CONDENSATION OF HEXACHLOROCYCLOPENTADIENE WITH UNSATURATED NITRO COMPOUNDS

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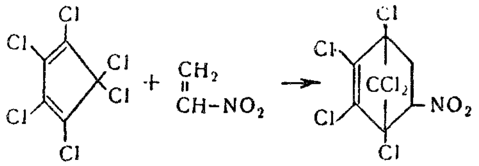
Only one compound has been reported which contains simultaneously chlorine atoms and a nitro group in its molecule and is obtained by the diene synthesis, namely the adduct formed by hexachloropentadiene with m-nitrostyrene [1]. Such compounds, however, may be of considerable interest from the point of view of physiological activity [2]. We considered it to be of interest to study the condensation of hexachlorocyclopentadiene with unsaturated nitro compounds. Of the latter, compounds of two types may be used: $CH_2 = CHR$ (in which R = e. g. NO_2, $COOR'-NO_2$) and $NO_2CH = CHR''$ (in which R" = e. g. H, alkyl, aryl, $COOCH_3$, CN). The presence of the sterically active voluminous chlorine atoms in hexachlorocyclopentadiene, particularly in the 5-position, renders its condensation with dienophiles difficult [3].

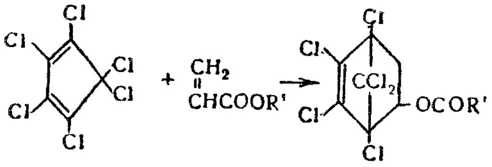
As Tamelen and Thiede showed [4], the nitro and methyl groups of 1-nitropropene are in the trans positions. This is clearly true also for other nitro dienophiles of the type $NO_2CH = CHR$. Diene condensation with such dienophiles will probably proceed with difficulty. On the basis of these facts it may be supposed that disubstituted nitro dienophiles of the type $NO_2CH = CHR$ would condense with hexachlorocyclopentadiene with very great difficulty. As regards monosubstituted nitro dienophiles it may be predicted that they will condense more readily with hexachlorocyclopentadiene than disubstituted nitro dienophiles, but the rate of such condensation will probably be low. The experimental results fully confirmed our suppositions.

When a solution of nitroethylene and hexachlorocyclopentadiene in chlorobenzene was heated at 100-102° for 14 hours, we obtained a good yield of 1,2,3,4,7,7-hexachloro-5-nitro-2-norbornene (I):



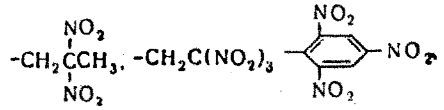
(I)

Good yields of the corresponding adducts were obtained also when hexachlorocyclopentadiene was heated for many (10-28) hours with 2-nitroethyl, 2,2-dinitropropyl, 2,2,2-trinitroethyl, and 2,4,6-trinitrophenyl acrylates:



(II)

in which R' = $-CH_2CH_2NO_2$



$-CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_3$, $-CH_2C(NO_2)_3$

On the other hand, all our attempts to cause hexachlorocyclopentadiene to react with 1-nitropropene, 2-nitropropene, β-nitrostyrene, methyl 3-nitroacrylate, and 3-nitroacrylonitrile were unsuccessful. When the components were heated together both in solvent (chlorobenzene, toluene, glacial acetic acid, propionitrile) and in absence of solvent, and also in presence of Cl_3CCOOH as catalyst, for as long as 20-30 hours, the diene was recovered unchanged quantitatively.

We decided to test our adducts, which contained chlorine atoms and nitro groups, for insecticidal activity, since it is known that many adducts synthesized from hexachlorocyclopentadiene and also various compounds containing both a chlorine atom and a nitro group in the molecule will function as insecticides. The tests* showed that all the adducts that we obtained show insecticidal activity.

EXPERIMENTAL

Condensation of Hexachlorocyclopentadiene with Nitroethylene. A solution of 7.3 g (0.1 mole) of nitroethylene, 9.03 g (0.033 mole) of hexachlorocyclopentadiene, and a little pyrogallol in 10 ml of chlorobenzene and 1 ml of glacial acetic acid was heated under reflux at 100-102° for 14 hours. When the reaction had ceased, solvent was vacuum-distilled off (12-15 mm) and unchanged hexachlorocyclopentadiene was steam-distilled off. When allowed to stand, the residue crystallized. Yield 8.4 g (73%). After being crystallized from aqueous methanol (one part of methanol to two parts of water) it had m. p. 160-161.5°. Found: C 24.94; 25.05; H 1.01; 1.27; N 4.21; 3.97; Cl 61.39; 61.14%. $C_7H_3NO_2Cl_6$. Calculated: C 24.27; H 0.867; N 4.04; Cl 61.56%.

