CONDENSATION OF CYCLOPENTADIENE WITH MONO- AND DISUBSTITUTED NITROOLEFINS

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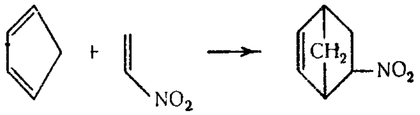
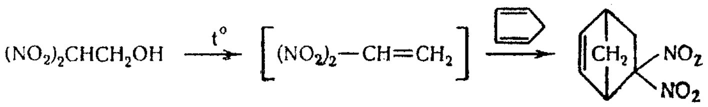
We have previously [1] carried out condensation of hexachlorocyclopentadiene with mono- and 1,2-disubstituted nitroolefins and have shown that the former react with the diene forming adducts in good yields, and that the disubstituted compounds do not give adducts with hexachlorocyclopentadiene even on heating for 30 hours.

In this work we studied the reaction of cyclopentadiene with monosubstituted ethylenes (nitroethylene and nitroallyl), 1,2-disubstituted ethylenes (β-nitrostyrene, β-nitroacrylic acid, its methyl ester and nitrile, and β-trichloromethylnitroethylene), and 1,1-dinitroethylene. As would be expected and as seen from the data in the literature [2], nitroethylene reacts smoothly with cyclopentadiene even at 0°, giving an adduct in 73% yield.

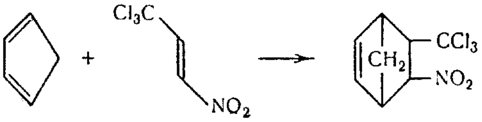


In contrast to 2-nitroalkenes-1, which can be regarded as 1,1-disubstituted phylodienes and which condense with cyclopentadiene with great difficulty [3, 4], 1,1-dinitroethylene (formed by dehydrating 1,1-dinitroethanol-2 under the reaction conditions) gives an adduct in 65% yield with cyclopentadiene on boiling for 15-20 minutes in chlorobenzene



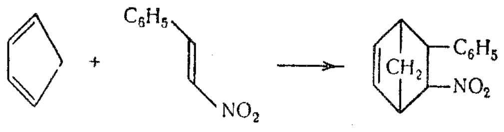
The cause of this different behavior of phylodienes of the same type must evidently be sought in the nature of the substituents: if in 2-nitroalkenes-1 and NO_2 and an alkyl-group are attached to the same carbon atom and the latter group partially "extinguishes" the activating effect of the nitro-group exerted on the double bond, then in 1,1-dinitroethylene both substituents are of the same nature and exert a "coordinated" effect.

We have not observed 1,1-dinitroethanol-2 in special detail, as this has been done by Gold, Hammel, and Klager [5], but have obtained the direct condensation product of dinitromethane with formaldehyde [6]. On comparing the experimental results of condensing cyclopentadiene with 1,2-disubstituted phylodienes: β-nitrostyrene, β-nitroacrylic acid, its nitrile and methyl ester, and β-trichloromethylnitroethylene, we noticed the fact that the latter reacts with much greater difficulty than the remaining phylodienes of this type. To obtain a high yield (86%) of adduct it is necessary to boil the mixture of diene and phylodiene in benzene for 17 hours.



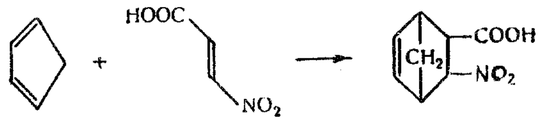
On carrying out the reaction under the conditions used by us in condensing cyclopentadiene with β-nitrostyrene and β-nitroacrylic acid (boiling in benzene for 5 hours), the adduct was formed in lower yield (~60%).

