

STUDIES IN THE CYCLOHEXANE SERIES

Part VI. The Stereoisomeric Forms of 4-Methyl-, and 3-Methylcyclohexane-1: 1-Dicarboxylic Acids and a Conclusive Chemical Evidence for the Multiplanar Cyclohexane Ring

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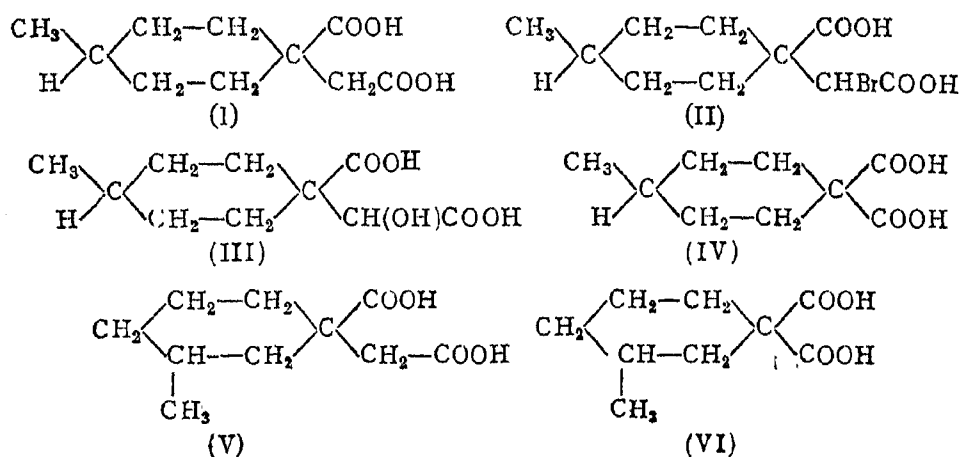
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WHILE summing up the position of the vexed question of the chemical evidence for the multiplanar forms of the cyclohexane derivatives in Part V of this series,¹ we came to the conclusion that conclusive evidence was still lacking. Vogel and co-workers² have tried to advance physical evidence such as boiling point, density, and refractive index in favour of the boat and arm-chair forms of the methylcyclohexane ring, but these observations have been challenged and contradicted by Wibaut and others.³ We do not wish to comment anything on the amazing but unconfirmed claims of Qudart-i-khuda and Co-workers⁴ because we are publishing a separate paper on this subject as we have convinced ourselves that none of their claims stands the tests of experimental verifications.

Contradictory to the observations of Qudart-i-khuda,⁵ Desai, Hunter, Khan and Sahariya⁶ showed that it was possible to isolate 1-carboxy-4-methylcyclohexane-1-acetic acid (I) only in two isomeric forms, and assumed that these represented the *cis* and *trans* forms of the acid containing the uniplanar cyclohexane ring. However, there is the possibility of these two acids being the stable modifications derived from the *boat* and *arm-chair* forms of the multiplanar six-membered ring. With a view to getting evidence on this point, we brominated one of the isomeric forms of the acid (I) by the Hell-Volhard-Zelinsky method, and converted the monobromo acid (II) into the hydroxy derivative (III) which, on oxidation with alkaline potassium permanganate gave 4-methylcyclohexane-1: 1-dicarboxylic acid (IV). The second isomeric form of the acid (I) furnished, under identical conditions a new isomeric 4-methylcyclohexane-1: 1-dicarboxylic acid (IV). Similarly the two isomeric forms of 1-carboxy-3-methylcyclohexane-1-acetic acid (V) gave a pair of isomeric 3-methylcyclohexane-1: 1-dicarboxylic acid (VI).

The isolation of pairs of isomeric 4-methyl-, and 3-methylcyclohexane-1:1-dicarboxylic acids is the first conclusive chemical evidence in favour of the strainless forms of the cyclohexane ring, though fifty years have elapsed since the theoretical predictions of Sachse.⁷ Despite the completion of this work in the summer of 1938, and the appearance of the preliminary note by us,⁸ in *Nature*, the detailed publication was hitherto delayed owing to unavoidable circumstances.



