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1-VINYL- AND 1-ETHYL-2-(VINYLOXYMETHYL)IMIDAZOLES

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The synthesis, structure, and reactivity of 1-vinyl(ethyl)-2-(vinyloxymethyl)imidazoles are studied. The chemical properties of vinyl ethers of the imidazole series have been little studied previously. There is described only one example of the synthesis of 1-alkyl-2-β-(hydroxyvinyl)benzimidazole in liquid ammonia [1].

The synthesis of new N,O-divinyl and O-vinyl derivatives of imidazoles was conducted by the reaction of 1-vinyl-2-(hydroxymethyl)imidazole (I), 1-vinyl-2-(hydroxymethyl)benzimidazole (II), 1-ethyl-2-(hydroxymethyl)imidazole (III), and 1-ethyl-2-(hydroxymethyl)benzimidazole (IV) with acetylene under pressure. During vinylation of imidazole (I) in the presence of 45% KOH at 180°C for 1 h in dioxane, 1-vinyl-2-(vinyloxymethyl)-imidazole (V) is formed in 85% yield. On replacing KOH with $Cd(AcO)_2$, up to 92% (V) is obtained. Reaction of (II) with acetylene in the presence of 30% $Cd(AcO)_2$ at 200°C for 2 h gives 75% 1-vinyl-2-(vinyloxymethyl)-benzimidazole (VI) and with 30% KOH, only 47%. In analogous optimal conditions, 1-ethyl derivatives of 2-(hydroxymethyl)imidazoles (III) and (IV) react with acetylene with the formation of 1-ethyl-2-(vinyloxymethyl)-imidazole (VII) and 1-ethyl-2-(vinyloxymethyl)benzimidazole (VIII) with yields up to 70%. The obtained compounds were identified by thin-layer chromatography, IR, UV, and NMR methods, by elemental analysis, and also by hydrogenation to the corresponding 1-ethyl-2-(ethoxymethyl)imidazole (IX) and 1-ethyl-2-(ethoxymethyl)benzimidazole (X). The properties of the N,O-divinyl- and O-vinylimidazoles and their PMR spectra are presented in Tables 1 and 2. The values for chemical shifts and spin–spin coupling constants of olefinic protons bonded to O and N atoms in compounds (V)-(VIII) are characteristic [2].

The IR spectra of imidazoles (V)-(VIII) (Table 3) contain absorption bands for stretching vibrations of N-vinyl groups at 1648-1649 cm^{-1}. The stretching vibrations of vinyloxy groups are characterized by doublet bands with maxima at 1640 and 1620 cm^{-1}, apparently, due to the presence of two rotomers, similar to vinyl alkyl ethers [3, 4]. Deformation vibrations of the CH bond in N- and O-vinyl groups are characterized by absorption at 960 and 830 cm^{-1}, respectively. The band at 1190 cm^{-1} is caused by stretching vibrations of the COC group.

In order to explain the mutual influence of substitution in the 1 and 2 positions of the heterocycle on the electron state of N- and O-vinyl groups, the integral intensities of bands ($E_{\nu_1}^{\nu_2}$) in spectra for (V)-(VIII) was measured in comparison with 1-vinyl derivatives of imidazole (XI) and benzimidazole (XII) using a method in [5]. The introduction of a CH_2OH group in position 2 of the imidazole ring leads to a decrease in the intensity of the bands for $N-CH=CH_2$ (see Table 3). The bands for vinyloxy and N-vinyl groups make an additive contribution to the overall intensity of the bands in spectra for (V) and (VI). The band at 1620 cm^{-1} in spectra for the ethers (VI) and (VIII) is superimposed by the band for the benzazole ring (ν 1612 cm^{-1}). In view of this, the $E_{\nu_1}^{\nu_2}$ for the hydroxymethylimidazole (II) was measured for the band at 1649 cm^{-1} and for the sum of the bands at 1649 and 1614 cm^{-1}. The overall integral intensity of the bands for N- and O-vinyl groups of imidazoles (V) and (VI) is significantly more than the values for the integral intensities of the bands for the N-vinyl group of 2-hydroxymethyl derivatives of imidazoles and the O-vinyl group of 1-ethylimidazoles.