The lower reactivity of β-trichloromethylnitroethylene evidently results from steric hindrance caused by the presence of trichloromethyl group. Under the same conditions, β-nitrostyrene condenses practically quantitatively with cyclopentadiene on heating the components on a boiling water bath for 5 hours. In this case, steric hindrance plays a lesser part, because of as a result of the planar structure of the benzene ring and its free rotation around the C−C bond, while electronic factors begin to play a considerably greater part,

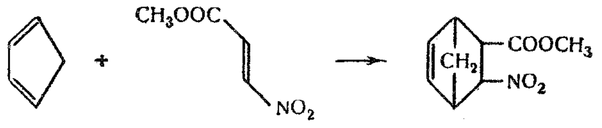


β-Nitroacrylic acid, its nitrile and methyl ester, react vigorously with cyclopentadiene. This evidently is a result of the activating effect exerted on the double bond by the two electronegative groups of the phylodiene.

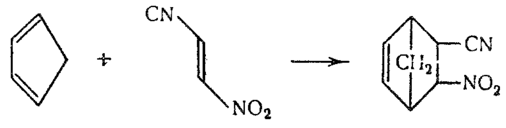
Thus, on boiling a mixture of β-nitroacrylic acid and cyclopentadiene in benzene for 5 hours, a bicylic acid is formed in 90% yield.



The methyl ester of the latter was obtained in 43% yield by reacting the methyl ester of β-nitroacrylic acid with cyclopentadiene.

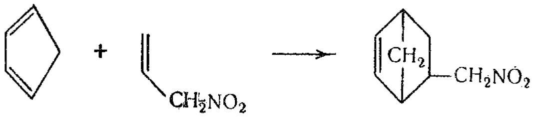


The nitrile of β-nitroacrylic acid reacts vigorously on mixing it with cyclopentadiene in benzene at 20°, but the adduct is formed in low yield (~ 25%). A similar low yield of this adduct (24%) was also obtained on heating the nitrile of β-nitroacrylic acid with cyclopentadiene in benzene at 80° for 5 hours.



The low yields of adducts from the nitrile and methyl ester of β-nitroacrylic acid are evidently related to the low stability of the initial phylodienes [7].

In nitroallyl the double bond is very weakly activated by the nitro group situated in the β-position, and thus it condenses with cyclopentadiene with much greater difficulty; on heating a mixture of nitroallyl and cyclopentadiene in chlorobenzene at 130-150° for 9 hours, an adduct was obtained in 24% yield.



EXPERIMENTAL

Condensation of Cyclopentadiene with Nitroethylene. To a solution of 82.5 g (1.26 M) of cyclopentadiene in 100 ml of absolute benzene with addition of pyrogallol was added dropwise a solution of 18.45 g (0.253 M) of nitroethylene in 100 ml of absolute benzene at a temperature of 0° over a period of 1 hour. The mixture was allowed to stand overnight at room temperature, the solvent evaporated off and the residue distilled. 25.2 g (73% theoretical) of 2-nitrobicyclo(2,2,1)-heptene-5 was obtained with b.p. 104-109° (12-14 mm); it solidified at room temperature. Data in the literature [2]: 92-94° (8 mm).

Condensation of Cyclopentadiene with Nitroallyl. To obtain nitroallyl, to a solution of 72 g (0.5 M) of freshly distilled allyl bromide in 120 ml of hexane was added without delay 83 g (0.54 M) of silver nitrite at room temperature. After several minutes the temperature of the reaction mixture was raised to the boiling point of the solvent. To avoid losing the reaction mixture, cooling it with ice water was necessary. The reaction mixture was then cooled to 40° and stirred at the temperature for 3 hours. The precipitate was filtered off, and hexane distilled off under weak vacuum (40 mm Hg) at room temperature. 22 g of nitroallyl was obtained with b.p. 42° (24 mm). Data in the literature [8]: b.p. 87-89° (180 mm); 125-130° (760 mm).

