SYNTHESIS AND TRANFORMATIONS OF TRINITROETHYL ESTERS OF PYRAZOLINE-CARBOXYLIC ACIDS*

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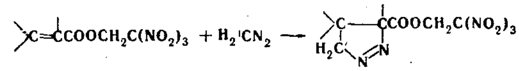
Trinitroethyl esters of pyrazolinecarboxylic acids were synthesized by the reaction of trinitroethyl esters of unsaturated carboxylic acids with diazomethane. The reaction is stereospecific. The trinitroethyl esters of pyrazolecarboxylic acids and N-acyl derivatives of pyrazolines were isolated during a study of the chemical properties of the compounds obtained.

Depending on the structures of the reagents, the reaction of diazoalkanes with unsaturated compounds leads to pyrazolines, pyrazoles, cyclopropanes [2, 3], or 3-nitroisoxazoline N-oxides [4]. It seemed of interest to study the behavior of trinitroethyl esters of unsaturated acids in the reaction with diazomethane. These compounds have not previously been investigated in this reaction. The behavior of diazomethane in the reaction with gem-dinitroalkenes is distinguished by its great peculiarity [4].

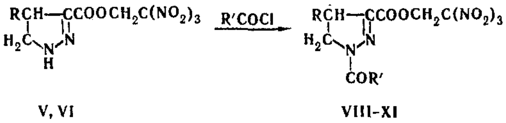
Trinitroethyl esters of acrylic, methacrylic, cinnamic, fumaric, mesaconic, citraconic, and itaconic acids were selected for the study. In all cases, the addition of diazomethane to the activated double bond proceeded according to the Auwers rule [5] with the formation of the trinitroethyl esters of the corresponding pyrazoline-carboxylic acids [6] (Table 1).



In the case of the trinitroethyl esters of citraconic and mesaconic acids, retention of configuration of the starting stereoisomers (II and III) was observed in the reaction products.

Intense absorption bands at ~ 1600 and ~ 1300 cm^{-1}, which are characteristic for the trinitromethyl group, and absorption bands of an ester carbonyl group (1730-1778 cm^{-1}) are present in the IR spectra of the compounds obtained. A band at ~ 1550 cm^{-1}, which is characteristic for the N=N bond of Δ^1-pyrazolines [7-9], is observed in the spectra (Fig. 1) of I-IV, which have substituents in the 3-position. Compounds V-VII have bands at ~ 3350 (the N-H bond of Δ^2-pyrazoline) and at ~ 1550 cm^{-1}. The latter band is sometimes assigned to the valence vibrations of the C=N bond of Δ^2-pyrazoline [10-13]. However, the possibility of the presence of a tautomeric equilibrium between the Δ^1 and Δ^2 forms of the pyrazolines [2, 14] does not exclude the possibility that this band is affiliated with the valence vibrations of the N=N bond of Δ^1-pyrazoline.

High yields of N-acyl derivatives (VIII-XI) are obtained in the reaction of Δ^2-pyrazolines with acetyl γ,γ,γ-trinitrobutyryl chlorides. The IR spectra of VIII-XI contain a band characteristic for the N-H group, and a carbonyl absorption band appears at 1670-1687 cm^{-1}).



V, VI VIII-XI

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* Communication VIII of the series "Reactions of Aliphatic Diazo Compounds." See [1] for communication VII.

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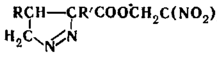
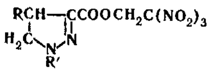
TABLE 1. Trinitroethyl Esters of Pyrazoline Carboxylic Acids and Their N-Acyl Derivatives