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TABLE 1. Properties of 1-Vinyl- and 1-Ethyl-2-(vinyloxymethyl)imidazoles (V)-(X)

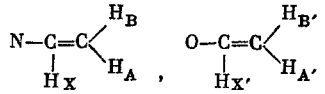
Compound	Yield, %	n_D^{20}	d_4^{20}	bp, °C (p, mm Hg)	R_f	Found, %			Molecular formula	Calculated, %		
						C	H	N		C	H	N
(V)	92	1,5260	1,1710	104(5)	0,90	63,91	6,75	18,39	$C_8H_{10}N_2O$	64,02	6,66	18,66
(VI)	75	1,5910	1,2060	173(10)	0,89	72,26	6,32	14,34	$C_{12}H_{12}N_2O$	72,00	6,05	14,01
(VII)	70	1,4962	1,1190	117(10)	0,83	63,11	8,04	18,39	$C_8H_{12}N_2O$	63,15	7,88	18,42
(VIII)	68	1,5709	1,2190	138(2)	0,92	71,62	6,84	13,65	$C_{12}H_{14}N_2O$	71,31	6,91	13,83
(IX)	64	1,4750	0,9475	121(17)	0,86	61,31	9,09	17,86	$C_8H_{14}N_2O$	61,03	9,09	18,13
(X)	70	1,5550	1,1879	146(4)	0,88	70,84	7,82	14,21	$C_{12}H_{16}N_2O$	70,52	7,83	13,75

The electron spectra for the absorption of vinyl and ethyl derivatives of imidazoles (see Table 3) are characterized by a band with λ_{max} 217 nm, the position and intensity of which depends on the substituents in the heterocycle. Introduction of CH_2OH and $CH_2OCH=CH_2$ groups in position 2 of ethylimidazole (XIII) leads to a similar bathochromic shift of the band by 2.7 nm. The atomic orbitals of the vinyl group participate to a significant degree in the electron transition of 1-vinylimidazole (XI) [6]. In spectra for the 2-substituted imidazoles (I) and (V), a bathochromic shift of the band by 8 nm in comparison with the spectra for compound (XI) indicates a high sensitivity of the energy of this transition to the inductive influence of substituents. Substitution in 1-vinyl- and 1-ethylbenzimidazole (XII) and (XIV) molecules does not lead to noticeable changes in λ_{max}. The absorption coefficients for 1-vinyl(ethyl)imidazoles and benzimidazoles do not change on transition to their 2-substituted derivatives.

The electrophilic addition of halides and hydrogen halides to compounds (V)-(VIII) can occur both through the vinyl group on an O or N atom and at the N atom in position 3. It is found that hydrochlorination of imidazoles (V)-(VIII) in absolute CCl_4 occurred best at 0-5°C with formation of air-stable white powders. IR spectra of the hydrochlorination products of (V)-(VIII) are identical to the spectra of the hydrochlorides of (I)-(VI) [7]. The spectra contain absorption bands for an N-vinyl group and a very broad absorption band at 2600-3000 cm^{-1}, characteristic for an ammonium cation $\geq NH^+$. A substantial shift of the vibration bands for the heterocycle to the short-frequency region occurs, indicating coordination at the N^3 atom. Absorption at 3220-3240 cm^{-1} confirms the appearance of an OH group bonded via intramolecular H bond; bands with frequency 1048-1052 cm^{-1} are caused by the stretching vibrations of C—OH bonds. The PMR spectra (Table 2) of the hydrochlorination products of (I) and (V) are identical.

