CONCLUSIONS

1. The rate of the thermal decomposition of tert-butyl hydroperoxide (TBH) to the free radicals in N,N-dimethylacetamide (DMA) as the medium is directly proportional to the hydroperoxide concentration and inversely proportional to the DMA concentration. A more complex dependence on [DMA] was obtained for cumyl hydroperoxide (CH). A scheme was proposed and the effective initiation rate constants were determined in the range 52.5-90.3° (TBH) and 80-110° (CH).

2. The empirical decomposition rate (W_p) for TBH and CH in DMA as the medium obeys the equation: $W_p \sim [ROOH]_0^{3/2}$. For TBH, $W_p \sim [DMA]^{-1.5}$ when $[DMA] > 7$ mole/liter. Acceptors of alkyl radicals, like benzoquinone and 2,2,6,6-tetramethylpiperdin-1-oxyl, effectively inhibit the empirical decomposition of hydroperoxides. A scheme was proposed for the induced decomposition and the effective rate constants at 132° were determined.

LITERATURE CITED

1. T. I. Drozdova, A. L. Aleksandrov, and E. T. Denisov, Izv. Akad. Nauk SSSR, Ser. Khim., 1978, 965.
2. T. I. Drozdova, A. L. Aleksandrov, and E. T. Denisov, Izv. Akad. Nauk SSSR, Ser. Khim., 1978, 967.
3. V. I. Vedeneev and A. A. Kibalko, Rate Constants of Gas-Phase Monomolecular Reactions [in Russian], Nauka (1972).
4. V. L. Antonovskii, E. T. Denisov, and L. V. Solntseva, Kinet. Katal., 6, 815 (1965).
5. V. V. Zharkov and N. K. Rudnevskii, Opt. Spektrosk., 12, 479 (1962).
6. I. I. Shabalin and E. A. Kiva, Opt. Spektrosk, 24, 703 (1968).
7. O. P. Yablonskii, M. S. Lastochkina, and V. A. Belyaev, Neftekhimiya, 13, 851 (1973).
8. E. T. Denisov, Zh. Fiz. Khim., 38, 2085 (1964).
9. N. I. Solomko, V. F. Tsepalov, and A. I. Yurzhenko, Kinet. Katal., 9, 766 (1965).
10. D. F. Doehnert and O. L. Mageli, Modern Plastics, 36, 142 (1959).
11. B. A. Redoshkin, V. A. Shushunov, and N. I. Kurochkin, Tr. po Khim. Tekhnol., Gor'kii, 1961, No. 1, 157.

REACTION OF MONOETHANOLAMINE VINYL ETHER WITH ALDEHYDES

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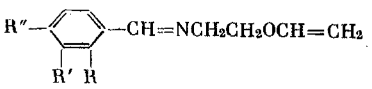
UDC 542.953.4:547.435:547.281:547.571

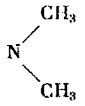
The condensation of amino alcohols with aldehydes, which leads to oxazolidines, is well known [1], but information on the condensation of monoethanolamine vinyl ether is restricted to the statement made in [2] that the reaction products with acetaldehyde immediately turn to a tar when fractionally distilled in vacuo. In order to ascertain the behavior of monoethanolamine vinyl ether in nucleophilic addition reactions we deemed it of interest to study its condensation with carbonyl compounds. The presence of a vinyl group in hydroxyethylamine made it possible to expect obtaining new derivatives of vinyl monomers. The latter can have biological activity as defoliants, herbicides, and plant growth stimulants by analogy with the condensation products of amino alcohols with furfural [3] and benzaldehydes [4].

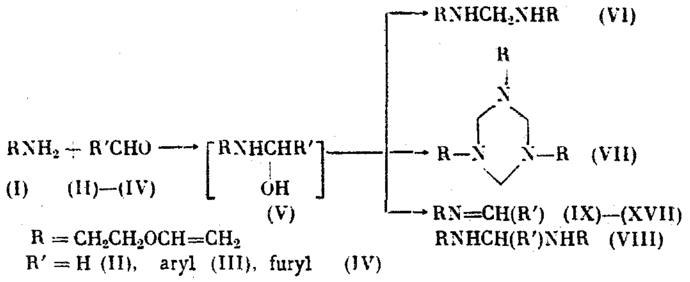
In the present paper it was shown on the example of reacting monoethanolamine vinyl ether with aldehydes that the vinyl ethers of amino alcohols can be used successfully as the amino components for obtaining derivatives of hexahydro-1,3,5-triazine and Schiff bases that contain the fragments of vinyl ethers in their composition.

