·45401; Vogel and Oommen, *loc. cit.*, give b. p. 171°/747 mm., $d_{4^\circ}^{19\cdot3^\circ}$ 0·9159, $n_D^{19\cdot3^\circ}$ 1·4455, *P* 289·6.)

cyclo*Heptanone*.—Suberic acid, m. p. 140—141°, is slowly distilled with iron filings and a little baryta (Vogel, J., 1928, 2034); there is a vigorous evolution of hydrogen during the first three hours, due to the formation of the iron salt; it is advisable to attach a long glass tube to the side arm of the cooled filter-flask acting as receiver and to pass it directly into the exhaust pipe of the fume chamber. The distillate was added to excess of saturated sodium bisulphite solution, shaken vigorously, the separated solid collected after 12 hours, and washed with alcohol and ether. The ketone was regenerated from the bisulphite compound with sodium hydroxide solution, well washed with water, dried (anhydrous sodium sulphate), and distilled. B. p. 180°/760 mm.; *M* = 112·17; n_C 1·45725, n_D 1·45976, n_F 1·46575, $n_{G'}$ 1·47306; R_C 32·21, R_D 32·36, R_F 32·52, $R_{G'}$ 33·00; $R_{G'-C}$ 0·79, R_{F-C} 0·31, $Mn_D^{20^\circ}$ 163·75. Densities determined (J., 1928, 2030): $d_{4^\circ}^{20^\circ}$ 0·9491, $d_{4^\circ}^{61\cdot7^\circ}$ 0·9160, $d_{4^\circ}^{86\cdot8^\circ}$ 0·8954.

γ_{20° = 34·70 (0·11). Apparatus *B*.

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
15·5°	15·99	15·75	0·9527	35·19	286·7	86·0°	13·48	13·24	0·8960	27·82	287·5
61·2	14·28	14·04	0·9164	30·17	286·9					Mean	287·0

(Wallach, *Annalen*, 1907, **353**, 331, gives b. p. 180°, $d^{21°}$ 0·9500, $n_D^{21°}$ 1·4604; v. Auwers, Hinterseber, and Treppmann, *loc. cit.*, give $d_{4°}^{21·9°}$ 0·9495, $n_\alpha^{21·9°}$ 1·45801, $n_D^{21·9°}$ 1·46027, $n_\beta^{20·9°}$ 1·46646, $n_\gamma^{21·9°}$ 1·47149; Vogel, *loc. cit.*, gives b. p. 181°/769 mm., $d_{4°}^{15·0°}$ 0·9526, $n_D^{15·0°}$ 1·4635, *P* 288·0.)

* trans-β-*Decalone*.—The ketone, b. p. 117°/16 mm., from pure trans-β-decalol (cf. Part II, *loc. cit.*) was purified through the semicarbazone, m. p. 192—193° (*ex* alcohol). B. p. 117°/16 mm.; M = 152·23; n_C 1·48015, n_D 1·48282, n_F 1·48922, $n_{G'}$ 1·49384; R_C 44·18, R_D 44·38; R_F 44·88, $R_{G'}$ 45·24; $R_{G'-C}$ 1·06, R_{F-C} 0·64; $Mn_D^{20°}$ 225·73. Densities determined: $d_{4°}^{20°}$ 0·9792, $d_{4°}^{60·7°}$ 0·9485, $d_{4°}^{85·6°}$ 0·9312.

$\gamma_{20°}$ = 36·16 (0·10). Apparatus *A*.

t.	*h.*	*H.*	$d_{4°}^{t°}$.	γ.	*P.*	*t.*	*h.*	*H.*	$d_{4°}^{t°}$.	γ.	*P.*
18·5°	20·02	19·78	0·9804	36·31	381·2	86·4°	17·43	17·19	0·9306	29·95	382·7
61·2	18·36	18·12	0·9481	32·17	382·4						Mean 382·1

(Hückel, *Annalen*, 1925, **441**, 20, gives b. p. 126°/30 mm., $d_{4°}^{15·7°}$ 0·9797, $n_D^{19°}$ 1·48088; Rao, J., 1929, 1961, b. p. 117°/16 mm., $d_{4°}^{22·2°}$ 0·97624, $n_D^{22·2°}$ 1·48337; Vogel, *loc. cit.*, b. p. 106°/12 mm., $d_{4°}^{17·7°}$ 0·9800, $n_D^{17·7°}$ 1·4843, *P* 382·4.)

trans-*Hexahydro*-β-*hydrindone*.—The ketone, b. p. 91—92°/13 mm., from *trans-cyclo*hexane-1 : 2-diacetic acid, m. p. 167° (cf. Part II, *loc. cit.*), was purified through the semicarbazone, m. p. 242° (*ex* alcohol). B. p. 92°/13 mm.; M = 138·20, n_C 1·47429, n_D 1·47686, n_F 1·48316, $n_{G'}$ 1·48782; R_C 39·70, R_D 39·88, R_F 40·33, $R_{G'}$ 40·66; $R_{G'-C}$ 0·96, R_{F-C} 0·63; $Mn_D^{20°}$ 204·11. Densities determined : $d_{4°}^{20°}$ 0·9791, $d_{4°}^{63·6°}$ 0·9463, $d_{4°}^{86·0°}$ 0·9298.

$\gamma_{20°}$ = 35·13 (0·10). Apparatus *A*.

t.	*h.*	*H.*	$d_{4°}^{t°}$.	γ.	*P.*	*t.*	*h.*	*H.*	$d_{4°}^{t°}$.	γ.	*P.*
24·9°	19·23	18·99	0·9742	34·64	344·2	86·9°	16·84	16·60	0·9291	28·88	344·9
64·2	17·64	17·40	0·9458	30·81	344·3						Mean 344·5

(Hückel and Friedrich, *Annalen*, 1926, **451**, 132, give b. p. 98°/19 mm., $d_{4°}^{17·0°}$ 0·9807, $n_D^{17·0°}$ 1·47687; Kandiah, J., 1931, 922, gives b. p. 90°/11 mm.; $d_{4°}^{16°}$ 0·9815, $n_D^{16°}$ 1·47692.)

*Methylene*cyclo*pentane*.—This was prepared by the catalytic decomposition of pure *cyclo*pentane-1 : 1-diacetic acid (Vogel, J., 1933, 1030), and fractionated over sodium. B. p. 75—76°/760 mm.; M = 82·14; n_C 1·42808, n_D 1·43078, n_F 1·43743, $n_{G'}$ 1·44257; R_C 27·15, R_D 27·29, R_F 27·66, $R_{G'}$ 27·94; $R_{G'-C}$ 0·79, R_{F-C} 0·51; $Mn_D^{20°}$ 117·80. Densities determined: $d_{4°}^{20°}$ 0·7787, $d_{4°}^{44·8°}$ 0·7518.

$\gamma_{20°}$ = 24·36 (0·11). Apparatus *C*.

t.	*h.*	*H.*	$d_{4°}^{t°}$.	γ.	*P.*	*t.*	*h.*	*H.*	$d_{4°}^{t°}$.	γ.	*P.*
20·8°	12·81	12·57	0·7778	24·27	234·6	42·7°	11·96	11·72	0·7541	21·94	236·0
											Mean 235·3

(Wallach, *Annalen*, 1906, **347**, 325, gives b. p. 78—81°, $d^{19°}$ 0·78, $n_D^{19°}$ 1·4355.)

*Methylene*cyclo*hexane*.—This was prepared by the thermal decomposition of pure *cyclo*hexane-1 : 1-diacetic acid (Vogel, J., 1933, 1030), and repeatedly fractionated over sodium. B. p. 102—103°/764 mm.; M = 96·17; n_C 1·44916, n_D 1·45227, n_F 1·45973, $n_{G'}$ 1·46567; R_C 31·96, R_D 32·15, $R_{G'}$ 32·97; $R_{G'-C}$ 1·01, R_{F-C} 0·64; $Mn_D^{20°}$ 139·67. Densities determined : $d_{4°}^{20°}$ 0·8074, $d_{4°}^{41·5°}$ 0·7867, $d_{4°}^{61·0°}$ 0·7704.

$\gamma_{20°}$ = 25·68 (0·11). Apparatus *A*.

t.	*h.*	*H.*	$d_{4°}^{t°}$.	γ.	*P.*	*t.*	*h.*	*H.*	$d_{4°}^{t°}$.	γ.	*P.*
17·5°	17·36	17·12	0·8097	25·96	268·1	61·5°	14·94	14·70	0·7699	21·19	268·3
40·9	16·16	15·92	0·7872	23·47	269·1						Mean 268·5

(Wallach, *Annalen*, 1906, **347**, 329, gives b. p. 105—106°, $d^{20°}$ 0·8025, $n_D^{20°}$ 1·4501; v. Auwers and Ellinger, *ibid.*, 1912, **387**, 200, give b. p. 104°/749 mm., $d_{4°}^{20°}$ 0·7992, $n_D^{20°}$ 1·4502; v. Auwers, Hinterseber, and Treppmann, *loc. cit.*, give, *inter alia*, b. p. 102·5°/756 mm., $d_{4°}^{17·8°}$ 0·8034, $n_\alpha^{17·8°}$ 1·44803, $n_D^{17·8°}$ 1·45092, $n_\beta^{17·8°}$ 1·45820, $n^{17·8°}$ 1·46430; Rosanow, *Centr.*, 1924, i, 2425, gives b. p. 103—104°, $d_{4°}^{20°}$ 0·8032, $n_D^{20°}$ 1·4528; Alexandrovitch, *Centr.*, 1933, ii, 2261, for compound from *cyclo*hexylcarbinol through the xanthate, gives b. p. 101—102°/760 mm., $d_{4°}^{20°}$ 0·8034, $n^{20°}$ 1·4490.)

