## 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.

## LITERATURE CITED

1. S. S. Novikov, G. A. Shvekhgeimer, and A. A. Dudinskaya, Izv. AN SSSR, Otd. Khim. N. 1961, 524.
2. E. G. Kataev and P. S. Matveeva, Zh. Obshch. Khimii 23, 405 (1953).
3. W. G. Wildman, R. B. Wildman, W. T. Norton, and J. B. Fine, J. Amer. Chem. Soc. 75, 1912 (1953).
4. H. Burkett and W. Wright, J. Organ. Chem. 25, 276 (1960).
5. R. L. Frank, R. D. Emmick, and R. S. Johnson, J. Amer. Chem. Soc. 69, 2313 (1947).

---

# "CONDENSATION OF BUTADIENE WITH NITROOLEFINS"

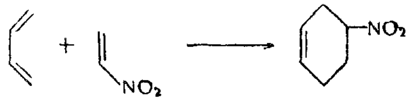
A. A. Dudinskaya, G. A. Shvekhgeimer, and S. S. Novikov

N. D. Zelinskii, Institute of Organic Chemistry, Academy of Sciences of the USSR

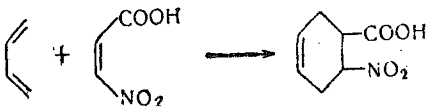
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk 1961,
No. 3, pp. 524-525, March, 1961

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.

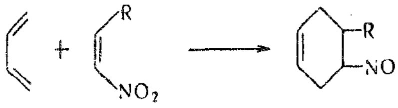
Reports published in the literature describe the condensation of butadiene with 1-nitropentene-1 [3], 2-nitrobutylene-1 [4], 2-(α-thienyl)nitroethylene [4], β-nitrostyrene [5, 6], and homologs and derivatives of β-nitrostyrene [7-9]. The reaction was carried out by heating the ingredients for many hours 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%:



R = $CH_3$, $CCl_3$, $C_6H_5$

While the work described was in progress an article [10] appeared in which the preparation of an addition product from butadiene and β-trichloromethylnitroethylene was described.

## EXPERIMENTAL

4-Nitrocyclohexene-1. a) A mixture of 39.55 gr (0.54 M) of nitroethylene, 54 gr (1.0M) of butadiene, and a small quantity of pyrogallol, which had been dissolved in 100 ml of pure and dry chlorobenzene, was heated in a rotating autoclave at 60-65° for 11 hours. After completion of the reaction the solvent was distilled off and the residue subjected to fractional distillation in vacuum. The product consisted of 65 gr (approx. 95% of theory) of 4-nitrocyclohexene-1 with b.pt. 63-64° (2 mm); $n^{20}D$ 1.4868; $d^{20}_4$ 1.1168; Found MR 32.69; calculated MR 32.93. Found: C 56.65; 56.93; H 7.23; 6.98; N 11.00; 10.63%. $C_6H_9NO_2$. Calculated: C 56.69; H 7.08; N 11.02%. b) A mixture of 5 gr (0.068M) of nitroethylene, 10 gr (0.18 M) of butadiene, a small quantity of pyrogallol and 20 ml of pure and dry chlorobenzene was sealed in a glass tube. The glass tube was placed in a protective steel jacket and heated for 11 hours at a temperature of the bath equal to 60°. After completion of the reaction the glass tube was cooled and opened. The solvent was distilled off and the residue fractionated in vacuum. The yield of 4-nitrocyclohexene-1 amounted to 6.47 gr (74% of theory). The product had a b.pt. of 63-64° (2 mm). In all other preparations a mixture of the diene and the dienophilic nitro compound was heated in a sealed glass tube placed into a boiling water bath; the heating was continued for 38 hours.

4-Nitro-5-methylcyclohexene-1. By reacting a mixture of 4.35 gr (0.05M) of 1-nitropropylene-1 with 5.4 gr (0.1M) of butadiene in the presence of a small quantity of pyrogallol in 10 ml of dry and pure chlorobenzene 3.7 gr (53% of theory) of 4-nitro-5-methylcyclohexene-1 were obtained; b.pt. 87° (13 mm); $n^{20}D$ 1.4742; $d^{20}_4$ 1.0646; found MR 37.22; calculated MR 37.58. Found: C 59.21; 59.05; H 7.89; 8.02; N 9.53; 9.77%. $C_7H_{11}NO_2$. Calculated: C 59.57; H 7.80; N 9.92%.

4-Nitro-5-phenylcyclohexene-1. From a mixture of 2.98 gr (0.02M) of β-nitrostyrene and 2.16 gr (0.04 M) of butadiene to which a small quantity of pyrogallol had been added and which was dissolved in 10 ml of dry and pure chlorobenzene, 1.73 gr (42% of theory) of 4-nitro-5-phenylcyclohexene-1 with m.pt. of 103-104° were obtained. Data published in the literature [6]: m.pt. 103-104°.

4-Nitro-5-carbomethoxycyclohexene-1. From a mixture of 4.9 gr (0.037M) of methyl ester of β-nitroacrylic acid and 3.78 gr(0.07M) of butadiene to which a small quantity of pyrogallol had been added and which was dissolved in 10 ml of pure and dry chlorobenzene, 4.6 gr (68% of theory) of 4-nitro-5-carboxymethoxycyclohexene-1 with b.pt. of 117° (2 mm) were obtained. The substance crystallized on standing; m.pt. 29-30°. Found: C 51.82; 51.80; H 5.92; 5.94; N 7.31; 7.24%. $C_8H_{11}O_4N$. Calculated: C 51.89; H 5.94; N 7.56%.

