REACTION OF TRINITROMETHANE AND ITS HALO DERIVATIVES WITH DIAZOMETHANE

A. A. Onishchenko, I. E. Chlenov, L. M. Makarenkova, and V. A. Tartakovskii UDC 542.91:547.414

The alkylation of the ambident anion of trinitromethane (TNM) with diazomethane (DM) is accomplished by two possible directions, in which connection, depending on the nature of the solvent, the reaction can go toward the predominant formation of either the O-alkylation product, namely, the O-methyl ester of trinitromethane (I), or the C-alkylation product, namely, trinitroethane (II) [1, 2]. In addition, besides (I) and (II), from the reaction mixture is also isolated in some cases the N-oxide of 3-nitroisoxazoline (III) in 15-20% yield [3]



The question remained unanswered of whether (III) is formed by an independent route or whether it is the product of the further transformations of (I). (It was shown in advance that (II) does not react with DM.) We studied the reaction of (I) with DM. It is known that (I) is formed instantly and in practically quantitative yield when a benzene solution of TNM is treated with an equimolar amount of DM [2]. To the benzene solution of (I) obtained in this manner was immediately added a 2-fold excess of DM. As a result, (III) was isolated in 25% yield. Consequently, when TNM is reacted with excess DM the formation of (III) occurs as the result of the further transformations of (I), which must be taken into account when making a material balance of the C- and O-alkylation products.

The transformation of (I) to (III) is obviously a multistep process, and a study of its mechanism is of independent interest.*

Recently a communication appeared in which it was stated that the formation of (III) also occurs when halo-trinitromethanes are treated with a 4-5-fold excess of DM [4]. It was interesting to ascertain if the

corresponding halomethyl esters of TNM of the type $(NO_2)_2C = N - OCH_2X$ (where X = Cl, Br, I), which then, similar to (I), are converted to (III), are formed in this case in the first step of the reaction, or whether the reaction goes in a different manner.

For this we reacted DM with the Cl-, Br- and I-TNM (1:1 ratio of the reactants) in the presence of the dimethyl ester of 7-oxa-bicyclo[2,2,1]heptenedicarboxylic acid (IV) in order to fix the corresponding α -halomethyl esters of TNM (if they are formed) as the products of their cyclo-addition to (IV). In the reaction

*One of the possible paths of this transformation can be depicted by the following sequence of reactions:



N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1560-1562, July, 1971. Original article submitted July 16, 1970.

© 1972 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.

with Cl-TNM we were actually able to isolate the cyclo-addition product of the chloromethyl ester of TNM to (IV) in 13% yield



The formation of (V) gives reason to believe that the first step in the reaction of DM with Cl-TNM, the same as when reaction is with TNM, is the formation of the corresponding nitronic ester, which then under the influence of excess DM is converted to (III). However, in the case of the Br- and I-TNM, instead of the corresponding Br- and I-methyl derivatives, the cyclo-addition product of (I) to (IV), namely, (VI), was isolated in 10% yield



It is known that in reactions with compounds, in which the halogen has a positive charge, DM easily exchanges its hydrogen for halogen [5]. It is most likely that in the reaction with the Br- and I-TNM, due to the presence of positively charged bromine and iodine in them [6], such exchange primarily takes place. Here is formed TNM and the Br- or I-diazomethane, respectively. The latter decompose instantly under the reaction conditions, while the TNM reacts with a second molecule of DM, giving (I), which under our conditions adds to (IV), while under the conditions of [4] it gives (III)

$$(NO_{2})_{3} CX \xrightarrow{CH_{2}N_{2}} [CHXN_{2}] + (NO_{2})_{3} CH \xrightarrow{CH_{2}N_{2}} (NO_{2})_{2} C = N \xrightarrow{\uparrow} (III)$$

$$X = Br I \qquad (I) \qquad OCH_{3} \xrightarrow{(IV)} (VI)$$

If this assumption is true, then for the formation of (I) is required two moles of DM per mole of Bror I-TNM. Actually, when the reaction is run with a double amount of DM the yield of (VI) is approximately doubled (from 10 up to 20-28%).

EXPERIMENTAL

Preparation of 3-Nitroisoxazoline N-Oxide (III) from the O-Methyl Ester of TNM (I). An anhydrous benzene solution (43 ml) of (I), prepared from 1.6 g of TNM and 0.45 g of CH_2N_2 at 6-8° [3], was added at one time to a solution of 1.35 g of CH_2N_2 in 69 ml of absolute benzene. The mixture was stirred for 1 h and then the solvent was distilled off. Recrystallization from alcohol gave 0.32 g (23% of theory) of (III), mp 96-97°. From [7]: mp 96.5°. The mixed melting point with an authentic sample was not depressed. Analogous results were obtained when (I) was reacted with two moles of CH_2N_2 .

