

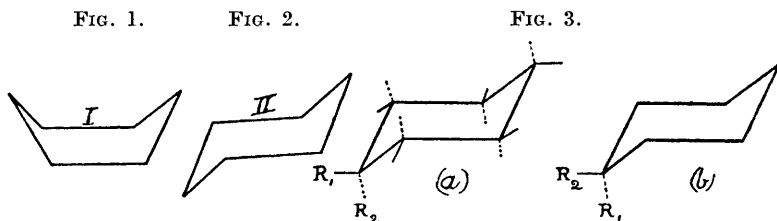
CCCXXXIV.—*The Spatial Structure of cycloParaffins.*
Part II. The Structure of 1:1-Disubstituted
cycloHexanes.

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IN Part I of this series (J., 1925, 127, 1421) it was shown that Sachse's strain-free structures for *cyclohexane* are consistent with the non-existence of isomeric mono-substitution products, because (a) relative strain-free rotation of the atoms in type I annihilates isomerism in this form, and (b) the interconvertibility (assumed by Mohr) of types I and II by the forces due to molecular collisions removes the need for isomerides corresponding to each. While the first point is proved by the study of suitable models (*loc. cit.*), the second rests on negative evidence only, and instances have recently been found in which it is evidently not applicable, or only partly applicable. The case of *dicyclohexyl* is of particular significance. Condensation methods using *cyclohexyl iodide* give a product of b. p. 234—236° (Kursanoff, *J. Russ. Phys. Chem. Soc.*,

1902, **34**, 221; Borsche and Lange, *Ber.*, 1905, **38**, 2769; Hell and Schaal, *Ber.*, 1907, **40**, 4165), while Wallach (*Ber.*, 1907, **40**, 70), by condensing *cyclohexanone* with itself and reducing the product, obtained a *dicyclohexyl*, b. p. 227°. Schrauth and Gorig (*Ber.*, 1923, **56**, 1900), by reduction of the products of condensation of *cyclohexanol* with phenol, obtained three different forms of *dicyclohexyl*, b. p. 235—237°, 227—228°, and 219.5—221.5°. One of these is stable, whilst the other two are transformed into mixtures of the three by the action of aluminium chloride or of light. Since two of these forms appear to correspond with those previously obtained by other methods, it would seem that we have a clear case of a mono-substitution derivative of *cyclohexane* existing in more than one form.

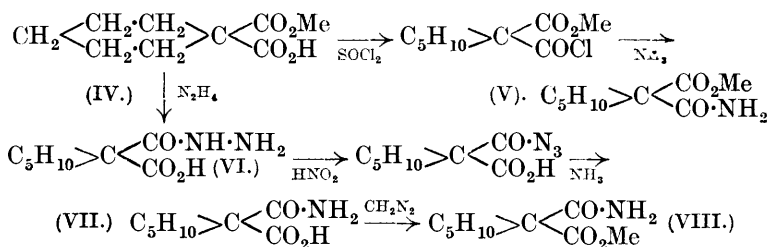
Now of Sachse's structures, type I (Fig. 1), by virtue of strainless motion, has all its hydrogen atoms equivalent and is stereochemically indistinguishable from a plane ring. In type II (the rigid form)



(Fig. 2), each hydrogen atom is equivalent to its *trans*-neighbours on the adjoining carbon atoms, but not to its *cis*-neighbours or to its partner on its own carbon atom, *i.e.*, the hydrogen atoms fall into two sets of six as indicated in Fig. 3a, and this form should give rise to two mono-substituted isomerides. The existence of three *dicyclohexyls* is thus in accord with the spatial possibilities.

Differences in the stereochemistry of types I and II at once arise. For instance, *cis-cyclohexane-1:2-dicarboxylic acid* can have only one form in the flexible modification, but in the rigid modification it can exist in two forms which are non-superposable mirror images. Attempts to resolve this compound have hitherto failed (Werner and Conrad, *Ber.*, 1899, **32**, 3046; Böeseken and Peek, *Rec. trav. chim.*, 1925, **44**, 841), but Derx (*ibid.*, 1922, **41**, 312) was led to conclude, from experiments on the effect of *cis-cyclohexane-diols* and *cis-tetrahydronaphthalenediols* on the conductivity of boric acid solutions, that the *cyclohexane* ring exists in the form of an equilibrium mixture in which type II predominates. It therefore becomes of interest to endeavour to obtain some positive evidence on the spatial structure of simple *cyclohexane* derivatives.

Fig. 3 shows that if a 1 : 1-disubstituted *cyclohexane*, $C_6H_{10}R_1R_2$ (*a*), has the rigid structure, then interchange of R_1 and R_2 will give a substance (*b*) which differs from (*a*) and is not its mirror image. If the original substance has the flexible structure, the interchange will make no difference. The present investigation was devised to test this point by carrying through the following series of changes (compare Fischer and Brauns, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, 1, 714).



