

hols in the presence of silicon tetrafluoride. Practically the theoretical yields of methyl and of ethyl acetate are obtained.

Alcohols absorb silicon tetrafluoride in the ratio of four moles of alcohol to one mole of tetrafluoride,

the products being unstable addition compounds. Acetamide, ammonia and tributylamine form other stable white solids with silicon tetrafluoride.

NOTRE DAME, IND.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

## Contribution to the Multiplanar Isomerism of Cyclohexanes

BY R. F. MILLER<sup>1</sup> AND ROGER ADAMS

Quadrat-I-Khuda<sup>2</sup> reported the isolation of four forms of 4-methyl-1-carboxycyclohexyl acetic acid and explained their existence on the basis of the Sachse theory of two multiplanar rings. Goldschmidt and Gräfinger<sup>3</sup> and Desai and Hunter<sup>4</sup> however, have repeated these experiments without successfully obtaining more than two compounds. All other apparent compounds were mixtures of these two.

Quadrat-I-Khuda<sup>5</sup> has also reported two forms of  $\beta,\beta$ -dimethylcyclohexanone but Dey and Linstead<sup>6</sup> have shown one of these to be 2,2,4-trimethylcyclopentanone.

Although other authors have investigated types of compounds which might exist in the form of multiplanar isomers, no satisfactory evidence has as yet been offered to establish that such forms of cyclohexane or its derivatives can exist.<sup>7</sup> Cohen<sup>8</sup> on the basis of a geometrical analysis believes in two configurations for cyclohexane, one a "fixed" represented by the "Z" or chair modification and the other a "mobile" having an infinite number of modifications of which the "C" or boat form is one. Mills<sup>9</sup> on the other hand, has pointed out

that the energy changes involved in the interconversion of one form to the other are so small as to exclude the likelihood of isolating the isomers as individuals.

The investigation described in this communication was undertaken to supplement the researches of Quadrat-I-Khuda,<sup>2</sup> from which he deduced that multiplanar isomers may be isolated in certain substituted cyclohexanes. The compound studied by Quadrat-I-Khuda, 4-methyl-1-carboxycyclohexyl acetic acid (I) exists in *cis-trans* modifications of the classical type. It may, therefore, hardly be considered ideal for the investigation of possible multiplanar forms since the stereochemical character of the product becomes more complex when *cis-trans* isomerism is possible. No attempt was made to repeat Quadrat-I-Khuda's experiments, the procedure followed by Goldschmidt and Gräfinger, and by Desai and Hunter, but analogous compounds were selected which would eliminate the complication just mentioned.

(1) Part of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Quadrat-I-Khuda, *J. Ind. Chem. Soc.*, **8**, 277 (1931); *Nature*, **136**, 301 (1935).

(3) Goldschmidt and Gräfinger, *Ber.*, **68**, 279 (1935).

(4) Desai and Hunter, *Nature*, **136**, 608 (1935).

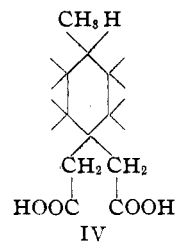
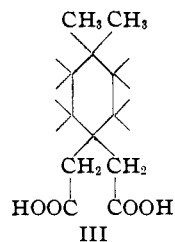
(5) Quadrat-I-Khuda, *ibid.*, **132**, 210 (1933).

(6) Dey and Linstead, *J. Chem. Soc.*, 1063 (1935).

(7) Schrauth and Görg, *Ber.*, **56**, 1900 (1923); Kursanoff, *J. Russ. Phys.-Chem. Soc.*, **34**, 221 (1902); Borsche and Lange, *Ber.*, **38**, 2766 (1905); Hell and Schaal, *ibid.*, **40**, 4162 (1907); Wallach, *ibid.*, **40**, 70 (1907); Werner and Conrad, *ibid.*, **32**, 3046 (1899); Böseken and Peek, *Rec. trav. chim.*, **44**, 841 (1925); Derx, *ibid.*, **41**, 312 (1922); Wightman, *J. Chem. Soc.*, **126**, 2541 (1926); Hopff, *Ber.*, **64B**, 2739 (1931); **65B**, 482 (1932); Unger, *ibid.*, **65B**, 467 (1932); Nenitzescu and Jonescu, *Ann.*, **491**, 189, 210 (1931); Zelinsky and Tarassova, *Ber.*, **65B**, 1249 (1932); *Ann.*, **508**, 115 (1934); Cornubert and Borrel, *Bull. soc. chim.*, **46**, 1148 (1929); Cornubert and Maurel, *ibid.*, **49**, 1498 (1931); Cornubert and de Demo, *Compt. rend.*, **197**, 1656 (1933); Desai, *Nature*, **136**, 434 (1935).

