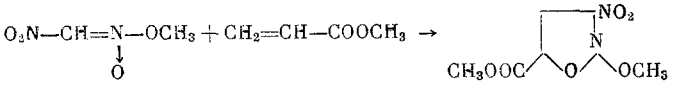
O-METHYL ETHER OF DINITROMETHANE IN THE REACTION OF 1,3-DIPOLAR CYCLOADDITION

(UDC 542.91+547.232)

V. A. Tartakovskii, I. E. Chlenov,
N. S. Morozova, and S. S. Novikov

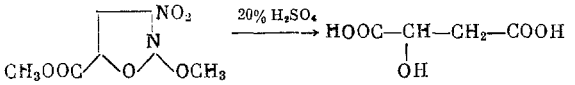
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2,
pp. 370-372, February, 1966
Original article submitted July 14, 1965

Continuing our study of the O-ethers of nitro compounds in the reaction of 1,3-dipolar cycloaddition [1-4], we investigated the behavior of the O-methyl ether of dinitromethane (I) in this reaction. To synthesize the previously unknown (I) we resorted to the method used to obtain the O-methyl ether of trinitromethane [2], and specifically, the treatment of dinitromethane with diazomethane in benzene. (I), the same as the O-methyl ether of trinitromethane, cannot be isolated in the free state because of its instability. The conclusion that (I) was obtained was made on the basis of studying its cycloaddition product (II) to methyl acrylate. The infrared spectrum of (II) contains the frequencies characteristic for the mononitro group (1570, 1370 cm^{-1}) and the carbonyl group (1740 cm^{-1}), while the hydrolysis of (II) with 20% H_2SO_4 solution gives malic acid in 79.5% yield. These results, combined with the elemental analysis data, demonstrate that (II) has the structure of N-methoxy-3-nitro-5-carbomethoxyisoxazolidine.



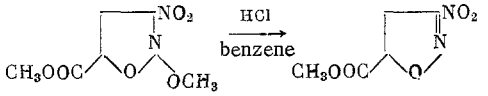
(I) (II)

The reaction for the hydrolysis of (II) can be depicted by the scheme.



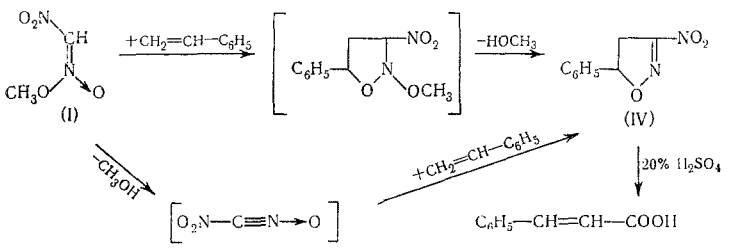
(II)

Cleavage of the elements of methyl alcohol, characteristic for N-methoxyisoxazolidine derivatives [4], occurs when (II) is treated with gaseous HCl in benzene, and 3-nitro-5-carbomethoxyisoxazolidine (III) is obtained as a reaction result, the structure of which is confirmed by the elemental analysis and the infrared spectrum.



(II) (III)

The infrared spectrum of (III) exhibits the frequencies characteristics for a NO_2 group attached to a C=N double bond (1530, 1370 cm^{-1}), and for the C=N (1640 cm^{-1}) and C=O (1750 cm^{-1}) groupings. The reaction of (I) with styrene gave, instead of the expected N-methoxyisoxazolidine, 3-nitro-5-phenylisoxazoline (IV), the structure of which was proved by the elemental analysis data and the infrared spectrum, and also by acid cleavage to cinnamic acid. The formation of (IV) could be the result of the cleavage of methyl alcohol under the reaction conditions either from the intermediately formed normal cycloaddition product, or from (I) with the subsequent cycloaddition of nitrocyanogen oxide to styrene.



The question of which of these schemes is actually realized is being studied at the present time. Since (III) and (IV) are the first members in the 3-nitroisoxazoline series, it was interesting to study some of their chemical properties. Thus, for example, the nitro group is replaced by the ethoxyl moiety when (IV) is reacted with ethanolic KOH solution and 3-ethoxy-5-phenylisoxazoline (V) is formed. It should be mentioned that when (I) is reacted with methyl acrylate, as well as with styrene, both the carbomethoxy group and the phenyl group show up in the 5-position of the ring, i.e., the cycloaddition reaction exhibits the same structural specificity as in the case of the O-ethers of other nitro compounds [2-4].

EXPERIMENTAL

A solution of dinitromethane in ether was obtained as described in [5]. The dinitromethane was transferred to benzene by distilling off the ether using a water-jet pump without heating, with the simultaneous addition of benzene to the flask.

Preparation of O-Methyl Ether of Dinitromethane (I). With stirring, a benzene solution of diazomethane (taken in 10% excess) was added in drops to a solution of dinitromethane (DNM) in benzene at 6-8°C, after which the mixture was stirred for another 10-20 min. The obtained solution of (I) was reacted with the unsaturated compound. The yields of the adducts are based on the DNM.