To prepare 2-nitromethylbicyclo(2,2,1)heptene-5, a solution of 2.7 g (0.03 M) of freshly distilled nitroallyl [b.p. 37° (20 mm)] and 3.96 g (0.06 M) of freshly distilled cyclopentadiene in 10 ml of chlorobenzene was boiled under reflux condenser for 7 hours; pyrogallol was added to prevent polymerization. After completion of the reaction, chlorobenzene and unreacted cyclopentadiene and nitroallyl were distilled off under the vacuum of a water-jet pump. The residue was distilled in a stream of nitrogen. 1.1 g (24% theoretical) of 2-nitromethylbicyclo(2,2,1)heptene-5 was obtained with b.p. 102° (8 mm); 92° (4 mm); $n^{20}D$ 1.4953; d^{20}_4 1.1253. Found: C 63.00; 63.07; H 7.16; 7.04; N 9.11; 9.37%. $C_8H_{11}NO_2$. Calculated: C 62.74; H 7.18; N 9.15%.

Condensation of Cyclopentadiene with 1,1-Dinitroethylene. For the reaction we took not 1,1-dinitroethylene, but 1,1-dinitroethanol-2, which, as is known, is readily dehydrated under condensation conditions [5]. 1,1-Dinitroethanol was prepared as described in an article by Duden and Pondorf [6]. To a boiling solution of 9.8 g (0.148 M) of cyclopentadiene (freshly distilled) in 15 ml of chlorobenzene was added dropwise over a period of 10 minutes to a solution of 7.4 g (0.054 M) of 1,1-dinitroethanol-2 in 30 ml of chlorobenzene, and then stirred at boiling point for 20 minutes. The solution was stirred with activated carbon at 40° for 30-40 minutes, filtered from the carbon, and chlorobenzene removed in vacuo; the residue crystallized on cooling. Yield of technical 2,2-dinitrobicyclo(2,2,1)-heptene-5 was 6.9 g (65% theoretical), m.p. 117-118° [subliming at 145° (2-3 mm)]. Data in the literature: m.p. 117-118° [5]. Found: C 45.41; 45.34; H 4.47; 4.45%. $C_7H_8N_2O_4$. Calculated: C 45.65; H 4.34%.

Condensation of β-Nitrostyrene with Cyclopentadiene. A mixture of 7.95 g (0.05 M) of β-nitrostyrene and 6.6 g (0.1 M) of freshly distilled cyclopentadiene with addition of pyrogallol was heated on a boiling water bath for 5 hours with reflux condenser and distilled. 10.8 g (96% theoretical) of 2-nitro-3-phenylbicyclo(2,2,1)heptene-5 was obtained with b.p. 142-145° (1-2 mm); $n^{20}D$ 1.5640; data in the literature [9, 10]: 145° (1 mm); $n^{20}D$ 1.5641.

Condensation of Cyclopentadiene with β-Nitroacrylic Acid. β-Nitroacrylic acid, its methyl ester and nitrile were prepared by the method described previously [7]. To a solution of 1.2 g (0.02 M) of freshly distilled cyclopentadiene in 5 ml of absolute benzene was added dropwise a solution of 2.34 g (0.02 M) of β-nitroacrylic acid in 10 ml of absolute benzene in presence of inhibitor. The temperature was then lowered to 32°. The solution was boiled for 5 hours, and benzene evaporated off; the residue crystallized on cooling. 3.2 g (90.5% theoretical) of 2-nitro-3-carboxybicyclo(2,2,1)heptene-5 was obtained with m.p. 95-96° (from hexene). Found: C 52.85; 52.66; H 5.24; 5.27; N 7.64; 7.69%. $C_8H_9NO_4$. Calculated: C 52.45; H 4.91; N 7.65%.

Condensation of Cyclopentadiene with the Methyl Ester of β-Nitroacrylic Acid. To a solution of 2 g (0.03 M) of cyclopentadiene in 5 ml of absolute benzene with addition of pyrogallol was added a solution of 3.8 g (0.029 M) of the methyl ester of β-nitroacrylic acid in 2 ml of absolute benzene at room temperature. The mixture was then boiled on a water bath for 5 hours. After solvent evaporation, the residue was distilled in vacuo. 2.45 g (43% theoretical) of 2-nitro-3-carbomethoxybicyclo(2,2,1)heptene-5 was obtained with b.p. 106-107° (2 mm); $n^{20}D$ 1.4912; d^{20}_4 1.2551. Found: C 54.45; 54.44; H 5.68; 5.60; N 7.09; 6.97%. $C_9H_{11}NO_4$. Calculated: C 54.82; H 5.58; N 7.10%.