(8) Cohen, *Proc. Roy. Acad. Amsterdam*, **37**, 532 (1934).

(9) Mills, "Inst. intern. chim. Solvay Conseil chim." 4th Conseil, Brussels, 1931, p. 1-60.

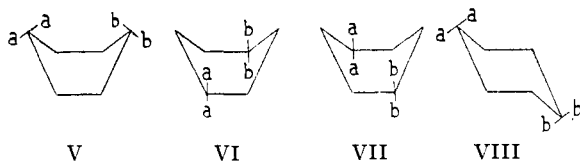


Compounds II, III and IV in which no *cis-trans*

isomerism is possible were prepared. If the compound I exists in multiplanar forms, then certainly the similarly constituted compounds (II, III and IV) should also show similar isomerism.

4,4-Dimethyl-1-carboxycyclohexyl acetic acid (II) was prepared from 4,4-dimethylcyclohexanone by the same series of reactions used by Quadrat-I-Khuda.<sup>2</sup> 4,4-Dimethylcyclohexane-1,1-diacetic acid (III) and 4-methylcyclohexane-1,1-diacetic acid (IV) were synthesized from the proper ketones by the method of Desai.<sup>10</sup> The products in each instance were subjected to very careful fractional crystallizations as ammonium salts, as free acids and also as anhydrides, but in no instance was there the slightest indication of more than a single individual compound corresponding to each of the formulas II, III or IV.

Although multiplanar forms of cyclohexanes have been recognized as a possibility for many years, on the basis of such isomerism the number of theoretically possible isomers in various substituted compounds of this type<sup>11</sup> have not been discussed. Groups in the 1,1- and 4,4-positions have usually been pictured only on the end carbons of the "Z" or "C" forms. The "Z" form is symmetrical and consequently similar substituents on any two carbons on opposite sides of the molecule will lead to identical structures. On the other hand, the "C" form is unsymmetrical and hence if the configuration is a "fixed" one, several isomeric modifications can result. Thus, for the mole  $a_2C_6H_8b_2$ , four forms may be written, three of the "C" and one of the "Z" type. Compounds VI and VII are mirror images. The "C" form



however, may be "mobile" since the interconversion of models constructed for V, VI and VII takes place with essentially no strain. This conforms to the geometrical deductions of Cohen previously mentioned. Much more distortion is necessary to transform the "C" to a "Z" modification. The existence of merely two forms, therefore, one "C" and one "Z" might not be unexpected.

(10) Desai, *J. Chem. Soc.*, 1047 (1932).

(11) Freudenberg, "Stereochemie," Franz Deuticke, Wien, 1933, p. 107; Goldschmidt, "Stereochemie," Akademische Verlagsgesellschaft, M. B. H., Leipzig, 1933, p. 57; Wittig, "Stereochemie," *ibid.*, 1930, p. 139.

With two different substituents on one of the carbons as in  $a_2C_6H_8bc$ , eight forms, six "C" and two "Z" might result. These include two pairs of mirror images. If it is assumed that because of mobility only one "C" form is possible, there should still be three multiplanar isomers.

Each isomeric "Z" form should represent an individual compound, since interconversion of one "Z" form to another "Z" form necessitates considerable strain. Such interchange requires an intermediate transition either through a "C" form or through a completely planar form. The latter intermediate would involve more temporary strain than passage through a "C" modification.

A compound of the formula  $abC_6H_8cd$  may be written in sixteen isomeric forms, twelve "C" and four "Z," including four pairs of mirror images. On the basis of only one "C" form, five isomers remain.

The compound studied by Quadrat-I-Khuda, 4-methyl-1-carboxycyclohexyl acetic acid, is a representative of the  $abC_6H_8cd$  type. The previous assumption of four modifications must consequently be modified.

