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Abstract

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CHEMISTRY

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O-ESTERS OF TRINITROMETHANE IN THE 1,3-DIPOLAR CYCLOADDITION REACTION

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In recent years, intensive study has begun of a complex of reactions united under the term "1,3-dipolar cycloaddition reactions" ([1]), which has already led to the creation of a general method for the synthesis of a wide variety of heterocycles.

One of the main tasks in the development of this synthetic method is the discovery or selection of new classes of compounds capable of acting as 1,3-dipoles. We have recently established ([2]) that O-esters of nitro compounds, in which the system $C \equiv N \rightarrow O$ is realized, can react according to the scheme of 1,3-dipolar cycloaddition:

(Reaction scheme of 1,3-dipolar cycloaddition)

The great variety of nitro compounds and their relative accessibility substantially broaden the range of substances that can now be involved in this reaction. It should also be noted that the products of addition of O-esters to dipolarophiles contain a previously unknown structural fragment—a nitrogen atom covalently bonded to two oxygen atoms. In addition to its synthetic significance, the 1,3-addition reaction provides a sufficiently convenient method for fixing unstable O-esters of nitro compounds. Of particular interest is the application of this method to the study of the previously practically unknown O-esters of polynitro compounds. In the present work we used the 1,3-dipolar cycloaddition reaction to clarify the question of the existence of O-esters of trinitromethane (TNM).

There are no sufficiently reliable data in the literature on the existence of O-esters of TNM. Thus, reports on the preparation of aci-TNM and on the preparation of its O-methyl ester by the action of CH_3I on the Ag salt of TNM ([3,4]) were not confirmed in subsequent work ([5]). The assumption of the intermediate formation of unstable O-esters of TNM in the interaction of its Ag salt with certain halogen derivatives was recently put forward by American investigators (^{6}). However, the authors do not provide strict proof of the formation of these esters.

For the synthesis of the O-methyl ester of TNM we used the method of O-methylation of mononitro compounds with diazomethane, proposed by Arndt and Rose (^{7}). Benzene was used by us as the solvent.

A second approach to the synthesis of alkyl esters of TNM was the alkylation of its K salt with trialkyloxonium borofluoride in methylene chloride solution. Such a method was recently proposed by Kornblum for obtaining nitronic esters of mononitro compounds (^{8}). In our case triethyloxonium borofluoride was used. These methods led to the synthesis of the methyl-

and, respectively, the ethyl esters of TNM. Both esters are stable in solutions at $t < 10°$ for several hours, but upon removal of the solvent they decompose violently, which did not allow us to isolate them in pure form. The conclusion that they had been formed was confirmed by analysis of the products of cycloaddition of these esters at the double bond of methyl acrylate. It turned out that they readily react with methyl acrylate, forming derivatives of *N*-alkoxy-3,3-dinitroisoxazolidine:

$$(\mathrm{NO_2})_2\mathrm{C{=}N(OR)O} + \mathrm{CH_2{=}CHCO_2CH_3} \xrightarrow{\text{(reaction scheme)}} \text{methyl } N\text{-alkoxy-3,3-dinitroisoxazolidine carboxylate}$$
$$R = \mathrm{CH_3}-,\ \mathrm{C_2H_5}-$$

The conclusion concerning the structure of the compounds obtained was made on the basis of their elemental analysis, determination of molecular weight, chemical transformations, and study of their IR and NMR spectra. In the IR spectra of the substances obtained there are frequencies characteristic of the carboxyl grouping, and frequencies relating to a double bond are absent, which indicates that the reaction proceeds exclusively at the $C{=}C$ double bond. In addition, there are frequencies characteristic of the gem-dinitro grouping; moreover, the absence of salt formation in the interaction of the adducts with bases indicates the internal character of the gem-dinitro group. The structure of the adduct of the *O*-methyl ester of TNM with methyl acrylate was proved by its chemical transformations. First, the homogeneity of this substance was shown by thermographic analysis (degree of purity 98.94%). When it was heated with 20% H_2SO_4, d,l-malic acid was isolated. Consequently, acid cleavage proceeds according to the scheme:

$$\text{methyl } N\text{-methoxy-3,3-dinitro-5-carbomethoxyisoxazolidine} \xrightarrow[\text{5 hr, } 80^\circ]{20\%\ \mathrm{H_2SO_4}} \mathrm{HOOC{-}CH(OH){-}CH_2{-}COOH}$$

and the carbomethoxy group is in position 5 of the isoxazolidine ring.

