SYNTHESIS OF 1-ALKENYL-3,5-DICHLORO-1,2,4-TRIAZOLES AND INVESTIGATION OF THEIR NITRATION BY NITRIC ACID

A. A. Stotskii, N. P. Lebedeva, and V. V. Fomina

UDC 547.32'792.07:542.958.1

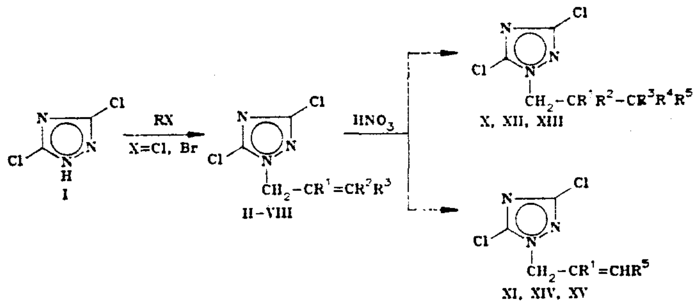
A method for obtaining 1-alkenyl-3,5-dichloro-1,2,4-triazoles by alkylation of 3,5-dichloro-1,2,4-triazole with chloro- and bromoalkenes was developed. The nitration of 1-alkenyl-3,5-dichloro-1,2,4-triazoles takes place at the double bond of the alkenyl radical; the concentration of the HNO_3 and the percentage of nitrogen oxides in it affect the character and yields of the products.

1-Alkenyl-3,5-dichloro-1,2,4-triazoles are unknown. The presence of a chlorine-containing alkenyl group bonded to a triazole ring is of interest in connection with the possibility of the synthesis of polymeric materials with increased thermal stability and fire resistance.

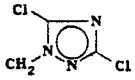
1-Alkenyl-3,5-dichloro-1,2,4-triazoles II-V were obtained by the reaction of 3,5-dichloro-1,2,4-triazole (I) with chloro- or bromoalkenes in the presence of sodium alkoxides in absolute alcohols (preferably in methanol or ethanol) at pH 8.0-8.5. Neither an exchange reaction nor cyclization involving the 5 position occurs at pH > 8.5, but the triazole ring undergoes decomposition.

The reaction of I with 2-chloromethyl-1,3-butadiene leads to 2-(3,5-dichloro-1,2,4-triazolylmethyl)-1,3-butadiene (VI).

1,4-Bis(3,5-dichloro-1,2,4-triazolyl)-2-methyl-2-butene (VII, 60%) and 1-(2-methyl-4-epoxy-2-butenyl)-3,5-dichloro-1,2,4-triazole (VIII, 20%) are formed with 1,4-dichloro-2-methyl-2-butene in the presence of sodium ethoxide in ethanol. Product VIII is formed as a result of reaction of the chloro derivative with unchanged sodium ethoxide. This is also confirmed by the fact that the reaction of 3,5-dichloro-1,2,4-triazone with a genuine sample of the 1,4-dialkoxy derivative does not lead to replacement of the alkoxy groups by I. If the reaction is carried out in methanol in the presence of methoxide, VII and 1-(2-methyl-4-methoxy-2-butenyl)-3,5-dichloro-1,2,4-triazole (IX) are formed.



II $R^1=R^2=R^3=H$; III $R^1=R^2=H$, $R^3=CH_3$; IV $R^1=CH_3$, $R^2=R^3=H$; V $R^1=H$, $R^2=R^3=CH_3$; VI $R^1=CH=CH_2$, $R^2=R^3=H$; VII $R^1=CH_3$, $R^2=H$; VIII $R^1=CH_3$, $R^2=H$, $R^3=CH_2OCH_2CH_3$; X $R^1=R^2=R^3=H$; $R^4=ONO_2$, $R^5=NO_2$; XI $R^1=R^5=NO_2$; XII $R^1=H$, $R^2=R^5=CH_3$, $R^3=ONO_2$, $R^4=NO_2$; XIII $R^1=CH_3$, $R^2=CH_2ONO_2$, $R^3=NO_2$, $R^4=ONO_2$, $R^5=H$; XIV $R^1=CH_3$, $R^5=NO_2$; XV $R^1=CH_2NO_2$, $R^5=H$; VII $R^3=$



S. M. Kirov Leningrad Institute of the Textile and Light Industries, Leningrad 191019. Blagoveshchensk Technological Institute, Blagoveshchensk 675007. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 933-936, July, 1987. Original article submitted January 13, 1986; revision submitted October 4, 1986.