Preparation of N-Methoxy-3-nitro-5-carbomethoxyisoxazolidine (II). A benzene solution of (I) (150 ml), obtained from 3.52 g of DNM and 1.53 g of CH_2N_2, and 10 ml of methyl acrylate was stirred at room temperature for 18 h, after which the solvent was distilled off, and the residue was dissolved in ethanol. By cooling, we obtained 4.45 g (65%) of (II), m.p. 47.5-48.5° (from CCl_4). Found %: C 34.96, 35.16; H 5.18, 5.23; N 13.58, 13.41. $C_6H_{10}N_2O_6$. Calculated %: C 34.95; H 4.84; N 13.59. Infrared spectrum, cm^{-1}: 1740 (C=O); 1570, 1370 (NO_2); 1020 (O–N–O).

Preparation of 3-Nitro-5-phenylisoxazoline (IV). A benzene solution of (I) (120 ml), obtained from 2.82 g of DNM and 1.23 g of CH_2N_2, and 10 ml of styrene was stirred at room temperature for 30 h, after which the solvent was distilled off,* and the residue was dissolved in a mixture of hexane and $CHCl_3$. By cooling, we obtained 1.8 g (34%) of (IV), m.p. 64.5-65.5° (from CCl_4). Found %: C 56.00, 55.88; H 4.23, 4.32; N 14.66, 14.77. $C_9H_8N_2O_3$. Calculated %: C 56.25; H 4.16; N 14.58. Infrared spectrum, cm^{-1}: 1615 (C=N); 1540, 1365 (NO_2).

Preparation of 3-Nitro-5-carbomethoxyisoxazoline (III). Gaseous HCl was passed into a solution of 4 g of (II) in 20 ml of benzene for 45 min, after which the benzene was distilled off, and the residue was neutralized with Na_2CO_3 in alcohol. After distilling off the alcohol the residue was taken up in ether and dried over $MgSO_4$. The oil remaining after distilling off the ether was distilled. We obtained 1.62 g (48%) of (III), b.p. 101-103° (0.5 mm); n_D^{20} 1.4884. Found %: C 34.90, 34.99; H 3.95, 3.94; N 15.51, 15.76. $C_5H_6N_2O_5$. Calculated %: C 34.48; H 3.45; N 16.09.

(III) contains 0.5% of chlorine, which is apparently explained by a partial replacement of the nitro group attached to the C=N double bond by chlorine [6]. Infrared spectrum cm^{-1}: 1750 (C=O); 1640 (C=N); 1530, 1350 (NO_2).

Cleavage of (II) to Malic Acid. A mixture of 2 g of (II) and 40 ml of 20% H_2SO_4 solution was stirred for 4 h at 70-80°, and then extracted with ether in a Soxhlet apparatus for 30 h. We obtained 1.05 g (79.5%) of malic acid. Descending paper chromatography disclosed that the obtained product is identical with authentic malic acid ("B" chromatographic paper, R_f 0.37 in the system n-amyl alcohol: 85% formic acid, 1:1).

* Care should be taken in isolating the reaction product, since in one instance violent decomposition of the reaction mixture occurred while distilling off the solvent.

Cleavage of (IV) to Cinnamic Acid. A mixture of 0.37 g of (IV) and 15 ml of 20% H_2SO_4 solution was stirred for 20 h at 80-90°. The solution on cooling deposited 0.1 g (35%) of cinnamic acid, m.p. 132°. The substance does not depress the mixed melting point with authentic cinnamic acid.

Preparation of 3-Ethoxy-5-phenylisoxazoline (V). To a solution of 2 g of (IV) in 40 ml of benzene was added a solution of 0.6 g of KOH in 25 ml of ethanol, after which the mixture was stirred for 1 h, and then the solvent was distilled off. The residue was distilled. We obtained 1.37 g (75%) of (V), b.p. 94-95° (0.5 mm); n_D^{20} 1.5320. Found %: C 69.00, 69.06; H 6.78, 6.89; N 7.30, 7.45. $C_{11}H_{13}NO_2$. Calculated %: C 69.11; H 6.81; N 7.33. Infrared spectrum, cm^{-1}: 1610 (C=N).

CONCLUSIONS

1. The O-methyl ether of dinitromethane was synthesized and its ability to react by the scheme of 1,3-dipolar cycloaddition was shown.

2. The first members of the 3-nitroisoxazoline series were obtained.

LITERATURE CITED

1. V. A. Tartakovskii, I. E. Chlenov, S. S. Smagin, and S. S. Novikov, Izv. AN SSSR, Otd. khim. n., 1964, 583.
2. V. A. Tartakovskii, I. E. Chlenov, G. V. Lagodzinskaya, and S. S. Novikov, DAN SSSR, 161, 136 (1965).
3. V. A. Tartakovskii, S. S. Smagin, I. E. Chlenov, and S. S. Novikov, Izv. AN SSSR, Otd. khim. n., 1965, 552.
4. V. A. Tartakovskii, E. E. Chlenov, S. L. Ioffee, A. A. Onishchenko, and S. S. Novikov, Soviet Author's Application No. 1011958/23-4.
5. P. Duden, Ber., 26, 3003 (1893).
6. J. Belew, C. Grabiel, and L. Clapp, J. Amer. Chem. Soc., 77, 1110 (1955).