* 1-*Methyl*-3-*methylene*cyclo*hexane*.—This was prepared by the thermal decomposition of pure 3-methyl*cyclo*hexane-1 : 1-diacetic acid, m. p. 140—141° (unpublished observation), and had b. p. 123—124°/762 mm. after two distillations over sodium. M = 110·19; n_C 1·44337,

n_D 1·44626, n_F 1·45336, $n_{G'}$ 1·45887; R_C 36·98, R_D 37·19, R_F 37·70, $R_{G'}$ 38·10; $R_{G'-C}$ 1·12, R_{F-C} 0·72; $Mn_D^{20°}$ 160·67. Densities determined : $d_{4°}^{20°}$ 0·7970, $d_{4°}^{42·1°}$ 0·7778, $d_{4°}^{61·9°}$ 0·7610.

$\gamma_{20°}$ = 24·72 (0·10). Apparatus *B*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	*γ*.	*P*.	*t*.	*h*.	*H*.	$d_{4°}^{t°}$.	*γ*.	*P*.
16·3°	13·61	13·37	0·8003	25·09	310·7	61·5°	11·80	11·56	0·7614	20·64	311·2
42·1	12·60	12·36	0·7778	22·54	311·2						Mean 311·0

(Wallach, *Annalen*, 1906, **347**, 342, gives b. p. 123—124°, $d_{4°}^{20°}$ 0·794, $n_D^{20°}$ 1·4461.)

* 1-*Methyl*-4-*methylene*cyclo*hexane*.—This was prepared by the decomposition of 4-methyl-*cyclo*hexane-1 : 1-diacetic acid, m. p. 158°, in the presence of iron filings and a little baryta (unpublished observation), and after two distillations over sodium had b. p. 124—125°/772 mm. M = 110·19; n_C 1·44339, n_D 1·44626, n_F 1·45338, $n_{G'}$ 1·45890; R_C 36·94, R_D 37·07, R_F 37·58, $R_{G'}$ 37·97; $R_{G'-C}$ 1·03, R_{F-C} 0·64; $Mn_D^{20°}$ 160·67. Densities determined : $d_{4°}^{20°}$ 0·7996, $d_{4°}^{60·9°}$ 0·7634, $d_{4°}^{86·7°}$ 0·7412.

$\gamma_{20°}$ = 24·72 (0·10). Apparatus *B*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	*γ*.	*P*.	*t*.	*h*.	*H*.	$d_{4°}^{t°}$.	*γ*.	*P*.
15·9°	13·58	13·34	0·8033	25·13	309·6	87·3°	10·66	10·42	0·7407	18·10	310·1
60·9	11·79	11·55	0·7634	20·68	310·5						Mean 310·1

(Perkin and Pope, J., 1911, **99**, 1514, give b. p. 122°, $d_{19°}^{19°}$ 0·7923, $n_D^{18°}$ 1·4465; Alexandrovitch, *loc. cit.*, for compound from 4-methyl*cyclo*hexylcarbinol through the xanthate, gives b. p. 120—121°/750 mm., $d_{4°}^{20°}$ 0·7945, $n^{20°}$ 1·4483.)

* 2-*Methylene*-trans-*decalin*.—This was prepared by the thermal decomposition of pure *trans*-decahydronaphthalene-2 : 2-diacetic acid (Tudor and Vogel, J., 1934, 1252) and fractionated over sodium. B. p. 82—82·5°/10 mm.; M = 150·25; n_C 1·48398, n_D 1·48695, n_F 1·49448, $n_{G'}$ 1·50047; R_C 48·31, R_D 48·57, R_F 49·20, $R_{G'}$ 49·71, $R_{G'-C}$ 1·40, R_{F-C} 0·89; $Mn_D^{20°}$ 223·42. Densities determined : $d_{4°}^{20°}$ 0·8897, $d_{4°}^{63·0°}$ 0·8577, $d_{4°}^{85·2°}$ 0·8415.

$\gamma_{20°}$ = 30·86 (0·09). Apparatus *A*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	*γ*.	*P*.	*t*.	*h*.	*H*.	$d_{4°}^{t°}$.	*γ*.	*P*.
20·5°	18·74	18·50	0·8893	30·81	398·1	84·9°	16·02	15·78	0·8417	24·87	398·7
61·2	17·02	16·78	0·8594	26·99	398·7						Mean 398·5

(Tudor and Vogel, *loc. cit.*, give b. p. 82—82·5°/10 mm., $d_{4°}^{20°}$ 0·8897, $n_D^{20°}$ 1·4870.)

* 2-*Methylene*-trans-*hexahydrohydrindene*.—This was prepared by the thermal decomposition of pure *trans*-hexahydrohydrindene-2 : 2-diacetic acid and fractionated over sodium. B. p. 59—60°/9·5 mm.; M = 136·23; n_C 1·46921, n_D 1·47204, n_F 1·47902, $n_{G'}$ 1·48436; R_C 43·81, R_D 44·05, R_F 44·59, $R_{G'}$ 45·02; $R_{G'-C}$ 1·21, R_{F-C} 0·78; $Mn_D^{20°}$ 200·53. Densities determined : $d_{4°}^{20°}$ 0·8663, $d_{4°}^{62·0°}$ 0·8347, $d_{4°}^{85·8°}$ 0·8163.

$\gamma_{20°}$ = 28·83 (0·09). Apparatus *A*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	*γ*.	*P*.	*t*.	*h*.	*H*.	$d_{4°}^{t°}$.	*γ*.	*P*.
21·3°	17·96	17·72	0·8653	28·71	364·5	85·5°	15·16	14·92	0·8165	22·81	364·7
63·0	16·24	16·00	0·8339	24·98	365·2						Mean 364·8

(Tudor and Vogel, *loc. cit.*, give b. p. 59—60°/9·5 mm., $d_{4°}^{20°}$ 0·8663, $n_D^{20°}$ 1·4720.)

cyclo*Pentanol*.—60 G. of *cyclo*pentanone, purified through the bisulphite compound, were mixed with 300 c.c. of ether and 300 c.c. of water in Pyrex 3-litre round-bottomed flask provided with a long reflux condenser with a wide inner tube. The flask was cooled in running water, and 72 g. of sodium were added slowly during 5 hours. The white solid which separated at first passed into solution upon vigorous shaking. After a further 12 hours, all the sodium had reacted, the ethereal layer was removed, the aqueous layer saturated with "AnalaR" sodium chloride, and extracted twice with ether. The combined ethereal solutions were washed with water, dried (anhydrous sodium sulphate), and distilled; *cyclo*pentanol (25—30 g.) passed over at 138—139°, and a yellow viscid liquid (*cyclo*pentyl*cyclo*pentanol, 20—25 g.) remained in the flask. The *cyclo*pentanol was tested with semicarbazide acetate but no trace of ketone could be detected. Upon redistillation from a fractionating Claisen flask, it boiled constantly at 139°/760 mm. M = 86·13; n_C 1·45087, n_D 1·45317, n_F 1·45863, $n_{G'}$ 1·46271; R_C 24·46, R_D 24·57, R_F 24·82, $R_{G'}$ 25·01; $R_{G'-C}$ 0·55, R_{F-C} 0·36; $Mn_D^{20°}$ 125·16. Densities determined: $d_{4°}^{20°}$ 0·9478, $d_{4°}^{63·4°}$ 0·9138, $d_{4°}^{87·0°}$ 0·8925.

$\gamma_{20^\circ} = 32\cdot14$ (0·08). Apparatus *A*.

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
21·0°	18·32	18·08	0·9470	32·06	216·4	86·6°	16·04	15·80	0·8928	26·41	218·7
62·0	17·11	16·87	0·9149	28·90	218·3					Mean	217·8

(Wislicenus and Hentzschel, *Annalen*, 1893, **275**, 322, give b. p. 139°, $d_{4^\circ}^{21\cdot5^\circ}$ 0·9395; v. Auwers, *ibid.*, 1918, **415**, 143, gives b. p. 140·6—140·8°, $d_{4^\circ}^{12\cdot9^\circ}$ $n_{\alpha}^{13\cdot5^\circ}$ 1·45387, $n_{D}^{13\cdot5^\circ}$ 1·45600, $n_{\beta}^{13\cdot5^\circ}$ 1·46169, $n_{\gamma}^{13\cdot5^\circ}$ 1·46649; Vavon, *Ann. Chim.*, 1914, **1**, 186, gives b. p. 140—141°, $d_{4^\circ}^{18^\circ}$ 0·946, $n_{D}^{18^\circ}$ 1·453; Eisenlohr, *loc. cit.*, gives b. p. 139°/735 mm.)

cyclo*Pentyl*cyclo*pentanol*.—The high-b. p. residues from several preparations of *cyclo*pentanol were combined and distilled twice under diminished pressure. The pure compound passed over at 100°/3 mm. $M = 152\cdot24$; n_{C} 1·48930, n_{D} 1·49194, n_{F} 1·49840, $n_{G'}$ 1·50314; R_{C} 45·00, R_{D} 45·20, R_{F} 45·71, $R_{G'}$ 46·07; $R_{G'-C}$ 1·07, R_{F-C} 0·71; $Mn_{D}^{20^\circ}$ 230·11. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9898, $d_{4^\circ}^{63\cdot5^\circ}$ 0·9586, $d_{4^\circ}^{87\cdot2^\circ}$ 0·9393.

$\gamma_{20^\circ} = 36\cdot20$ (0·09). Apparatus *C*.