Condensation of Cyclopentadiene with the Nitrile of β-Nitroacrylic Acid.

Experiment 1. To a solution of 3.96 g (0.06 M) of freshly distilled cyclopentadiene in 6 ml of absolute benzene with pyrogallol addition was added dropwise with stirring at 20° (cooling) 4.25 g (0.04 M) of distilled nitrile of β-nitroacrylic acid. A white, crystalline precipitate then settled out. The reaction mixture was stirred for 2 hours at 20-22°, then for 2 hours at 50-60°; the precipitate was filtered off. 1.6 g (~25% theoretical) of 2-nitro-3-cyanobicyclo(2,2,1)heptene-5 was obtained with m.p. 142-142.5° (from ethyl alcohol). Found: C 58.46; 58.57; H 4.98; 4.96; N 17.01; 17.05%. $C_8H_8N_2O_2$. Calculated: C 58.53; H 4.87; N 17.07%.

Experiment 2. A mixture of 3.5 g (0.036 M) of the nitrile of β-nitroacrylic acid, 3.6 g (0.054 M) of freshly distilled cyclopentadiene, and 15 ml of absolute benzene was boiled under reflux condenser for 5 hours, pyrogallol being added to prevent polymerization. The solvent was evaporated off, the resinous residue crystallizing on standing. 1.4 g (24% theoretical) of 2-nitro-3-cyanobicyclo(2,2,1)heptene-5 was obtained m.p. 142-142.5° (from ethyl alcohol).

Condensation of Cyclopentadiene with β-Trichloromethylnitroethylene. β-Trichloromethylnitroethylene was prepared by the method described in the literature [11].

Experiment 1. A mixture of 5.23 g (0.027 M) of β-trichloromethylnitroethylene, 5 g of freshly distilled cyclopentadiene, 10 ml of absolute benzene, and 1 ml of acetic acid was boiled under reflux condenser for 17 hours in the presence of pyrogallol. After completion of reaction, solvent and unreacted dicyclopentadiene were evaporated off, and the residue distilled. 6.02 g (~86% theoretical) of 2-nitro-3-trichloromethylbicyclo(2,2,1)heptene-5 was obtained with b.p. 120-123° (2 mm); $n^{20}D$ 1.5342; d^{20}_4 1.4908. Found: C 37.27; 37.56; H 3.07; 3.12 ; Cl 41.52; 41.32%. $C_8H_8NO_2Cl_3$. Calculated: C 37.13; H 3.08; Cl 41.18%.

Experiment 2. A mixture of 3.9 g (0.02 M) of β-trichloromethylnitroethylene, 2.6 g (0.04 M) of freshly distilled cyclopentadiene, 7 ml of absolute benzene, and 0.5 ml of glacial acetic acid was boiled under reflux condenser for 5 hours in presence of pyrogallol. After reaction completion, solvent and unreacted dichclopentadiene were evaporated off, and the residue distilled. 3.12 g (~60% theoretical) of 2-nitro-3-trichloromethylbicyclo(2,2,1)-heptene-5 was obtained with b.p. 124-126° (3 mm); $n^{20}D$ 1.5346.

SUMMARY

1. Condensation was achieved of cyclopentadiene with monosubstituted (nitroethylene and nitroallyl), and 1,1,- and 1,2-disubstituted (1,1-dinitroethylene, nitrostyrene, β-nitroacrylic acid, its nitrile and methyl ester, and β-trichloromethylnitroethylene) nitroolefins.

2. Both the nature of the substituents and their volume affected the reactivity of the nitrophylodiene.

3. For the first time, a series of bicyclic adducts containing functional groups together with a nitro-group was prepared and characterized.

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