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RESEARCHES ON REACTIONS OF ALPHA OXIDES OF CYCLIC OLEFINS

I. Reactions of 1-Vinylcyclohexene-3 Dioxide with Alpha Chloroethers, Dialkylphosphorous Chloroanhydrides, and Amines

L. A. Mukhamedova, T. M. Malyshko, and R. R. Shagidullin

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The reactions of 1-vinylcyclohexene-3 dioxide with chloroethers (chlorodimethyl ether, chloromethylethyl ether, chloromethylpropyl ether) in the presence of zinc chloride, with diethyl and dipropylphosphorous chloroanhydrides, and with propylamine, butylamine and ethanolamine are described. IR absorption spectra show that the chloroethers and dialkylphosphorous chloroanhydrides add to 1-vinylcyclohexene-3 dioxide with opening of the oxide ring at the 6-carbon ring, while the amines add at the oxide ring across the exocyclic double bond.

The present authors previously showed how the reaction of 1-vinylcyclohexene-3 dioxide with alcohols varies with reaction medium [1], addition taking place at the cyclohexane epoxy group in acid medium, and at the exocyclic epoxy group in alkaline medium.

As a development of this work, it was of interest to investigate the reaction of 1-vinylcyclohexene-3 dioxide with other acidic and basic reagents. The acidic reagents selected were alpha chloroethers, and dialkylphosphorous chloroanhydrides. It is known from the literature that in the presence of mercuric or zinc chloride, alpha chloroethers readily add to olefin alpha oxides [2, 3, 4]. Dialkylphosphorous chloroanhydrides also react easily with olefin alpha oxides [5, 6].

The chloroethers (chlorodimethyl, chloromethylethyl, chloromethylpropyl) have been reacted with 1-vinylcyclohexane-3 dioxide in the presence of zinc chloride. Reaction does not occur in the presence of boron trifluoride etherate. The first two of the above-mentioned chloroethers gave products of addition to one oxide ring, and no products of addition to both rings could be isolated, because of the small amounts of the high boiling materials.

However, both types of products were obtained when the dioxide reacted with chloromethylpropyl ether. The reaction products were viscous colorless liquids, soluble in organic solvents. Table 1 gives their physical constants.

1-Vinylcyclohexene-3 dioxide reacts readily with dialkylphosphorous chloroanhydrides (diethyl- and dipropylphosphorous chloroanhydrides) one oxide ring being opened. A slight excess of dioxide was used, otherwise there was extensive resinification. The reaction products were colorless viscous liquids, soluble in organic solvents. Table 2 gives their physical constants.

Table 1

Properties of the Compounds Made by Reacting 1-Vinylcyclohexene-3 Dioxide with Alpha Chloroethers

Ether added	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D		Yield, %
				Found	Calculated	
CH_2ClOCH_3	89—90 (0.015)	1.4828	1.1704	53.83	53.78	30.6
$CH_2ClOC_2H_5$	93—95 (0.01)	1.4749	1.1275	58.61	58.39	50.6
$CH_2ClOC_3H_7$	103—105 (0.009)	1.4803	1.1241	62.94	63.01	12.2
	125—126* (0.009)	1.4747	1.1172	90.05	90.20	24.6

*Product of addition at both oxide rings.

The basic reactants used were amines (propylamine, butylamine, ethanolamine). There is an extensive literature [6] dealing with the reaction of amines with oxides. Reaction of dioxides with amines gives products of addition at one oxide ring. The reaction products are colorless, glass-like substances, which darken on storage. The amino alcohols synthesized do not give picrates. Their properties are given in Table 3.

The IR absorption spectra of the reaction products from the dioxide and the above reactants showed that chloroethers and dialkylphosphorous chloroanhydrides add with opening of the oxide ring on the six-membered ring. Reaction

Table 2

Properties of the Compounds Made by Reacting 1-Vinylcyclohexene-3 Dioxide with Dialkylphosphorous Chloroanhydrides

Chloroanhydride added	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D		Yield, %
				Found	Calculated	
$(C_2H_5O)_2PCl$ . . .	103—104 (0.012)	1.4790	1.1491	73.23	72.80	61.1
$(C_3H_7O)_2PCl$ . . .	110—112 (0.007)	1.4764	1.1112	82.50	82.01	39.3