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
22·1°	14·92	14·68	0·9880	36·01	382·4	87·0°	13·10	12·86	0·9395	30·00	384·2
63·5	13·72	13·48	0·9586	32·08	382·9					Mean	383·2

cyclo*Pentene*.—100 G. of phosphoric oxide were placed in a 250 c.c. Claisen flask, which was attached by means of a condenser to a Perkin triangle; the receiver (100 c.c. round-bottomed flask) was cooled in a mixture of ice and salt. 50 G. of pure redistilled *cyclo*pentanol were added during 90 minutes; a liquid passed over at 41—46°. The distillate was dried with anhydrous sodium sulphate and distilled from a fractionating Claisen flask; the whole of the liquid passed over at 44·3—44·4°/761 mm. A middle fraction, b. p. 44·3°/761 mm., was collected for the measurement of the physical properties. $M = 68\cdot11$; n_{C} 1·41984, n_{D} 1·42246, n_{F} 1·42904, $n_{G'}$ 1·43398; R_{C} 22·27, R_{D} 22·40, R_{F} 22·70, $R_{G'}$ 22·93; $R_{G'-C}$ 0·66, R_{F-C} 0·43; $Mn_{D}^{20^\circ}$ 96·89. Density determined: $d_{4^\circ}^{20^\circ}$ 0·7736 (temp. coeff., assumed, 0·0008 per 1°).

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	
17·2°	16·13	15·89	0·7756	23·08	192·7	App. *A*
17·9	12·25	12·01	0·7753	23·11	192·8	App. *C*
				Mean	192·8	

(Harries and Tank, *Ber.*, 1908, **41**, 1703, give b. p. 45—46°, $d_{4^\circ}^{14^\circ}$ 0·7754, $n_{D}^{14^\circ}$ 1·4208; Filipow, *Centr.*, 1915, i, 1057, gives b. p. 44·1—44·6°/752 mm., $d_{4^\circ}^{18^\circ}$ 0·7743, $n_{D}^{18^\circ}$ 1·4218; v. Auwers, *Annalen*, 1918, **415**, 144, b. p. 43·6—43·8°, $d_{4^\circ}^{6\cdot75^\circ}$ 0·7864, $n_{\alpha}^{7\cdot1^\circ}$ 1·4282, $n_{D}^{7\cdot1^\circ}$ 1·4305, $n_{\beta}^{7\cdot1^\circ}$ 1·4375, $n_{\gamma}^{7\cdot1^\circ}$ 1·4431; Eisenlohr, *loc. cit.*, b. p. 45°/760 mm.; Godchot, *loc. cit.*, b. p. 44—45°/763 mm., $d_{13\cdot5^\circ}^{13\cdot5^\circ}$ 0·7783, $n_{D}^{13\cdot5^\circ}$ 1·4256, $n_{Hg\text{-}\alpha}^{13\cdot5^\circ}$ 1·4371, *P* 193.)

cyclo*Pentane*.—16 G. of pure *cyclo*pentene, 80 c.c. of absolute alcohol, and 0·4 g. of Adams's platinum catalyst were shaken in hydrogen. The absorption was theoretical after 6 hours. The liquid was poured off from the platinum, 800 c.c. of water added, the mixture saturated with "AnalaR" sodium chloride, and the hydrocarbon layer (14 g.) removed. The latter was dried with calcium chloride and then distilled from sodium in a fractionating Claisen flask. The whole boiled constantly at 48·4—48·6°/763 mm. $M = 70\cdot13$; n_{C} 1·40464, n_{D} 1·40672, n_{F} 1·41166, $n_{G'}$ 1·41520; R_{C} 22·97, R_{D} 23·09, R_{F} 23·34, $R_{G'}$ 23·51; $R_{G'-C}$ 0·54, R_{F-C} 0·37; $Mn_{D}^{20^\circ}$ 98·65. Density determined: $d_{4^\circ}^{20^\circ}$ 0·7471 (temp. coeff. assumed, 0·0008 per 1°).

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	
17·1°	16·58	16·34	0·7494	22·93	205·0	App. *A*
17·5	13·24	13·00	0·7491	22·84	204·9	App. *B*
				Mean	205·0	

(Wislicenus and Hentzschel, *loc. cit.*, give b. p. 50·2—50·8°, $d_{4^\circ}^{20\cdot5^\circ}$ 0·7506, $n_{D}^{20^\circ}$ 1·4039; Eykman, *Chem. Weekblad*, 1906, **3**, 687, gives $d_{4^\circ}^{20\cdot1^\circ}$ 0·7543, $n_{\alpha}^{20\cdot1^\circ}$ 1·4064, $n_{\beta}^{20\cdot1^\circ}$ 1·41173, $n_{\gamma}^{20\cdot1^\circ}$ 1·42589; Eykman, *Naturk. Verhandel. Haarlem*, 1919, 3, **8**, 505, $d_{4^\circ}^{14\cdot7^\circ}$ 0·7500, $n_{\alpha}^{14\cdot7^\circ}$ 1·40770, $n_{He}^{14\cdot7^\circ}$ 1·40981, $n_{\beta}^{14\cdot7^\circ}$ 1·41481, $n_{\gamma}^{14\cdot7^\circ}$ 1·41891; Rosanow, *Centr.*, 1916, i, 925, $d_{4^\circ}^{20^\circ}$ 0·7447, $n_{D}^{20^\circ}$ 1·4075; Eisenlohr, *loc. cit.*, b. p. 50·0°/756 mm., $d_{4^\circ}^{20^\circ}$ 0·7510, $n_{\alpha}^{20^\circ}$ 1·40383, $n_{He}^{20^\circ}$ 1·40609, $n_{\beta}^{20^\circ}$ 1·41126, n^{20° 1·41536; Godchot, *loc. cit.*, b. p. 49°/760 mm., $d_{13\cdot5^\circ}^{13\cdot5^\circ}$ 0·7502, $n_{D}^{13\cdot5^\circ}$ 1·4100, $n_{Hg\text{-}\alpha}^{13\cdot5^\circ}$ 1·4193, *P* 205.)

3-*Methyl*cyclo*pentanol*.—This was prepared from 75 g. of pure 3-methyl*cyclo*pentanone, 500 c.c. of ether, 375 c.c. of water, and 80 g. of sodium in a 4-litre flask; the experimental details were similar to those described under *cyclo*pentanol. Upon working the product up in the usual manner, 43 g. of the alcohol, b. p. 151—154°, and 19 g. of a high-b. p. residue were obtained. Redistillation gave pure 3-methyl*cyclo*pentanol, b. p. 152°/766 mm. M = 100·16; n_C 1·44485, n_D 1·44736, n_F 1·45253, $n_{G'}$ 1·45656; R_C 29·22, R_D 29·37, R_F 29·66, $R_{G'}$ 29·89; $R_{G'-C}$ 0·67, R_{F-C} 0·44; $Mn_D^{20°}$ 144·97. Densities determined: $d_{4°}^{20°}$ 0·9120, $d_{4°}^{61·7°}$ 0·8807, $d_{4°}^{85·9°}$ 0·8601.

$\gamma_{20°}$ = 28·24 (0·07). Apparatus *A*.

t.	*h.*	*H.*	$d_{4°}^{t°}$.	γ.	*P.*	*t.*	*h.*	*H.*	$d_{4°}^{t°}$.	γ.	*P.*
18·5°	16·82	16·58	0·9132	28·35	253·1	85·6°	14·91	14·67	0·8603	23·63	256·7
62·3	15·59	15·35	0·8803	25·30	255·2						Mean 255·0

(Godchot and Taboury, *Bull. Soc. chim.*, 1913, **13**, 592, give b. p. 148—149°, $d^{16°}$ 0·9158, $n_D^{16°}$ 1·4487.)

1-*Methyl*-Δ^2-cyclo*pentene*.—This was prepared similarly to *cyclo*pentene from 70 g. of the pure alcohol and 150 g. of phosphoric oxide. The Claisen flask was immersed in a glycerol-bath at 110—115°, the alcohol added during 2 hours, and heating continued for a further hour; a liquid which passed over at 69—74° (23 g.) was dried with anhydrous sodium sulphate and distilled. Pure 1-methyl-Δ^2-*cyclo*pentene passed over at 72°/770 mm.; a small high-b. p. residue (2·4 g.) remained in the flask. M = 82·14; n_C 1·42214, n_D 1·42476, n_F 1·43120, $n_{G'}$ 1·43573; R_C 27·10, R_D 27·25, R_F 27·51, $R_{G'}$ 27·86; $R_{G'-C}$ 0·76, R_{F-C} 0·41; $Mn_D^{20°}$ 117·03.

$\gamma_{20°}$ = 22·68 (0·12).

t.	*h.*	*H.*	$d_{4°}^{t°}$.	γ.	*P.*	
20·0°	12·79	12·55	0·7705	22·68	232·8	App. *B*
18·9	16·04	15·80	0·7715	22·81	232·9	App. *A*
					Mean 232·9	

*Methyl*cyclo*pentane*.—14·5 G. of pure 1-methyl-Δ^2-*cyclo*pentene, 75 c.c. of absolute alcohol, and 0·4 g. of Adams's platinum catalyst were shaken in hydrogen for 20 hours; the absorption of hydrogen was theoretical. When the product was worked up as usual and distilled from sodium in a fractionating Claisen flask, the whole passed over at 70·8—71·1°/751 mm. A middle fraction, b. p. 70·9—71·0°/751 mm., was collected for the physical measurements. M = 84·16; n_C 1·40788, n_D 1·40998, n_F 1·41511, $n_{G'}$ 1·41824; R_C 27·63, R_D 27·77, R_F 28·07, $R_{G'}$ 28·24; $R_{G'-C}$ 0·81, R_{F-C} 0·44; $Mn_D^{20°}$ 118·67. Densities determined: $d_{4°}^{20°}$ 0·7510, $d_{4°}^{41·2°}$ 0·7293.

