REACTION OF 3(5)-DIAZO-1,2,4-TRIAZOLES WITH NITROALKANE ANIONS

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The 1,2,4-triazolylhydrazones of the corresponding nitro aldehydes were obtained by the reaction of the anions of nitromethane, nitroethane, and 1-nitropropane with diazo-1,2,4-triazoles. 2-Nitropropane, 1,1-dinitroethane, 1,1-dinitropropane, and trinitromethane form 1,2,4-triazolylazonitro compounds.

It is well-known [1, 2] that diazo compounds of the benzene series react with primary aliphatic nitro compounds to form hydrazones of nitro aldehydes (A) and with secondary aliphatic nitro compounds to give arylazonitro compounds (B).

$$\underset{A}{ArNHN{=}CRNO_2} \quad \underset{B}{ArN{=}NCRR'NO_2} \quad \underset{C}{Ar\overset{+}{N}_2\overset{-}{C}R(NO_2)_2}$$

Either arylazodinitro compounds and arylazotrinitromethanes (B, $R = NO_2$, $R' = Alk$; $R = R' = NO_2$) or the corresponding diazonium salts (C, $R = NO_2$) [3, 4] can be obtained with 1,1-dinitro aliphatic compounds and trinitromethane, depending on their acidities and the properties of the substituents in the benzene ring. Information on the reaction of aliphatic nitro compounds with heterocyclic diazo compounds is extremely scanty. Quilico [5] obtained a product from the reaction of an α-isoxazolediazonium salt with trinitromethane and assigned an azo compound structure (B, $R = R' = NO_2$) to it, but he did not present direct proof of the structure. The coupling of 3-diazo-1,2,4-triazole with methazonic acid was recently described [6]. We did not find other data on this problem in the literature.

The aim of the present research was to synthesize and investigate the structures of the products of the reaction of some diazo-1,2,4-triazoles with mono- and polynitroalkanes that have acidic properties. Nitromethane, nitroethane, 1,1-dinitropropane, and trinitromethane were introduced into the reaction with diazotriazoles. The structures of the compounds obtained were studied by IR and UV spectroscopy.

The IR spectra of the products of the reaction of diazotriazoles with nitromethane, nitroethane, and 1-nitropropane contain absorption bands at 1620-1660 cm^{-1}, which correspond to the vibrations of the $C=N$ bond, and absorption bands at 1520-1570 and 1320-1360 cm^{-1}, which correspond, respectively, to the antisymmetrical and symmetrical stretching vibrations of the nitro group (Fig. 1, curves 1, 2, 3, 5, and 6). Absorption bands at 1620-1660 cm^{-1} are absent in the IR spectra of the products of coupling of diazotriazoles with 2-nitropropane. Bands corresponding to the absorption of a nitro group are observed at 1360 and 1560 cm^{-1} (Fig. 1, curves 4 and 7). Thus the nitro aldehyde hydrazone structure (A, I-V) can be assigned to the products of the reaction of diazotriazoles with primary mononitroalkanes, while the azo structure (B, VI and VII) can be assigned to the products obtained from the reaction with 2-nitropropane.

The position of the maxima in the UV spectra of aqueous solutions of the triazolylhydrazones of the nitro aldehydes (I-V) and triazolylazonitropropanes (VI and VII) depends on the pH of the medium (Fig. 2, curve 3). In acid media ($pH < 1$) I-V are protonated at the ring heteroatom to form the corresponding cation (λ_{max} 225 nm). Neutral forms I-V absorb at 330-345 nm (Table 1). Transition to alkaline media ($pH > 8$) causes dissociation of the hydrazones to give the monoanion (λ_{max} 250 and 445 nm) and dianion (λ_{max} 250

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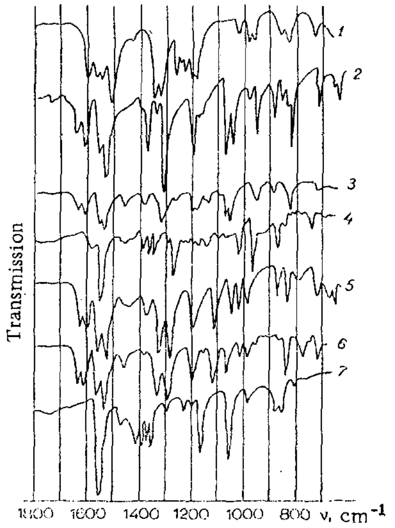