Experimental

The isomeric forms of 1-carboxy-4-methylcyclohexane-1-acetic acid and 1-carboxy-3-methylcyclohexane-1-acetic acid were prepared by the method already described by Desai, Hunter, Khan and Sahariya (*loc. cit.*).

Bromination of 1-Carboxy-4-methylcyclohexane-1-acetic Acid (A), m.p. 173 and formation of 1-Carboxy-4-methylcyclohexane-1- α -bromacetic acid (A).— Phosphorous pentachloride (21 g.) was slowly added to the above acid (10 g.) contained in a round bottom flask with constant cooling and shaking and the mixture was warmed on the water-bath till the evolution of hydrogen chloride ceased (6 hours). After adding bromine (3 c.c.) in three lots to the cooled mixture (6 hours) and a crystal of iodine, the mixture was left overnight at the room temperature, exposed to bright sunlight for 6 hours, and finally warmed at 50–60° under reflux for 36 hours. The cooled bromo-acid chloride was poured into anhydrous formic acid (100 c.c.) and the decomposition of the acid chloride was completed by warming on the water-bath for 3–4 hours, after the initial vigour of the reaction had abated. The crude *bromo-acid* which separated out on cooling was refluxed with hexane and finally crystallised from benzene when white plates, m.p. 152°, were obtained. (Found: Br, 28.5; C₁₅H₂₀O₄Br requires Br, 28.7 per cent.)

The β -lactone of 1-carboxy-4-methylcyclohexane-1-glycollic acid was deposited in long, white needles, m.p. 110° (previous sintering) when the

above hexane solution was kept at the room temperature after concentration. (Found: C, 60.8; H, 7.1; $C_{10}H_{14}O_4$ requires C, 60.6; H, 7.1 per cent.).

The Aniline Salt prepared by adding the above lactonic acid (1.5 g.) to the benzene solution (5 c.c.) of aniline (1.5 g.) separated out in white, tiny needles, m.p. 160°. (Found: C, 62.4; H, 7.6; $C_{16}H_{21}O_4N, H_2O$ requires C, 62.1; H, 7.4 per cent.).

Action of Sodium Carbonate Solution on the Bromo-acid (A) and Formation of 1-Carboxy-4-methylcyclohexane-1-glycollic acid (A).—The bromo-acid (5 g.) was neutralised with 2 N-sodium carbonate solution (20 c.c.), and then heated on the sand-bath under reflux for four hours. The alkaline solution was concentrated to a small bulk, cooled in ice, acidified with concentrated hydrochloric acid, saturated with ammonium sulphate and extracted with ether (thrice). The dried ethereal solution gave, on the removal of the solvent, *the acid* which solidified in a vacuum to a white solid, and crystallised from benzene in white scales, m.p. 134°. [Found: C, 55.6; H, 7.6; equiv. = 107.8; $C_{10}H_{16}O_5$ requires C, 55.6; H, 7.4 per cent.; equiv. = 108 (dibasic).]

Oxidation of 1-Carboxy-4-methylcyclohexane-1-glycollic Acid (A) by Alkaline Potassium Permanganate to 4-Methylcyclohexane-1:1-dicarboxylic Acid (A).—A solution of potassium permanganate (4 g.) in water (500 c.c.) was slowly added during 4 hours to the aqueous solution of the glycollic acid (2 g.) neutralised with N/20 barium hydroxide solution. After allowing the mixture to stand for 15 hours at the room temperature, the excess of potassium permanganate was destroyed with sulphur dioxide, and the filtered solution after being made alkaline with caustic soda solution was concentrated, acidified with concentrated hydrochloric acid, saturated with ammonium sulphate, extracted with ether (thrice), dried and the acid recovered. The recovered acid which solidified immediately crystallised from benzene in small plates, m.p. 170° (effer.), and did not react with -phenylene-diamine, semicarbazide acetate and *p*-nitrophenylhydrazine showing the absence of a keto group. [Found: C, 57.6; H, 7.7; equiv. = 93.4; $C_9H_{14}O_4$ requires C, 58.1; H, 7.5 per cent.) equiv. = 93.0 (dibasic).]