$\gamma_{20°}$ = 22·30 (0·12).

t.	*h.*	*H.*	$d_{4°}^{t°}$.	γ.	*P.*	
19·5°	12·88	12·64	0·7515	22·27	243·5	App. *B*
41·2	11·87	11·63	0·7293	19·88	244·0	App. *B*
14·8	16·48	16·24	0·7562	23·00	243·9	App. *A*
40·2	14·81	14·57	0·7303	19·92	243·8	App. *A*
					Mean 243·8	

(Zelinsky and Moser, *Ber.*, 1902, **35**, 2686, give b. p. 71°/743 mm., $d_{4°}^{19·5°}$ 0·7488, $n_D^{19·5°}$ 1·4096; Zelinsky, *Ber.*, 1911, **44**, 2781, gives b. p. 72—72·2°, $d_{4°}^{21°}$ 0·7474, $n_D^{21°}$ 1·4088; Eisenlohr, *loc. cit.*, b. p. 70·0—70·5°/755 mm., $d_{4°}^{20°}$ 0·7459, $n_{\alpha}^{20°}$ 1·40750, $n_{He}^{20°}$ 1·40947, $n_{\beta}^{20°}$ 1·41465, $n_{\gamma}^{20°}$ 1·41868; Godchot, *loc. cit.*, b. p. 71·5—72·5°/760 mm., $d_{13·5°}^{13·5°}$ 0·7511, $n_D^{13·5°}$ 1·4111, $n_{Hg\text{-}\alpha}^{13·5°}$ 1·4202, *P* 244.)

cyclo*Hexanol*.—This was prepared from 50 g. of *cyclo*hexanone (*ex* bisulphite compound), 250 c.c. of 10% sodium hydroxide solution, 300 c.c. of ether, and 60 g. of sodium. 45 G. of a liquid, b. p. 158—161°, and about 3 g. of a high-b. p. residue were obtained (compare Bentley, J., 1895, **67**, 264). The crude alcohol was shaken with a large excess of aqueous-alcoholic sodium bisulphite solution, but no solid separated after standing for 20 hours. The upper layer was removed, and the aqueous layer saturated with " AnalaR " sodium chloride and extracted three times with ether. The combined extracts were then distilled and the fraction, b. p. 159—161°, collected. This was dried over anhydrous sodium sulphate and again distilled; it passed over constantly at 159°/755 mm. M = 100·6; n_C 1·46390, n_D 1·46600, n_F 1·47196, $n_{G'}$ 1·47639; R_C 29·04, R_D 29·16, R_F 29·48, $R_{G'}$ 29·71; $R_{G'-C}$ 0·67, R_{F-C} 0·44; $Mn_D^{20°}$ 148·88.*

Apparatus *A*.

t.	*h.*	*H.*	$d_{4°}^{t°}$.	γ.	*P.*	*t.*	*h.*	*H.*	$d_{4°}^{t°}$.	γ.	*P.*
†18·5°	18·95	18·71	0·9527	33·38	252·6	86·3°	16·33	16·09	0·8967	27·02	254·8
61·8	16·89	16·65	0·9178	28·61	252·4						Mean 253·3

* The observations at 20° were made with the supercooled liquid.
† Supercooled liquid.

(v. Auwers, Hinterseber, and Treppmann, *loc. cit.*, give, *inter alia*, b. p. 66—69°/15 mm., $d_{4°}^{22·6°}$ 0·9463, $n_{\alpha}^{22·6°}$ 1·46330, $n_{D}^{22·6°}$ 1·46560, $n_{\beta}^{22·6°}$ 1·47141, $n_{\gamma}^{22·6°}$ 1·47623.)

cyclo*Hexene*.—36 G. of pure *cyclo*hexanol were dehydrated with a little concentrated sulphuric acid ("Organic Syntheses," 1925, **5**, 33), and 20 g. of the crude hydrocarbon obtained. This was dried with anhydrous sodium sulphate and distilled; b. p. 83°/777 mm. M = 82·14; n_C 1·44369, n_D 1·44646, n_F 1·45326, $n_{G'}$ 1·45854; R_C 26·96, R_D 27·11; R_F 27·47, $R_{G'}$ 27·74; $R_{G'-C}$ 0·78, R_{F-C} 0·51; $Mn_D^{20°}$ 118·82. Densities determined: $d_{4°}^{20°}$ 0·8088, $d_{4°}^{41·2°}$ 0·7896, $d_{4°}^{59·8°}$ 0·7731

$\gamma_{20°}$ = 26·56 (0·12).

t.	h.	H.	$d_{4°}^{t°}$.	γ.	P.	
22·7°	17·61	17·37	0·8064	26·23	230·6	App. *A*
41·9	16·46	16·22	0·7890	23·96	230·5	App. *A*
61·8	15·26	15·02	0·7713	21·69	230·3	App. *A*
17·4	13·59	13·35	0·8111	26·88	230·6	App. *B*
42·1	12·44	12·20	0·7888	23·89	230·2	App. *B*
61·1	11·53	11·29	0·7720	21·64	229·9	App. *B*
				Mean	230·4	

(v. Auwers, Hinterseber, and Treppmann, *loc. cit.*, give b. p. 83—83·5°/760 mm., $d_{4°}^{15·1°}$ 0·8147, $n_{\alpha}^{15·1°}$ 1·44653, $n_{D}^{15·1°}$ 1·44921, $n_{\beta}^{15·1°}$ 1·45620, $n_{\gamma}^{15·1°}$ 1·46194; Godchot, *loc. cit.*, gives b. p. 83·5°/758 mm., $d_{13·5°}^{13·5°}$ 0·8183, $n_D^{13·5°}$ 1·4494, $n_{Hg\text{-}\alpha}^{13·5°}$ 1·4619, P 230.)

cyclo*Hexane*.—14 G. of pure *cyclo*hexene, 150 c.c. of rectified spirit, and 0·2 g. of Adams's platinum catalyst were shaken in hydrogen; the absorption was theoretical after 6 hours. After being worked up as before and distilled over sodium, pure *cyclo*hexane (13 g.) passed over at 80·2°/763 mm. M = 84·16; n_C 1·42437, n_D 1·42656, n_F 1·43184, $n_{G'}$ 1·43580; R_C 27·63, R_D 27·75, R_F 28·05, $R_{G'}$ 28·27; $R_{G'-C}$ 0·64, R_{F-C} 0·42; $Mn_D^{20°}$ 120·06. Densities determined: $d_{4°}^{20°}$ 0·7780, $d_{4°}^{44·6°}$ 0·7555.

$\gamma_{20°}$ = 25·05 (0·11). * Apparatus *A*. ** Apparatus *C*.

t.	h.	H.	$d_{4°}^{t°}$.	γ.	P.	t.	h.	H.	$d_{4°}^{t°}$.	γ.	P.
25·6°	16·87	16·63	0·7730	24·07	241·3*	20·8°	13·23	12·99	0·7772	25·06	242·3**
42·9	15·93	15·69	0·7570	22·24	241·7*	43·6	12·18	11·94	0·7564	22·42	242·4**
22·4	17·13	16·89	0·7758	24·53	241·4*					Mean	241·8

[Zelinsky, *Ber.*, 1901, **34**, 2802, gives b. p. 80·8—80·9°, $d_{4°}^{19·5°}$ 0·7788, $n_D^{19·5°}$ 1·4266; Eykman, *loc. cit.*, 1906, gives $d_{4°}^{16·1°}$ 0·7820, $n_{\alpha}^{16·1°}$ 1·42626, $n_{\beta}^{16·1°}$ 1·43381, $n_{\gamma}^{16·1°}$ 1·43820; v. Auwers, Hinterseber, and Treppmann, *loc. cit.*, give, for a purified commercial specimen, b. p. 80·0—80·2°/749 mm., $d_{4°}^{10·85°}$ 0·7872, $n_{\alpha}^{10·85°}$ 1·42910, $n_D^{10·85°}$ 1·43119, $n_{\beta}^{10·85°}$ 1·43668, $n_{\gamma}^{10·85°}$ 1·44116; Eisenlohr, *loc. cit.*, gives b. p. 80·3°/750 mm., $d_{4°}^{20°}$ 0·7783, $n_{\alpha}^{20°}$ 1·42476, $n_{He}^{20°}$ 1·42680, $n_{\beta}^{20°}$ 1·43229, $n_{\gamma}^{20°}$ 1·43668 (from benzene and platinum-black in acetic acid solution): b. p. 80·5°/756 mm., $d_{4°}^{20°}$ 0·7782, $n_{\alpha}^{20°}$ 1·42496, $n_{He}^{20°}$ 1·42700, $n_{\beta}^{20°}$ 1·43260, $n_{\gamma}^{20°}$ 1·43705 (from benzene and nickel at 180—190°); Timmermans and Martin, *loc. cit.*, give b. p. 80·80°, $d^{15°}$ 0·78310, $n_{\alpha}^{15°}$ 1·42670, $n_D^{15°}$ 1·42886, $n_{He}^{15°}$ 1·42890, $n_{\beta}^{15°}$ 1·43430, $n_{\gamma}^{15°}$ 1·43870; Godchot, *loc. cit.*, gives b. p. 80·5°/758 mm., $d_{13·5°}^{13·5°}$ 0·7820, $n_D^{13·5°}$ 1·4272, $n_{Hg\text{-}\alpha}^{13·5°}$ 1·4368, P 240·14.]