TABLE 1. PMR Spectra of 1-Alkenyl-3,5-dichloro-1,2,4-triazoles and the Products of their Nitration

Compound	PMR spectrum, ppm				SSCC, Hz
	CH_3	CH_2	$=CH_2$	$=CH$	
II		4,75	5,14; 5,22	5,94	$J_{AB(=CH_2)}=1{,}5$; $J_{CA(=CH_2)}==16{,}5$; $J_{CB(=CH)}=10{,}5$; $J_{C_{CH_2}}=6{,}0$
III	1,68	4,62	—	5,72	$J_{AB(=CH)}=15$; $J_{A(CH_3)}=5$; $J_{B(CH_3)}=1{,}0$; $J_{A(CH_2)}=1{,}0$; $J_{B(CH_2)}=5{,}0$
IV	1,70	4,62	4,76; 4,97	—	$J_{CH_2}=1{,}0$; $J_{CH_3}=1{,}0$
V	1,69; 1,72	4,62	—	5,26	$J_{CH_2}=7{,}0$; $J_{CH_3}=1{,}5$
VI	—	4,87	5,24	6,37	
VII	1,76	4,65; 4,74	—	5,52	$J_{CH_2}=7{,}0$; $J_{CH_3}=1{,}0$
VIII	1,12; 1,73; 1,12; 1,59	3,97; 4,75; 3,79; 4,60	— —	5,50; 5,08	
IX	1,78; 1,65	3,87; 4,63; 4,04; 4,79	— —	5,05; 5,45	
X	—	4,51; 4,60; 4,77	5,96	—	
XI	—	2,92	—	5,76	
XII	1,65	4,33; 4,99	5,78	—	

Substances VIII and IX are produced in the form of two isomers (Tables 1 and 2); this is explained by the equally likely substitution by the alkoxy group and the triazole radical at both ends of the dihalo-substituted ethylene compound.

The nitration of 1-alkenyl- [4] and 1-alkenyl-3,5-dinitro-1,2,4-triazoles [5, 6] has been previously investigated. In a further investigation it was expedient to introduce halogen atoms into the 3 and 5 positions of the triazole ring, i.e., to replace the nitro groups by chlorine atoms.

The addition of nitrating agents to the double bond to give 1-(3-nitro-2-nitratopropyl)-3,5-dichloro-1,2,4-triazole (X) occurs in the nitration of II with nitric acid. The yield of nitro nitrate X as a function of the concentration of HNO_3, which contains 0.08-0.09% nitrogen oxides (based on N_2O_3), is presented in Fig. 1, while the yield as a function of the percentage of nitrogen oxides in 98.1% HNO_3 is presented in Fig. 2. The formation of 1-(2,3-dinitro-2-propenyl)-3,5-dichloro-1,2,4-triazole (XI) rather than nitro nitrate X is observed in the nitration of II with HNO_3 containing more than 2.2% nitrogen oxides and only over the concentration range 95-96%.

A nitro nitroso compound is probably initially formed in a medium with an increased percentage of nitrogen oxides. The nitroso group in the reaction medium is converted to an oxime group, which is nitrated by weak nitric acid to a pseudonitrol [7, 8]. This transition can also be explained by a change in the direction of dissociation of HNO_3 [7-9]. That the formation of XI occurs through a nitroso nitrate is also attested to by the green-blue color of the solution after the nitrating mixture is poured over ice: the color vanishes after a few hours.

The PMR spectrum of XI contains only two singlets of protons: of methylene (2.99 ppm) and methylidyne (5.76 ppm) groups affiliated with a double bond bonded to a nitro group. The ^{13}C NMR spectrum contains a signal of a carbon atom of a methylene fragment at strong field (40.4 ppm) and three signals of atoms at weak field (107.1, 143.4, and 157.1 ppm) corresponding to carbon atoms of a double bond and a triazole ring.

In V, as compared with II, the methyl groups attached to the carbon atom of the double bond increase the nucleophilicity of the double bond, but this affects only the yield of nitro nitrate XII (Fig. 1, curve 2). The nitration of VIII and IX with nitric acid gives the same product, viz., 1-(2-methyl-3-nitro-2,4-dinitratobutyl)-3,5-dichloro-1,2,4-triazole (XIII), i.e., nitration of the double bond and replacement of an alkoxy group by a nitrate group occur.