Chemical and Metallurgical Institute, Academy of Sciences of the Kazakh SSR, Karaganda. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1217-1220, May, 1978. Original article submitted October 5, 1977.

TABLE 1. Vinyl Ethers of Schiff Bases



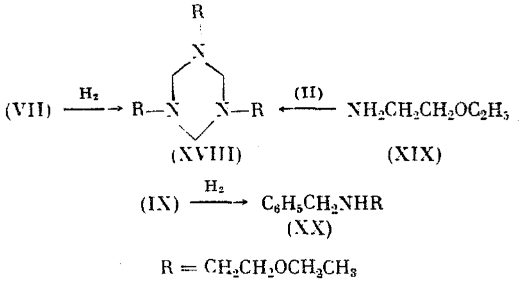
Compound	R	R′	R″	Yield, %	bp, °C (p, mm of Hg) mp, °C	d_4^{20}	n_D^{20}	Found, %			Empirical formula	Calculated, %		
								C	H	N		C	H	N
(IX)	H	H	H	87,1	125–127 (2,5)	1,0144	1,5440	75,27	7,19	7,85	$C_{11}H_{13}NO$	75,42	7,42	8,00
(X)	H	H	OCH_3	83,4	145–146 (1,5)	1,0579	1,5610	70,05	7,13	6,64	$C_{12}H_{15}NO_2$	70,24	7,31	6,82
(XI)	OCH_3	H	OCH_3	81,7	187–189 (3,0)	1,0924	1,5650	66,17	7,09	5,51	$C_{13}H_{17}NO_3$	66,38	7,23	5,95
(XII)	OH	H	H	89,3	145–146 (1,5)	1,0753	1,5640	68,97	6,67	7,08	$C_{11}H_{13}NO_2$	69,10	6,80	7,35
(XIII)	H	OCH_3	OCH_3	92,1	157–159 (1,5)	1,1110	1,5640	66,27	7,18	5,70	$C_{13}H_{17}NO_3$	66,38	7,23	5,95
(XIV)	H	H	NO_2	91,3	47–48	–	–	59,87	5,23	12,55	$C_{11}H_{12}N_2O_3$	60,00	5,45	12,72
(XV)	H	NO_2	H	95,9	60–61	–	–	59,83	5,19	12,49	$C_{11}H_{12}N_2O_3$	60,00	5,45	12,72
(XVI)	H	H		93,7	38–39	–	–	71,33	8,12	12,47	$C_{13}H_{18}N_2O$	71,56	8,25	12,84



When monoethanolamine vinyl ether (MEAVE) is reacted with paraform (II) the stoichiometric amount of water is liberated and the trivinyl ether of 1,3,5-tris(hydroxyethyl)hexahydrotriazine (VII) is formed in 91% yield. Depending on the concentration of (II), the competing condensation of aminomethylol (V) with another MEAVE molecule, which leads to methylenediamine (VI), proceeds in parallel with the main direction. To suppress this side reaction it is necessary to use an excess of (II). The reaction with benzaldehydes (III) and furfural (IV), taken in equimolar amounts, proceeds with the formation of the corresponding vinyl ethers of Schiff bases in 81-96% yield. The formation of the aminals (VIII) of furfural and benzaldehydes was not detected.

The reaction products (VII), (IX)–(XIII), (XVII) (Table 1) are viscous oily liquids that can be readily distilled in vacuo, whereas (XIV)-(XVI) are crystalline. They are readily soluble in benzene, acetone, dioxane, alcohol, chloroform, or ether, and in water are hydrolyzed to the starting products. The molecular refraction exaltations are positive, which is explained by the presence of conjugation of the π electrons of the aromatic ring and the azomethine group.

The structure of the obtained compounds was proved by catalytic hydrogenation. The amount of absorbed H_2 corresponds to the presence of three double bonds in the (VII) molecule, and two double bonds in (IX). In addition, (XVIII) was obtained by counter synthesis starting with (XIX).



The IR spectra of all of the obtained compounds are in full agreement with their structure. The constants and elemental analysis data for the vinyl ethers of the Schiff bases of hydroxyethylamines (IX)-(XVI) are given in Table 1.

EXPERIMENTAL

Monoethanolamine vinyl ether was obtained as described in [5]. The IR spectra were taken on a UR-20 spectrophotometer as KBr pellets and as a microlayer.