Condensationof Hexachlorocyclopentadiene with 2-Nitroethyl Acrylate. A solution of 2.5 g (0.017 mole) of 2-nitroethyl acrylate, 4.7 g (0.017 mole) of hexachlorocyclopentadiene, and a little pyrogallol in 10 ml of chlorobenzene was boiled under reflux for 21 hours. When the reaction had ceased, low-boiling substances were vacuum-distilled off (12-15 mm). The residue crystallized when cool. The weight of adduct obtained was 6.4 g (89%). After being crystallized from aqueous alcohol (one part of water to two parts of alcohol) it had m. p. 93-94°. The condensation product (II)(R' = $CH_2CH_2NO_2$) is soluble in ether, alcohol, benzene, chloroform, and isopropyl alcohol; it is insoluble in water. Found: C 28.78; 28.78; H 1.81; 1.82; Cl 50.29; 50.29%. $C_{10}H_7NO_4Cl_6$. Calculated: C 28.70; H 1.67; Cl 50.88%.

Condensation of Hexachlorocyclopentadiene with 2,4,6-Trinitrophenyl Acrylate. A mixture of 12.55 g (0.046 mole) of hexachlorocyclopentadiene, 13.0 g (0.046 mole) of 2,4,6-trinitrophenyl acrylate, and a little pyrogallol was heated at 100-110° with stirring for 28 hours. When the reaction had ceased, unchanged diene (1.93 g) was steam-distilled off. The resinous residue was separated from water and dissolved in ether; the ethereal solution was dried with anhydrous sodium sulfate. Ether was distilled off under reduced pressure, and the residual oil crystallized. This gave 16.6 g (65%) of (II)(R' = 2,4,6-$(NO_2)_3C_6H_2$), m. p. 116.5-117.5° (from isopropyl alcohol). The adduct is soluble in alcohol, ether, benzene, and chloroform; it is insoluble in petroleum ether and water. Found: C 31.58; 31.32; H 1.25; 1.20; Cl 37.06; 36.86%. $C_{14}H_4O_8N_3Cl_6$. Calculated: C 32.19; H 0.89; Cl 38.30%.

Condensation of Hexachlorocyclopentadiene with 2,2-Dinitropropyl Acrylate. A mixture of 5.46 g (0.02 mole) of hexachlorocyclopentadiene, 4.08 g (0.02 mole) of 2,2-dinitropropyl acrylate, and a little pyrogallol was heated at 100-110° with stirring for ten hours. When cool, the reaction mixture crystallized. We obtained 9.5 g (about 100%) of (II)(R" = $CH_2C(NO_2)_2CH_3$). After being crystallized from alcohol it had m. p. 114-115°. The adduct is soluble in ether, benzene, and warm alcohol; it is insoluble in water. Found: C 27.97; 27.29; H 1.76; 1.80; Cl 44.60; 44.56%. $C_{11}H_8O_6N_2Cl_6$. Calculated: C 27.67; H 1.67; Cl 44.65%.

Condensation of Hexachlorocyclopentadiene with 2,2,2-Trinitroethyl Acrylate. A solution of 5.35 g (0.019 mole) of hexachlorocyclopentadiene, 4.6 g (0.019 mole) of 2,2,2-trinitroethyl acrylate, and a little pyrogallol in 15 ml of chlorobenzene was refluxed for 20 hours. When reaction ceased, solvent was vacuum-distilled off (12-15 mm) and unchanged diene was steam-distilled off. The resinous residue was separated from water, and dissolved in ether; the ethereal solution was dried with anhydrous sodium sulfate. Ether was distilled off, and

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* Toxicological tests were carried out by N. M. Permyakova.

the residual oil crystallized after long standing. We obtained 7.2 g (72%) of (II)(R' = $CH_2C(NO_2)_3$). The condensation product is readily soluble in alcohol, ether, benzene, and isopropyl alcohol; it is insoluble in water. For purification the adduct was dissolved in boiling aqueous alcohol or hexane, from which it then separated as an oil, which crystallized on standing; m. p. 55-57°. Found: Cl 41.62; 41.31%. $C_{10}H_5O_8N_3Cl_6$. Calculated: Cl 41.92.

SUMMARY

1. Hexachlorocyclopentadiene was brought into reaction with unsaturated nitro compounds, and as a result some adducts were prepared for the first time.

2. It was suggested that steric hindrance exists in the diene condensation of hexachlorocyclopentadiene with unsaturated nitro compounds of the types $RCH = CH_2$ and $NO_2CH = CHR''$, and this hypothesis was confirmed.

3. The adducts synthesized possess insecticidal activity.

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