We have established that during the reaction of (V) with HCl, the 1-vinyl-2-(vinyloxymethyl)imidazole hydrochloride is formed after 2-5 min, in which, according to IR and PMR spectra, the N- and O-vinyl groups

TABLE 2. Parameters of PMR Spectra of Imidazoles (V)-(VII), (X) and Their Hydrochlorinated Products



Compound*	Chemical shift, δ, ppm										Spin–spin coupling constants, J, Hz							
	H_A	H_B	H_X	$H_{A'}$	$H_{B'}$	$H_{X'}$	H_4	H_5	H_{N-CH_2}	H_{OCH_2}	H_AH_X	H_BH_X	H_AH_B	$H_{A'}H_{X'}$	$H_{B'}H_{X'}$	$H_{A'}H_{B'}$	H_4H_5	$H_{CH_2}H_{CH_2}$
(V)	4,05	4,38	6,27	4,83	5,19	7,05	7,13	6,82			6,9	14,38	2,48	9,00	15,92	1,56		
(VII)	4,00	4,37	6,42				6,77	6,77		4,73	7,12	14,62	2,50					7,52
(X)							6,80	6,60	3,80	4,00							5,26	7,32
(VI)	4,09	4,46	6,48	5,13	5,56	7,21					7,08	14,13	2,48	9,38	14,76	0,99		
HC-(V)	4,28	4,55	6,55	5,50	5,86	7,23	7,97	7,60			9,56	14,38	3,00	8,80	15,66	2,24		
HC-(I)	5,38	5,77	7,16				7,83	7,45	4,75 (H_{OH})	4,85								
HC-(I)*	5,49	5,88	7,28				7,96	7,58	4,90 (H_{OH})		8,10	15,4	2,45					
HC-(II)**	5,95	6,03	7,28						4,92 (H_{OH})	5,16								

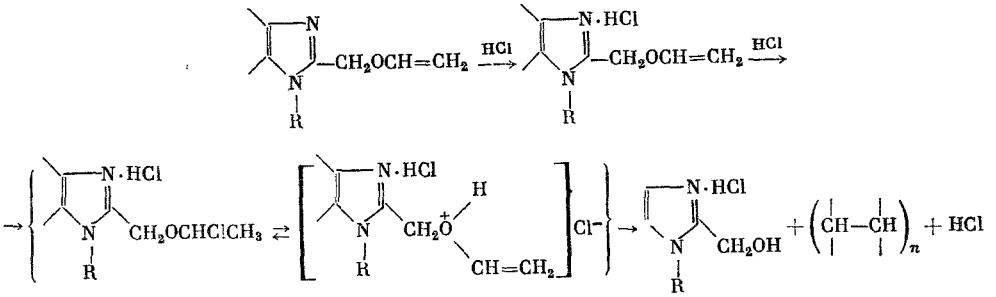
HC-(V), HC-(I), HC-(I), HC-(II)** are the hydrodrochlorination products of (V), (I), (V), and (VI).

TABLE 3. Parameters of UV and IR Spectra of Imidazoles (I)-(VIII), (XI)-(XIV)

Compound	λ, nm	ε	ν, cm⁻¹ N—CH=CH₂ O—CH=CH₂	$E^{\nu_2}_{\nu_1}$ (liters/mole·cm²)	Compound	λ, nm	ε	ν, cm⁻¹ N—CH=CH₂ O—CH=CH₂	$E^{\nu_2}_{\nu_1}$ (liters/mole·cm²)
(I)	237,4	12320	1648	2487	(VII)	219,7	9400	1640 1620	4923
(II)	232	16701	1649	2393					
	259,6	9055			(VIII)	250	7682		
	283,2	5391	1649	3644		256	7864		
	292,1	3501	1612			277	6712	1640	3902
(III)	219,7	7318				283	5819	1620	
						286	4526		
(IV)	250	7153			(XI)	230	10970	1650	2722
	256	7733							
	270,2	5964			(XII)	226,7	16729		
	277,7	6919				232,6	17104		
	285,7	5488				253	11043	1655	3648
						281	5134		
(V)	238	11500	1648 1641 1620	7811	(XIII)	217	5160		
					(XIV)	249	6044		
(VI)	231	18238				255	6221		
	260	10135	1649	8021		267	4181		
	282	6404	1620			276	4836		
	291	2433				282	5188		