Fig. 1

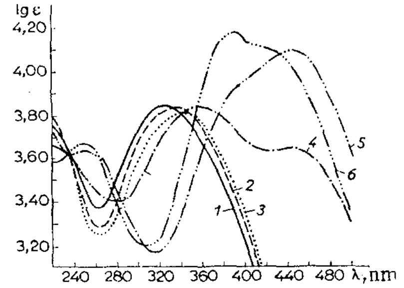
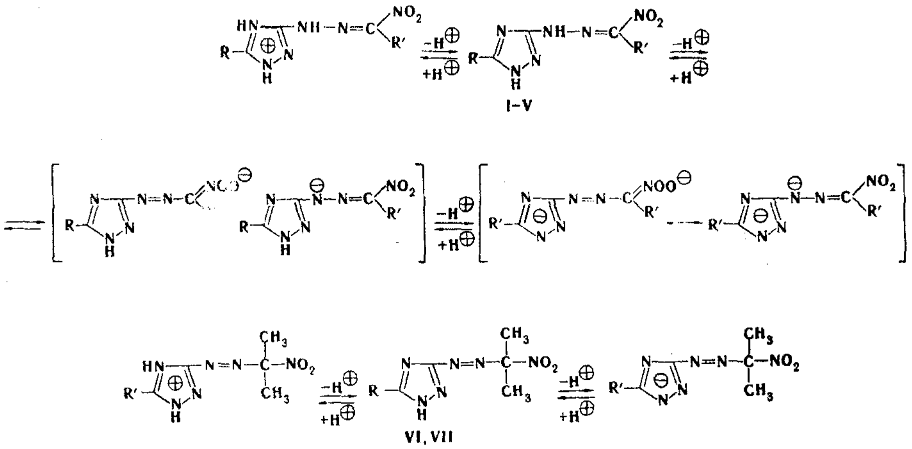


Fig. 2

Fig. 1. IR spectra: 1) I; 2) II; 3) III; 4) VI; 5) IV; 6) V; 7) VII.

Fig. 2. UV spectra of nitroformaldehyde 1,2,4-triazolyl-3-hydrazone (I) in aqueous solutions with pH: 1) 0.64; 2) 0.98; 3) 1.25; 4) 6.32; 5) 9.32; 6) 11.05.

and 390 nm). Triazolylazonitropropanes (VI and VII) are also protonated in acidic media to give the cation (λ_{max} 252 nm), while in alkaline media (pH > 7) they give the anion (λ_{max} 290-295 nm).



I-III, VI R=H; IV, V, VII R=CH$_3$; I R′=H; II, IV R′=CH$_3$; III, V R′=C$_2$H$_5$

The sequence of the splitting off and addition of protons may be different in hydrazones I-V, since cleavage of a proton from both the hydrazone group and from the ring nitrogen is possible. In our opinion, a proton is first split off from the hydrazone group, since the participation of the nitro group in delocalization of the negative charge is possible in the resulting anion.

The reaction of diazotriazoles with 1,1-dinitroethane and 1,1-dinitropropane gave the corresponding 1,2,4-triazolyl-3-azodinitro compounds (VIII-XIII). Absorption bands at 1330 cm^{-1} and 1580-1590 cm^{-1}, which correspond to gem-nitro groups, are observed in the IR spectra of these compounds.

The production of both the covalent azotrinitromethane (B) and diazonium salts (C) might have been expected in the reaction of diazotriazoles with trinitromethane. A study of the IR spectra of the compounds obtained demonstrated the absence of the absorption of the diazonium group at 2200-2300 cm^{-1} and of absorption bands at 700-1500 cm^{-1}, which might have been assigned to the absorption of the trinitromethane anion. At the same time, intense bands at 800, 1300, and 1600 cm^{-1}, which are characteristic for the covalently bonded

