2. The selective oxidation with nitrogen oxides of the OH group at C_6 in the cellulose molecule is due to the presence and nature of the glucopyranoside ring.

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"CONDENSATION OF PIPERYLENE WITH NITROOLEFINS"

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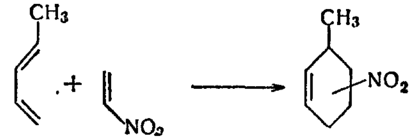
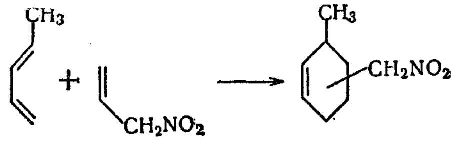
In the preceeding article we described the condensation of mono- and disubstituted nitroolefins with butadiene [1]. The present report deals with the interaction of some mono- and disubstituted nitroolefins with piperylene. Only two articles were available in the literature in regard to the condensation of piperylene with nitroolefins at the time when our work was begun. One of these articles described the preparation of addition products derived from piperylene and 1-nitropentene [2], 2-(α-furyl)nitroethylene [2], or β-nitrostyrene [2, 3]. When the experimental work of the investigation reported by us in this instance was completed an article appeared which described the condensation of piperylene with β-trichloromethylnitroethylene [4].

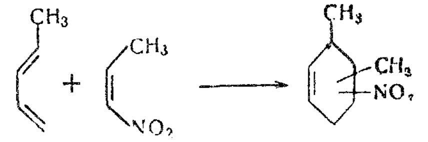
We investigated the interaction of piperylene with mono-substituted dienophilic nitro compounds (nitroethylene and 1-nitropropylene-2) and di-substituted dienophilic nitro compounds (1-nitropropylene-1,β-dichloromethylnitroethylene, and the methyl ester of β-nitroacrylic acid). On heating of a mixture of nitroethylene with piperylene in benzene for 11 hours, the addition product was obtained with a yield of 89-91%.



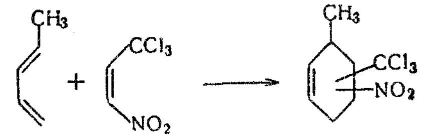
As was to be expected, 1-nitropropylene-2 condenses with much greater difficulty with piperylene: after a mixture of the reacting substances was heated in a sealed tube for 26 hours at 100°, the addition product formed with a yield of only 18%.



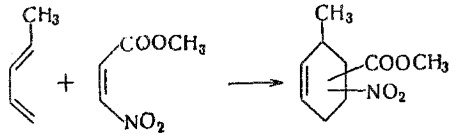
Heating of a mixture of piperylene with 1-nitropropylene-1 in a sealed tube for 12 hours at 100° resulted in the formation of the addition product with a yield of 55%. Under analogous conditions



(time of the reaction 12 hours) the yield of the addition product from piperylene and β-trichloromethylnitroethylene reached 81%



Heating of piperylene with the methyl ester of β-nitroacrylic acid in a sealed tube for 12 hours at 110° resulted in formation of the addition product with a yield of 85%.



When the condensation of piperylene with di-substituted dienophilic nitro compounds was carried out in a chlorobenzene solution at 100° for 38 hrs, the yields of the addition products comprised 50-60%.

EXPERIMENTAL

Trans-piperylene with b.p. of 41-42°; $n^{20}D$ 1.4320 [5] was used in all syntheses.

Condensation with nitroethylene. A solution of 30 gr (0.41 M) of nitroethylene and 54.4 gr (0.8 M) of piperylene in 100 ml of dry and pure benzene was boiled under reflux for 7 hrs. To prevent polymerization, pyrogallol was added. The yield was 53.1 gr (approx. 91% of theory) of 3-methyl-4(5)-nitrocyclohexene-1 with b.p. of 93-93.5° (8 mm); $n^{20}D$ 1.4798; d^{20}_4 1.0751. Found: C 59.55; 59.40; H 8.02; 8.05; N 9.95; 9.99%. $C_7H_{11}NO_2$. Calculated: C 59.57; H 7.80; N 9.93%.

Condensation with 1-nitropropylene-2. A mixture of 4 gr (0.046 M) of freshly distilled 1-nitropropylene-2, 4.7 gr (0.069 M) of piperylene, and a small quantity of pyrogallol was heated in a sealed tube for 26 hours at 100°. The yield was 1.3 gr of 3-methyl-4(5)-nitromethylcyclohexene-1 (18% of theory) with b.p. of 63° (1 mm); $n^{20}D$ 1.4731; d^{20}_4 1.0371. Found: C 61.45; 61.43; H 8.21; 8.47; N 9.38; 9.44%. $C_8H_{13}NO_2$. Calculated: C 61.93; H 8.38; N 9.03%.

