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SYNTHESIS OF TRIPHENYLENE DERIVATIVES

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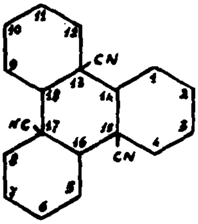
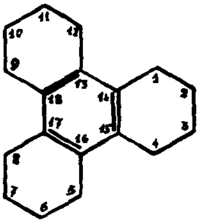
Radical and ionic polymerisations of 1-cyclohexene derivatives were unknown.

In attempting to obtain a polymer of 1-cyanocyclohexene, we have now found that alkali metal amides, such as lithium dimethylamide, lead mainly to cyclic trimerization of 1-cyanocyclohexene, that is to 13,15,17-tricyanoperhydrotriphenylene:



Furthermore, dodecahydrotriphenylene:



together with methanol, have been found the main reaction products when 1-methoxycyclohexene is contacted with boron trifluoride diethyletherate at room temperature.

1) - Synthesis of 13,15,17- tricyanoperhydrotriphenylene

$LiN(CH_3)_2$ (0,95 g) and anhydrous toluene (160 cm^3) are introduced, under nitrogen atmosphere, in a 250 cm^3 three- necked flask, equipped with mechanical stirrer. A toluene solution of 1-cyanocyclohexene (20 g in 40 cm^3) is then slowly added through a dropping funnel. After 48 hours at 25°C, benzene (100 cm^3) and 3 M HCl (100 cm^3) are added, the upper layer is removed and washed with water. Solvents are then removed by distillation and the solid residue (14 g) is purified by crystallization from benzene. Colorless needles (m.p. = 268 - 8,5°C), soluble in chloroform, methylene chloride, ketones, aromatic hydrocarbons, aliphatic alcohols and dimethylformamide, slightly soluble in diethylether and cyclohexane, insoluble in aliphatic hydrocarbons, are thus obtained (found: C, 78,20; H, 8,74; N, 13,32; calc. for $(C_7H_9N)_n$: C, 78,54; H, 8,40; N, 13,06%). The molecular weight as determined by cryoscopic measurements of benzene solutions, is 323. The product is therefore a trimer of 1-cyanocyclohexene (calc. for $(C_7H_9N)_3$ = 321,5) to which either a linear or a cyclic structure might be attributed. I.R. spectrum of the trimer (fig. 1) does not show any absorption band of carbon - carbon double bond. Furthermore, dehydrogenation of the trimer by heating at 300°C with palladium-carbon for 10 hours under nitrogen atmosphere, yields a diethylether very soluble compound, whose melting point after crystallization from n-heptane

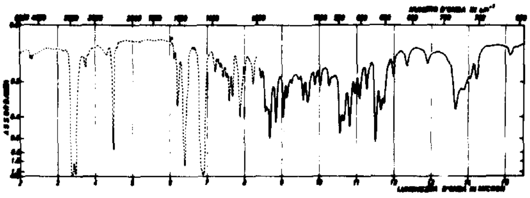


Fig. 1 - I.R. spectrum of 13,15,17-tricyanoperhydrotriphenylene in hexachlorobutadiene (------) and Nujol (———).

is 197 - 8°C (found: C, 96,64; H, 5,35; calc. for triphenylene $C_{18}H_{12}$: C,94,70; H, 5,30%; m.p. with authentic sample of triphenylene: 197–8°C; picrate m.p. = 223°C). Since this dehydrogenation product is recognized as triphenylene, we can conclude for a cyclic structure of the trimer, that is to say (in the ~~very~~ likely hypothesis of a head-to-tail enchainment of the monomeric units) for: 13,15,17-tricyanoperhydrotriphenylene.

Like perhydrotriphenylene (1), 13,15,17-tricyanoperhydrotriphenylene can form with several compounds, such as aliphatic and aromatic hydrocarbons, alcohols etc., clathrate inclusion compounds from which included compounds may be removed by heating, optionally under reduced pressure.

2) - Synthesis of dodecahydrotriphenylene

1-methoxycyclohexene (30 mmoles), anhydrous toluene (10 cm^3) and boron trifluoride diethyletherate (15 mmoles) are introduced, under nitrogen atmosphere, in a 50 cm^3 two-necked tube.

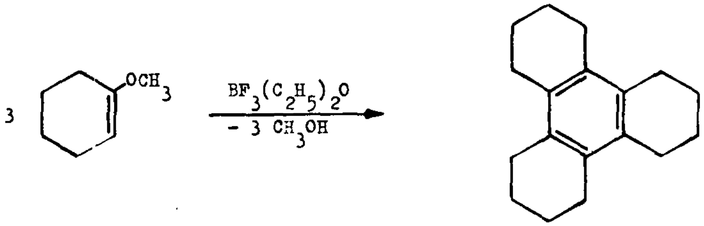
After 48 hours at 25°C, the crude reaction product (1,6 g) is isolated by following the description of par. 1).

Crystallization from boiling n-buthyl alcohol yields colorless needles (m.p. = 232 - 3°C) soluble in chloroform, benzene, acetone and n-heptane; slightly soluble in cold aliphatic alcohols (found: C, 89,88; H,10,06%; molecular weight from benzene solution, 240; calc. for dodecahydrotriphenylene $C_{18}H_{24}$: C, 89,94; H, 10,06%; molecular weight: 240,37).

A mixture of the purified product with authentic sample of dodecahydrotriphenylene (2) melts at 233°C.

Trimerization run afore-mentioned is repeated and the reaction mixture, when examined by gas-cromatography, shows the presence of methyl alcohol.

We can therefore conclude for the following total reaction:



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