From the experiments described in this communication and from those previously published, no evidence has as yet been made available to establish that cyclohexanes may exist in multiplanar forms.

### Experimental

4,4-Dimethylcyclohexanone was synthesized in two ways. The better of the two was a modification of that described by Von Auwers and Keil.<sup>12</sup> From chloroform, potassium hydroxide and *p*-cresol, 1-methyl-1-dichloromethylcyclohexadiene-2,5-one-4 was produced. The above-mentioned authors converted this product by reduction, first with palladium and hydrogen, and then with sodium and moist ether, through the intermediate 4-methyl-4-dichloromethyl cyclohexanol to 4,4-dimethylcyclohexanol. A much improved yield and a more convenient procedure consisted in the reduction of the dichloro compound in one step with active nickel and sodium hydroxide. Oxidation of 4,4-dimethylcyclohexanol gave excellent yields of 4,4-dimethylcyclohexanone.

The second method for preparing this ketone was by cyclization of 4,4-dimethylpimelic acid. This acid was synthesized by the following series of reactions: (1) dimethyldihydroresorcinol, (2) 4,4-dimethylglutaric acid, (3) diethyl-4,4-dimethylglutarate, (4) 4,4-dimethylheptandiol-1,7, (5) 4,4-dimethyl-1,7-dibromoheptane, (6) 4,4-dimethyl-1,7-dicyanoheptane, (7) 4,4-dimethylpimelic acid, (8) 4,4-dimethylcyclohexanone.

The preparation of 4,4-dimethylpimelic acid from 3,3-dimethylpentandiol-1,5 through the dihalide followed by a malonic ester synthesis and hydrolysis or followed by con-

(12) Von Auwers and Keil, *Ber.*, **35**, 4207 (1902).

version to the dicyanide and hydrolysis could not be used because of the unreactivity of the dihalide.

**4,4-Dimethylcyclohexanol and 4,4-Dimethylcyclohexanone.**—A solution of 15 g. of 1-methyl-1-dichloromethylcyclohexadiene-2,5-one-4<sup>13</sup> in 100 cc. of alcohol was reduced with 1 g. of Raney nickel<sup>13</sup> and hydrogen at 2 to 3 atm. pressure. At the end of thirty minutes, three-fifths of the calculated amount of hydrogen had been absorbed when it ceased to react. After addition of 6.4 g. (calculated amount to neutralize the hydrochloric acid) of powdered sodium hydroxide to the mixture, the reduction was continued and was complete in eight hours. Essentially a quantitative yield of 4,4-dimethylcyclohexanol was obtained, b. p. 68° (7 mm.), m. p. 37°.

The sodium hydroxide may be added at the beginning of the reduction with equally successful results.

The hexanol was oxidized as described by Von Auwers to 4,4-dimethylcyclohexanone,<sup>12</sup> m. p. 40–42°.

**3,3-Dimethylpentanediol-1,5.**—3,3-Dimethylglutaric acid was prepared by oxidation of dimethyldihydroresorcinol<sup>14</sup> with sodium hypobromite, according to the method of Komppa.<sup>15</sup> The dimethylglutaric acid was kindly reduced for us with copper–chromium oxide catalyst and hydrogen at 250 atm. by Dr. Homer Adkins of the University of Wisconsin: colorless liquid, b. p. 132° (1 mm.).

*Anal.* Calcd. for C<sub>8</sub>H<sub>16</sub>O<sub>2</sub>: C, 63.63; H, 12.12. Found: C, 63.66; H, 12.33.

**3,3-Dimethyl-1,5-dichloropentane.**—To 30 g. of 3,3-dimethylpentane-diol-1,5, 60 g. of thionyl chloride was added slowly, with stirring, and the mixture then refluxed for four hours. Upon pouring into water, an oily layer separated which was extracted with ether. The 3,3-dimethyl-1,5-dichloropentane boiled at 135° (80 mm.); yield 26 g. (80%).

