1-VINYL-4-ALKYL-1,2,4-TRIAZOLIUM SALTS

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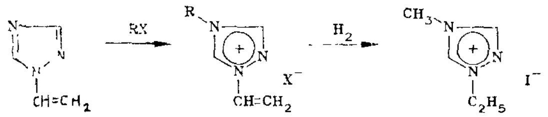
Quaternary salts based on 1-vinyl-1,2,4-triazole have been synthesized. Alkyl iodides and bromides and dimethyl sulfate served as the quaternizing agent. Polymeric quaternary salts of 1-vinyl-1,2,4-triazole have been obtained by alkylation of its polymer.

1-Vinylazoles are known to undergo quaternization under the action of alkyl bromides and iodides or dialkyl sulfates [1-6]. Since there is no information on the quaternization of 1-vinyl-1,2,4-triazole (VT), we studied its alkylation reactions with various agents, viz., alkyl iodides and bromides, as well as dimethyl sulfate.



I–XI

XII

As in the case of other 1-alkyl-1,2,4-triazoles [7], quaternization takes place at the $N_{(4)}$ nitrogen atom, as was demonstrated by converting I into 4-methyl-1-ethyl-1,2,4-triazolium iodide (XII).

The quaternization of VT by alkyl bromides proceeds with considerably more difficulty than its quaternization by alkyl iodides, and the reaction with dimethyl sulfate is accompanied by spontaneous polymerization. 4-Methyl-1-vinyl-1,2,4-triazolium methosulfate (XI) could be obtained only at reduced temperatures, and only poly-1-vinyl-4-methyl-1,2,4-triazolium methosulfate forms under other conditons.

In the IR spectrum of salts I-XI the band of the stretching vibrations of the vinyl group is located at 1650 cm^{-1}. The displacement of the band of the stretching vibrations of the heterocycle (at 1510 cm^{-1}) to 1590 cm^{-1} and of the bands of the deformations of the ring (1290, 1150, and 1010 to 1350, 1170, and 1060 cm^{-1}, respectively), which is charac-

TABLE 1. Quaternary Salts of 1-Vinyl-1,2,4-triazole I-XI

Compound	Quaternizing agent	Reaction temp., °C	Reaction time, h	mp, * °C	Found, %				Empirical formula	Calculated, %				Yield, %
					C	H	N	Hal(S)		C	H	N	Hal(S)	
I	CH_3I	40	120	130	25,3	3,7	18,3	52,8	$C_5H_8IN_3$	25,3	3,4	17,7	53,5	86
II	C_3H_7I	95	90	122—124	31,7	4,6	15,9	47,9	$C_7H_{12}IN_3$	31,9	4,5	15,7	47,8	65
III	C_4H_7I	120	80	97	34,3	5,4	15,0	45,4	$C_8H_{14}IN_3$	34,8	5,1	14,9	45,2	87
IV	$C_5H_{11}I$	130	25	84	36,0	6,0	14,7	43,3	$C_9H_{16}IN_3$	35,9	5,7	14,3	44,1	53
V	$C_6H_{13}I$	120	30	110	39,0	6,2	13,6	41,2	$C_{10}H_{18}IN_3$	39,0	5,9	13,4	41,6	84
VI	$C_8H_{17}I$	110	25	122	42,9	6,8	12,5	37,8	$C_{12}H_{22}IN_3$	41,7	6,8	11,3	37,8	76
VII	C_2H_5Br	45	180	167	35,3	4,9	20,6	39,2	$C_6H_{10}BrN_3$	35,2	5,0	20,4	39,3	Trace
VIII	C_3H_7Br	80	300	117—118	38,6	5,5	19,5	37,0	$C_7H_{12}BrN_3$	39,9	5,3	19,3	34,2	Trace
IX	C_3H_5Br	80	60	98	38,9	4,7	19,5	37,0	$C_7H_{10}BrN_3$	39,6	4,6	19,0	37,4	Trace
X	$C_6H_{13}Br$	130	30	112	46,2	7,0	16,2	30,7	$C_{10}H_{18}BrN_3$	48,2	6,8	15,3	29,7	12
XI	$(CH_3)_2SO_4$	−20	20	49	—	—	—	—	$C_6H_{11}N_3O_4S$	32,6	5,0	19,0	(14,5)	66

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*The solvents for crystallization were 2-propanol (I-IV) and n-butanol (VII).

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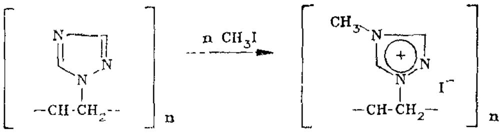
teristic of salts of azoles and their derivatives [8], is evidence of the delocalization of the positive charge over the triazole ring. These shifts are considerably greater than the shifts of donor-acceptor complexes of vinylazoles with salts of transition metals [9], which amount to 10-20 cm^{-1} for the band at 1510 cm^{-1}. An increase in the frequency of the γCH band for the deformation vibrations of the heterocycle from 680 to 720 cm^{-1} is also observed.