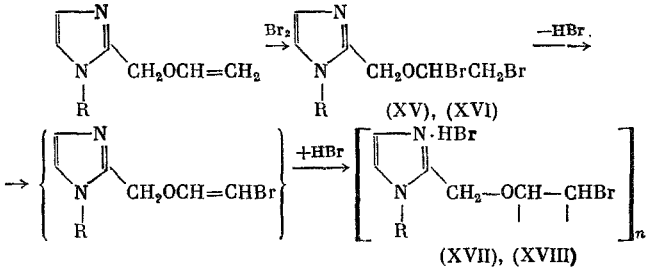
are retained. In products of further hydrochlorination, a mixture of the hydrochlorides of (I) and (V) in a ratio of 30 and 70% is found. The PMR spectrum of the mixture contains signals for protons of the $OCH=CH_2$ group and, in a weak field, two doublets belonging to the protons of the ring of (I) hydrochloride. On termination of the reaction, only one product, the hydrochloride of imidazole (I), is separated. The obtained data suggest that in the reaction of N,O-divinylimidazoles (V)-(VIII) with HCl, formation of the hydrochlorides of 1-vinyl(ethyl)-2-(vinyloxymethyl)imidazoles are formed initially from the reaction with an unshared pair of electrons of the N^3.

Later, a second molecule of HCl is added at the double bond of the O-vinyl group, with formation of unstable hydrochlorides of 1-vinyl-2-(α-chloroethoxymethyl)imidazoles. As the result of redistribution of the electron density of the imidazole ring during protonation at the N^3, they are decomposed to the hydrochlorides of 1-vinyl-2-(hydroxymethyl)imidazoles and resins similar to α-haloethyl alkyl ethers [8].



R = $CH=CH_2$; C_2H_5

Bromine adds readily to the mono- and divinyl derivatives of the hydroxymethylimidazoles (V)-(VIII). The reaction occurs without heating in absolute CCl_4 at the double bond of the O-vinyl group with formation of 1-vinyl(ethyl)-2-(α,β-dibromoethoxymethyl)imidazoles (XV) and (XVI):

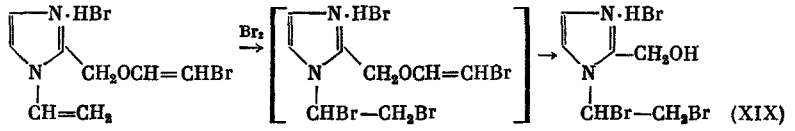


(XVII), (XVIII)

R = $CH=CH_2$ (XV), (XVII); C_2H_5 (XVI), (XVIII)

The dibromo derivatives (XV) and (XVI) are similar to the bromination products of alkyl and aryl vinyl ethers [9] and decompose to unstable 1-vinyl(ethyl)-2-(β-bromovinyloxymethyl)imidazoles with the elimination of HBR. These imidazoles are capable of spontaneous polymerization at the vinyl group attached to the oxygen; the HBr itself enters into reaction with the unshared pair of electrons at the N^3. The polymers of the hydrobromides of 1-vinyl(ethyl)-2-(β-bromovinyloxymethyl)imidazoles (XVII) and (XVIII) were isolated and characterized. Elemental analysis data agree fully with the proposed structure. In their IR spectra, absorption bands for the $OCH=CH_2$ double bond disappear and a broad band appears at 2600-3000 cm^{-1}, caused by the vibrations of an ammonium cation [10]. The absorption characteristic of an N-vinyl group is retained and a shift to the short-wavelength region is observed for the vibration frequencies of the heterocycle.