**3,3-Dimethyl-1,5-dicyanopentane.**—A mixture of 30 g. of 3,3-dimethyl-1,5-dichloropentane, 200 cc. of 50% alcohol and 30 g. of sodium cyanide was refluxed for ninety-six hours. The alcohol and water were removed under diminished pressure and the residue extracted with ether. After removal of unchanged dichloro- and monocyno derivative by distillation, the dicyano derivative was obtained as a colorless liquid, b. p. 155–157° (7 mm.); *n*<sup>20</sup><sub>D</sub> 1.4404; *d*<sup>20</sup><sub>4</sub> 1.0936; yield 10.5 g. (40%).

*Anal.* Calcd. for C<sub>9</sub>H<sub>14</sub>N<sub>2</sub>: N, 18.66. Found: N, 18.47.

**Diethyl 4,4-Dimethylpimelate.**—A mixture of 9 g. of 3,3-dimethyl-1,5-dicyanopentane, 19 g. of ethyl alcohol and 19 g. of concentrated sulfuric acid was refluxed for twenty hours, cooled, diluted with water and extracted with ether. The ester boiled at 135° (7 mm.); *n*<sup>20</sup><sub>D</sub> 1.5632; *d*<sup>20</sup><sub>20</sub> 0.9732; yield 11 g. (70%).

*Anal.* Calcd. for C<sub>18</sub>H<sub>24</sub>O<sub>4</sub>: C, 63.93; H, 9.83. Found: C, 63.94; H, 9.62.

**4,4-Dimethylcyclohexanone.**—A mixture of 15 g. of diethyl 4,4-dimethylpimelate and 28 g. of barium hydroxide in 150 cc. of water was refluxed for twenty-four hours. The product, consisting of barium salt and barium hydroxide, obtained by evaporation of the solution *in vacuo*

to dryness was distilled from a 50-cc. flask gradually heated to 300° in a Wood's metal bath. Water, ketone and a small amount of oily material collected in the receiver. The ketone was filtered and recrystallized from low-boiling petroleum ether, m. p. 38°; yield, 3 g. (33%).

**Ethyl 4,4-Dimethylcyclohexylidene-cyanoacetate.**—A mixture of 8 g. of 4,4-dimethylcyclohexanone, 9.04 g. of ethyl cyanoacetate and 8 drops of piperidine was allowed to stand for forty hours, and then heated on the steam-bath for two hours.<sup>16</sup> The mixture was poured into normal hydrochloric acid and the oily layer extracted with ether. By vacuum distillation, unchanged starting materials were removed and the ethyl 4,4-dimethylcyclohexylidene-cyanoacetate obtained as a colorless oil, b. p. 155° (7 mm.); m. p. 50°; yield 10.3 g. (75%).

*Anal.* Calcd. for C<sub>13</sub>H<sub>19</sub>O<sub>2</sub>N: N, 6.33. Found: N, 6.43.

**Ethyl 4,4-Dimethylcyclohexane-1-cyano-1-α-cyanoacetate.**—To a solution of 35 g. of ethyl 4,4-dimethylcyclohexylidene-cyanoacetate in 125 cc. of alcohol, a solution of 15 g. of potassium cyanide in 35 cc. of water was added. After two days at room temperature, the potassium salt of the product had separated. The alcohol was removed under diminished pressure and the crude potassium salt used directly in the next reaction.

**4,4-Dimethyl-1-carboxycyclohexylacetic Acid.**—The crude potassium salt just described was boiled for ten hours with 250 cc. of concentrated hydrochloric acid to complete the hydrolysis. The mixture was cooled, extracted with ether and the cyclohexylacetic acid removed from the ether by means of aqueous sodium carbonate. Upon acidification with hydrochloric acid and filtration, the product was obtained.

*Anal.* Calcd. for C<sub>11</sub>H<sub>18</sub>O<sub>4</sub>: C, 61.68; H, 8.41. Found: C, 61.32; H, 8.21.

The corresponding anhydride was prepared by the action of acetic anhydride. Purified from ligroin, it was obtained in the form of white crystals, m. p. 124°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>16</sub>O<sub>3</sub>: C, 67.34; H, 8.11. Found: C, 67.20; H, 8.02.