1-*Methyl*-Δ^1-cyclo*hexene*.—*cyclo*Hexanone was converted by methylmagnesium iodide into 1-hydroxy-1-methyl*cyclo*hexane (Wallach, *Annalen*, 1908, **359**, 298); upon distillation, this suffered dehydration by the trace of iodine present and gave the unsaturated hydrocarbon in good yield. To a Grignard reagent prepared from 15 g. of magnesium, 89 g. of methyl iodide, and 250 c.c. of ether in a 1500-c.c. three-necked flask were added 49 g. of *cyclo*hexanone (*ex* bisulphite compound) in 150 c.c. of dry ether during 3 hours, the whole being mechanically stirred. Stirring was continued for a further hour, and the whole gently refluxed for 2 hours. The mixture was cooled in ice, decomposed with dilute sulphuric acid during 3 hours, the ethereal layer separated, the aqueous layer extracted with ether, and the combined ethereal solutions dried with anhydrous sodium sulphate. The ether was removed, and the resultant yellowish-brown liquid (the brown colour was due to iodine arising from the decomposition of the excess of Grignard reagent present) was distilled until a brown liquid commenced to pass over; a brown viscid residue remained in the flask. The distillate passed over below 110° and consisted of a mixture of water and an organic liquid; it was added to 1 l. of water, the upper layer removed (32 g.), washed with a little sodium thiosulphate solution, dried (anhydrous sodium sulphate), and distilled from sodium in a fractionating Claisen flask. The whole distilled constantly at 110·0°/769 mm. and was obviously homogeneous. This is the most convenient method for preparing this hydrocarbon. M = 96·17; n_C 1·44766, n_D 1·45067, n_F 1·45745, $n_{G'}$ 1·46259; R_C 31·66,

R_D 31·84, R_F 32·26, $R_{G'}$ 32·57; $R_{G'-C}$ 0·91, R_{F-C} 0·60; $Mn_D^{20°}$ 139·51. Densities determined: $d_{4°}^{20°}$ 0·8127, $d_{4°}^{42·1°}$ 0·7912, $d_{4°}^{62·1°}$ 0·7734.

$\gamma_{20°}$ = 20·66 (0·11). Apparatus *A*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*
14·2°	18·06	17·82	0·8182	27·30	269·3	61·1°	15·49	15·25	0·7743	22·11	269·6
41·4	16·49	16·25	0·7918	24·10	269·2					Mean	269·4

[Wallach, *Annalen*, 1908, **359**, 298, gives b. p. 111—112°, $d^{20°}$ 0·8110, $n_D^{20°}$ 1·4496 (dehydration with zinc chloride); v. Auwers and Ellinger, *ibid.*, 1912, **387**, 220, give b. p. 109·1—109·3°/772 mm., $d_{4°}^{20°}$ 0·8103, $n_D^{20°}$ 1·4497 (dehydration with oxalic acid at 150°); Roth and v. Auwers, *ibid.*, 1915, **407**, 154, b. p. 109·5—110·5°/767 mm., $d_{4°}^{17·9°}$ 0·8117, $n_\alpha^{17·9°}$ 1·44763, $n_D^{17·9°}$ 1·45042, $n_\beta^{17·9°}$ 1·45735, $n_\gamma^{17·9°}$ 1·46328 (dehydration with potassium bisulphate); Nametkin and Jarzew, *Ber.*, 1923, **56**, 1803, b. p. 109—110°/753 mm., $d_{4°}^{20·0°}$ 0·8122, $n_D^{20°}$ 1·4503 (dehydration with dilute nitric acid or 50% sulphuric acid); Eisenlohr, *loc. cit.*, gives b. p. 108·0—108·5°/769 mm., $d_{4°}^{20°}$ 0·8106, $n_{He}^{20°}$ 1·45017 (dehydration with phosphoric oxide); Godchot, *loc. cit.*, gives b. p. 110·6°/760 mm., $d_{13·5°}^{13·5°}$ 0·8257, $n_D^{13·5°}$ 1·4543, $n_{Hg\text{-}\alpha}^{13·5°}$ 1·4668, *P* 267 (dehydration with phthalic anhydride).]

*Methyl*cyclo*hexane from* 1-*Methyl*-Δ^1-cyclo*hexene*.—20 G. of the pure unsaturated hydrocarbon and 0·4 g. of Adams's platinum catalyst were shaken in hydrogen, theoretical absorption taking place in 84 hrs. (reduction was extremely slow and incomplete when absolute alcohol was used as solvent). The liquid was decanted from the platinum, and distilled from sodium in a small fractionating Claisen flask, the whole passing over at 100·3—100·9°/773 mm.; a middle fraction, b. p. 100·4—100·7°/773 mm., was collected for the physical measurements. M = 98·18; n_C 1·42167, n_D 1·42410, n_F 1·42915, $n_{G'}$ 1·43301; R_C 32·36, R_D 32·53, R_F 32·87, $R_{G'}$ 33·12; $R_{G'-C}$ 0·76, R_{F-C} 0·51; $Mn_D^{20°}$ 139·82. Densities determined: $d_{4°}^{20°}$ 0·7704, $d_{4°}^{42·1°}$ 0·7512, $d_{4°}^{62·1°}$ 0·7344.

$\gamma_{20°}$ = 23·59 (0·10). Apparatus *A*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
20·2°	16·58	16·34	0·7702	23·57	281·0	61·1°	14·34	14·10	0·7353	19·41	280·6
41·7	15·44	15·20	0·7516	21·39	281·1					Mean	280·9

(Godchot, *loc. cit.*, gives b. p. 100·25°/758 mm., $d_{13·5°}^{13·5°}$ 0·7738, $n_D^{13·5°}$ 1·4255, $n_{Hg\text{-}\alpha}^{13·5°}$ 1·4352, *P* 280.)

2-*Methyl*cyclo*hexanol*.—90 G. of 2-methyl*cyclo*hexanone (*ex* bisulphite compound), 500 c.c. of ether, 375 c.c. of water, and 75 g. of sodium yielded 78 g. of the alcohol, b. p. 165—169° (chiefly 165—167°), and 5 g. of a high-b. p. residue. Upon redistillation, pure 2-methyl*cyclo*hexanol passed over constantly at 165°/762 mm. M = 114·18; n_C 1·45844, n_D 1·46085, n_F 1·46646, $n_{G'}$ 1·47060; R_C 33·69, R_D 33·85, R_F 34·20, $R_{G'}$ 34·46; $R_{G'-C}$ 0·77, R_{F-C} 0·51; $Mn_D^{20°}$ 166·80. Densities determined: $d_{4°}^{20°}$ 0·9254, $d_{4°}^{62·3°}$ 0·8914, $d_{4°}^{85·3°}$ 0·8706.

$\gamma_{20°}$ = 30·75 (0·07). Apparatus *A*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
24·7°	17·87	17·63	0·9215	20·42	291·0	86·6°	15·95	15·71	0·8697	25·58	295·3
61·2	17·04	16·80	0·8923	28·07	294·5					Mean	293·6

(Sabatier and Mailhe, *Ann. Chim.*, 1907, **10**, 549, give b. p. 164·5—165·5°, $d_{4°}^{14°}$ 0·936, $n_D^{14°}$ 1·462; Murat, *ibid.*, 1909, **16**, 108, gives b. p. 165—166°, $d^{20°}$ 0·9332, $n_D^{20°}$ 1·461; v. Auwers, Hinterseber, and Treppmann, *loc. cit.*, give b. p. 167·4—167·6°, $d_{4°}^{13·4°}$ 0·9333, $n_\alpha^{13·4°}$ 1·46352, $n_D^{13·4°}$ 1·46585, $n_\beta^{13·4°}$ 1·47180, $n_\gamma^{13·4°}$ 1·47665; Skita, *Annalen*, 1923, **431**, 4, gives for *cis*-compound, b. p. 169·5—170·5°, $d_{4°}^{20°}$ 0·934, $n_D^{20°}$ 1·4623; for *trans*-compound, b. p. 116·2—166·7°, $d_{4°}^{20°}$ 0·929, $n_D^{20°}$ 1·4590; Eisenlohr, *loc. cit.*, gives for *cis*-compound, b. p. 170·0°/755 mm., $d_{4°}^{20°}$ 0·9280, $n_\alpha^{20°}$ 1·46003, $n_{He}^{20°}$ 1·46225, $n_\beta^{20°}$ 1·46841, $n_\gamma^{20°}$ 1·47353; for *trans*-compound, b. p. 168·5°/750 mm., $d_{4°}^{20°}$ 0·9254, $n^{20°}$ 1·45943, $n_{He}^{20°}$ 1·46165, $n_\beta^{20°}$ 1·46771, $n_\gamma^{20°}$ 1·47284.)

Hydrocarbon (I) *from* 2-*Methyl*cyclo*hexanol*.—70 G. of the pure alcohol and 165 g. of phosphoric oxide were heated in a glycerol-bath at 155—165°; liquid passed over at 105—110° (24 g.). This was dried over anhydrous sodium sulphate and distilled from a fractionating Claisen flask; most of the distillate (*ca.* 85%) passed over at 105·5—106·5°/758 mm., and there was a small fraction (*ca.* 10%), b. p. 108—109°/758 mm., $d_{4°}^{20°}$ 0·8013, $n_D^{20°}$ 1·4435. The main fraction was redistilled, and that of b. p. 106°/758 mm. was collected for the physical measurements. M = 96·17; n_C 1·44357, n_D 1·44616, n_F 1·45245, $n_{G'}$ 1·45711; R_C 31·19, R_D 32·32, R_F 32·72, $R_{G'}$ 33·00; $R_{G'-C}$ 0·81, R_{F-C} 0·53; $Mn_D^{20°}$ 139·08. Densities determined: $d_{4°}^{20°}$ 0·7938, $d_{4°}^{42·5°}$ 0·7760, $d_{4°}^{62·9°}$ 0·7584.

$\gamma_{20°} = 25{\cdot}24$ (0·10). Apparatus *A*.

t.	*h*.	*H*.	$d^{t°}_{4°}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d^{t°}_{4°}$.	γ.	*P*.
23·3°	17·06	16·82	0·7911	24·91	271·6	62·3°	14·92	14·68	0·7589	20·86	271·1
42·0	16·06	15·82	0·7764	23·00	271·5						Mean 271·4

(Wallach, *Annalen*, 1908, **359**, 298, gives, for hydrocarbon obtained by dehydration of 2-methyl*cyclo*hexanol with zinc chloride, b. p. 106—108°, $d^{17°}$ 0·7990, $n_D^{17°}$ 1·4428, and states that it is largely the Δ^1-compound.)