TABLE 1. Products of the Reaction of Diazo-1,2,4-triazoles with Nitroalkanes

Compound	R	R′	Mp (dec.), °C*	IR spectrum, cm^{-1}	λ_{max}, nm(lg ε)†	Empirical formula	Found, %			Calc., %			Yield, %
							C	H	N	C	H	N	
I	H	H	158	1620, 1525, 1360	345 (3,83)	$C_3H_4N_6O_2$	23,7	2,5	53,7	23,1	2,6	53,8	35
II	H	CH_3	152	1660—1630, 1570—1545, 1320	345 (3,80)	$C_4H_6N_6O_2$	28,1	3,5	49,2	28,2	3,5	49,4	65
III	H	C_2H_5	133	1650—1625, 1560—1545, 1330	335 (3,81)	$C_5H_8N_6O_2$	32,3	4,3	45,8	32,6	4,4	45,6	55
IV	CH_3	CH_3	143	1640—1615, 1570—1540, 1330	330 (3,90)	$C_5H_8N_6O_2$	32,6	4,3	45,9	32,6	4,3	45,6	60
V	CH_3	C_2H_5	125	1640—1615, 1565—1540, 1335	330 (3,86)	$C_6H_{10}N_6O_2$	36,4	5,1	42,0	36,4	5,0	42,4	55
VI	H	—	165	1560, 1360	255 (3,87)	$C_5H_8N_6O_2$	32,4	4,7	45,8	32,6	4,4	45,6	65
VII	CH_3	—	155	1555, 1360	260 (3,85)	$C_6H_{10}N_6O_2$	36,1	5,0	42,4	36,4	5,0	42,4	50
VIII	H	CH_3	115	1580, 1330	288 (3,83)	$C_4H_5N_7O_4$	22,4	2,5	45,4	22,3	2,3	45,6	68
IX	CH_3	CH_3	125	1590, 1330	297 (3,69)	$C_5H_6N_7O_4$	26,5	3,3	42,6	26,2	3,0	42,8	60
X	COOH	CH_3	105	1748, 1240, 1590, 1330	—	$C_5H_5N_7O_6$	22,6	2,4	37,6	23,2	1,9	37,8	25
XI	$COOCH_3$	CH_3	110	1750, 1230, 1590, 1340	—	$C_6H_7N_7O_6$	26,2	2,4	36,0	26,4	2,6	35,9	42
XII	H	C_2H_5	100	1590, 1330	—	$C_5H_7N_7O_4$	26,1	3,2	42,5	26,2	3,0	42,8	66
XIII	CH_3	C_2H_5	110	1580, 1330	—	$C_6H_9N_7O_4$	29,3	3,5	40,0	29,6	3,7	40,3	45
XIV	H	NO_2	75	1600, 1300	310 (3,79)‡	$C_3H_2N_8O_6$	14,4	0,8	45,3	14,6	0,8	45,5	50
XV	CH_3	NO_2	60	1615, 1300	—	$C_4H_4N_8O_6$	18,6	1,3	43,2	18,5	1,5	43,1	46
XVI	COOH	NO_2	52	1755, 1255, 1600, 1300	—	$C_4H_2N_8O_8$	16,4	0,9	38,7	16,6	0,7	38,9	26
XVII	$COOCH_3$	NO_2	77	1755, 1240, 1600, 1300	—	$C_5H_4N_8O_8$	19,5	1,2	36,6	19,7	1,3	36,9	30

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*Compounds II, III, V, and VI were recrystallized from dioxane, IV and VII were recrystallized from alcohol, and VIII, IX, and XI-XIII were recrystallized from aqueous alcohol.

† The UV spectra were recorded from aqueous solutions, and the λ_{max} values are given for the neutral forms of the compounds.

‡ The value is too low because of partial dissociation during recording of the spectrum.

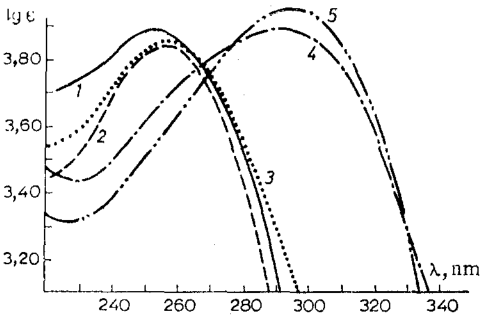
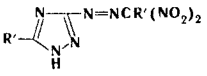


Fig. 3. UV spectra of 2-(1,2,4-triazolyl-3-azo)-2-nitropropane (VI) in aqueous solutions with pH: 1) 0.70; 2) 1.04; 3) 6.54; 4) 8.71.

trinitromethyl group, are observed in the IR spectra. Thus the 1,2,4-triazolyl-3-azotrinitromethane structure (XIV-XVII) should be assigned to the compounds obtained.



