INTERACTION OF 1-VINYLCYCLOHEXENE-3 DIOXIDE WITH ALCOHOLS

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Abstract

Full Text

CHEMISTRY

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INTERACTION OF 1-VINYLCYCLOHEXENE-3 DIOXIDE WITH ALCOHOLS

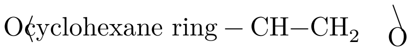
(Presented by Academician B. A. Arbuzov, June 12, 1964)

The addition of alcohols to the α-oxides of unsymmetrical olefins has now been studied in sufficient detail, owing to the investigations of A. A. Petrov and other authors (^{1}). There is no information in the literature on the addition of alcohols to the dioxides of cycloolefins.

The study of the addition of alcohols to 1-vinylcyclohexene-3 dioxide is of interest, since the literature contains an indication of the different reactivity of the epoxycyclohexane group and the epoxyethyl part of the dioxide molecule depending on the medium (^{2}). However, the literature gives no experimental substantiation of this statement (^{2}). The preparation of 1-vinylcyclohexene-3 dioxide is described in a patent (^{3}) and without a description of the reaction conditions in the above-cited article (^{2}). We obtained 1-vinylcyclohexene-3 dioxide by the action of acetyl hydroperoxide according to the method of B. A. Arbuzov (^{4}). The reaction proceeded in two stages: first, monoepoxide I was isolated with the following constants:

Fig. 1. IR spectra of 1-vinylcyclohexene-3 dioxide (1), 1-oxyethyl-3-oxypropyl-3-oxy-4-propoxy (or 3-propoxy-4-oxy)cyclohexane (2), 1-oxyethyl-3-oxypropoxyethyl-3-epoxycyclohexane (3).

$$\text{O¢yclohexane ring} - \text{CH=CH}_2 \qquad \text{(I)}$$



$$\text{O¢yclohexane ring} - \text{CH}-\text{CH}_2 \; \underset{\text{O}}{\diagdown} \qquad \text{(II)}$$

reaction scheme

Figure 2: reaction scheme

b.p. 43.5-44.5°/7 mm, n_D^{20} 1.4684, d_4^{20} 0.9574; MR_D found 36.08; calculated for $C_8H_{12}OF_1$, 35.93.

In the IR absorption spectrum of substance I there are $\nu_{\text{C-H}} = 3090$ cm^{-1}, $\nu_{\text{C=C}} = 1650$ cm^{-1}, and an intense peak at ~ 900 cm^{-1} (out-of-plane deformation vibrations of $= CH_2$), characteristic of the vinyl part of the molecule, as well as intense absorption at 3000 cm^{-1} of a symmetrically disubstituted epoxide ring (^{5}). Further, on repeated action of acetyl hydroperoxide on monoepoxide I, diepoxide II was obtained (b.p. 97-99°/9 mm, n_D^{20} 1.4782, d_4^{20} 1.0967, MR_D found 36.17; calculated for $C_8H_{12}O_2$ 35.84). In the spectrogram of the dioxide (Fig. 1, 1) the $\nu_{\text{C=C}}$ band disappears and appear-

peaks ν_{as} $CH_2 = 3050$ (medium), 1260 (medium), and 870 (strong) cm^{-1} of the pulsation and asymmetric vibrations of a monosubstituted epoxy ring (^{5}). From comparison of the spectrograms it may be concluded that the epoxide group condensed with the six-membered ring corresponds to an absorption maximum of medium intensity with $\nu = 920$ cm^{-1}.