The structure adopted by us for *N*-methoxy-3,3-dinitro-5-carbomethoxyisoxazolidine is also confirmed by consideration of its NMR spectrum (see Fig. 1). Here the intense line with $\delta = 3.81$ belongs to the two OCH_3 groups. A weak triplet with $\delta = 5.2$ belongs to the proton of the CH group, connected by spin-spin interaction with the CH_2 group. The protons of the CH_2 group give a doublet (splitting by the proton of the CH group) in the region $\delta = 3.8$, distorted by the superposition on it of the lines from the two OCH_3 groups. Since the 5-position of the carbomethoxy group in this compound is known from chemical data, the chemical shift $\delta = 3.8$ should be assigned to the CH_2 group in position 4, and the chemical shift $\delta = 5.2$ to the CH group in position 5.

Thus, the experimental data obtained allow us to conclude that the interaction of TNM with diazomethane and of the potassium salt of TNM with triethyloxonium fluoroborate under the selected conditions proceeds according to the scheme of *O*-alkylation of nitro compounds, and the TNM esters formed in this process are capable of entering into the 1,3-dipolar cycloaddition reaction.

In continuation of our investigations of this reaction with nitronic esters, we studied in greater detail the interaction of the *O*-methyl ester of TNM with unsaturated compounds.

It turned out that this ester is very active in the 1,3-dipolar cycloaddition reaction. As dipolarophiles for it there may serve both olefins containing an activated double bond and olefins

with an unactivated double bond, vinyl ethers, cyclenes, and functional olefins (see Table 1). Apparently, this reaction cannot be carried out with olefins containing a free amino group. However, benzoylated amines react smoothly. The reaction is carried out by adding the unsaturated component to a freshly prepared solution of the O-ether of TNM. Gaseous olefins react when passed through the solution of the O-ether.

Fig. 1. NMR spectrum of N-methoxy-3,3-dinitro-5-methoxyisoxazolidine

Determination of the molecular weight, elemental-analysis data, and IR spectra confirm the conclusions concerning the structure of the isoxazolidines obtained.

A convenient chemical method for proving the structure of compounds of this type is their acid hydrolysis to the corresponding unsaturated acids (via intermediately formed -hydroxy acids). Thus, for example, hydrolysis of the adduct with cyclopentene leads to cyclopentenecarboxylic acid, and upon hydrolysis of the adduct with styrene, cinnamic acid was isolated.

$$\text{cyclopentene adduct} \longrightarrow \text{ -hydroxy acid} \longrightarrow \text{cyclopentenecarboxylic acid,}$$

$$\text{styrene adduct} \longrightarrow [C_6H_5{-}CH(OH){-}CH_2{-}COOH] \longrightarrow C_6H_5{-}CH{=}CH{-}COOH.$$

The NMR spectra of all the substances obtained contain an intense narrow line in the range from $\delta = 3.62$ to $\delta = 3.84$, which belongs to the $-OCH_3$ group. The

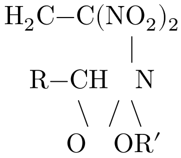
NMR spectrum of N-methoxy-3,3-dinitro-5-phenylisoxazolidine, whose structure was unambiguously established by the chemical method, has a doublet in the region $\delta = 3.8$ from the protons of the CH_2 group in the 4-position of the ring and a triplet in the region $\delta = 5.5$ from the proton of the CH group in the 5-position of the ring. (Compare with analogous data obtained from the NMR spectrum of N-methoxy-3,3-dinitro-5-carbomethoxyisoxazolidine.)

The NMR spectra of the isoxazolidines were recorded on a UVR-1 spectrometer operating at a frequency of 21.05 MHz; the resolving power of the instrument was $\sim 10^{-7}$. Solid products were analyzed as saturated solutions in chloroform; all chemical shifts are given in ppm from TMS.