I-IV


V-XI

Compound	R	R′	Mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
					C	H	N	C	H	N	
I	H	CH_3	83—84	$C_7H_9N_5O_8$	29,1	3,1	23,9	28,9	3,1	24.1	96
II*	$(NO_2)_3CCH_2OCO$	CH_3	85—86	$C_{10}H_{10}N_8O_{16}$	24,1	1,9	22,7				86
III†	$(NO_2)_3CCH_2OCO$	CH_3	118—119	$C_{10}H_{10}N_8O_{16}$	24,3	2,1	22,9	24,1	2,0	22,5	89
IV	H	$CH_2COOCH_2C(NO_2)_3$	84—85	$C_{10}H_{10}N_8O_{16}$	24,2	2,2	22,5				93
V	H	H	138‡	$C_6H_7N_5O_8$	26,3	2,8	25,5	26,0	2,5	25,3	92
VI	C_6H_5	H	117—118‡	$C_{12}H_{11}N_5O_8$	41,3	3,2	21,7	40,8	3,1	21,3	93
VII	$(NO_2)_3CCH_2OCO$	H	128‡	$C_9H_8N_8O_{16}$	22,6	1,7	23,6	22,3	1,7	23,1	90
VIII	H	$COCH_3$	151—152	$C_8H_9N_5O_9$	30,4	2,7	22,4	30,1	2,8	21,9	95
IX	H	$COCH_2CH_2C(NO_2)_3$	132—133	$C_{10}H_{10}N_8O_{15}$	25,1	2,1	23,5	24,9	2,1	23,2	96
X	C_6H_5	$COCH_3$	148—149	$C_{14}H_{13}N_5O_9$	43,0	3,3	18,0	42,5	3,3	17,9	92
XI	C_6H_5	$COCH_2CH_2C(NO_2)_3$	127—128	$C_{16}H_{14}N_8O_{15}$	34,8	2,5	20,3	34,4	2,5	20,1	90

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* trans isomer.

† cis isomer.

‡ This compound melts with decomposition.

TABLE 2. Trinitroethyl Esters of Pyrazolecarboxylic Acids

Compound	R	R′	Mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
					C	H	N	C	H	N	
XII	H	H	158—159*	$C_6H_5N_5O_8$	26,1	1,8	26,0	26,2	1,8	25,5	93
XIII	C_6H_5	H	156*	$C_{12}H_9N_5O_8$	41,4	2,6	20,2	41,0	2,6	19,9	91
XIV	$(NO_2)_3CCH_2OCO$	H	150—151*	$C_9H_6N_8O_{16}$	22,7	1,3	23,4	22,4	1,2	23,2	87
XV	H	$COCH_3$	104—105	$C_8H_7N_5O_9$	32,0	2,3	23,8	32,1	2,3	23,4	87

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* This compound melts with decomposition.

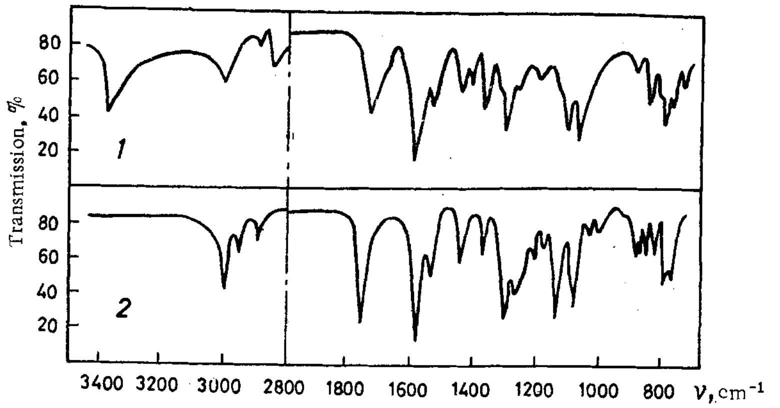
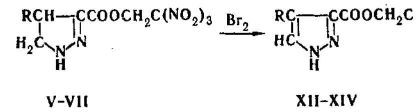
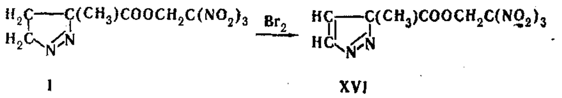


Fig. 1. IR spectra (films from acetone); 1) trinitroethyl ester of pyrazoline-3-carboxylic acid (V); 2) trinitroethyl ester of 3-methyl-Δ^1-pyrazoline-3-carboxylic acid (I).