**The ω-Imide of α,α'-Dicyano-4,4-dimethylcyclohexane-1,1-diacetic Acid.**—Ammonia was passed into a solution of 30 g. of 4,4-dimethylcyclohexanone, 53 g. of ethyl cyanoacetate and 125 cc. of absolute alcohol until the saturation point was reached. After twenty-four hours in the refrigerator, the ammonium salt separated and was filtered. More salt was obtained by evaporation of the filtrate to small volume. The imide was obtained by treatment of the salt with hot, dilute, hydrochloric acid. It was purified from alcohol, m. p. 230° (dec.); yield 46 g. (75%).

*Anal.* Calcd. for C<sub>14</sub>H<sub>17</sub>O<sub>4</sub>N<sub>2</sub>: N, 16.21. Found: N, 15.86.

**4,4-Dimethylcyclohexane-1,1-diacetic Acid.**—A mixture of 125 cc. of 70% sulfuric acid, 25 g. of the imide of α,α'-dicyano-4,4-dimethylcyclohexane-1,1-diacetic acid was refluxed until no more carbon dioxide was evolved (ten hours). Upon cooling, diluting with water and filtering, the acid was obtained and extracted with ether. The

(13) Adkins and Covert, *This Journal*, **54**, 4116 (1932).

(14) Shriner, "Org. Syn.," Vol. XV, 1935, p. 14.

(15) Komppa, *Ber.*, **32**, 1421 (1899).

(16) General method described by Lapworth and McRae, *J. Chem. Soc.*, **121**, 2741 (1922).

ether, in turn, was extracted with aqueous sodium carbonate and then acidified with hydrochloric acid; white crystals from alcohol, m. p. 213–218° (capillary tube); m. p. 230° (bloc Maquenne); yield 14.3 g. (65%).

*Anal.* Calcd. for  $C_{12}H_{20}O_4$ : C, 63.15; H, 8.77. Found: C, 62.90; H, 8.75.

**4,4 - Dimethylcyclohexane - 1,1 - diacetic Anhydride.**—A mixture of 2 g. of 4,4-dimethylcyclohexane-1,1-diacetic acid and 10 g. of acetic anhydride was refluxed for two and one-half hours. The excess of acetic anhydride was removed under diminished pressure and the residue purified from low-boiling petroleum ether, m. p. 86°.

*Anal.* Calcd. for  $C_{12}H_{18}O_3$ : C, 68.57; H, 8.57. Found: C, 68.30; H, 8.78.

The  $\omega$ -imide of  $\alpha, \alpha'$ -dicyano-4-methylcyclohexane-1,1-diacetic acid, 4-methylcyclohexane-1,1-diacetic acid and its anhydride were prepared according to the directions of Desai.<sup>10,17</sup> The melting points were identical with those reported.

#### Fractional Crystallization of the Acids

**4,4 - Dimethyl - 1 - carboxycyclohexylacetic Acid.**—A. The crude acid (14 g.) was neutralized with ammonia and the solution evaporated to dryness on a steam-bath. The dry salt was dissolved in 100 cc. of absolute alcohol and filtered. The filtrate was evaporated to 60 cc. and then boiled gently under reflux until solution was complete. Upon cooling to room temperature a fraction of the salt crystallized which was filtered and washed with a few cubic centimeters of cold absolute alcohol. This fraction was converted to the acid which melted at 189° (bloc Maquenne).<sup>18</sup> By gradual evaporation of the alcohol four different fractions of the acid were obtained, all of which melted at 189° (bloc Maquenne). Mixed melting points gave no depression. These fractions (5.5 g.) were combined and dissolved in 80 cc. of chloroform. When this solution was evaporated to half its original volume, one fraction was obtained and, upon evaporation to near dryness, another fraction separated. Both melted at 189°. The first fraction from chloroform was converted to the anhydride and fractionally crystallized from 20 cc. of ligroin. All fractions from this solution melted at 123–124° (capillary tube).