When this series of operations had been carried out, it was found that the two ester-amides (V) and (VIII), which were solids, m. p. 91.5° and $90-91^\circ$, respectively, were identical, giving a mixed m. p. $90-91^\circ$.

Positive proof is thus obtained that in this series of derivatives the rigid form of the *cyclohexane* ring does not exist as a static modification. The possibility of dynamic equilibrium is not, however, excluded.

EXPERIMENTAL.

Dimethyl Ester of cycloHexane-1 : 1-dicarboxylic Acid.—This ester was prepared from pentamethylene dibromide and methyl disodiummalonate in the manner described by Dox and Yoder for the diethyl ester (*J. Amer. Chem. Soc.*, 1921, 43, 1368). The yield of crude ester (b. p. $110-125^\circ/14$ mm. after repeated fractionation) was 22%. It was purified by hydrolysis and re-esterification: colourless liquid, b. p. $119^\circ/14$ mm. (Found: C, 59.9; H, 8.0. $C_{10}H_{16}O_4$ requires C, 60.0; H, 8.0%).

Constitution. Hydrolysis with methyl-alcoholic potash gave *cyclohexane-1 : 1-dicarboxylic acid*, m. p. 176° (decomp.) (Found: C, 55.3; H, 7.3. Calc. for $C_8H_{12}O_4$: C, 55.8; H, 7.0%). On heating to 190° , this substance lost carbon dioxide, giving an acid, m. p. $30.5-31.5^\circ$, which proved to be identical with a specimen of hexahydrobenzoic acid prepared from magnesium *cyclohexyl bromide* and carbon dioxide (mixed m. p. $30-31.5^\circ$).

1-Methyl 1'-Hydrogen cycloHexane-1 : 1'-dicarboxylate (IV).—This substance was prepared by partial hydrolysis of the dimethyl ester

according to Walker's method for acid esters of dialkylmalonic acids (J., 1892, **61**, 710). Acidification of the solution of the potassium salt gave an insoluble oil which solidified when the residue from its dried and evaporated ether solution was kept in a vacuum. It crystallised from low-boiling ligroin in rhombic plates, m. p. 75°, yield 42% (Found: C, 58.1; H, 7.4. $C_9H_{14}O_4$ requires C, 58.1; H, 7.5%).

1-Methyl 1'-Carbamylcyclohexane-1-carboxylate (V).—The acid ester (IV) (3 g.) was refluxed with an excess of thionyl chloride on the steam-bath, and after distillation of the excess of thionyl chloride the residual oil was poured into cooled aqueous ammonia. The resulting white precipitate was twice recrystallised from acetone; prisms, m. p. 91.5°, yield 1.5 g. (Found: C, 57.7; H, 8.1. $C_9H_{15}O_3N$ requires C, 58.4; H, 8.1%).

cycloHexane-1'-carboxylic Acid 1-Hydrazide (VI).—The acid ester (IV) (2.1 g.) was shaken with hydrazine (2.6 g., 92% N_2H_4), cooled to 0° in an atmosphere of hydrogen, until it dissolved. After standing for a day at the ordinary temperature, excess of hydrazine was removed in a vacuum at 30°, whereupon the residue solidified to a white, crystalline mass. This was dissolved in water, acidified with acetic acid, and precipitated with lead acetate at 80°. The resulting lead salt was suspended in water and decomposed with hydrogen sulphide at 80°. After thorough extraction of the lead sulphide with hot water, the cooled and concentrated filtrate yielded 1.5 g. of a solid, which on recrystallisation from water gave m. p. 156° (decomp.).

1-Carbamylcyclohexane-1'-carboxylic Acid (VII).—Sodium nitrite (0.5 g.) was added to the acid hydrazide (VI) (1 g.) suspended in 15 c.c. of water and ice, and shaken till solution was complete. On acidifying with 5*N*-sulphuric acid the azoimide was precipitated as an oil. This was immediately dissolved in ether and dry ammonia gas was passed into the ether solution cooled in a freezing mixture. A precipitate was formed which, after removal of the ether by suction, was dissolved in water and acidified with hydrochloric acid. Hydrazoic acid was evolved, and the amic acid precipitated. It was recrystallised twice from water, insufficient to dissolve the whole being used; yield, 0.5 g., prisms, m. p. 149° (decomp.) (sintering at 139°).

1'-Methyl 1-Carbamylcyclohexane-1'-carboxylate (VIII).—The amic acid (VII) was suspended in ether and esterified by addition of diazomethane. The residue after removal of the ether consisted of prismatic crystals similar to (V), m. p. 90–91°, mixed m. p. with (V) 90–91.5°. The identity of the compounds (V) and (VIII) was thus clearly established.

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