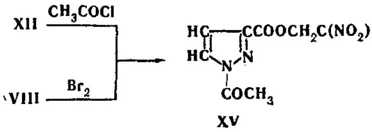
The trinitroethyl esters of the corresponding pyrazolecarboxylic acids (XII-XIV) (Table 2) were obtained by the oxidation of the pyrazolines with bromine. The absorption band of the N–H group in the IR spectra of the pyrazoles is shifted to ~3150 cm^{-1}.



The trinitroethyl ester of 3-methyl-Δ^1-pyrazoline-3-carboxylic acid (I) is oxidized by bromine to give the pyrazolenine derivative (XVI).



An N-acylated product (XV) was isolated in good yield when XII was refluxed in acetyl chloride. Compound XV was also prepared by alternative synthesis – by oxidation of VIII with bromine.



EXPERIMENTAL

Trinitroethyl Esters of Pyrazoline Carboxylic Acids (I-VIII). An ether solution of diazomethane was added dropwise at 0-10°C with stirring to a solution of 0.02 mole of the trinitroethyl ester of the unsaturated acid [15, 16] in 120-140 ml of ether until a light-yellow coloration appeared. The mixture was allowed to stand for 1 hour, and the solvent and excess diazomethane were removed by distillation. The residue was air dried. Compounds IV, V, and VII were recrystallized from chloroform, while I-III and VI were recrystallized from carbon tetrachloride. The reaction of diazomethane with the trinitroethyl ester of fumaric acid was carried out in acetone.

Trinitroethyl Esters of Pyrazolecarboxylic Acids (XII-XIV). A solution of 0.01 mole bromine in 5 ml of dichloroethane was added dropwise with stirring to a solution of 0.01 mole of the trinitroethyl ester of the pyrazolinecarboxylic acid in 10-15 ml of dichloroethane. The resulting precipitate was centrifuged, washed with cold dichloroethane, and recrystallized from chloroform (XII and XIV) or carbon tetrachloride (XIII). Compounds XII, XIII, and XIV were obtained at 20°, 35-40°, and 40-45° for reaction times of 0.5, 1, and 2 h, respectively.

Pyrazolenine XVI was similarly obtained in 88% yield at 20-25° and had mp 110-111° (from carbon tetrachloride). Found: C 27.3; H 2.3; N 28.9%. $C_7H_7N_5O_8$. Calculated: C 27.2; H 2.3; N 29.1%.

Acylation of Trinitroethyl Esters of Δ^2-Pyrazolinecarboxylic Acids (VIII-XI). A) The trinitroethyl esters of Δ^2-pyrazolinecarboxylic acids (V and VI) were added with stirring to a 10-fold excess of acetyl chloride. At the end of the reaction, the excess acetyl chloride was removed by distillation, and the residue was dried. Compounds VIII and X were obtained at 20 and 35-40° for reaction times of 0.5 and 2 h, respectively, and were recrystallized from ethanol and carbon tetrachloride, respectively.

B) Equimolecular amounts of V and VI were stirred with freshly distilled trinitrobutyryl chloride in benzene. At the end of the reaction (35-40° and 40-45° for reaction times of 0.5 and 3 h, respectively), the benzene was removed by distillation, and the residue was dried over calcium chloride. Compounds IX and XI were recrystallized from chloroform.

Trinitroethyl 1-Acetylpyrazole-3-carboxylate (XV). A mixture of 4 g (0.015 mole) of XII and 15 ml of acetyl chloride was refluxed for 8 h. The acetyl chloride was removed, and the residue was recrystallized from petroleum ether to give XV. Compound XV was also obtained by oxidation of VIII with bromine via the method described above. The product of the latter reaction did not depress the melting point of a sample obtained by the former method.

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