4-Nitro-5-trichloromethylcyclohexene-1. From a mixture of 1.9 gr (0.01M) of β-trichloromethylnitroethylene and 1.08 gr(0.02M) of butadiene to which a small quantity of pyrogallol had been added and which was dissolved in 10 ml of pure and dry chlorobenzene, 4-nitro-5-trichloromethylcyclohexene-1 was obtained with a yield of 1.35 gr (55.5% of theory): b.pt. 134-135° (2 mm); $n^{20}D$ 1.5330; $d^{20}_4$ 1.4630; found MR 51.87; calculated MR 52.03. Found: C 34.34; 34.24; H 3.27; 3.08; Cl 43.43; 43.32%. $C_7H_8NO_2Cl_3$. Calculated: C 34.35; H 3.27; Cl 43.55%.

## SUMMARY

The diene condensation of butadiene with some dienophilic nitro compounds was investigated. The addition products which formed were prepared for the first time.

## LITERATURE CITED

1. S. S. Novikov, G. A. Shvekhgeimer, and A. A. Dudinskaya, Izv. AN SSSR, Otd. Khim. N. 1960, 1858.
2. S. S. Novikov, G. A. Shvekhgeimer, and A. A. Dudinskaya, Izv. AN SSSR, Otd. Khim. N. 1961, No. 4.
3. K. Alder, H. F. Rickert, and E. Windemuth, Ber. 71, 2451 (1938).
4. D. V. Naightingale, M. Maienthal, and J. A. Gallagher, J. Amer. Chem. Soc. 75, 4852 (1953).

5. W. C. Wildman, and R. B. Wildman, J. Organ. Chem. 17, 581 (1952).
6. C. F. H. Allen, A. Bell, and J. W. Gates, J. Organ. Chem. 8, 373 (1943).
7. J. A. Barltrop, and J. S. Nicholson, J. Chem. Soc. 1951, 2524.
8. Sh. Sugasawa, and K. Kodama, Ber. 72, 675 (1939).
9. S. J. Rhoads, Ch. B. Hopkins, and V. M. Hylton, J. Organ. Chem. 22, 321 (1957).
10. H. Burkett, and W. Wright, J. Organ. Chem. 25, 276 (1960).

---

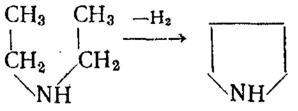
# "CATALYTIC DEHYDROCYCLIZATION OF DIETHYLAMINE WITH THE FORMATION OF A FIVE-MEMBERED HETEROCYCLIC RING"

A. L. Liberman, O. V. Bragin, and B. A. Kazanskii,

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR

Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk 1961
No. 3, pp. 525-527, March, 1961
Original article submitted July 21, 1960

We demonstrated in earlier work [1] that at 310° in the presence of platinized carbon paraffins, alkyl benzenes, and alkyl cyclopentenes undergo a $C_5$-dehydrocyclization, i.e., their straight hydrocarbon chain closes, forming a five-membered ring. It appeared of interest to establish whether this reaction is restricted to hydrocarbons or whether compounds of a different composition may also undergo the same transformation – for instance, compounds containing hetero-atoms in the straight chain, such as dialkylamines. In the case of compounds of this type one might expect that formation of a new C–C bond would lead to pyrrolidines



or products resulting from subsequent transformations of the pyrrolidines. To find the answer to this question, we conducted diethylamine over platinized carbon. We found that there was a considerable amount of decomposition and that the yield of liquid catalyzate amounted to only 30%. Investigation of this catalyzate by gas-liquid chromatography showed that it had a complex composition: the chromatogram contained nine peaks (Fig. 1), some of which could be identified by adding to the catalyzate small quantities of the reaction products expected and observing the increase in the area of the corresponding peak (see, for instance, Fig. 2). In this manner it was possible to demonstrate the presence in the catalyzate of pyrrole and of significant quantities of butylamine and acetonitrile. The presence of pyrrolidine could not be established, although it is not out of the question that this substance was present. No separate peak corresponding to pyrrolidine was found. However, a special experiment showed that in chromatography with the use of the liquid stationary phase applied by us acetonitrile and pyrrolidine could not be separated. One must further emphasize that under the conditions of our experiments, pyrrolidine would have been capable of undergoing further reactions. Thus, Zelinskii and Yur'ev [2] established that at 300° pyrrolidine is dehydrogenated to pyrrole on palladium, while Yur'ev and Shen'yan [3] found that under much milder conditions than those applied in our experiments hydrogenolysis of the pyrrolidine ring takes place in a hydrogen atmosphere with the formation of amines. In addition to the dehydrocyclization of diethylamine and the dehydrogenation of pyrrolidine, the process of the formation of acetonitrile

$$CH_3CH_2NHCH_2CH_3 \xrightarrow{-C_2H_4} CH_2CH_2NH_2 \xrightarrow{-2H_2} CH_3CN$$

could have served as a source of hydrogen in our experiments.