384. *Physical Properties and Chemical Constitution. Part IV. Methyl*cyclo*hexane and the Multiplanar Structure of the Methyl*cyclo*hexane Ring.*

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Decomposition of either of the semicarbazones of 2- and 4-methyl*cyclo*hexanones by the Wolff method yielded the same methyl*cyclo*hexane *B*; this passed on keeping for several days or on warming for a short time at 40—60° into another form (*B'*), which was exclusively obtained by the Clemmensen reduction of pure 2-, 3-, and 4-methyl*cyclo*hexanones. The experimental results with 3-methyl*cyclo*hexanonesemicarbazone were somewhat erratic but they may indicate the presence of considerable quantities of a third form of the methyl*cyclo*hexane ring. The results support the view that the methyl*cyclo*hexane ring exists in multiplanar forms.

Further experimental work has shown that the methyl*cyclo*hexanes *A* of Part III (J., 1938, 1323) are, in fact, slightly impure forms of *B'*, for their physical properties changed appreciably during 6 months' keeping, and redistillation over sodium afforded material having properties agreeing closely with those originally recorded for *B'*. Furthermore, the physical properties of form *B'* remained unchanged after 1 year's keeping. The view that *A* was a stable form of methyl*cyclo*hexane being no longer tenable, we directed our experiments with a view to obtain independent experimental evidence for the existence of forms *B* and *B'*.

Clemmensen reduction of pure 2-, 3-, and 4-methyl*cyclo*hexanones gave products which differed widely in physical properties (compare Morgan and Hickinbottom, J., 1921, **119**, 1886, who obtained similar results in the reduction of 4-chlorophenyl *n*-propyl ketone), but this was found to be due to the presence of small quantities of methyl*cyclo*hexenes, since on further reduction with hydrogen and Adams's platinum catalyst the physical properties agreed closely with those originally found for *B'* (see Experimental). These results seem to establish beyond all doubt the existence of the *B'* form, but no evidence could be obtained in these experiments of the *B* modification.

The reduction of the pure semicarbazones of 2- and 4-methyl*cyclo*hexanones with sodium ethoxide by a modification of the Wolff–Kishner method (compare Bennett and Linstead, J., 1935, 442; Cook and Linstead, J., 1934, 956) led in both cases to the *B* form, which passed on standing for several days into the *B'* form (see Experimental). 3-Methyl*cyclo*hexanonesemicarbazone yielded apparently anomalous results for which no satisfactory explanation can be offered; they do not, however, exclude the possibility of the presence of varying quantities of another isomeride of methyl*cyclo*hexane.

The experiments with 2- and 4-methyl*cyclo*hexanones seem to establish the existence of two forms of methyl*cyclo*hexane, one of which (*B*) is comparatively unstable and passes easily into a stable form (*B'*) and thus provides direct evidence for the existence of the methyl*cyclo*hexane ring in multiplanar forms. The exact number of theoretically possible forms of methyl*cyclo*hexane has been discussed by Brodetsky (*Proc. Leeds Phil. Soc.*, 1929, **1**, 370; cf. Wightman, *Chem. and Ind.*, 1939, **58**, 604) and by Cohen Henriquez (*Proc. Roy. Acad. Amsterdam*, 1934, **37**, 532). According to the former, the " chair " or " *Z* " form of the methyl*cyclo*hexane ring can give rise to two isomeric monosubstituted derivatives, whilst the latter finds that there is one fixed (" *Z* ") modification and an infinite number of mobile modifications of which the " *C* " form is one. Both mathematical analyses appear to be in agreement that more than two forms of the monosubstituted six-membered ring are theoretically capable of existence.

It should be pointed out that the form *B* is particularly sensitive to chemical reagents; *e.g.*, of some 18 preparations from the semicarbazones it was only possible to prepare the *B* form 6 times, the *B'* form being obtained in every other case. It is significant that the *B* form was isolated at the beginning of the autumn term when the laboratory was comparatively free from fumes: most subsequent attempts yielded the *B'* form, presumably owing to the presence of catalysts in the atmosphere. Furthermore, it is essential to employ a ground-glass joint in the hydrogenation bottle in the preparation from 2-methyl*cyclo*hexanol; if a rubber stopper is used, the *B'* form is invariably obtained.