Reaction of $\text{ClC}(\text{NO}_2)_3$ with Diazomethane. To a solution of 1.5 g of $\text{ClC}(\text{NO}_2)_3$ and 1.73 g of (IV) in 50 ml of absolute benzene was added dropwise a solution of 0.35 g of CH_2N_2 in 24 ml of absolute benzene at 8-10°. The mixture was allowed to stand at room temperature for three days. Here the solvent gradually volatilized. The unreacted (IV) was extracted from the residue with hot hexane. Recrystallization from methanol gave 0.45 g (13.5%) of (V), mp 99.5-100°. Found: C 34.28; 34.31; H 3.45; 3.29; Cl 8.61; 8.48; N 9.87; 10.07%. C₁₂H₁₄N₃O₁₁Cl. Calculated: C 35.00; H 3.42; Cl 8.62; N 10.20%. Infrared spectrum (ν , cm⁻¹): 1720 (CO); 1590; 1360 (gem-di-NO₂); 1020 (O - N - O).

<u>Reaction of BrC(NO₂)₃ with Diazomethane</u>. To a stirred solution of 1.23 g of BrC(NO₂)₃ in 25 ml of anhydrous benzene at 8-10° was rapidly added a stream of 0.22 g of CH₂N₂ in 24 ml of absolute benzene, and to the obtained mixture was added at one time a solution of 1.13 g of (IV) in 50 ml of absolute benzene. The mixture was kept at room temperature for 20 h and then the solvent was distilled off. Recrystallization from ethanol gave 0.2 g (10%) of (VI) with mp 172-174° (decompn.) (from ethyl acetate). Found: C 38.11; 38.37; H 4.28; 4.26; N 11.22; 11.12%. C₁₂H₁₅N₃O₁₁. Calculated: C 38.20; H 4.01; [From [8]: mp 172-174°. The mixed melting point with an authentic sample was not depressed. Infrared spectrum (ν , cm⁻¹): 1740 (CO); 1580, 1350 (gem-dinitro); 1015 (O-N-O).] When the reaction was run with 1.23 g of BrC(NO₂)₃ and 0.44 g of CH₂N₂ we obtained 0.42 g (21.2%) of (VI). Reaction of IC(NO₂)₃ with Diazomethane. The reaction was run in the same manner as the preceding. From 2.35 g of IC(NO₂)₃, 0.36 g of CH_2N_2 and 1.78 g of (IV) was obtained 0.36 g (11.5%) of (VI). From 1.7 g of IC(NO₂)₃, 0.52 g of CH_2N_2 and 1.28 g of (IV) was obtained 0.7 g (~28%) of (VI).

CONCLUSIONS

1. The formation of 3-nitroisoxazoline N-oxide in the reaction of diazomethane with trinitromethane goes through the intermediate step of the O-methyl ester of trinitromethane.

2. The O-chloromethyl ester of trinitromethane is formed when chlorotrinitromethane is reacted with an equimolar amount of diazomethane.

3. The O-methyl ester of trinitromethane is formed when the bromo- and iodotrinitromethanes are reacted with a double amount of diazomethane.

LITERATURE CITED

- 1. A.A. Onishchenko and V.A. Tartakovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 948 (1970).
- 2. V. A. Tartakovskii, I. E. Chlenov, G. V. Lagodzinskaya, and S. S. Novikov, Dokl. Akad. Nauk SSSR, 161, 136 (1965).
- 3. I.E. Chlenov, Dissertation [in Russian], Moscow (1965).
- 4. F. A. Gabitov and A. L. Fridman, Zh. Organ. Khim., 4, 2259 (1968).
- 5. G. L. Closs and J J. Coyle, J. Am. Chem. Soc., 87, No. 19, 4270 (1965).
- 6. A. N. Shidlovskaya, Ya. K. Syrkin, S. S. Novikov, A. A. Fainzil berg, V. V. Sevost yanova, and V. I. Gulevskaya, Dokl. Akad. Nauk SSSR, 132, 1367 (1960).
- 7. V.A. Tartakovskii, V.G. Gribov, and S.S. Novikov, Izv. Akad. Nauk SSSR, Ser. Khim., 1074 (1965).
- 8. V. A. Tartakovskii, Dissertation [in Russian], Moscow (1966).