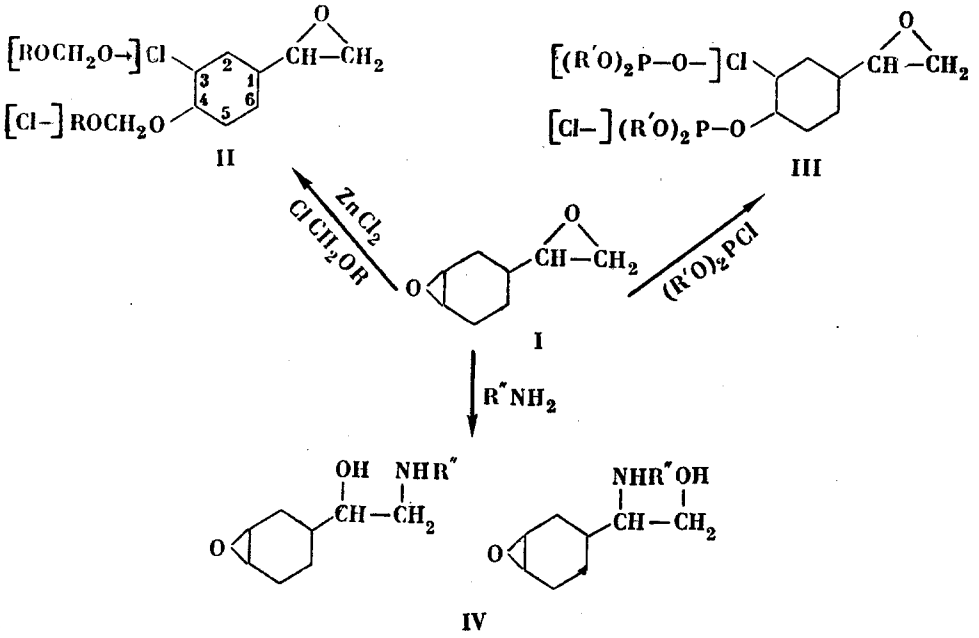
Table 3

Properties of Compounds Made by Reacting 1-Vinylcyclohexene Dioxide with Amines

Amine added	Property				Yield, %
	Bp, °C (pressure, mm)	n_D^{50}	N, %		
			Found	Calculated	
n-$C_3H_7NH_2$ . . .	121—122 (0.02)	1.5150*	7.23 7.21	7.03	30.3
n-$C_4H_9NH_2$ . . .	125—127 (0.03)	1.5102	6.21 6.38	6.57	38.8
$NH_2CH_2CH_2OH$ . .	182—183.5 (0.05)	1.5245	6.78 6.70	6.96	45.5