The physical properties of the *B'* form are in excellent agreement with those recorded by Wibaut, Hoog, Langedijk, Overhoff, and Smittenberg (*Rec. Trav. chim.*, 1939, **58**, 329), who found for methyl*cyclo*hexane prepared by the hydrogenation of pure toluene under pressure in the presence of a nickel catalyst: b. p. 100·80°/760 mm., $d_{4^\circ}^{20^\circ}$ 0·76944, $n_{C}^{20^\circ}$ 1·42085, $n_{D}^{20^\circ}$ 1·42310, $n_{F}^{20^\circ}$ 1·42838, $n_{G'}^{20^\circ}$ 1·43285.

EXPERIMENTAL.

Pure 2-, 3-, and 4-methyl*cyclo*hexanones were specially prepared by Messrs. Howards from the pure cresols; the 3-compound was also obtained from Messrs. Ronsheim and Moore. All the physical measurements were made as described in earlier papers of this series.

Reduction of Semicarbazones with Sodium Ethoxide.—The pure semicarbazone was placed in a 250-c.c. Pyrex Claisen flask connected to a Pyrex condenser and Pyrex Perkin triangle, and a solution of sodium ethoxide added; a thermometer was inserted with its bulb about 2 cm. from the bottom of the flask, and the mixture was slowly distilled from a special glass-fronted air-bath, the temperature of which could be maintained constant within ± 2°. When most of the alcohol had passed over, the temperature was raised slowly until no further liquid distilled over. Most of the hydrocarbon passed over at 180—220° for the 2- and the 4-compound, and at 160—180° for the 3-compound. Great care must be exercised in the early stages of the distillation owing to excessive frothing. In all cases the liquid distilling above 100° was poured into water, the upper layer separated, treated successively with excess of 3N-sulphuric acid, water, saturated sodium bisulphite solution (shaken in mechanical shaker for 30—60 mins.), and water, and dried over calcium chloride. The product was then distilled over sodium in an all-glass Pyrex apparatus, and the middle fraction collected.

4-*Methyl*cyclo*hexanone*. 28 G. of the semicarbazone, m. p. 196° (crystallised from equal vols. of methyl and ethyl alcohols), and 12 g. of sodium in 130 c.c. of alcohol yielded 9·9 g. of hydrocarbon, b. p. 100·3—100·4°/760 mm. This had $d_{4^\circ}^{20^\circ}$ 0·7676, $n_{C}^{20^\circ}$ 1·42090, $n_{D}^{20^\circ}$ 1·42311, $n_{F}^{20^\circ}$ 1·42847, $n_{G'}^{20^\circ}$ 1·43238.* Upon standing for five days the physical properties were $d_{4^\circ}^{20^\circ}$ 0·7695, $n_{C}^{20^\circ}$ 1·42104, $n_{D}^{20^\circ}$ 1·42326, $n_{F}^{20^\circ}$ 1·42856, $n_{G'}^{20^\circ}$ 1·43256; these remained unchanged on further keeping for fifty days or upon distillation.

2-*Methyl*cyclo*hexanone*. 34 G. of the semicarbazone, m. p. 196° (ex rectified spirit), and 14·5 g. of sodium in 180 c.c. of absolute alcohol gave 13·5 g. of methyl*cyclo*hexane, b. p. 100·4°/763 mm. Immediately after distillation this had $d_{4^\circ}^{20^\circ}$ 0·7678, $n_{C}^{20^\circ}$ 1·42083, $n_{D}^{20^\circ}$ 1·42306, $n_{F}^{20^\circ}$ 1·42835, $n_{G'}^{20^\circ}$ 1·43224; 3—4 days later, these values had changed to 0·7694, 1·42099, 1·42321, 1·42853, and 1·43253, respectively, and were then unchanged after a further 28 days.

3-*Methyl*cyclo*hexanone*. The semicarbazone prepared from ketone from either source (see above) and recrystallised from pure methyl alcohol had m. p. 186°, unchanged by repeated recrystallisation from this solvent or from ethyl alcohol, ethyl acetate, or benzene–methyl alcohol–light petroleum (b. p. 40—60°). The purity of the semicarbazones was confirmed as follows. The mixed m. p. was 186°. The semicarbazone from Howard's ketone was converted into the ketone by means of oxalic acid in the usual way, and after thorough drying by anhydrous sodium sulphate (shaking machine, 1 hour) it had b. p. 169°/756 mm., $d_{4^\circ}^{20^\circ}$ 0·9181, $n_{C}^{20^\circ}$ 1·44284, $n_{D}^{20^\circ}$ 1·44586, $n_{F}^{20^\circ}$ 1·45113, $n_{G'}^{20^\circ}$ 1·45554. (Eisenlohr, *Fortschr. Chem. Physik*, 1925, **18**, 46, 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, from semicarbazone m. p. 190°; for other values see Vogel, J., 1938, 1333; the pure ketone is appreciably hygroscopic, and unless it is thoroughly dried and the measurements performed within 24 hours of distillation, somewhat lower values for the density will be obtained.)

