HOMOLYTIC ADDITION OF ISOPROPYL ALCOHOL TO DIVINYL ETHERS OF 1,1- AND 1,2-DIOLS

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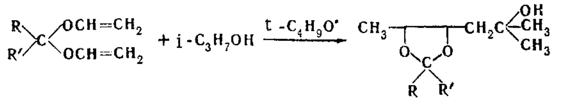
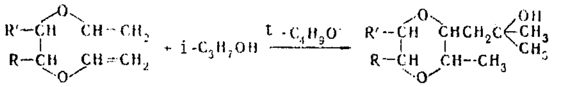
UDC 547.729.7'841

The reaction of divinyl ethers of 1,1- and 1,2-diols with isopropyl alcohol in the presence of tert-butyl peroxide gave, in addition to telomers, cyclic adducts (1 : 1), to which the 5-methyl-4-(2-hydroxy-2-methylpropyl)-1,3-dioxolane structure (in the case of divinyl ethers of gem-diols) or the 2-methyl-3-(2-hydroxy-2-methylpropyl)-1,4-dioxane structure (in the case of the vic-diols) was assigned.

The reactions of vinyl ethers with alcohols under acid catalysis conditions have been studied in detail [1]. However, nothing is known regarding the possibility of the addition of alcohols to vinyl ethers in the presence of radical initiators.

Our investigations have demonstrated that the divinyl ethers of 1,1- and 1,2-diols can undergo homolytic reactions with alcohols. We obtained cyclic adducts in yields of 40-50% by the action of excess isopropyl alcohol on these ethers under conditions involving initiation by tert-butyl peroxide (Table 1). A high degree of dilution is necessary because of the small chain-transfer constants for the alcohols [2].


I-III


IV, V

I, IV R=R'=H; II, V R=H, R'=CH_3, III R=H, R' i-C_3H_7

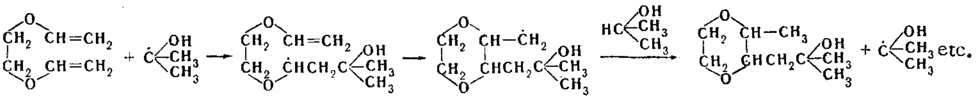
The selection of isopropyl alcohol was deliberate. according to the data in [2], this alcohol adds more readily, by a radical mechanism, to olefins than other aliphatic alcohols and is less inclined to undergo telomerization reactions

The formation of the cyclic adducts can be represented by the following scheme:

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO$$

$$(CH_3)_3CO^{\cdot} + HC(CH_3)_2(OH) \rightarrow (CH_3)_3COH + \dot{C}(CH_3)_2(OH) \text{ or}$$

$$(CH_3)_3CO^{\cdot} + HC(CH_3)_2(OH) \rightarrow CH_4 + CH_3COCH_3 + \dot{C}(CH_3)_2(OH)$$



We observed a similar cyclization in the reaction of the same ethers with dialkyl phosphites under homolytic catalysis conditions [3-5]. Unambiguous conclusions regarding the structures of the phosphonomethyl-1,3-dioxolanes and 1,4-dioxanes were drawn from an analysis of the IR and PMR spectra and several chemical transformations. These results provide a basis for assuming that the reaction of divinyl ethers of

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Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 298-302, March, 1972. Original article submitted September 10, 1970.

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gem- and vic-diols with isopropyl alcohol would lead to cyclic adducts (1 : 1) of similar structure, i.e., 1,3-dioxolanes (I-III) and 1,4-dioxanes (IV, V).

This is in good agreement with the fact that the addend in radical ractions generally attacks the β-carbon atom of the vinyloxy group [6] and is also in good agreement with the known ease of formation of 5- and 6-membered rings.

An analysis of the IR spectra (Fig. 1) indicates that linear structures of the $CH_2=CHO-R-OCH_2CH_2C(CH_3)_2OH$ [$R = -CH_2-, -(CH_2)_2-, >CH-CH_3, >CHCH(CH_3)_2, -CH_2CH(CH_3)$] type are excluded, since all of the characteristic frequencies of the vinyloxy group are absent. The strong band at 3450-3510 cm^{-1} corresponds to the stretching vibrations of the tertiary hydroxyl group. However, the identification of the in-plane deformation vibrations of the hydroxyl group (1300-1400 cm^{-1}) and of the band at 1150 cm^{-1}, which is characteristic for tertiary alcohols [7], is complicated because of the presence of bands of the 1,3-dioxolane and 1,4-dioxane ring, which lie in the same regions and complicate the spectral picture. The purities of the products were confirmed by gas-liquid chromatography. Acetaldehyde, determined as the 2,4-dinitrophenylhydrazone, was isolated from the hydrolysis of II.

Additional information regarding the structures of I-V can be obtained by investigating the IR spectra of dilute solutions. Two major absorption bands are observed in the IR spectra of I, II, IV, and V (Table 2, Fig. 2) at 3547-3615 cm^{-1}; the high-frequency bands (3610-3615 cm^{-1}) correspond to the absorption of the unbonded tertiary hydroxyl group [8] [which is yet another confirmation of the assumed structures (I-V)], while the low-frequency bands (3530-3550 cm^{-1}) are affiliated with intramolecular hydrogen bonds.