VIII–XVII

VIII, XII, XIV R=H; IX, XIII, XV R=CH_3; X, XVI R=COOH; XI, XVII R=$COOCH_3$;
VIII–XI R′=CH_3; XII, XIII R′=C_2H_5; XIV–XVII R′=NO_2

In aqueous solutions, triazolylazotrinitromethanes are readily decomposed to the starting triazolyl cation and the trinitromethane anion. Thus XIV in a freshly prepared solution (at pH 1) has an absorption maximum at 310 nm (ε 6100), which decreases in 20-40 min with the simultaneous appearance of absorption at 350 nm, which corresponds to the trinitromethyl anion. A maximum in the UV spectrum of XIV in a nonpolar solvent (CCl_4) is observed at 295 nm, during which ionization does not occur, but rather rapid decomposition of the compound to form unidentified products does occur. All of the trinitromethyl derivatives obtained are unstable and decompose at room temperature in a few days.

EXPERIMENTAL

Nitroformaldehyde 1,2,4-Triazolyl-3-hydrazone (I). A 1.05 g (12.5 mmole) sample of 3-amino-1,2,4-triazole was diazotized in 15 ml of 20% nitric or fluoboric acid at 0° with an equimolar amount of sodium nitrite (0.86 g). The diazonium solution was filtered, recooled to 0°, and added all at once to an alkaline solution of nitromethane obtained from 1.5 g (37 mmole) of sodium hydroxide and 2.3 g (37 mmole) of nitromethane in a mixture of 50 ml of water and 20 ml of ethanol. The mixture was stirred at 0° for 45-60 min, and the precipitate was removed by filtration, washed with cold water and cold acetone, and air dried.

The reactions with nitroethane and 1- and 2-nitropropanes were accomplished similarly (I-VII, Table 1). In the synthesis of IV and V, the pH of the medium was brought up to 6.5-7 to isolate the reaction products.

Reaction of Diazotriazoles with Dinitroalkanes. A solution of 10 mmole of the ammonium salt of the dinitroalkane [7] in 25-30 ml of water was added with stirring at 0° to a diazonium solution obtained from 12 mmole of the aminotriazole by the method described above, and the precipitated reaction products (VIII-XIII, Table 1) were removed by filtration, washed with water, and crystallized.

In the synthesis of X, the product was isolated as the sodium or ammonium salt, which are difficult to purify. To obtain the free acid, the salt of X was treated with 25% sulfuric acid, and the product was removed by filtration and washed with water. The acid underwent decarboxylation during crystallization from aqueous ethanol to give 1,2,4-triazolyl-3-azodinitroethane (VIII).

Reaction of Diazotriazoles with Trinitromethane. A solution of 10 mmole of trinitromethane in 30 ml of water was added with stirring at 0° to a diazonium solution obtained as described above from 10 mmole of the aminotriazole. The precipitated products were removed by filtration, washed with ice water containing several drops of hydrochloric acid, and air dried. This method was used to obtain XIV and XV (Table 1).

5-Carboxy-1,2,4-triazolyl-3-azotrinitromethane (XVI). A 1.6 g (10 mmole) sample of diazotriazolecarboxylic acid [8] was suspended in 10 ml of water at 0°, and 5 g (33 mmole) of trinitromethane in 10 ml of water was added to the suspension with stirring. After 15-20 min, almost all of the acid had gone into solution. A small amount of residue was removed by filtration, and the clear solution was held at 0° for another 50-60 min. The yellow, crystalline precipitate was removed by filtration, washed with ice water, and air dried.

5-Carbomethoxy-1,2,4-triazolyl-3-azotrinitromethane (XVII). A 20% solution of sodium hydroxide was added with stirring at 0° to a suspension of 1.53 g (10 mmole) of methyl diazotriazolecarboxylate [8] in 20 ml of water until the diazo ester had dissolved (pH 5-6). A solution of 4.53 g (30 mmole) of trinitromethane in 20 ml of water was then added to the cooled (to 0°) solution. After 10-15 min, the yellow, crystalline precipitate was removed by filtration, washed with water, and air dried.

The IR spectra of films of the substances were recorded with a UR-10 spectrometer. The UV spectra were recorded with an SF-16 spectrophotometer by the generally accepted method.

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