26·2 G. of semicarbazone (from Howard's ketone) and 11·5 g. of sodium in 123 c.c. of absolute ethyl alcohol yielded 9·4 g. of hydrocarbon, b. p. 100·0°/750 mm., $d_{4^\circ}^{20^\circ}$ 0·7699, $n_{C}^{20^\circ}$ 1·42102, $n_{D}^{20^\circ}$ 1·42326, $n_{F}^{20^\circ}$ 1·42854, $n_{G'}^{20^\circ}$ 1·43248; after 5 days it had $d_{4^\circ}^{20^\circ}$ 0·7718, $n_{D}^{20^\circ}$ 1·42321. In another experiment with the same semicarbazone the methyl*cyclo*hexane had b. p. 99·5°/743 mm., $d_{4^\circ}^{20^\circ}$ 0·7716, $n_{C}^{20^\circ}$ 1·42096, $n_{D}^{20^\circ}$ 1·42321, $n_{F}^{20^\circ}$ 1·42855, $n_{G'}^{20^\circ}$ 1·43240; these properties were unchanged on keeping for several months.

In a similar experiment with 26·0 g. of semicarbazone from Ronsheim and Moore's ketone, 9·4 g. of hydrocarbon were obtained; b. p. 100·4°/769 mm., $d_{4^\circ}^{20^\circ}$ 0·7687, $n_{C}^{20^\circ}$ 1·42098, $n_{D}^{20^\circ}$ 1·42321, $n_{F}^{20^\circ}$ 1·42848, $n_{G'}^{20^\circ}$ 1·43239, and after 7 days' keeping, $d_{4^\circ}^{20^\circ}$ 0·7701, $n_{C}^{20^\circ}$ 1·42099, $n_{D}^{20^\circ}$ 1·42321, $n_{F}^{20^\circ}$ 1·42852, $n_{G'}^{20^\circ}$ 1·43247. The last values remained unchanged upon further keeping or upon distillation over sodium.

Clemmensen Reduction of Ketones.—General procedure. The reductions were effected in an all-Pyrex glass apparatus (cf. Linstead and Meade, J., 1934, 945; Meade, Ph.D. Thesis, London, 1933). 60 G. of zinc wool were placed in the 250 c.c. flask and treated successively with hot 10% sodium hydroxide solution, water, and 5% mercuric chloride solution for one hour, and the amalgam was thoroughly washed with water; 75 c.c. of glacial acetic acid, 25 c.c. of concentrated hydrochloric acid, and 20 g. of the ketone (*ex* bisulphite compound) were then added, and the mixture refluxed until fuming ceased (½ hr.) and then for a further 8—9 hours in a gentle stream of hydrogen chloride. The mixture was distilled in steam, the upper layer of the distillate separated, washed with water, shaken mechanically with saturated sodium bisulphite solution (no crystalline bisulphite compound separated), washed with water, dried with calcium chloride, and distilled. The resultant hydrocarbon (60% yield) invariably contained some unsaturated compound and was shaken with hydrogen in the presence of Adams's platinum catalyst until no further absorption took place; it was then dried with calcium chloride and distilled from sodium in all-Pyrex glass apparatus.

2-*Methyl*cyclo*hexanone*. The crude dried reduction product had b. p. 100—102°/760 mm.; this was redistilled over sodium, and a middle fraction, b. p. 100·2°/760 mm., collected; this had $d_{4^\circ}^{20^\circ}$ 0·7735, $n_{C}^{20^\circ}$ 1·42291, $n_{D}^{20^\circ}$ 1·42516, $n_{F}^{20^\circ}$ 1·43061, $n_{G'}^{20^\circ}$ 1·43466. 15·5 G. were reduced with

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* For data here and subsequently, 20° is used for brevity, although the temperature was accurately 20·0°.

hydrogen in the presence of 0·3 g. of Adams's platinum catalyst; absorption (360 c.c.) was complete in 5 hours. The product on distillation over sodium distilled completely at 100·3—100·4°/754 mm., and had $d_{4^\circ}^{20^\circ}$ 0·7694, $n_{C}^{20^\circ}$ 1·42091, $n_{D}^{20^\circ}$ 1·42316, $n_{F}^{20^\circ}$ 1·42844, $n_{G'}^{20^\circ}$ 1·43242.

