

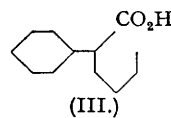
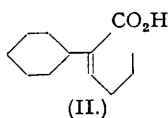
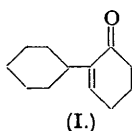
149. α -cycloHexyl- β -propylacrylic Acid from cycloHexanol.

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The acid formed from cyclohexanol at 300° in presence of sodium cyclohexyloxide has been shown to be 1-cyclohexylpent-1-ene-1-carboxylic (α -cyclohexyl- β -propylacrylic) acid. The mechanism of its formation is discussed.

GUERBET (*Compt. rend.*, 1912, **155**, 1156) observed that if a solution of sodium cyclohexyloxide in excess of cyclohexanol was heated at about 300°, an acid was formed to which he ascribed the formula $C_{11}H_{21} \cdot CO_2H$. This acid, which was obtained in our experiments in an average yield of 0.21 mol. per mol. of sodium cyclohexyloxide, was found to have the formula $C_{12}H_{20}O_2$ and to contain one double bond and, therefore, one ring. Its hydrogenation product has been identified as 1-cyclohexylpentane-1-carboxylic acid (III). It is submitted that Guerbet's acid is the corresponding 1-cyclohexylpent-1-ene-1-carboxylic acid (α -cyclohexyl- β -propylacrylic acid) (II) and that it originates from the hydrolytic fission of 2-cyclohexyl-2-cyclohexenone (I). This is in accord with the view put forward by Weizmann, Bergmann, and Haskelberg (*Chem. and Ind.*, 1937, **56**, 587) that the Guerbet condensations of alcohols proceed *via* the corresponding carbonyl compounds and the self-condensation (crotonisation) products of the latter. The so-called "cyclohexylidene-cyclohexanone" which would be expected to be formed from cyclohexanol on the basis of this mechanism is, according to Wallach (*Annalen*, 1911, **381**, 96), in equilibrium with (I).

The synthesis of (III) was carried out by butylation of ethyl cyclohexenylcyanoacetate, simultaneous hydrolysis and half-decarboxylation of the product so obtained, and finally catalytic hydrogenation. An attempt to butylate ethyl cyclohexylmalonate was unsuccessful.



EXPERIMENTAL.

1-cycloHexylpent-1-ene-1-carboxylic Acid (II).—The acid was obtained according to Guerbet (*loc. cit.*); b. p. 180°/14 mm.; 168°/6 mm.; d_{20}^{20} 0.9822; n_D^{20} 1.4848 (Found: C, 74.0; H, 10.5; bromine number, 80.6; M (in camphor) 196, (by titration) 208; $[R]$, 57.76. $C_{12}H_{20}O_2$ requires C, 73.5; H, 10.2%; bromine number, 80.0; M , 196; $[R]$, 56.51). The molecular refraction is in accord with (II); a molecular exaltation of about 0.6 would be expected for such a highly-substituted conjugated system. An alcoholic solution of *p*-bromophenacyl bromide (2.8 g.) was added to an aqueous solution (10 c.c.) of the sodium salt of the acid (2 g.), and the mixture was boiled for 4 hours. The oil, which separated upon cooling, solidified spontaneously. From light petroleum, the *p*-bromophenacyl ester crystallised in shiny leaflets, m. p. 67°. Yield, almost quantitative (Found: C, 61.2; H, 6.4; Br, 21.0. $C_{20}H_{25}O_3Br$ requires C, 61.1; H, 6.4; Br, 20.4%).

Hydrogenation.—A solution of the Guerbet acid (14.5 g.) in propyl alcohol (100 c.c.) was hydrogenated with palladium-barium sulphate as catalyst at ordinary temperature. In 3 hours, the theoretical quantity of 1700 c.c. of hydrogen had been absorbed. Distillation gave the hydrogenated acid, b. p. 182.5—183°/14 mm., which was later identified as 1-cyclohexylpentane-1-carboxylic acid (Found: C, 72.8; H, 11.0. $C_{12}H_{22}O_2$ requires C, 72.7; H, 11.1%). The *p*-bromophenacyl ester, prepared as above, solidified at 0° after addition of water, and crystallised in large, shiny leaflets from light petroleum; m. p. 45—46° (Found: C, 60.9; H, 6.3; Br, 20.6. $C_{20}H_{27}O_3Br$ requires C, 60.8; H, 6.8; Br, 20.3%).

Synthesis.—Ethyl cyclohexenylcyanoacetate (Harding, Haworth, and Perkin, *J.*, 1908, **93**, 1958) (b. p. 165°/16 mm.) (58 g.) and butyl bromide (41.1 g.) were added to a solution of sodium (7 g.) in absolute propyl alcohol (150 c.c.). After 4 hours at the boiling point of the solution, reaction was complete. The sodium bromide was removed by filtration, the solvent under reduced pressure, and the residue was treated with water and ether. Ethyl cyclohexenylbutylcyanoacetate boiled at 173°/16 mm. Yield, 42 g. (Found: C, 72.6; H, 9.6; N, 6.0. $C_{18}H_{22}O_2N$ requires C, 72.0; H, 9.2; N, 5.6%).

Hydrolysis of the ester presented unusual difficulties. Boiling alcoholic potassium hydroxide was practically without effect. The ester (21 g.) was heated with potassium hydroxide (40 g., 8 mols.) in water (50 c.c.), in an oil-bath at 180° for 24 hours. The cooled reaction product consisted of a solid precipitate and an oily top layer which dissolved on dilution with some water. Acidification liberated carbon dioxide, and extraction with ether then gave 1-cyclohexenylpentane-1-carboxylic acid, b. p. 156°/7 mm., after a substantial head fraction which was not further investigated. Yield, 8 g. (Found: C, 73.0; H, 9.9. $C_{13}H_{20}O_2$ requires C, 73.5; H, 10.2%).

1-cyclohexenylpentane-1-carboxylic Acid (III).—The unsaturated acid (4 g.) was hydrogenated in propyl alcohol (25 c.c.) with palladium-barium sulphate as catalyst at room temperature. The theoretical quantity of hydrogen was absorbed in 4 hours. The reduction product boiled at 159–160°/9 mm. (Found: C, 72.6; H, 11.1. Calc. for $C_{13}H_{22}O_2$: C, 72.7; H, 11.1%).

The *p*-bromophenacyl ester had m. p. 46–47° and proved identical with that prepared from the hydrogenation product of the Guerbet acid.

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