The remaining alcohol solution of the ammonium salt was evaporated to dryness, and the salt changed to the acid. The acid (7.3 g.) was then extracted with 400 cc. of boiling water, and the hot solution filtered. The two, slightly colored, non-crystalline fractions obtained from the water melted at 183 and 180°, respectively. The first fraction was extracted with 40 cc. of hot benzene, and the benzene solution, when allowed to cool, gave a small fraction which melted at 189°. The acid which did not dissolve in benzene was combined with the portion that did not dissolve in the water extraction. These two fractions (6 g.) were dissolved in 150 cc. of chloroform. The solution was evaporated to 70 cc. and allowed to cool when a

portion of the acid crystallized which melted at 189°. By gradual evaporation, two more fractions were obtained which melted at 189 and 188°, respectively. The remaining chloroform was evaporated to dryness and a trace of oil was found which was alkali insoluble. The second chloroform fraction was converted to the anhydride which melted at 123–124°.

B. The crude acid (15 g.) was dissolved in 1 liter of hot benzene, and the solution evaporated to 600 cc. and allowed to cool. The acid that crystallized from the solution (10 g.) was filtered and washed with 50 cc. of cold benzene. It melted at 189°. This material was then converted to the anhydride and dissolved in 200 cc. of boiling ligroin. When this solution was cooled to room temperature, a fraction of the anhydride was obtained which melted at 123–124° (capillary tube). By subsequent evaporation and cooling, two more fractions were obtained. Both melted at 123–124°.

The first fraction (2 g.) obtained from the ligroin solution was dissolved in 100 cc. of fresh ligroin and the solution evaporated to 60 cc. As the solution cooled, the anhydride crystallized which, when filtered and dried, melted at 123–124°. The remaining mother liquor was used to dissolve the second fraction from the original solution of 10 g. of anhydride in 200 cc. of ligroin. This was done by boiling the second fraction in the mother liquor until it had dissolved, and then allowing the solution to cool. The fraction obtained here melted at 123–124°. This type of fractional crystallization, an accepted method of separating compounds with different solubilities, was used until a total of nine fractions of the anhydride had been obtained. They all possessed the same melting point, 123–124°.

The mother liquor from the original benzene solution was evaporated gradually in order to obtain two fractions of the acid. Both fractions melted at 189° (bloc Maquenne). The remaining benzene solution was evaporated to dryness and the small residue (0.2 g.) recrystallized once from chloroform. It melted at 189°.

The first fraction (3 g.) obtained from the benzene was converted to the anhydride and fractionated from 100 cc. of ligroin according to the procedure described above. All of the fractions melted at 123–124°.

**4-Methylcyclohexane - 1,1-diacetic Acid.**—The acid from the reaction mixture (40 g.) was neutralized with aqueous ammonia and the solution evaporated to dryness on the steam-bath. The dry ammonium salt was dissolved in 100 cc. of boiling absolute alcohol. Upon cooling, about half of the salt crystallized. The salt was converted to the acid and it melted at 156–158°. This acid was dissolved in 400 cc. of boiling benzene, and the solution allowed to cool. A fraction separated which melted at 157–158°. Two more fractions were obtained by evaporation and cooling which melted at the same temperature, 157–158°. The second fraction was dissolved in 200 cc. of benzene and three fractions were obtained which gave the same melting points.

The original solution of ammonium salt in alcohol was evaporated to dryness and the dry salt changed to the free acid which melted from 150–155°. This portion of the acid (17.6 g.) was extracted with 300 cc. of boiling benzene. The portion that did not dissolve melted at 151–156°. This fraction was dissolved in 1 liter of benzene at 45° and

(17) Thorpe and Wood, *J. Chem. Soc.*, 103, 1586 (1913).

(18) The melting points of the dimethylcyclohexyldibasic acids, as determined by the capillary tube method, were unsatisfactory. Very slight changes in rates of heating caused wide changes in melting point. Under any condition, the acids melted over a range because the acids decomposed to the anhydrides with the loss of water.

evaporated under reduced pressure to 400 cc. Upon cooling, most of the acid crystallized. This fraction melted at 156–158°. Two more fractions from this solution obtained by further evaporation melted at 157–158°.

Two fractions were obtained from the first benzene extraction. Both melted at 157–158°.