Bromination of 1-Carboxy-4-methylcyclohexane-1-acetic Acid (B), m.p. 137°, and Formation of 1-Carboxy-4-methylcyclohexane 1- α -bromacetic Acid (B).—This was carried out by following all the details of the acid (A). The crude bromo-acid (m.p. 128–30°) crystallised from benzene in white rectangular plates, m.p. 132°. (Found: Br, 28.5; $C_{10}H_{18}O_4Br$ requires Br, 28.7 per cent.)

1-Carboxy-4-methylcyclohexane-1-glycollic Acid (B).—Obtained by the action of sodium carbonate on the bromo-acid (*B*) crystallised from benzene in white scales, m.p. 138° (depressed to 115° by admixture with 1-carboxy-4-methylcyclohexane-1-acetic acid (*B*), m.p. 137°. (Found: C, 55.2; H, 7.5; $C_{10}H_{16}O_5$ requires C, 55.5; H, 7.4 per cent.)

4-Methylcyclohexane-1:1-dicarboxylic Acid (B).—Prepared by oxidising the above glycollic acid (*B*) crystallised from benzene in white, rectangular plates, m.p. 175° (effer.), depressed by admixture with 4-methylcyclohexane-1:1-dicarboxylic acid (*A*) to 148°, and gave negative tests for the keto-acid. [Found: C, 57.7; H, 7.4; equiv. = 93.5; $C_9H_{14}O_4$ requires C, 58.1; H, 7.5; equiv. = 93.0 (dibasic).]

Derivatives of 1-Carboxy-3-methylcyclohexane-1-acetic Acid (A), m.p. 163°, and *1-Carboxy-3-methylcyclohexane-1-acetic Acid (B)*, m.p. 108.09°, *1-Carboxy-3-methylcyclohexane-1- α -brom-acetic Acid (A)*, prepared in the usual manner, crystallised from benzene in white plates, m.p. 142°. (Found: Br, 28.6; $C_{10}H_{15}O_4Br$ requires Br, 28.7 per cent.)

1-Carboxy-3-methylcyclohexane-1-glycollic Acid (A), crystallised from benzene in white scales, m.p. 166°. (Found: C, 55.4; H, 7.5; $C_{10}H_{16}O_5$ requires C, 55.5; H, 7.4 per cent.)

3-Methylcyclohexane-1:1-dicarboxylic acid (A), crystallised from benzene in plates, m.p. 171–72° (effer.), and gave all the negative tests for the keto-acid. [Found: C, 57.8; H, 7.5; equiv. = 93.3; $C_9H_{14}O_4$ requires C, 58.1; H, 7.5 per cent., equiv. = 93.0 (dibasic).]

1-Carboxy-3-methylcyclohexane-1- α -bromacetic acid (B), crystallised from benzene in white plates, m.p. 155°. (Found: Br, 28.5; $C_{10}H_{15}O_4Br$ requires Br, 28.7 per cent.)

1-Carboxy-3-methylcyclohexane-1-glycollic acid (B), crystallised from benzene in white scales, m.p. 134°. [Found: C, 55.4; H, 7.4; equiv. = 109.0; $C_{10}H_{16}O_5$ requires C, 55.3; H, 7.4 per cent.; equiv. = 108 (dibasic).]

3-Methylcyclohexane-1:1-dicarboxylic acid (B), crystallised from benzene in white, rectangular plates, m.p. 185° (effer.), and did not respond to the tests for the keto-acid. [Found: C, 58.2; H, 7.6; $C_{19}H_{14}O_4$ requires C, 58.1; H, 7.5 per cent.)]

Summary

A pair of stereo-isomeric 4-methylcyclohexane-1:1-dicarboxylic acids has been prepared from a pair of isomeric 1-carboxy-4-methylcyclohexane-1-acetic acids. Similarly two isomeric 3-methylcyclohexane-1:1-dicarboxylic

acids have been obtained from the two isomeric 1-carboxy-3-methylcyclohexane-1-acetic acids. These results supply the first convincing proof of the multiplanar forms of the cyclohexane ring.

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