A mixture of conjugated and unconjugated nitro enes XIV and XV was obtained in the nitration of III with HNO_3. Chromatography on Silufol [with hexane—acetone (15:1)] reveals two

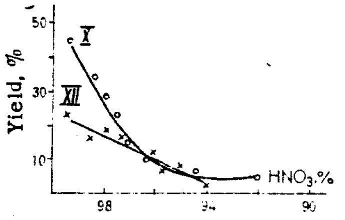


Fig. 1

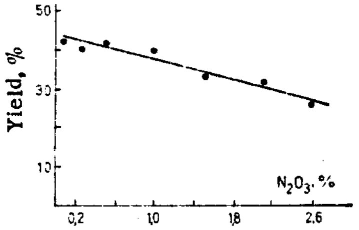


Fig. 2

Fig. 1. Dependence of the yields of X and XII on the HNO_3 concentration.

Fig. 2. Dependence of the yield of X on the percentage of nitrogen oxides in 98.1% NHO_3.

TABLE 2. Physicochemical Constants of 1-Alkenyl-3,5-dichloro-1,2,4-triazoles

Compound	bp, °C (hPa) [mp, °C]	d_4^{20}	n_D^{20}	Found, %				Empirical formula	Calculated, %				Yield, %
				C	H	Cl	N		C	H	Cl	N	
II	69 (1,33—2,7)	1,3345	1,5070	36,3	2,8	39,8	23,7	$C_5H_5Cl_2N_3$	33,7	2,8	39,8	23,8	80
III	83 (1,3—2,7)	1,2883	1,5064	38,8	3,5	39,8	22,0	$C_6H_7Cl_2N_3$	38,5	3,6	39,8	21,8	80
IV	71 (10,4—11,7)	1,1310	1,5014	38,5	3,6	39,7	21,8	$C_6H_7Cl_2N_3$	38,5	3,6	39,9	21,8	80
V	103 (2,7)	1,2365	1,5052	42,0	4,5	34,1	20,5	$C_7H_9Cl_2N_3$	41,7	4,3	34,4	20,3	75
VI	107—108 (4,0)	1,2495	1,5232	41,3	3,4	34,8	20,6	$C_7H_7Cl_2N_3$	41,1	3,4	34,8	20,6	75
VII	[78]	—	—	31,8	2,5	41,3	24,5	$C_9H_8Cl_4N_6$	31,6	2,3	41,5	24,5	60
VIII	127 (1,3—2,7)	1,2907	1,5112	43,2	5,5	28,1	16,9	$C_9H_{13}Cl_2N_3O$	43,2	5,2	28,4	16,8	20
IX	121 (4,0)	1,2896	1,5106	41,8	4,8	30,0	17,8	$C_9H_{11}Cl_2N_3O$	40,7	4,7	30,0	17,8	20
X	[82—83]*	—	—	21,2	1,7	24,7	24,6	—	20,9	1,7	24,8	24,4	60
XI	[159—160]**	—	—	22,0	0,9	26,1	26,0	—	22,3	1,1	26,4	26,1	30
XII	[116—117]***	—	—	26,9	2,9	22,4	22,3	—	26,7	2,8	22,6	22,2	25
XIII	[124—125]**** (dec.)	—	—	22,4	2,0	20,0	22,7	—	22,4	2,1	19,8	22,4	35

---

*Found: M 280. Calculated: M 286.

**Found: M 268. Calculated: M 268.

***Found: M 320. Calculated: M 314.

****Found: M 375. Calculated: M 371.

compounds with R_f 0.53 and 0.41. Evidence that substitution at the double bond rather than addition to it occurs as a result of nitration with HNO_3 is provided by the absence of nitrate nitrogen (Lunge analysis) and of absorption bands of a nitrato group in the IR spectrum, which contains bands of vibrations of a double bond (1634 cm^{-1}) and lines of vibrations of nitro groups (1565, 1360 cm^{-1}).

EXPERIMENTAL

The IR spectra of suspensions of the compounds in minearl oil were recorded with a UR-75 spectrometer. The PMR spectra of solution in $CDCl_3$, CD_3OD, and C_2D_6CO were obtained with a Tesla BS-497 spectrometer (100 MHz), the concentration of the compounds was 10-15%, and the internal standard was hexamethyldisiloxane (HMDS). The ^{13}C NMR spectrum of a solution of the compound in $CDCl_3$ was obtained with an FX-90 spectrometer with tetramethylsilane (TMS) as the internal standard; the spectrum was obtained under conditions of complete suppression of spin-spin coupling of carbon with the protons.

3,5-Dichloro-1,2,4-triazole was obtained by the method in [10].

1-Alkenyl-3,5-dichloro-1,2,4-triazoles II-IX. A 0.83-g sample of sodium metal was dissolved in 80 ml of absolute alcohol (methanol or ethanol), the solution was cooled, and 5 g of I and 5 g of the chloroalkene were added successively. The reaction was carried out at pH 8.0-8.5. The reaction mixture was refluxed for 2 h with constant monitoring of the pH and adjusting to it 8.0-8.5 by means of a solution of sodium methoxide or ethoxide. Refluxing was carried out until the pH remained constant. The precipitate was removed by filtration, and the alcohol was removed by distillation. Extraction was carried out with ether or $CHCl_3$.