3-*Methyl*cyclo*hexanone*. The crude dried reduction product had b. p. 100—101°/760 mm.; this was redistilled over sodium, and a middle fraction, b. p. 99·6°/741 mm., collected: $d_{4^\circ}^{20^\circ}$ 0·7770, $n_{C}^{20^\circ}$ 1·42504, $n_{D}^{20^\circ}$ 1·42737, $n_{F}^{20^\circ}$ 1·43296, $n_{G'}^{20^\circ}$ 1·43725. 17·0 G. were reduced as before in the presence of 0·3 g. of platinum: 440 c.c. of hydrogen were absorbed. The hydrocarbon thus obtained distilled constantly at 100·4°/749 mm., and had $d_{4^\circ}^{20^\circ}$ 0·7693, $n_{C}^{20^\circ}$ 1·42093, $n_{D}^{20^\circ}$ 1·42316, $n_{F}^{20^\circ}$ 1·42847, $n_{G'}^{20^\circ}$ 1·43243.

4-*Methyl*cyclo*hexanone*. The dried product from the Clemmensen reduction had b. p. 100—101·5°/760 mm.; this was redistilled over sodium, and a middle fraction, b. p. 100·3—100·4°/755 mm., had $d_{4^\circ}^{20^\circ}$ 0·7704, $n_{C}^{20^\circ}$ 1·42196, $n_{D}^{20^\circ}$ 1·42426, $n_{F}^{20^\circ}$ 1·42962, $n_{G'}^{20^\circ}$ 1·43365. 18·6 G. were reduced as before in the presence of 0·3 g. of platinum: 600 c.c. of hydrogen were absorbed. The hydrocarbon thus obtained distilled constantly from sodium at 100·2°/746 mm., and had $d_{4^\circ}^{20^\circ}$ 0·7692, $n_{C}^{20^\circ}$ 1·42092, $n_{D}^{20^\circ}$ 1·42316, $n_{F}^{20^\circ}$ 1·42848, $n_{G'}^{20^\circ}$ 1·43238.

Preparation from 1-*Methyl*-Δ^1-cyclo*hexene*.—The unsaturated hydrocarbon prepared from *cyclo*hexanone (*ex* bisulphite compound) as in Part III had b. p. 110—110·4°/744 mm. 20 G. were shaken with hydrogen in the presence of 0·4 g. of Adams's platinum catalyst until absorption became very slow. Addition of further catalyst only slightly increased the rate of absorption, and it was found best to redistil the liquid and reduce it again in the presence of fresh catalyst, these processes being repeated (4 times) until the theoretical absorption was obtained. The final product after distillation over sodium had b. p. 100·3°/750 mm., $d_{4^\circ}^{20^\circ}$ 0·7698, $n_{C}^{20^\circ}$ 1·42121, $n_{D}^{20^\circ}$ 1·42346, $n_{F}^{20^\circ}$ 1·42880, $n_{G'}^{20^\circ}$ 1·43237.

*Parachor of Methyl*cyclo*hexane* (B′ *form*), *b. p.* 100·4°/755 *mm.*—The measurements were carried out in the usual manner. The constant *K* of the apparatus was 1·8725. The symbols have their usual significance (cf. Part III).

Densities determined: $d_{4^\circ}^{20^\circ}$ 0·7694, $d_{4^\circ}^{41\cdot9^\circ}$ 0·7511.

$\gamma_{20^\circ} = 23{\cdot}74\ (0{\cdot}10)$.

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
18·8°	16·78	16·54	0·7705	23·86	281·6
40·7	15·54	15·30	0·7522	21·55	281·2
					Mean 281·4

(Wibaut *et al.*, give γ_{20° 23·73, *P* 281·6.)

It is hoped to obtain further evidence of the existence of the various forms of methyl*cyclo*hexane by the determination of their freezing points.

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