The addition of isopropyl alcohol to divinyl ethers of glycols is accompanied by telomerization. The oligomers obtained are thick, viscous liquids, some of which are soluble in water. The IR spectra of the telomers are characterized by absorptions at 3440-3500 (stretching vibrations of the OH group), and at 1640 and 1715-1735 cm^{-1}, which are peculiar to the carbonyl group.

Monoadducts could not be isolated from the reaction of isopropyl alcohol with the divinyl ethers of 1,3- and 1,4-butylene glycols; very viscous telomers were primarily obtained in yields of 50-70%.

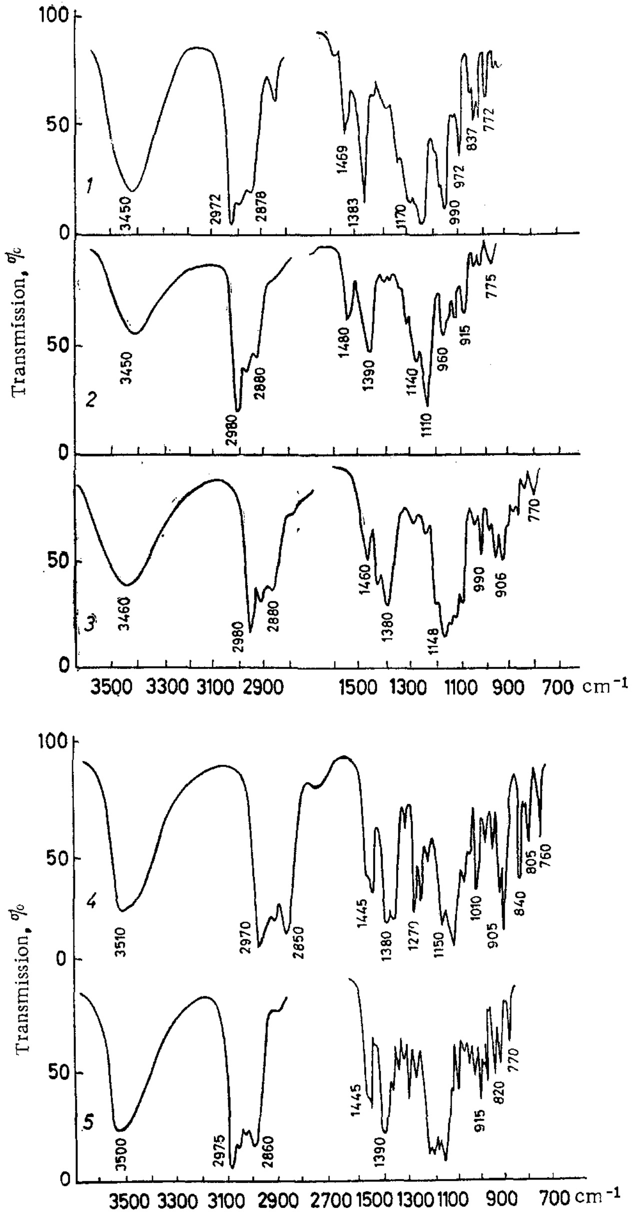

Fig. 1. IR spectra: 1) 5-methyl-4-(2-hydroxy-2-methylpropyl)-1,3-dioxolane; 2) 2-isopropyl-5-methyl-4-(2-hydroxy-2-methylpropyl)-1,3-dioxolane; 3) 2,5-dimethyl-4-(2-hydroxy-2-methylpropyl)-1,3-dioxolane; 4) 2-methyl-3-(2-hydroxy-2-methylpropyl)-1,4-dioxane; 5) 2,5-dimethyl-3-(2-hydroxy-2-methylpropyl)-1,4-dioxane.

EXPERIMENTAL

2-Methyl-5-methyl-4-(2-hydroxy-2-methylpropyl)-1,3-dioxolane (II). A mixture of 9.5 g (0.083 mole) of 1,1-divinyloxyethane, 157 g (2.6 moles) of isopropyl alcohol, and ~2 g of tert-butyl peroxide was heated in an ampul at 120-125° C for 48 h. Removal of the excess isopropyl alcohol and the unchanged ether (156.3 g) by fractionation gave 5.3 g (44% based on the recovered divinyl ether of the glycol) of cyclic product II with bp 52.5-53.5° C (1.5-2 mm) (Table 1) and 5 g of a very viscous, yellow telomer. The recovered divinyl

TABLE 1. Adducts of Divinyl Ethers of 1,1- and 1,2-Diols with Isopropyl Alcohol (I-V, formulas in the text)