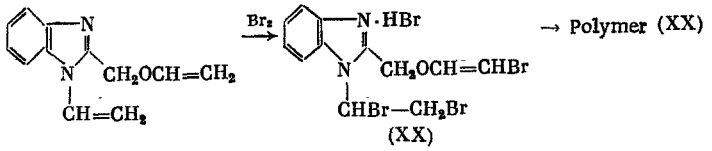
In the case of imidazole (V), the ratio of initial components has a significant influence on the direction of the reaction. Thus, during excess Br_2, addition at the double bond of the N-vinyl group is also observed and the hydrobromide of 1-(α,β-dibromoethyl)-2-(hydroxymethyl)imidazole (XIX) is isolated in addition to the polymer of the imidazole (XVII):



(XIX)

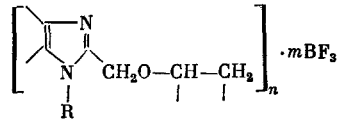
The IR spectrum for (XIX) contains no absorption bands for vibrations of N- and O-vinyl groups. Absorption characteristic for the ammonium cation at 2600-3000 cm^{-1} and associated OH group at 3220-3240 cm^{-1} is observed.

During reaction of the imidazole (VI) with Br_2 even in equimolar ratio of the initial components, addition occurs at both vinyl groups with formation of the halogenated product (XX), which is converted to the polymer of the 1-(α,β-dibromoethyl)-2-(β-bromovinyloxymethyl)benzimidazole hydrobromide (XX):



(XX)

Depending on the position of the vinyl group on the N or O atoms of the synthesized imidazoles (V)-(VIII), the polymerization occurs differently. In the presence of azobisisobutyronitrile (AIBN), the polymerization of (V) and (VI) occurs via scission of the double bond of the N-vinyl group. Conversion after 8 h at 80°C is 98 and 29%, respectively. The obtained polymers are light-yellow powders with a mp in the range 195-270°C and soluble in chloroform, dioxane, and DMF. The IR spectra of the polymers obtained from (V) and (VI) show a disappearance of absorption bands for the N-vinyl group, but bands for stretching and deformation vibrations of the $OCH = CH_2$ group at 1610-1640 and 830-835 cm^{-1} are retained. It should be noted that the N,O-divinylimidazoles (V) and (VI) can also be polymerized by a cationic mechanism. Thus, in the presence of BF_3 etherate, compound (VI) is polymerized at 49% conversion after 6 h at 140°C. In contrast to imidazoles (V) and (VI), the 1-ethyl derivatives of (VII) and (VIII) form polymers only in conditions of cationic polymerization with a yield of ~20%. In the IR spectra of the polymerization products of compounds (V)-(VIII) obtained in the presence of a cationic catalyst, a shift of the bands for vibrations of the heterocycle to the short-wavelength region is observed. In the given case, formation of polymer complexes occurs and complete with the polymerization. The composition of the complexes depends on catalyst concentration:



R = C_2H_5, CH = CH_2; $n = 3$—10, $m = 1$—3

Spectra for such polymers show the retention of bands for the vibrations of an N-vinyl group, but absorption bands for the double bond of a vinyl ether disappear.

EXPERIMENTAL

The PMR spectra were recorded on a BS 1878 instrument in a solution of CCl_4 and CD_3OD relative to HMDS; the IR spectra were recorded on a UR-20 spectrophotometer using KBR tablets and solutions in CCl_4

TABLE 4. Bromo Derivatives (XVII)-(XX)

Compound	Yield, %	mp., °C	Found, %			Molecular formula	Calculated, %		
			C	H	Br		C	H	Br
(XVII)	43	137–139	30,86	3,17	51,23	$C_8H_{10}N_2OBr_2$	30,90	3,21	51,61
(XVIII)	35	147–150	31,11	4,00	50.89	$C_8H_{12}N_2OBr_2$	30,70	3,84	51,20
(XIX)	10	176–177	20,11	2.35	65,33	$C_6H_9N_2OBr_3$	19,72	2,46	65,76
(XX)	49	110–140	27,91	2,67	61,41	$C_{12}H_{12}N_2OBr_4$	27,68	2,30	61,53

and $CHCl_3$. The electronic spectra of the absorption of the compounds in a solution of ethanol were obtained on a Specord UV-VIS spectrometer. The R_f values were determined in a nonreinforced layer of Al_2O_3 (activated II) in a system of 20 : 8 : 1 chloroform–benzene–ethanol.