Thus, the NMR spectra provide reliable information on the position of substituents in derivatives of 3,3-dinitroisoxazolidines. Analysis of the NMR spectra of the substances obtained by us shows that the addition of olefins to the O-methyl ether of TNM occurs in such a way that

Table 1

General formula



No.	R	Starting olefin	Boiling point, °C (mm Hg)	Melting point, °C	n_D^{20}	Yield, % (calculated on THM)	Found, % C	Found, % H	Found, % N	Calculated, % C	Calculated, % H	Calculated, % N
1	H	$H_2C=CH_2$	66 (0.33)	–	1.4603	73	24.93	3.84	21.42	24.93	3.62	21.78
2	CH_3	$CH_3-CH=CH_2$	85.5–87 (2.5)	–	1.4549	68	29.47	4.47	20.47	29.00	4.35	20.13
3	C_6H_5	$C_6H_5CH=CH_2$	–	–	1.5255	62.5	45.04	4.34	15.63	44.61	4.09	15.61
4	CH_2Cl	$CH_2=CH-CH_2Cl$	–	43–44	–	81.3	24.92	3.39	–	24.84	3.31	–

No.	R	Starting olefin	Boiling point, °C (mm Hg)	Melting point, °C	n_D^{20}	Yield, % (calculated on THM)	Found, % C	Found, % H	Found, % N	Calculated, % C	Calculated, % H	Calculated, % N
5	CH_2OH	$CH_2=CH-CH_2OH$		75–76	—	91	27.36	4.26	18.55	26.91	4.00	18.88
6	$C_6H_5\overset{O}{\overset{\|}{C}}NH$	$C_6H_5\overset{O}{\overset{\|}{C}}-NH-CH_2-CH=CH_2$		123–124		32.4	44.11	4.53	16.66	44.17	4.29	17.18
7	$CH_3\overset{O}{\overset{\|}{C}}O$	$CH_3\overset{O}{\overset{\|}{C}}-OCH=CH_2$		68		93	28.80	3.82	16.09	28.69	3.51	16.73
8	$CH_3\overset{O}{\overset{\|}{C}}$	$CH_3\overset{O}{\overset{\|}{C}}-CH=CH_2$		61.5–62	—	88	30.26	3.85	17.95	30.64	3.83	17.87
9	$-\overset{O}{\overset{\|}{C}}-OCH_3$	$CH_2=CH-\overset{O}{\overset{\|}{C}}-OCH_3$		52–53		71.5	28.68	3.87	16.50	28.69	3.51	16.73
10	$-\overset{O}{\overset{\|}{C}}-OH$	$CH_2=CH-COOH$		105–106	—	90.5	—	—	—	—	—	—
11	$-\overset{O}{\overset{\|}{C}}-OCH_3$	$CH_2=CH-\overset{O}{\overset{\|}{C}}-OCH_3$		43–44		38	32.18	4.28	15.97	31.70	4.15	15.87
12	—	cyclopentadiene		69.5–70.5	—	76.5	36.05	4.94	18.30	36.05	4.72	18.00
13	—	$(CH_3)_2C=C(CH_3)_2$	70 (0.3)		—	20	38.40	6.36	17.11	38.55	6.02	16.87

Note. a –Nos. 1–10 $R = CH_3$; No. 11 $-R' = C_2H_5$; b –the substance was purified on a column with silica gel; c –recrystallized from 75% ethanol; d –recrystallized from a mixture of hexane and chloroform; Cl found 14.71; 14.81. Calculated 14.70; e –the substance was not analyzed. The structure was proved by converting it under the action of CH_2N_2 into (8); g –N-methoxy-3,3-dinitrocyclopentanoisoxazolidine; z –N-methoxy-3,3-dinitro-4,4,5,5-tetramethylisoxazolidine.

The terminal carbon of the multiple bond adds to the oxygen end of the 1,3-

dipole, and the reaction with monosubstituted olefins always leads to isoxazolidines substituted in position 5. This is apparently connected with the predominant influence of steric factors. An indirect confirmation of this conclusion is the unsuccessful outcome of the reaction of the O-methyl ether of THM with styrene, methyl cinnamate, dimethyl fumarate, and dimethyl maleate. The interaction of the O-methyl ether of THM with tetramethylethylene proceeds with difficulty, and the yield of the corresponding isoxazolidine is low.

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Note: Figure translations are in progress. See original paper for figures.

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