In the reaction of 1-vinylcyclohexene-3 dioxide with alcohols, the formation of the following reaction products may be expected: III, IV, VI:

As the investigations showed, as a result of the addition of alcohols, addition products are formed both at one and at both epoxy rings, with predominant formation of the first product. No isomerization products were detected. The addition of ethyl, *n*- and iso-propyl, *n*- and iso-butyl alcohols to 1-vinylcyclohexene-3 dioxide was studied in the presence of BF_3 etherate and Na alcoholates. For the reaction, 1.0-1.2 moles of alcohol and 0.07 ml of BF_3 etherate were taken per 0.1 mole of dioxide. The reaction proceeds with evolution of heat; after cooling, the reaction mixture was kept for 3 hours at room temperature. In the case of using Na, for the same ratios of dioxide and alcohol, 0.6 g of Na was taken, and the reaction mixture was heated for 1 hour at 80-100°. Upon opening one oxirane ring in acidic and alkaline media, products with different constants are formed. Their characteristics are presented in Table 1. The order of addition of alcohols was studied in greater detail using the action of *n*-propyl alcohol as an example. In the IR spectrogram of the addition product in the presence of BF_3, the described features of the epoxyethyl part of the structure are clearly observed (ν_{as} CH 3050, 1260, and 870 cm^{-1}), which undoubtedly indicates structure III (Fig. 1, 2). A study aimed at choosing between the structures with a hydroxyl group at the 3- or 4-carbon atom of the cyclohexane ring (IIIa or IIIb) was not carried out. The product of addition of alcohols to the dioxide in an alkaline medium was assigned structure IV, since in the absorption spectrum (Fig. 1, 3) of the product of addition of propyl alcohol to the dioxide, the absorption bands at 3050 and 870 cm^{-1} of the epoxyethyl part are absent, and the peak at

917 cm^{-1}, assigned above to the epoxycyclohexane group, is retained.

Table 1

Characteristics of the products of alcohol addition to vinylcyclohexene dioxide

No.	Name of alcohol added to the dioxide	Catalyst	B.p., °C/mm	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated	C, %, found	C, %, calculated	H, %, found	H, %, calculated	Yield of theory, %
1	Ethyl	Na	93–94/0,01 101–103/0,008*	1,4819 [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible] 65,9
2	Ethyl	BF_3	88–89/0,01	1,4780	1,0762	48,98	48,79	64,15	64,48	9,84	9,74	27,8
3	*n*-Propyl	Na	94–95/0,007 118–120/0,01*	1,4798 [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible] 24,1
4	*n*-Propyl	BF_3	94–96/0,007 117–119/0,01*	1,4750 [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible] 16,8
5	*iso*-Propyl	Na	93–95/0,01	1,4752	1,0595	53,21	53,41	65,29	65,97	10,05	10,07	27,7
6	*iso*-Propyl	BF_3	91,5–93/0,008	1,4728	1,0477	53,59	53,41	65,80	65,97	9,98	10,07	36,6

No.	Name of alcohol added to the dioxide	Catalyst	B.p., °C/mm	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated	C, %, found	C, %, calculated	H, %, found	H, %, calculated	Yield of theory, %
7	*n*-Butyl	Na	102–104/0,007124–126/0,01 *	1,4763	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
8	*n*-Butyl	BF_3	101,5–103/0,007125–126/0,01 *	1,4739	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
9	*iso*-Butyl	Na	99–101/0,01	1,4737	1,0361	58,11	58,03	66,94	67,25	10,30	10,35	43,8
10	*iso*-Butyl	BF_3	103–104/0,01	1,4711	1,0268	58,03	58,03	66,97	67,25	10,32	10,35	42,5

* Constants of the products of addition of two moles of the corresponding alcohol.

To determine the order of addition to the epoxyethyl moiety of the dioxide, substance IV was oxidized with a pyridine-CrO_3 complex (6). Under these conditions the epoxide ring was not affected by the oxidizing agent. As a result of oxidation, a carbonyl compound of composition $C_{18}H_{11}O_3$ was isolated (b.p. 75-79/0.01, n_D^{20} 1.4728; d_4^{20} 1.0647; MR_D found 52.23; calculated for $C_{18}H_{11}O_3$ 51.99). The substance colors fuchsin-sulfurous acid and reduces ammoniacal silver oxide solution. In the absorption spectrum of substance V there is intense absorption at 1728 cm^{-1} with a shoulder at 1712 cm^{-1} ($\nu_{C=O}$). The indicated frequency is higher than that usually observed for liquid ketones (~1710 cm^{-1}) and is close to the frequency of aldehydes. It is known that a characteristic feature of aldehydes is a weak band in the IR spectrum at 2720 cm^{-1}. For all the compounds under discussion (including those without a carbonyl group), weak broad absorption maxima are observed in the range 2700-2850 cm^{-1}, which does not make it possible to use the above analytical characteristic of aldehydes from the IR spectrum. To determine whether substance V is an aldehyde (Va) or a mixture of aldehyde (Va) with ketone (Vb), the aldehyde content was quantitatively determined by method (7). The aldehyde content obtained was within the range 27-29%.