1-Vinyl-2-(vinyloxymethyl)imidazole (V). A mixture of 20 g (0.15 mole) 1-vinyl-2-(hydroxymethyl)-imidazole (I), 4 g (20%) $Cd(AcO)_2$ in 250 ml dioxane was kept in an autoclave for 5 h at 200°C under an acetylene pressure of 15 atm. A dark brown liquid was filtered off, the dioxane was distilled off, and the residue was placed in vacuum. Yield, 22.5 g (92%) (V) (see Table 1).

Hydrochlorination of 1-Vinyl-2-(vinyloxymethyl)imidazole (V). A solution of 1.2 g (0.008 mole) (V) in 30 ml abs. CCl_4 at −5°C was bubbled with dry HCl. After 2 min, the white precipitate was washed with absolute CCl_4 and ether. Yield, 1.1 g (73%) (V) hydrochloride, mp 164-165°C. Found: C 51.2; H 5.7; Cl 19.4%. $C_8H_{10}N_2O \cdot HCl$. Calculated: C 51.4; H 5.9; Cl 19.0%. On passing through HCl for 1 h, 1.45 g (95%) (I) hydrochloride was isolated with mp 206-208°C. Found: C 44.6; H 5.71; Cl 22.3%. $C_6H_8ON_2 \cdot HCl$. Calculated: C 44.8; H 5.6; Cl 22.1%.

Bromination of 1-Vinyl-2-(vinyloxymethyl)imidazole (V). A solution of 0.45 g (0.003 mole) (V) in 30 ml absolute CCl_4 was added dropwise to a solution of 0.96 g (0.006 mole) Br_2 in 30 ml absolute CCl_4 at −30°C over 1 h. After 2 h, the yellow precipitate was washed with dry acetone and ether. Yield, 0.3 g of the polymer of 1-vinyl-2-(β-bromovinyloxymethyl)imidazole hydrobromide (XVII). White crystalline precipitate of 1-(α,β-dibromoethyl)-2-(hydroxymethyl)imidazole (XIX) (0.1 g, 10%) was isolated from the filtrate. The properties of the bromination products of imidazoles (V)-(VIII) are given in Table 4.

Polymerization of 1-Vinyl-2-(vinyloxymethyl)imidazole (V). Compound (V) (0.5 g, 0.0033 mole) and 0.02 g (4%) AIBN were placed in an ampul for 8 h at 80°C. The polymer formed was washed with chloroform and ether and dried. Yield, 0.49 g (98%) poly[vinyl-2-(vinyloxymethyl)imidazole] with mp 240-272°C, insoluble in organic solvents. Found: C 64.1; H 6.78; N 18.62%. $(C_8H_{10}N_2O)_n$. Calculated: C 64.02; H 6.66; N 18.66%.

Polymerization of 1-Vinyl-2-(vinyloxymethyl)imidazole (VI). $BF_3 \cdot O(Et)_2$ (0.18 g, 9%) was added gradually under stirring to 2 g (VI). The mixture was maintained for 6 h at 140°C. Yield, 1.9 g (48%) (VI) polymer with dark brown color and mp 150-175°C. Found: C 64.7; H 5.69; N 8.10%. $(C_{12}H_{14}N_2O)_3 \cdot BF_3$. Calculated: C 64.6; H 5.39; N 8.53%.

CONCLUSIONS

1. 1-Vinyl and 1-ethyl-2-(hydroxymethyl)imidazoles form with acetylene under pressure the corresponding 2-vinyloxymethyl derivatives.