Reduction of hydrocarbon (I). 20 G. of (I), b. p. 105·5—106·5°/758 mm., 0·4 g. of Adams's platinum catalyst, and 125 c.c. of rectified spirit were shaken in hydrogen; only 60% of the theoretical volume was absorbed after 30 hours, reaction then having become very slow. The liquid was decanted from the platinum, poured into 700 c.c. of water, the upper layer separated (18 g.), and the aqueous liquid saturated with " AnalaR " sodium chloride, whereupon a further 1 g. of liquid was separated. The combined liquids were dried with calcium chloride and distilled from sodium; about 75% passed over at 100·7—101·2°/766 mm., and the remainder distilled up to 102·5°/766 mm. The liquid decolourised 1% potassium permanganate solution, and was clearly not homogeneous. 14·5 G. of this liquid and 0·3 g. of Adams's platinum catalyst were shaken with hydrogen in the absence of a solvent for 15 hours, the theoretical amount of hydrogen required for complete absorption then having been absorbed. The liquid was poured off from the catalyst and distilled from sodium; it boiled constantly at 100·2—100·4°/768 mm., the last 0·5 c.c. having b. p. 100·6—100·8°/768 mm. A middle fraction, b. p. 100·2—100·4°/768 mm., was collected for the physical measurements, which were determined after immersion in the thermostat for 8 hours. These were $d^{20°}_{4°}$ 0·7679, n_C 1·42081, n_D 1·42306, n_F 1·42839, n_G 1·43230; R_C 32·41, R_D 32·56, R_F 32·92, $R_{G'}$ 33·18; $R_{G'-C}$ 0·77; R_{F-C} 0·51; $Mn_D^{20°}$ 139·71. After standing in a Pyrex tube for 7 days at the laboratory temperature or after being heated for 2—3 hours at 40—60°, the hydrocarbon had $d^{20°}_{4°}$ 0·7694, n_C 1·42093, n_D 1·42316, n_F 1·42846, $n_{G'}$ 1·43250. These properties remained unchanged after 6 months' keeping. A detailed study of the influence of catalysts and temperature upon this hydrocarbon and those prepared by other methods is in progress.

3-*Methyl*cyclo*hexanol*.—70 G. of 3-methyl*cyclo*hexanone (*ex* bisulphite compound), 400 c.c. of ether, 300 c.c. of water, and 58 g. of sodium yielded 56 g. of the alcohol, b. p. 172—174°, and 6 g. of a high-b. p. residue. Upon redistillation, 3-methyl*cyclo*hexanol boiled constantly at 172°/763 mm. $M = 114{\cdot}18$; n_C 1·45516, n_D 1·45757, n_F 1·46330, $n_{G'}$ 1·46754; R_C 33·80, R_D 33·96, R_F 34·32, $R_{G'}$ 34·59; $R_{G'-C}$ 0·79, R_{F-C} 0·52; $Mn_D^{20°}$ 166·43. Densities determined: $d^{20°}_{4°}$ 0·9168, $d^{63·7°}_{4°}$ 0·8827, $d^{87·2°}_{4°}$ 0·8631.

$\gamma_{20°} = 27{\cdot}75$ (0·06). Apparatus *A*.

t.	*h*.	*H*.	$d^{t°}_{4°}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d^{t°}_{4°}$.	γ.	*P*.
23·1°	16·37	16·13	0·9143	27·62	286·3	85·3°	14·86	14·62	0·8646	23·67	291·3
61·3	15·51	15·27	0·8843	25·27	289·5						Mean 289·0

(Knoevenagel, *Annalen*, 1897, **297**, 182, gives for *cis*-form, b. p. 174—175°, $d^{16°}$ 0·9191, $n_D^{16°}$ 1·4579; for *trans*-form, *ibid.*, 1896, **289**, 142, b. p. 175—176°, $d^{15°}$ 0·9320, $n_D^{15°}$ 1·4695; Wallach, *ibid.*, 1896, **289**, 343, gives b. p. 175—176°, $d^{19°}$ 0·914, $n_D^{19°}$ 1·4581; Zelinsky, *Ber.*, 1897, **30**, 1534, gives b. p. 173—174°, $d^{21°}_{4°}$ 0·9137, $n_D^{21°}$ 1·4575; Kondakow and Schindelmeiser, *J. pr. Chem.*, 1900, **61**, 482, give b. p. 174°/764 mm., $d^{20°}_{4°}$ 0·9135, $n_D^{20°}$ 1·45809; Sabatier and Mailhe, *loc. cit.*, give b. p. 172·5°/745 mm., $d^{12°}_{4°}$ 0·9336, $n_D^{12°}$ 1·460; Gutt, *Ber.*, 1907, **40**, 2061, gives b. p. 91·5—92·5°/35 mm., $d^{20°}_{4°}$ 0·9144, $n_D^{20°}$ 1·4555; v. Auwers, Hinterseber, and Treppmann, *loc. cit.*, give, *inter alia*, b. p. 76—78°/14 mm., $d^{24·3°}_{4°}$ 0·9182, $n_\alpha^{24·3°}$ 1·45217, $n_D^{24·3°}$ 1·45444, $n_\beta^{24·3°}$ 1·46031, $n_\gamma^{24·3°}$ 1·46502; Skita, *loc. cit.*, gives for *cis*-compound, b. p. 174·6—175·2°, $d^{20°}_{4°}$ 0·922, $n_D^{20°}$ 1·455: for *trans*-compound, b. p. 171·5—172·5°, $d^{20°}_{4°}$ 0·918, $n_D^{20°}$ 1·458; Eisenlohr, *loc. cit.*, gives, for *cis*-form, b. p. 175·5°/760 mm., $d^{20°}_{4°}$ 0·9250, $n_\alpha^{20°}$ 1·45873, $n_{He}^{20°}$ 1·46086, $n_\beta^{20°}$ 1·46692, $n_\gamma^{20°}$ 1·47196: for *trans*-form, b. p. 174·5—174·7°/762 mm., $d^{20°}_{4°}$ 0·9234, $n_\alpha^{20°}$ 1·45723, $n_{He}^{20°}$ 1·45931, $n_\beta^{20°}$ 1·46544, $n_\gamma^{20°}$ 1·47020.)

Hydrocarbon (II) *from* 3-*Methyl*cyclo*hexanol*.—55. G. of the pure alcohol and 135 g. of phosphoric oxide were heated in a glycerol-bath at 165—175°; the liquid passed over at 102—106° (22 g.). This was dried over anhydrous sodium sulphate and distilled from a fractionating Claisen flask; over 85% passed over at 104·5—105·5°/761 mm., and about 10% at 107—109°/761 mm. The main fraction was redistilled, and a middle fraction, b. p. 105°/761 mm., was collected for the physical measurements. $M = 96{\cdot}17$; n_C 1·43848, n_D 1·44114, n_F 1·44757, n_G

1·45256; R_C 31·82, R_D 31·99, R_F 32·39, $R_{G'}$ 32·71; $R_{G'-C}$ 0·89, R_{F-C} 0·57; $Mn_D^{20°}$ 138·59. Densities determined: $d_{4°}^{20°}$ 0·7941, $d_{4°}^{42·1°}$ 0·7769, $d_{4°}^{62·4°}$ 0·7586.

$\gamma_{20°}$ = 25·50 (0·11). Apparatus *A*.

t.	*h.*	*H.*	$d_{4°}^{t°}$.	*γ.*	*P.*	*t.*	*h.*	*H.*	$d_{4°}^{t°}$.	*γ.*	*P.*
19·1°	17·31	17·07	0·7948	25·40	271·7	62·2°	14·94	14·70	0·7588	20·89	271·2
41·7	16·02	15·78	0·7772	22·97	271·1					Mean	271·3

Reduction of hydrocarbon (II). 20 G. of (II), b. p. 104·5—105·5°/761 mm., 125 c.c. of rectified spirit, and 0·35 g. of Adams's platinum catalyst were shaken in hydrogen, but only 80% of the theoretical volume had been absorbed in 30 hours, reaction then being extremely slow. The product was worked up as described under hydrocarbon (I) (18 g.) and was distilled from sodium; most passed over at 100·8—101·0°/759 mm., but *ca.* 10% distilled up to 102°/759 mm. This decolourised 1% potassium permanganate slightly. 14 G. of this liquid and 0·3 g. of Adams's platinum catalyst were shaken in hydrogen for 8 hours, the theoretical absorption having then taken place. The liquid was poured from the platinum and distilled from sodium; it boiled constantly at 100·5—100·7°/771 mm. This had $d_{4°}^{20°}$ 0·7703, n_C 1·42151, n_D 1·42377, n_F 1·42911, $n_{G'}$ 1·43303; these properties are in agreement with those for methyl*cyclo*hexane prepared from 1-methyl-Δ^1-*cyclo*hexene (p. 1333).

4-*Methyl*cyclo*hexanol*.—90 G. of 4-methyl*cyclo*hexanone (*ex* bisulphite compound), 500 c.c. of ether, 375 c.c. of water, and 80 g. of sodium yielded 82 g. of the alcohol, b. p. 171·5—173°, and 5 g. of a high-b. p. solid residue. Upon redistillation, pure 4-methyl*cyclo*hexanol boiled constantly at 172°/763 mm. M = 114·18; n_C 1·45395, n_D 1·45647, n_F 1·46203, $n_{G'}$ 1·46616; R_C 33·90, R_D 34·06, R_F 34·41, $R_{G'}$ 34·68; $R_{G'-C}$ 0·78, R_{F-C} 0·51; $Mn_D^{20°}$ 166·30. Densities determined: $d_{4°}^{20°}$ 0·9122, $d_{4°}^{61·7°}$ 0·8831, $d_{4°}^{87·2°}$ 0·8631.