A 2,4-dinitrophenylhydrazone of substance V, of composition $C_{17}H_{22}O_6N_4$, with m.p. 139.0-139.5°, was obtained. The authors did not establish whether the 2,4-dinitrophenylhydrazone is a derivative of the aldehyde or of the ketone.

Thus, the addition of alcohols to the epoxyethyl moiety of the dioxide in an alkaline medium proceeds with formation of both primary and secondary monoalkyl ethers of epoxy-3,4-cyclohexylethylene glycol, with predominant formation of the former. This agrees with studies on the addition of alcohols to isoprene oxide (8) and to styrene oxide (9).

In the case of addition of alcohols to the dioxide at both oxide rings, both in the presence of BF_3 and of sodium, the reaction products, as can be seen from the data in Table 1, proved to have identical constants. Their spectra are also identical.

Consequently, in the case of opening of both oxide rings of the dioxide, both in acidic and in alkaline media, the order of addition is the same.

As a result of oxidation with a pyridine-CrO_3 complex of product VI ($R = C_3H_7$), obtained in the presence of Na, a dicarbonyl compound of composition $C_{14}H_{24}O_4$ was obtained, with b.p. 80-83/0.008, n_D^{20} 1.4668, d_4^{20} 1.0452; MR_D found 68.03; calculated for $C_{14}H_{24}O_4$ 67.96. On oxidation of substance VI ($R = C_3H_7$), obtained in the presence of BF_3, a substance of composition $C_{14}H_{24}O_4$ was likewise isolated, with b.p. 83-86/0.01, n_D^{20} 1.4649; d_4^{20} 1.0375; MR_D found 68.31; calculated for $C_{14}H_{24}O_4$ 67.96.

Both substances show all the characteristic reactions for an aldehyde group. Determination of the percentage content of ketoaldehyde VIIa by method (7) showed that the first product (b.p. 80-83°/0.008) contains ~36% of it, and the second (b.p. 83-86°/0.01) ~32%.

Thus, summarizing the above, it may be said that the addition of alcohols to 1-vinylcyclohexene-3 dioxide in an alkaline medium proceeds at the epoxyethyl moiety of the molecule, whereas in an acidic medium it proceeds at the epoxycyclohexane group. On opening of both oxide rings, addition to the epoxyethyl moiety of the molecule, both in acidic and in alkaline media, takes place in both possible directions.

Elemental analysis was carried out by T. S. Krivova.

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CITED LITERATURE

1. M. S. Malinovskii, *Oxides of Olefins and Their Derivatives*, 1961, p. 161.
2. E. Guccione, *Chem. Eng.*, **67**, No. 17, 78 (1960).
3. U. S. Pat., 2 527 806; *Chem. Abstr.*, **45**, 13876 (1951).
4. B. A. Arbuzov, *Isomeric Transformations of Terpenes*, Dissertation, Kazan, 1936, p. 209.
5. *Physical Methods in Heterocyclic Chemistry*, 2, N. Y.—London, 1963, p. 179.
6. G. I. Poos, G. E. Arth et al., *J. Am. Chem. Soc.*, **75**, 422 (1953).
7. Gutenberg, *Methods of Organic Chemistry*, M., 1963, p. 460.
8. A. N. Pudovik, S. G. Denislamova, *Zhurn. obshch. khim.*, **27**, 2363 (1957).
9. W. Reeve, J. Christfeel, *J. Am. Chem. Soc.*, **72**, 1480 (1950).

Note: Figure translations are in progress. See original paper for figures.