Condensation with 1-nitropropylene-1. A mixture of 2.3 gr (0.025 M) of 1-nitroprolylene-1, 3.4 gr (0.05 M) of piperylene, and a small quantity of pyrogallol were heated in a sealed tube at 100° for 12 hours. The yield was 2.2 gr (55% of theory) of 3,5(4)-dimethyl-4(5)-nitrocyclohexene-1 with a b.pt. of 84-85.5° (8 mm); $n^{20}D$ 1.4719; d^{20}_4 1.0465. Found: C 61.71; 61.66; H 8.49; 8.50; N 9.03; 9.26%. $C_8H_{13}NO_2$. Calculated: C 61.93; H 8.38; N 9.03%.

Condensation with the methyl ester of β-nitroacrylic acid. A mixture of 4.8 gr (0.036 M) of the methyl ester of β-nitroacrylic acid, 2 gr (0.07M) of piperylene, and a small quantity of pyrogallol was heated in a sealed tube for 12 hours at 110°. The resulting yield was 4.95 gr (85% of theory) of 3-methyl-4(5)-nitro-5(4)-carbomethoxycyclohexene-1 with b.pt. of 108-108.5° (1 mm); $n^{20}D$ 1.4795; d^{20}_4 1.1819. Found: C 54.28; 54.42; H 6.51; 6.58; N 6.64; 6.54%. $C_9H_{13}NO_4$. Calculated: C 54.32; H 6.53; N 7.03%.

Condensation with β-trichloromethylnitroethylene. A mixture of 5.15 gr (0.027 M) of β-trichloromethylnitroethylene, 3.67 gr (0.054M) piperylene, and a small quantity of pyrogallol were heated in a sealed tube for 12 hours at 100°. The resulting yield of 3-methyl-4(5)-nitro-5(4)-trichloromethylcyclohexene-1 amounted to 5.65 gr (81% of theory); b.pt. 134-135° (2 mm); $n^{20}D$ 1.5246. On melting the substance crystallized; m.pt. 60-61°. Found: C 37.28; H 3.85; Cl 41.19; 41.09; 41.42%. $C_8H_{10}NO_2Cl_3$. Calculated: C 37.13; H 3.86; Cl 41.19%. According to data published in the literature [5], the b.pt. is 110-111.5° (1 mm); $n^{20}D$ 1.5232.

SUMMARY

The condensation of piperylene with nitroethylene, 1-nitropropylene-2, 1-nitropropylene-1, β-trichloromethylnitroethylene, and the methyl ester of β-nitroacrylic acid was investigated. The corresponding addition products were prepared.

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"CONDENSATION OF BUTADIENE WITH NITROOLEFINS"

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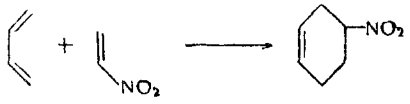
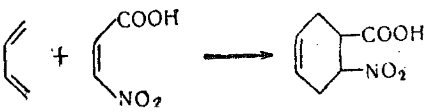
In prior work we investigated the condensation of mono- and disubstituted nitroolefins with cyclic dienes [1, 2]. It appeared of interest to investigate the interaction of same nitroolefins with non-cyclic dienes. We used butadiene as a diene in this case.

Reports published in the literature describe the condensation of butadiene with 1-nitropentene-1 [3], 2-nitrobutylene-1 [4], 2-(α-thienyl)nitroethylene [4], β-nitrostyrene [5, 6], and homologs and derivatives of β-nitrostyrene [7-9]. The reaction was carried out by heating the ingredients for many hours in an autoclave or in a sealed tube. We brought about the diene condensation of butadiene with nitroethylene, nitropropylene, β-nitrostyrene, β-trichloromethylnitroethylene, and the methyl ester of β-nitroacrylic acid under similar conditions. All reactions were carried out by heating a mixture of the components in sealed glass tubes on a boiling water bath for 38 hours. The sole exception was the reaction of butadiene with nitroethylene: in this case the mixture was heated for 11 hours at 60-65°. Nitroethylene reacted particularly smoothly with butadiene. When this condensation was carried out in a sealed tube, the yield of 4-nitrocyclohexene-1 amounted to 74%; when the reaction was carried out in a rotating autoclave the yield could be raised to 95%.



A somewhat lower yield (68%) of the addition product resulted when butadiene and methyl ester of β-nitroacrylic acid which had been dissolved in chlorobenzene were heated in a sealed tube:



The remaining three olefins, i.e., 1-nitropropylene-1, β-trichloromethylnitroethylene, and β-nitrostyrene, reacted under the same conditions with butadiene, giving yields of the addition products amounting to 42-55%: