324. *4-Phenyl*cyclo*hexylacetic Acid.*

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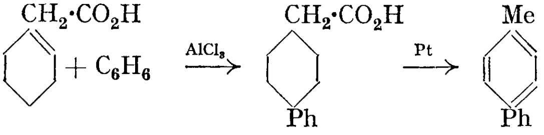
THE condensation between Δ^1-*cyclo*hexenylacetic acid and benzene in presence of aluminium chloride is attended by migration of a double bond (or its equivalent), for the only crystalline product isolated was 4-phenyl*cyclo*hexylacetic acid; the 2-phenyl*cyclo*hexylacetic acids which would be expected if migration did not occur were shown to be absent from the products.

ONE of us stated at a Meeting of the Society (Cook, *Chem. and Ind.*, 1937, **56**, 290) that condensation of Δ^1-*cyclo*hexenylacetic acid (I) with benzene in presence of aluminium chloride was accompanied by migration and gave, not 2-phenyl*cyclo*hexylacetic acid as claimed by Ghosh (*Science and Culture*, 1935, **1**, 299), but 4-phenyl*cyclo*hexylacetic acid (II). Ghosh (*ibid.*, 1937, **3**, 55) has recently remarked that " this does not seem plausible " and hence we wish to record the evidence on which the statement was based.

The two stereoisomeric 2-phenyl*cyclo*hexylacetic acids have m. p.'s 84—85° and 168—170° (Cook, Hewett, and Lawrence, J., 1936, 77). The acid obtained by Ghosh from benzene and *cyclo*hexenylacetic acid or hexahydro-α-coumaranone was stated to have m. p. 69—70°, but the mixed m. p. of the acids obtained from the two sources " was not observed as they did not have sharp melting points." If this acid were an impure specimen of the 2-phenyl*cyclo*hexylacetic acid of m. p. 85°, the reaction would furnish a convenient route to the hitherto almost inaccessible *trans*-hexahydrophenanthrone which it gives on dehydration (Cook, Hewett, and Lawrence, *loc. cit.*; compare Cook, *Chem. and Ind.*, 1937, **56**, 513). We have carried out condensations between Δ^1-*cyclo*hexenylacetic acid (I) and benzene in presence of aluminium chloride at 0°, at room temperature, and on the boiling water-bath, and in all cases have obtained in moderately good yield a liquid mixture of acids from which crystals could be obtained by dilution with ligroin. After two recrystallisations this crystalline acid, of which the yield was only 7%, melted constantly at 113°, and was shown to be *4-phenyl*cyclo*hexylacetic acid* (II) by dehydrogenation-decarboxylation with platinum-black to *p*-methyldiphenyl (III).



(I.) (II.) (III.)

The liquid mixture of acids which constituted the bulk of the reaction products we have not investigated, except to show that it was completely sulphonated by brief treatment with concentrated sulphuric acid at 100°, under which conditions the 2-phenyl*cyclo*hexylacetic acids are dehydrated to hexahydrophenanthrones. Therefore, 2-phenyl*cyclo*hexylacetic acids were not present in the reaction products. Pure 4-phenyl*cyclo*hexylacetic acid was likewise completely sulphonated by this treatment. Ghosh characterised his acid of m. p. 69—70° by conversion into its amide. This was stated to have m. p. 196—197°, in agreement with the value (195—196°) which we have found for the m. p. of the *amide* of 4-phenyl*cyclo*hexylacetic acid.

The formation of 4-phenyl*cyclo*hexylacetic acid in this reaction represents a type of migration which has not been much studied; it is, however, analogous to the production of 1 : 3- and 1 : 4-diphenyl*cyclo*hexanes, to the exclusion of the 1 : 2-compound, by condensation of benzene with 1 : 2-dibromo*cyclo*hexane in the presence of aluminium chloride (Nenitzescu and Curcăneanu, *Ber.*, 1937, **70**, 346).

Experimental.

Anhydrous aluminium chloride (10 g.) was gradually added to an ice-cold solution of Δ^1-*cyclo*hexenylacetic acid (10 g.) in pure dry benzene (50 c.c.). After ½ hour the mixture was kept at about 25° for 7 hours, the product decomposed with ice and hydrochloric acid, the benzene distilled in steam, and the residue extracted with ether. Acidic substances were removed from the extract by washing with dilute sodium carbonate solution, and were liberated by hydrochloric acid and re-extracted with ether. Distillation gave a colourless viscous oil (10 g.), b. p. 180°/0·8 mm., which yielded crystals, m. p. 106—108°, when diluted with ligroin (b. p. 80—100°). In another experiment a solution of the liquid distillate in light petroleum (b. p. 40—60°) was cooled in a freezing mixture; the m. p. of the crude crystalline material was then 80—106°. After two recrystallisations from ligroin *4-phenyl*cyclo*hexylacetic acid* (II) formed colourless elongated plates, m. p. 112·5—113·5° (Found: C, 76·7; H, 8·4. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%). Yield, 0·5—1 g. Substantially the same result was obtained when the reaction mixture was kept at 0° for 18 hours or heated on the water-bath for an hour.

A solution in benzene of the chloride of 4-phenyl*cyclo*hexylacetic acid (0·5 g.), prepared by means of thionyl chloride, was treated with gaseous ammonia. The resulting *amide* crystallised from benzene in colourless leaflets, m. p. 195—196° (Found: C, 77·1; H, 9·0. $C_{14}H_{19}ON$ requires C, 77·4; H, 8·8%).

4-Phenyl*cyclo*hexylacetic acid (1·25 g.) was heated with platinum-black (0·25 g.) in an atmosphere of carbon dioxide at 305—310° for 4 hours. The product was extracted with ether and washed with dilute sodium carbonate solution. A little of the original acid was recovered from the alkaline extract. The neutral material was distilled at 0·2 mm. from a bath at 140—160°. The crystals which separated from the distillate were drained on a tile and recrystallised from alcohol; they then had m. p. 45—46°, not depressed by *p*-methyldiphenyl prepared by the method of Gomberg and Pernert (*J. Amer. Chem. Soc.*, 1926, **48**, 1375).

We are indebted to Dr. John Iball for completing the identification of the two specimens of *p*-methyldiphenyl by crystallographic comparison. He reports that under the polarising microscope both specimens gave identical interference fringes, and an *X*-ray examination by the powder method gave identical photographs with the two specimens.

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