$\gamma_{20°}$ = 27·63 (0·06). Apparatus *A*.

t.	*h.*	*H.*	$d_{4°}^{t°}$.	*γ.*	*P.*	*t.*	*h.*	*H.*	$d_{4°}^{t°}$.	*γ.*	*P.*
20·9°	16·40	16·16	0·9116	27·58	287·1	86·1°	14·49	14·25	0·8639	23·05	288·5
60·4	15·27	15·13	0·8840	25·04	288·9					Mean	288·2

(Sabatier and Mailhe, *Compt. rend.*, 1904, **139**, 344, give b. p. 172·5—173°/745 mm., $d_{4°}^{12°}$ 0·924, $n_D^{14°}$ 1·462; Haller, *Bull. Soc. chim.*, 1905, **33**, 77, gives b. p. 173—173·5°, $d_{4°}^{20°}$ 0·9170, $n_D^{20°}$ 1·4573; v. Auwers, Hinterseber, and Treppmann, *loc. cit.*, give *inter alia*, b. p. 74·7—75·2°/12 mm., $d_{4°}^{22·5°}$ 0·9183, $n_\alpha^{22·5°}$ 1·45366, $n_D^{22·5°}$ 1·45594, $n_\beta^{22·5°}$ 1·46160, $n_\gamma^{22·5°}$ 1·46651; v. Auwers and Kolligs, *Ber.*, 1922, **55**, 45, give b. p. 172—173°, $d_{4°}^{16·3°}$ 0·9192, $n_\alpha^{16·3°}$ 1·45742, $n_{He}^{16·3°}$ 1·45959, $n_\beta^{16·3°}$ 1·46558, $n_\gamma^{16·3°}$ 1·47025; Skita, *loc. cit.*, gives for *cis*-compound, b. p. 173·5—173·8°, $d_{4°}^{20°}$ 0·920, $n_D^{20°}$ 1·4592: for *trans*-compound, b. p. 172·8—173·5°, $d_{4°}^{20°}$ 0·918, $n_D^{20°}$ 1·4586; Eisenlohr, *loc. cit.*, gives for *cis*-compound, b. p. 175·5°/760 mm., $d_{4°}^{20°}$ 0·9223, $n_\alpha^{20°}$ 1·45704, $n_{He}^{20°}$ 1·45926, $n_\beta^{20°}$ 1·46534, $n_\gamma^{20°}$ 1·47039; for *trans*-compound *inter alia*, b. p. 174·5°/760 mm., $d_{4°}^{20°}$ 0·9172, $n_\alpha^{20°}$ 1·45503, $n_{He}^{20°}$ 1·45727, $n_\beta^{20°}$ 1·46336, $n_\gamma^{20°}$ 1·46831.)

Hydrocarbon (III) *from* 4-*Methyl*cyclo*hexanol*.—80 G. of the pure alcohol and 165 g. of phosphoric oxide were heated in a glycerol-bath at 160—170°; 32 g. of liquid passed over at 104—111°. The liquid was dried with anhydrous sodium sulphate and distilled; over 80% had b. p. 105—106°/765 mm., and *ca.* 15% had b. p. 107·5—108°/765 mm., $d_{4°}^{20°}$ 0·8016, $n_D^{20°}$ 1·4449. The main fraction was redistilled, and the middle portion, b. p. 105·5°/765 mm., collected for the physical measurements. M = 96·17; n_C 1·43879, n_D 1·44144, n_F 1·44784, $n_{G'}$ 1·45267; R_C 31·79, R_D 31·96, R_F 32·36, $R_{G'}$ 32·67; $R_{G'-C}$ 0·88, R_{F-C} 0·57; $Mn_D^{20°}$ 138·62. Densities determined: $d_{4°}^{20°}$ 0·7953, $d_{4°}^{41·5°}$ 0·7797, $d_{4°}^{60·9°}$ 0·7628.

$\gamma_{20°}$ = 25·42 (0·10). Apparatus *A*.

t.	*h.*	*H.*	$d_{4°}^{t°}$.	*γ.*	*P.*	*t.*	*h.*	*H.*	$d_{4°}^{t°}$.	*γ.*	*P.*
23·5°	17·13	16·89	0·7926	25·07	271·5	60·7°	15·07	14·83	0·7630	21·19	270·6
41·7	16·08	15·84	0·7795	23·12	270·7					Mean	270·9

Reduction of hydrocarbon (III). 20 G. of (III), b. p. 105—106°/765 mm., 125 c.c. of absolute alcohol, and 0·3 g. of Adams's platinum catalyst were shaken in hydrogen, 80% of the theoretical quantity being absorbed in 24 hours and the reaction then becoming extremely slow. The product was worked up as described under hydrocarbon (I) and fractionated from sodium; most distilled at 101·0—101·5°/766 mm., but *ca.* 10% passed over up to 102·5°/766 mm. This decolourised 1% potassium permanganate slightly. 14·5 G. of this liquid and 0·2 g. of Adams's platinum catalyst were shaken in hydrogen for 7 hours, theoretical absorption of hydrogen taking place. The liquid was decanted from the platinum and distilled over sodium. It distilled constantly at 100·7—100·9°/776 mm., and had $d_{4°}^{20°}$ 0·7702, n_C 1·42132, n_D 1·42356, n_F 1·42891, $n_{G'}$ 1·43283.

cyclo*Heptanol*.—100 G. of suberone (*ex* bisulphite compound), 555 c.c. of ether, 420 c.c. of water, and 88 g. of sodium yielded 72 g. of the alcohol, b. p. 183—187°, and 24 g. of a crystalline high-b. p. residue (compare Markownikow, *Annalen*, 1903, **327**, 66). Upon redistillation, *cyclo*heptanol boiled constantly at 185°/761 mm. M = 114·18; n_C 1·47220, n_D 1·47470, n_F 1·48087, $n_{G'}$ 1·48502; R_C 33·75, R_D 34·00, R_F 34·28, $R_{G'}$ 34·53; $R_{G'-C}$ 0·78, R_{F-C} 0·53; $Mn_D^{20°}$ 168·38. Densities determined: $d_{4°}^{20°}$ 0·9478, $d_{4°}^{61·3°}$ 0·9152, $d_{4°}^{86·9°}$ 0·8946.

$\gamma_{20°}$ = 33·10 (0·09). Apparatus *A*.

t.	h.	H.	$d_{4°}^{t°}$.	γ.	P.	t.	h.	H.	$d_{4°}^{t°}$.	γ.	P.
13·5°	19·12	18·88	0·9530	33·69	288·7	85·7°	16·67	16·43	0·8956	26·93	290·4
61·4	17·53	17·29	0·9151	29·61	291·1					Mean	290·1

(Markownikow, *J. pr. Chem.*, 1894, **49**, 415, gives b. p. 184—185°, $d_{15°}^{15°}$ 0·9595; Willstätter, *Annalen*, 1900, **317**, 218, gives b. p. 184—185°.)

Action of Phosphoric Oxide upon cyclo*Heptanol*.—60 G. of *cyclo*heptanol and 135 g. of phosphoric oxide were heated in a glycerol-bath at 150—160°; 27 g. of a liquid passed over first at 109—110° and later at 114—116°. The distillate was dried over anhydrous sodium sulphate and fractionated. Distillation commenced at 107—108°/760 mm., practically the whole passed over at 109—110°/760 mm., and the last 2 c.c. at 111—113°/760 mm. A middle fraction, b. p. 109—110°/760 mm. had $d_{4°}^{20°}$ 0·8068, $n_D^{20°}$ 1·4473. For *cyclo*heptene Markownikow (*loc. cit.*) gives b. p. 114·5—115°, and Willstätter (*loc. cit.*) b. p. 115°. Harries and Tank (*Ber.*, 1908, **41**, 749) state that the distillation of *cyclo*heptanol with phosphoric oxide yields "*cyclo*heptene," $d_{4°}^{20°}$ 0·823, $n_D^{20°}$ 1·45301, but they do not give a b. p.; they were unable to isolate any pimelic acid upon ozonolysis. The b. p., physical properties, and catalytic reduction of the product (see below) prove conclusively that it consists of a mixture of *cyclo*heptene and a methyl*cyclo*hexene, isomerisation having occurred during the dehydration.

Catalytic reduction of liquid, b. p. 109—110°/760 *mm.* 15 G. of the liquid, 50 c.c. of absolute alcohol, and 0·4 g. of Adams's platinum catalyst were shaken in hydrogen, theoretical absorption occurring in 24 hours. The product was worked up as described under hydrocarbon (I), and the 14 g. of liquid thus obtained were distilled from sodium. Two fractions were obtained: (i) b. p. 104—106·5°/747 mm., 10 g., $d_{4°}^{20°}$ 0·7842, $n_D^{20°}$ 1·4306; (ii) b. p. 107—109°/747 mm., 3·5 g., $d_{4°}^{20°}$ 0·7870, $n_D^{20°}$ 1·4323. It consisted clearly of a mixture of methyl*cyclo*hexane and *cyclo*heptane.

cyclo*Heptyl Bromide*.—To 70 g. of pure *cyclo*heptanol, contained in a 1-litre three-necked flask provided with a mercury-sealed stirrer, a dropping funnel, and a thermometer, and cooled in a mixture of ice and salt, were added 60 g. (10% excess) of redistilled phosphorus tribromide, (b. p. 170·5—172°) during 2 hours, the temperature not being allowed to rise above 5° (compare Noller and Adams, *J. Amer. Chem. Soc.*, 1926, **48**, 1084). Stirring was continued for a further 4 hours, 500 c.c. of water were added after 12 hours, and the whole distilled in steam. The crude bromide (88 g.) was washed with 10% sodium carbonate solution, water, dried (anhydrous sodium sulphate), and distilled; practically the whole passed over at 62—63°/6 mm. (70 g.). A middle fraction, b. p. 62·5°/6 mm., was collected for the physical measurements. M = 177·09; n_C 1·49521, n_D 1·49911, n_F 1·50647, $n_{G'}$ 1·51023; R_C 41·16, R_D 41·43, R_F 41·95, R_G 42·23; $R_{G'-C}$ 1·17, R_{F-C} 0·79; $Mn_D^{20°}$ 265·47.