Trivinyl Ether of 1,3,5-Tris(hydroxyethyl)hexahydrotriazine (VII). A stirred mixture of 8.7 g of MEAVE, 3.4 g of paraform, and 60 ml of benzene was heated in a flask equipped with a water separator until the liberation of water ceased. After removal of the benzene the residue was vacuum-distilled to give (VII) in 91% yield, bp 165-167° (3 mm); d_4^{20} 1.0409; n_D^{20} 1.4960. Found: C 60.13; H 8.78; N 13.84%. $C_{15}H_{27}N_3O_3$. Calculated: C 60.60; H 9.09; N 14.14%. Infrared spectrum (ν, cm^{-1}); 1205, 1620, 3025, 3120 ($CH_2=CHO$); absorption in the 1570 and 3300-3500 cm^{-1} regions (NH) is absent.

Triethyl Ether of 1,3,5-Tris(hydroxyethyl)hexahydrotriazine (XVIII). a) Under the above described conditions, from 8.9 g of ethoxyethylamine (XIX) and 3.4 g of paraform we obtained (XVIII) in 80% yield, bp 175-176° (2.5 mm); d_4^{20} 0.9640; n_D^{20} 1.4630. Found: C 59.32; H 10.63; N 13.57%. $C_{15}H_{33}N_3O_3$. Calculated: C 59.40; H 10.89; N 13.86%.

b) The hydrogenation of 7.42 g of vinyl ether (VII) was run in 30 ml of ethanol using 1.0 g of skeletal Ni until saturation was complete. The ethanol was distilled off, and the residue was vacuum-distilled to give 6.5 g of (XVIII), **bp 167-168° (2 mm); d_4^{20} 0.9660; n_D^{20} 1.4615.**

Ethyl Ether of N-(Hydroxyethyl)benzylamine (XX). Under conditions similar to the preceding experiment, from 8.7 g of (IX) and 0.5 g of skeletal Ni we obtained 6.5 g of ethyl ether (XX), bp 115-117° (1.5 mm); d_4^{20} 0.9653; n_D^{20} 1.5075.

Vinyl Ether of N-(p-Nitrobenzylidene)hydroxyethylamine (XIV). A mixture of 7.5 g of p-nitrobenzaldehyde and 4.3 g of MEAVE in 30 ml of ethanol was stirred at 50-60° for 3 h. After removal of the solvent we obtained 10 g (91.3%) of vinyl ether (XIV), which was recrystallized from alcohol. Infrared spectrum (ν, cm^{-1}): 1205, 1620, 3030, 3125 ($CH_2=CHO$), 1640 ($C=N$), 700, 1518, 1580 (C_6H_5); absorption in the 3300-3500 cm^{-1} region is absent.

Hydrolysis of (XIV). A mixture of 8.0 g of vinyl ether (XIV) and 25 ml of water was shaken for 8 h. After the usual workup we isolated 2.5 g of MEAVE [2] with bp 115-117° and n_D^{20} 1.4420, and 3.8 g of p-nitrobenzaldehyde with mp 105-106°.

Vinyl Ether of N-(Furfurylidene)hydroxyethylamine (XVII). A mixture of 4.3 g of MEAVE, 4.8 g of freshly distilled furfural, and 50 ml of toluene was heated in a flask equipped with a water separator until the liberation of water ceased. After removal of the toluene the residue was vacuum-distilled to give 6.5 g of (XVII), bp 110-112° (5 mm); d_4^{20} 1.0045; n_D^{20} 1.5330. Found: C 65.27; H 6.34; N 8.83%. $C_9H_{11}NO_2$. Calculated: C 65.45; H 6.66; N 9.09%. Compounds (IX)-(XIII) were obtained in a similar manner (see Table 1).

CONCLUSIONS

The trivinyl ether of 1,3,5-tris(hydroxyethyl)hexahydrotriazine and some vinyl ethers of the Schiff bases of hydroxyethylamines were synthesized by the condensation of monoethanolamine vinyl ether with aliphatic and aromatic aldehydes.

LITERATURE CITED

1. E. D. Bergmann, Chem. Revs., 53, 309 (1953).
2. M. F. Shostakovskii, I. A. Chekulaeva, and I. V. Lipovich, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1963, 532.
3. Sh. A. Israilova and I. P. Tsukervanik, Dokl. Akad. Uzbek. SSR, 11, 29 (1966).
4. J. M. Arnaud, R. Dorme, P. Hampe, and C. Viel, Bull. Soc. Bot. France, 113, 105 (1966); R. Dorme, P. Hampe, J. Hernette, and C. Viel, Compt. Rend., 265, 128 (1967).
5. M. F. Shostakovskii, Vinyl Ethers [in Russian], Izd. Akad. Nauk SSSR (1952), p. 103.