2. On treatment of 1-vinyl(ethyl)-2-(vinyloxymethyl)imidazoles with HCl, the hydrochlorides of 1-vinyl-(ethyl)-2-(α-chloroethoxymethyl)imidazoles are formed with subsequent decomposition to the hydrochlorides of 1-vinyl(ethyl)-2-(hydroxymethyl)imidazoles.

3. Bromination of 1-vinyl-2-(vinyloxymethyl)imidazole leads to the formation of mainly the polymeric hydrobromide of 1-vinyl-2-(β-bromovinyloxymethyl)imidazole. Reaction of 1-vinyl-2-(vinyloxymethyl)benzimidazole with bromine occurs simultaneous at the N- and O-vinyl groups with formation of the hydrobromide 1-(α,β-dibromoethyl)-2-(β-bromovinyloxymethyl)benzimidazole, which is subsequently polymerized.

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HIGH-TEMPERATURE ORGANIC SYNTHESIS

9. THERMAL TRANSFORMATIONS OF DIMETHYL SULFIDE AND THIIRANE*

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The pyrolysis of dimethyl sulfide (DMS) and thiirane has not yet been studied in sufficient detail. It has only been known that DMS is converted to methane, CH_3SH, and H_2S at 700°C in a toluene stream [2]. Other dialkyl sulfides are decomposed in the gas phase at 400-800°C with the loss of hydrogen sulfide and olefins through the intermediate formation of thiols [3-5]. Thiophene is also found in the pyrolyzates. It was of interest to study the pyrolysis of DMS under the same conditions. The structure of DMS dictates a difference in the conversion scheme relative to other dialkyl sulfides. In particular, the direct elimination of olefins is impossible from DMS, and thiirane may be one of the intermediates. Sulfur-containing products of the pyrolysis of DMS and thiirane may be trapped by thermal condensation with halo-substituted aromatic, heteroaromatic, and unsaturated compounds [6, 7].

The pyrolysis of dimethyl sulfide in a flow system consisting of a hollow quartz tube in a nitrogen atmosphere begins above 500°C. The yield of liquid pyrolyzate at 500-600°C is low (from 15 to 40%) and decreases with increasing reaction temperature (Table 1). The major pyrolysis products of DMS are hydrogen, hydrogen sulfide, methane, ethane, propane, butane, and butene. Ethylene is not formed. Only vinylthiol and thiophene, according to PMR data, are formed as liquid pyrolyzate products. The yield and ratio of these products depend on temperature and contact time. The maximum yield of vinylthiol (4%) is observed at 500°C with 55-58 sec contact time. With an increase in the pyrolysis temperature to 600°C, only thiophene in 17% yield is found in the condensate in addition to unreacted DMS. The maximum yield of thiophene (20%) is observed at 550°C; 1% vinylthiol is formed at this temperature.

An increase in contact time at constant temperature (500°C) leads to a decrease in the yield of vinylthiol and increase in the yield of thiophene (the vinylthiol : thiophene ratio decreases from 2 to 0.4), which indicates the initial formation of vinylthiol from DMS and subsequent conversion of this product into thiophene apparently through the intermediate formation of divinyl sulfide [8].

$$CH_3SCH_3 \rightarrow CH_2{=}CHSH + H_2 \quad (1)$$

$$2CH_2{=}CHSH \xrightarrow[-H_2S]{\Delta} \left[\begin{array}{cc} H_2C & CH_2 \\ \| & \| \\ HC & CH \\ & S \end{array}\right] \xrightarrow[-H_2]{\Delta} \quad (2)$$

Thiirane is a likely intermediate in DMS pyrolysis; it subsequently isomerizes into vinylthiol:

$$CH_3SCH_3 \xrightarrow[-H_2]{} H_2C{-}CH_2 \rightarrow CH_2{=}CHSH \quad (3)$$

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