$\gamma_{20°}$ = 34·31 (0·09). Apparatus *A*.

t.	h.	H.	$d_{4°}^{t°}$.	γ.	P.	t.	h.	H.	$d_{4°}^{t°}$.	γ.	P.
15·7°	14·95	14·71	1·2599	34·70	341·1	87·4°	12·99	12·75	1·1839	28·26	344·9
61·9	13·91	13·67	1·2103	30·98	345·7					Mean	343·2

(Zelinsky, *Ber.*, 1902, **35**, 2691, gives b. p. 75°/12 mm., $d_{4°}^{22°}$ 1·2887, $n_D^{22°}$ 1·4996; Markownikow, *Annalen*, 1903, **327**, 63, gives b. p. 101·5°/40 mm., $d_{15°}^{15°}$ 1·299.)

Action of Alcoholic Potassium Hydroxide upon cyclo*Heptyl Bromide: Preparation of* cyclo*Heptene*.—A mixture of 50 g. of the bromide, 50 g. of potassium hydroxide, and 125 c.c. of rectified spirit was refluxed on the water-bath for 5 hours and then poured into 1 l. of water. The upper layer (27 g.) was separated, dried with calcium chloride, and distilled in a fractionating Claisen flask over sodium; 21 g. of *cyclo*heptene, b. p. 113·5—116°/774 mm. (chiefly 115—116°/774 mm.) were obtained, together with about 2 g. of a pleasant-smelling, halogen-free liquid, b. p. 172—181°; the latter was probably *cyclo*heptyl ethyl ether but was not further investigated.

The hydrocarbon was redistilled over sodium, and a middle fraction, b. p. 114·5—115°/774 mm., collected for the physical measurements. $M = 96{\cdot}17$; n_C 1·45450, n_D 1·45737, n_F 1·46438, $n_{G'}$ 1·46966; R_C 31·58, R_D 31·75, R_F 32·17, $R_{G'}$ 32·49; $R_{G'-C}$ 0·91, R_{F-C} 0·59; $Mn_D^{20°}$ 140·16. Densities determined : $d_{4°}^{20°}$ 0·8255, $d_{4°}^{41·4°}$ 0·8059, $d_{4°}^{62·1°}$ 0·7884.

$\gamma_{20°} = 28{\cdot}02$ (0·11). Apparatus *A*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
17·9°	18·48	18·24	0·8272	28·25	268·0	62·0°	16·00	15·76	0·7885	23·27	268·2
42·1	17·11	16·87	0·8052	25·44	268·4					Mean	268·2

(Willstätter, *Annalen*, 1901, **317**, 221, gives b. p. 115°; Markownikow, *J. pr. Chem.*, 1894, **49**, 429, b. p. 114·5—115·5°, $d_{20°}^{20°}$ 0·8245; Rosanow, *Centr.*, 1924, i, 2425, b. p. 113—115°, $d_{4°}^{20°}$ 0·8228, $n_D^{20°}$ 1·4552; Godchot, *loc. cit.*, b. p. 114—115°/752 mm., $d_{13·5°}^{13·5°}$ 0·8359, $n_D^{13·5°}$ 1·4607, $n_{Hg\text{-}a}^{13·5°}$ 1·4733, *P* 266·17.)

Reduction of cyclo*Heptene : Preparation of* cyclo*Heptane*.—14 G. of *cyclo*heptene, 75 c.c. of absolute alcohol, and 0·4 g. of Adams's platinum catalyst were shaken in hydrogen; theoretical absorption took place in 3 hours but shaking was continued for a further 5 hours. The product was worked up as before; the liquid (13·5 g.) was dried with calcium chloride and distilled from sodium in a fractionating Claisen flask. The whole distilled at 116·5—118·5°/758 mm., and a middle fraction, b. p. 117·5—118°/758 mm., was collected for the physical measurements. $M = 98{\cdot}18$; n_C 1·44090, n_D 1·44355, n_F 1·44906, $n_{G'}$ 1·45288; R_C 32·01, R_D 32·18, R_F 32·53, $R_{G'}$ 32·76; $R_{G'-C}$ 0·75, R_{F-C} 0·52; $Mn_D^{20°}$ 141·73. Densities determined : $d_{4°}^{20°}$ 0·8098, $d_{4°}^{41·0°}$ 0·7905, $d_{4°}^{61·0°}$ 0·7733.

$\gamma_{20°} = 27{\cdot}93$ (0·12). Apparatus *A*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
16·1°	18·89	18·65	0·8133	28·40	278·7	61·0°	16·18	15·94	0·7733	23·08	278·5
41·0	17·49	17·25	0·7905	25·53	279·3					Mean	278·8

(Markownikow, *Annalen*, 1903, **327**, 63, gives b. p. 117—117·5°/763 mm., $d_{0°}^{20°}$ 0·8093; Willstätter and Kametaka, *Ber.*, 1908, **41**, 1483, give b. p. 116·4—116·8°/726 mm., $d_{4°}^{20°}$ 0·8108, $n_D^{20°}$ 1·44521; Rosanow, *loc. cit.*, gives b. p. 118—120°, $d_{4°}^{20°}$ 0·8099, $n_D^{20°}$ 1·4440; Godchot, *loc. cit.*, b. p. 119—120°, $d_{13·5°}^{13·5°}$ 0·8136, $n_D^{13·5°}$ 1·4466, $n_{Hg\text{-}a}^{13·5°}$ 1·4563, *P* 278.)

Note on Cyclic Alcohols.—All the cyclic alcohols were viscid and somewhat hygroscopic liquids; the density and refractive index changed slightly on exposure to air. The measurements recorded were made upon freshly distilled specimens. The meniscuses in the capillary tubes at temperatures above that of the room were slightly hazy; it is possible that the contact angle is not quite zero in these cases

The following data complete those for substituted glutaric esters (Part II, *loc. cit.*).

* *Methyl and Ethyl 2-Methyl*cyclo*hexane-1 : 1-diacetate*.—These *esters* were prepared in good yield by refluxing the pure acid, m. p. 152° (German and Vogel, J., 1937, 1110), with the pure dry alcohol, pure sodium-dried benzene, and concentrated sulphuric acid for several hours (compare Vogel, J., 1928, 2021; 1933, 338). Methyl ester : b. p. 139°/4 mm.; $M = 242{\cdot}31$ (Found : C, 66·4; H, 9·1. $C_{13}H_{22}O_4$ requires C, 64·4; H, 9·2%); n_C 1·46688, n_D 1·46898, n_F 1·47477, $n_{G'}$ 1·47907; R_C 62·46, R_D 62·70, R_F 63·36, $R_{G'}$ 63·85; $R_{G'-C}$ 1·39, R_{F-C} 0·90; $Mn_D^{20°}$ 355·14. Ethyl ester (Found : C, 66·4; H, 9·6. $C_{15}H_{26}O_4$ requires C, 66·6; H, 9·7%), b. p. 145°/4 mm.; $M = 270{\cdot}36$; n_C 1·46077, n_D 1·46314, n_F 1·46885, $n_{G'}$ 1·47303; R_C 71·82, R_D 72·12, R_F 72·90, $R_{G'}$ 73·45; $R_{G'-C}$ 1·63, R_{F-C} 1·08; $Mn_D^{20°}$ 395·56.

Methyl ester.

Densities determined : $d_{4°}^{20°}$ 1·0738, $d_{4°}^{62·3°}$ 1·0417, $d_{4°}^{87·9°}$ 1·0224.

$\gamma_{20°} = 35{\cdot}70$ (0·10). Apparatus *A*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
21·0°	17·96	17·72	1·0730	35·60	550·4	86·1°	15·48	15·24	1·0234	29·21	549·1
61·3	16·42	16·18	1·0425	31·58	549·8					Mean	549·8

Ethyl ester.

Densities determined : $d_{4°}^{20°}$ 1·0326, $d_{4°}^{61·7°}$ 1·0000; $d_{4°}^{86·0°}$ 0·9829.

$\gamma_{20°} = 33{\cdot}33$ (0·09). Apparatus *B*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
20·5°	13·99	13·75	1·0332	33·28	629·1	87·4°	12·11	11·87	0·9818	27·33	629·6
62·1	12·77	12·53	0·9997	29·37	629·6					Mean	629·4

Note, added in proof, September 2nd, 1938.—Since this paper was written, Wibaut, Langedijk, Smittenberg, and Hoog (*Chem. and Ind.*, 1938, **57**, 753) have described the isolation of only one form of methyl*cyclo*hexane by the hydrogenation of pure toluene at 150° under 100 atm. pressure in the presence of nickel–kieselguhr as catalyst. This had b. p. 100·80°, $d_{4^\circ}^{20\cdot0^\circ}$ 0·76944, and $n^{20\cdot00^\circ}$ as follows:

C (6563)	d_{He} (5876)	F (4861)	G′ (4341)
1·42085	1·42310	1·42838	1·43285

These properties agree well with those of the (*B*′) form described on p. 1324. This would therefore seem to be a stable modification (compare Vogel, *Chem. and Ind.*, 1938, **57**, 541, 772).

The author's thanks are tendered to Imperial Chemical Industries, the Royal Society, and the Dixon Fund of the University of London for grants which have helped to defray the heavy expenses of this research.

WOOLWICH POLYTECHNIC, LONDON, S.E. 18. [*Received, June 8th,* 1938.]