Compound	R	Bp, °C (press., mm)	d_4^{20}	n_D^{20}	MR_D		Empirical formula	Found, %		Calc., %		Yield, %
					found	calc.		C	H	C	H	
I	H	104,5—105 (6)	1,0321	1,4469	41,47	41,96	$C_8H_{16}O_3$	59,9	10,0	60,0	10,1	47
II	CH_3	52,5—53,5 (1,5—2)	0,9890	1,4378	46,23	46,60	$C_9H_{18}O_3$	62,2	10,3	62,0	10,4	44
III	i-C_3H_7	70 —70,5 (1,5—2)	0,9687	1,4396	54,99	55,61	$C_{11}H_{22}O_3$	65,2	10,7	65,3	11,0	40
IV	H	89,5—90 (6)	1,0094	1,4492	46,32	46,60	$C_9H_{18}O_3$	62,0	10,3	62,0	10,4	43
V	CH_3	52 —52,5 (1—1,5)	0,9807	1,4435	50,94	51,25	$C_{10}H_{20}O_3$	63,1	10,6	63,8	10,8	38

TABLE 2. Frequencies of the Stretching Vibrations of the Hydroxyl Group in I-V

Compound	ν_{OH}^{free}, cm^{-1}	ν_{OH}^{bonded}, cm^{-1}	$\Delta\nu$, cm^{-1}
I	3612	3552	60
II	3615	3547	68
IV	3612	3535	77
V	3612	3532	80

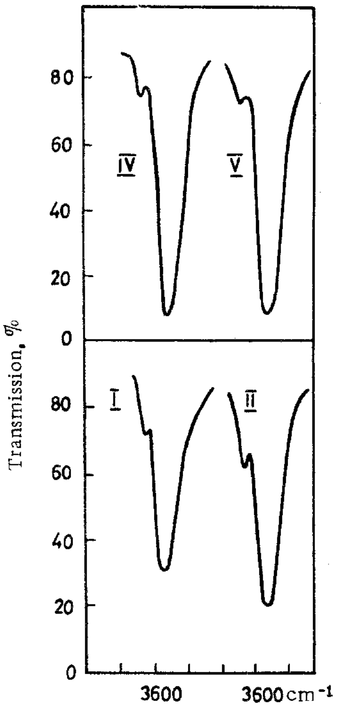

Fig. 2. IR spectra in the region of the OH stretching vibrations (0.002 M solutions in CCl_4, layer thickness 50 mm). The Roman numerals correspond to the numbers of the compounds in Table 1.

ether was determined by hydrolytic oximation [1]. The appropriate calculations demonstrated that 1.6 g of divinyl ether was recovered from the reaction.

The syntheses of I and III-V were carried out similarly. The compounds obtained (Table 1) are quite stable, transparent liquids, some of which are soluble in water.

Hydrolysis of 2-Methyl-5-methyl-4-(2-hydroxy-2-methylpropyl)-1,3-dioxolane (II). A mixture of 1 g of II, 10 ml of water, and five drops of concentrated hydrochloric acid was heated at 70-95° C for 2 h. The acetaldehyde, which was collected in a cooled receiver, was determined as the 2,4-dinitrophenylhydrazone [9]. A total of 0.3 g of the corresponding 2,4-dinitrophenylhydrazone with mp 147° C (orange form) was obtained (literature mp 146° C).

Reaction of 1,4-Butylene Glycol Divinyl Ether with Isopropyl Alcohol. A mixture of 9.5 g (0.066 mole) of 1,4-butylene glycol divinyl ether, 120 g (2.0 mole) of isopropyl alcohol, and 2 g of tert-butyl peroxide was heated in an ampul at 120-125° C for 46 h. The unchanged material (121 g, 78-81°C) and low-boiling products [2.5 g, 45-96° C (2 mm)] were removed by distillation, and 5.2 g (54%) of a very viscous, sticky, slightly water-soluble telomer was obtained in the residue. The yield of the telomer in the reaction of 1,3-butylene glycol divinyl ether with isopropyl alcohol under the same conditions was 70%.

The IR spectra were obtained with a UR-10 spectrometer.

LITERATURE CITED

1. M. F. Shostakovskii, Vinyl Ethers [in Russian], Moscow (1952).
2. W. H. Urry, F. W. Stacey, E. S. Huyser, and O. O. Juveland, J. Am. Chem. Soc., 76, 450 (1954).
3. B. A. Trofimov, A. S. Atavin, G. M. Gavrilova, and G. A. Kalabin, Zh. Obshch. Khim., 38, 2344 (1968).
4. B. A. Trofimov, A. S. Atavin, G. M. Gavrilova, and G. A. Kalabin, Izv. Akad. Nauk SSSR, Ser. Khim., 1200 (1969).

5. G. A. Kalabin, A. S. Atavin, G. M. Gavrilova, B. A. Trofimov, and M. F. Shostakovskii, Dokl. Akad. Nauk SSSR, 190, 849 (1970).
6. E. N. Prilezhaeva and M. F. Shostakovskii, Usp. Khim., 32, 897 (1963).
7. L. Bellamy, Infrared Spectra of Complex Molecules, Methuen (1958).
8. K. Nakanishi, Infrared Spectra and Structure of Organic Compounds [Russian translation] Mir, Moscow (1965), p. 36.
9. Houben-Weyl, Methoden der Organ. Chem. [Russian translation], Vol. 2, Goskhimizdat, Moscow (1963), p. 452.