**4,4-Dimethylcyclohexane-1,1-diacetic Acid.**—A. The acid (17 g.) was dissolved in aqueous ammonia, and this solution evaporated to dryness on a steam-bath. The dry salt formed was dissolved in 120 cc. of boiling absolute alcohol and the solution allowed to cool to room temperature. The crystalline precipitate formed was filtered and washed with cold absolute alcohol and then converted to the acid. This fraction melted at 227° (bloc Maquenne). The acid (13 g.) was then dissolved in 100 cc. of hot alcohol and the solution allowed to cool when part of the acid crystallized. This fraction melted at 230°. By gradual evaporation of the mother liquor three more fractions were obtained, and they melted at 230, 229 and 228°, respectively.

The first fraction of the acid from alcohol was dissolved in 30 cc. of hot alcohol and part of it recrystallized on cooling. This fraction melted at 230°. The mother liquor from this fraction was used to dissolve the second fraction from alcohol, etc. This procedure was followed until a total of nine fractions had been obtained, all of

which melted at 230°. The seventh fraction was converted to the anhydride and fractionated from ligroin. All of the fractions melted at 85–86°.

The original mother liquor from the ammonium salt was evaporated to dryness, and the salt converted to the acid (34 g.) which melted at 224° (bloc Maquenne). This portion of the acid was dissolved in 60 cc. of boiling alcohol, and three fractions were obtained from this solution by alternate evaporation and cooling. They all melted at 230°. The second fraction was converted to the anhydride which was fractionally crystallized from 80 cc. of ligroin. The fractions obtained all melted at 85°.

### Summary

1. 4,4-Dimethyl-1-carboxycyclohexylacetic acid, 4,4-dimethylcyclohexyl-1,1-diacetic acid and 4-methylcyclohexyl-1,1-diacetic acid have been prepared. Each was obtained in a single form only.

2. A discussion is given of the theoretical number of isomers in substituted cyclohexanes, on the assumption that multiplanar forms are possible.

URBANA, ILLINOIS

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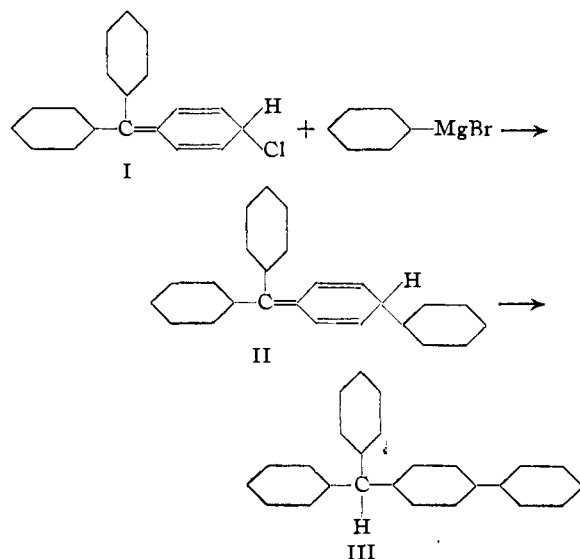
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

## The Reaction between Triarylmethyl Halides and Phenylmagnesium Bromide. II

BY C. S. SCHOEPFLE AND S. G. TREPP

Tetraphenylmethane is commonly prepared by the reaction of triphenylchloromethane and phenylmagnesium bromide,<sup>1</sup> although the yield is very poor. Gilman and Jones<sup>2</sup> found that biphenyldiphenylmethane (biphenyl = 4-phenyl-phenyl) is also formed in this reaction and that this compound is actually the principal product. The explanation offered by the present authors<sup>3</sup> for the formation of the two compounds is that triphenylchloromethane reacts partly in a benzenoid modification giving tetraphenylmethane, and partly in a quinonoid modification (I) giving biphenyldiphenylmethane (III). The relative amounts of the two products will therefore be dependent upon the equilibrium between the two forms of triphenylchloromethane, and the rate of reaction of each form with the Grignard reagent; it is assumed that the rate of transformation of the benzenoid form to the quinonoid form is rapid in com-

parison with the rate of reaction of the quinonoid form.



It might be expected then that the reaction of a given triarylchloromethane would vary with dif-

(1) (a) Gomberg and Cone, *Ber.*, **39**, 1461 (1906); (b) Freund, *ibid.*, **39**, 2237 (1906).

(2) Gilman and Jones, *THIS JOURNAL*, **51**, 2840 (1929).

(3) Schoepfle and Trepp, *ibid.*, **54**, 4059 (1932).