Compounds II-VI, VIII, and IX were colorless liquids that were stable on heating, while VII was a crystalline substance.

General Method of Nitration. A 1-g sample of the product was added to 7.5 ml of HNO_3 cooled to 5°C, and the mixture was allowed to stand at this temperature for 25 min. The solution was then poured over ice, and the aqueous mixture was allowed to stand overnight. A precipitated crystalline substance was removed by filtration, whereas an oil was extracted with $CHCl_3$, the extract was dried, and the solvent was removed in vacuo.

Absorption bands at 1646-1674 ($C{=}C$), 920-990 ($CH{=}$), and 710 cm^{-1} ($C{-}Cl$) and stretching vibrations of a triazole ring at 1288, 1380, 1470, and 1560 cm^{-1} were the most characteristic bands for the IR spectra of II-IX. The most characteristic bands for nitration products X-XII were found at 1570 and 1380 cm^{-1} (NO_2) and at 1625 and 1285 cm^{-1} (ONO_2).

LITERATURE CITED

1. R. H. Wiley, N. R. Smith, D. M. Johnson, and J. Moffat, J. Am. Chem. Soc., 77, 2572 (1955).
2. L. I. Bagal, M. S. Pevzner, N. I. Zheludkova, and V. M. Kerusov, Khim. Geterotsikl. Soedin., No. 2, 265 (1970).
3. T. P. Kofman, G. A. Zykova, V. I. Manuilova, T. N. Timofeeva, and M. S. Pevzner, Khim. Geterotsikl. Soedin., No. 7, 997 (1974).
4. A. A. Stotskii, N. P. Lebedeva, and V. V. Fomina, Zh. Org. Khim., 17, 1784 (1981).
5. A. A. Stotskii and N. P. Tkacheva, Zh. Org. Khim., 12, 655 (1976).
6. A. A. Stotskii, N. P. Tkacheva, and M. F. Shostakovskii, Dokl. Akad. Nauk SSSR, 231, 1370 (1976).
7. W. H. Lee and D. J. Millen, J. Chem. Soc., 11, 4463 (1956).
8. L. T. Eremenko and A. P. Genich, Izv. Akad. Nauk SSSR, Ser. Khim., No. 12, 2106 (1965).
9. O. Redlich, Chem. Rev., 39, 333, 346 (1946).
10. R. Stolle and W. Dietrich, J. Prakt. Chem., 139, 193 (1934).

DIRECTION OF GLYCOSYLATION OF 5-SUBSTITUTED 4-CHLORO-1,2,3-TRIAZOLES

I. D. Shingarova, A. T. Lebedev,
and M. N. Preobrazhenskaya

UDC 543.422.25'51:547.
455.522'791'963.32

The structures of previously obtained nucleosides of 5-substituted 4-chloro-1,2,3-triazoles were refined by means of high-resolution mass spectrometry and ^{13}C NMR spectroscopy. It is shown that fusion of 5-substituted 4-chloro,1,2,3-triazoles with tetra-O-acylribofuranoses in the presence of di(p-nitrophenyl) phosphate leads to the formation of 2-nucleosides of the corresponding triazoles. The signals of the carbon atoms in the ^{13}C NMR spectra of the 4,5-di-substituted triazoles and their nucleosides were assigned.

We have previously obtained nucleosides of 5-substituted 4-chloro-1,2,3-triazoles, to which 1-nucleoside structures were assigned [1]. Continuing our research on the glycosylation of triazoles, we have obtained 2-β-D-ribofuranosyl-4-methylthio-5-methoxycarbonyl-1,2,3-triazole and its derivatives involving the carboxy group by fusion of 4-methylthio-5-methoxycarbonyl-1,2,3-triazole with tetra-O-acetylribofuranose in the presence of catalytic amounts of di(p-nitrophenyl) phosphate [2]. Our attention was drown to the closeness of the characteristics of the PMR spectra of the newly obtained 2-nucleosides of sulfur-containing triazoles and the previously described 1-nucleosides of 5-substituted 4-chloro-1,2,3-triazoles.

All-Union Oncologic Research Center, Academy of Medical Sciences of the USSR, Moscow 115478. M. V. Lomonosov Moscow State University, Moscow 117234.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 937-940, July, 1987. Original article submitted January 27, 1986.