The quaternary salts of 1-vinyl-1,2,4-triazole are promising for the synthesis of water-soluble high-molecular-weight polyelectrolytes. Another path for their synthesis is the quaternization of the already known [10] water-soluble polymer poly-1-vinyl-1,2,4-triazole (PVT). Since PVT has a reduced basicity in comparison to poly-1-vinylimidazole (the pK_{BH^+} for 1-ethyl-1,2,4-triazole is 3.08 [11], and the pK_{BH^+} for 1-ethylimidazole is 8.87 [12]), it may be expected that reactions taking place at the nitrogen atom of the heterocycle, for example, the quaternization of PVT, would take place with greater difficulties than in the case of the more basic polyvinylimidazole.



In fact, PVT is quaternized with greater difficulty than is polyvinylimidazole [13]. Nevertheless, by using a large excess of the alkylating agent and by increasing the reaction time it is possible to obtain poly-1-vinyl-1,2,4-triazolium iodide with a practically quantitative yield.

EXPERIMENTAL

The IR spectra of the samples were recorded on a UR-20 spectrometer in tablets with potassium bromide.

The quaternization of VT was carried out in around-bottom flask equipped with a reflux condenser and a thermometer. The reaction was carried out in a threefold excess of the quaternizing agent at the boiling point of the reaction mixture. The salt precipitating after cooling was filtered out, washed with ether, and dried in a vacuum. The quaternization of vinyltriazole with dimethyl sulfate was carried out at -20°C.

1-Vinyl-4-methyl-1,2,4-trizolium Iodide (I). A 4.75-g portion (0.05 mole) of VT was given an addition of 15 ml of methyl iodide and heated with a reflux condenser for 1.5 h.

1-Ethyl-4-methyl-1,2,4-triazolium Iodide. A. A 0.5-liter rotating steel autoclave was charged with 9.5 g of salt I, 130 ml of absolute ethanol, and a catalyst, viz., Raney nickel and supplied with hydrogen under a pressure of 50 atm. The reaction mixture was held at 50°C for 5 h. The yield was 7.35 g (76%), and the mp 54°C. Found: C, 26.6; H, 2.9; N, 18.0; I, 52.5%. Calculated for $C_5H_{10}N_3I$: C, 25.4; H, 2.9; N, 17.0; I, 53.5%.

B. A 5.5-g portion (0.05 mole) of 4-methyl-1,2,4-triazole [7] was given an addition of 17 ml of ethyl iodide, and the mixture was boiled with a reflux condenser for 2 h. The subsequent treatement was carried out in a similar manner.

Poly-1-vinyl-4-methyl-1,2,4-triazolium Iodide. A mixture of 36 ml of methyl iodide and 6 g of a solution of poly-1-vinyl-1,2,4-triazole in 100 ml of methanol was held in an argon atmosphere for 30 h at 40°C. The precipitated polymeric salt was washed with methanol in a Soxhlet apparatus and dried to constant weight in a vacuum at 25°C. The yield was 84%, and the degree of quaternization was 95%. Found: C, 26.0; H, 4.0; I, 50.8; N, 18.8%. Calculated for $C_5H_8IN_3$: C, 25.3; H, 3.4, I, 53.5; N, 17.5%.

Poly-1-vinyl-4-methyl-1,2,4-triazolium Methosulfate. A. A mixture of 15.5 ml of dimethyl sulfate and 5 g of poly-1-vinyl-1,2,4-triazole in 40 ml of dimethyl sulfoxide was held in an argon atmosphere for 11 h at 60°C. The polymeric salt was diluted with dimethyl sulfoxide and precipitated by acetone. The salt was filtered out, washed with acetone, and dried in a vacuum at 25°C over phosphorus pentoxide. The yield was 85%. The degree of quaternization was 84%. Found: C, 33.9; H, 5.2; N, 20.5; S, 12.1%. Calculated for $C_6H_{11}N_3O_4S$: C, 32.6; H, 5.0; N, 19.0; S, 14.5%.

B. A 3.5-ml portion of 1-vinyl-1,2,4-trizole was given a dropwise addition of 1.89 ml of dimethyl sulfate at room temperature. At the conclusion of the reaction, which was accompanied by a sharp increase in temperature, the polymer was dissolved in methanol and precipitated by isopropanol, filtered out, washed, and dried in a vacuum at 25°C over phosphorus pentoxide. The yield was 95%. The degree of quaternization was 99%.

C. A solution of 5 g of 1-vinyl-1,2,4-triazole in 25 ml of methyl ethyl ketone was given a dropwise addition of 6.6 ml of dimethyl sulfate, and the reaction mixture was held in an argon atmosphere with stirring for 6 h at room temperature. The polymeric salt was precipitated by isopropanol, washed, and dried in a vacuum at 25°C. The yield was 97%. The degree of quaternization was 91%. Found: C, 34.7; H, 5.4; N, 19.9; S, 13.1%. Calculated for $C_6H_{11}N_3O_4S$: C, 32.6; H, 5.0; N, 19.0; S, 14.5%.

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