*At 70° C

with amines involves opening of the ethylenic oxide ring. The equations are

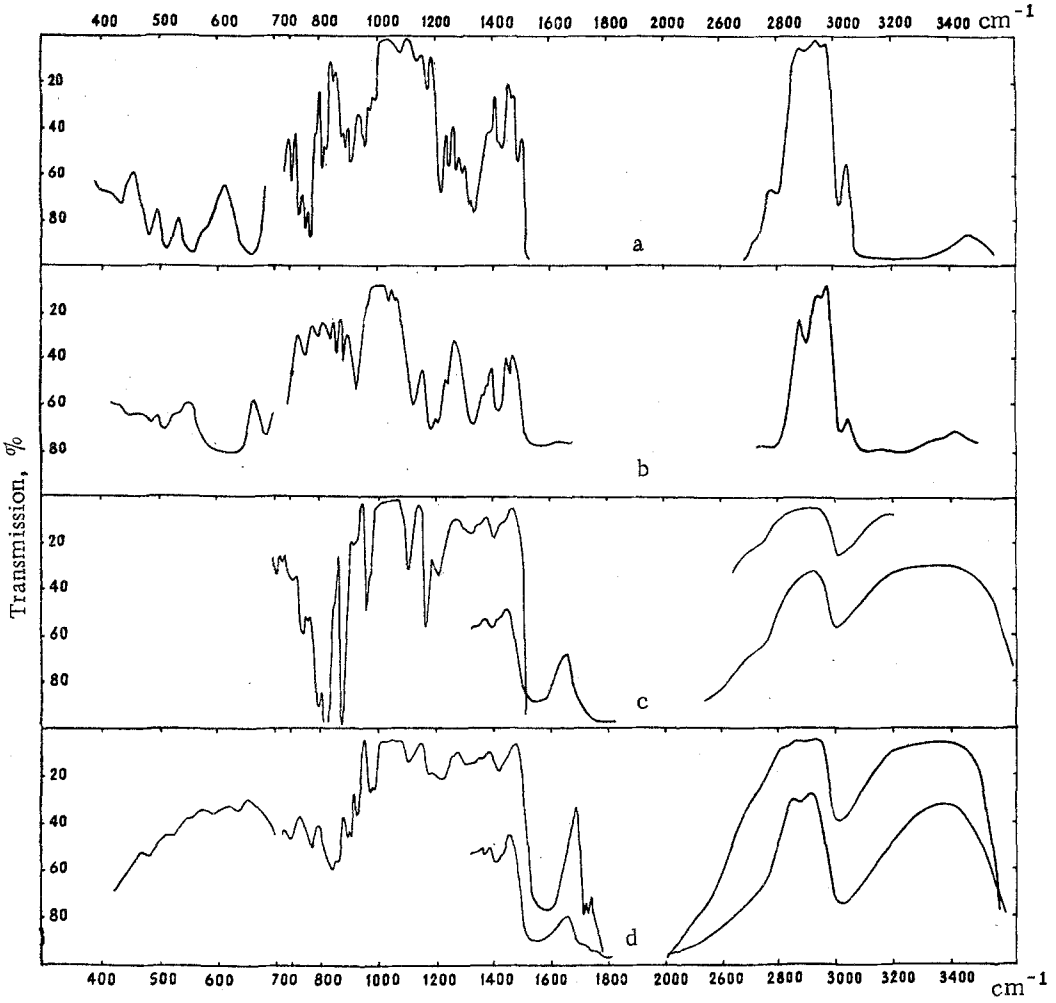


$R = CH_3$, C_2H_5, n-C_3H_7; $R' = C_2H_5$, n-C_3H_7; $R'' = n$-C_3H_7, n-C_4H_9, $OH—CH_2CH_2$.

The spectrogram of 1-vinylcyclohexene-3 dioxide [1] shows intense absorption at 3000 cm^{-1}, and a peak at γ_{max} 920 cm^{-1}, corresponding to the epoxy group, condensed with the six-membered ring. The ethylenic epoxy group is characterized by peaks at 3050, 1260 (average), and 870 cm^{-1} (strong), due to pulsating and asymmetrical vibrations of a monosubstituted epoxide ring.

It follows that addition to one or the other epoxide ring can be checked on the spectrograms, using the indications mentioned.

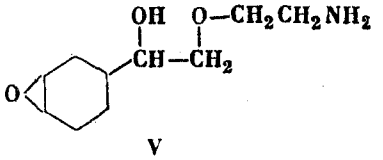
The figure below shows the spectrograms of reaction products from 1-vinylcyclohexene-3 dioxide with a) chlorodimethyl ether, b) dipropylphosphorous chloroanhydride, c) ethanolamine, and d) butylamine.



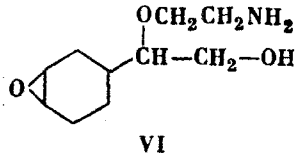
IR spectra: a) 1-epoxyethyl-3(or 4)-chloro-4(or 3)-methoxymethocyclohexane; b) dipropyl-[2-chloro-4(or 5)-epoxyethylcyclohexyl]phosphite; c) 2-(or 1)[3, 4-epoxycyclohexyl]diethanolamine; d) 2-(or 1)[3, 4-epoxycyclohexyl]-N butylethanolamine.

The spectra a and b show clearly the most convenient analytical indication of the epoxyethyl part of the molecule under consideration, viz., the peak 3050 cm^{-1} $\gamma_{as}CH_2$. This is because it is in the region very often devoid of absorption. The absorption bands at 870 and approximately 1250 cm^{-1}, mentioned above, can also be intensified. Thus in those cases the epoxyethyl part of the molecule is preserved, so that addition occurs at the oxide ring of the six-membered ring. In contrast to this, the spectra c and d do not have the just-mentioned indications, and it must be concluded that the corresponding reaction here took place with opening of the epoxyethyl ring. It was stated above that the epoxide ring condensed with the six-membered one, gives rise to absorptions at approximately 920 and 3000 cm^{-1}. However, in the particular case, due to overlap of bands of a number of groups, these regions cannot be used for analysis.

The absence of intense absorption peaks at 1600-1650 cm^{-1} (δ NH_2) in spectrum c (of ethanolamine-dioxide addition product) shows that there is no question of the presence of structures V and VI, containing primary amine groups, which are theoretically possible products of addition of ethanolamine to the dioxide.



V



VI

The structures of the products of addition of chloroethers and dialkylphosphorous chloroanhydrides to the dioxide were not determined as to whether the chlorine was at position 3 or position 4. Probably both structures are present, since there is no direct substitution at a carbon atom of the epoxide ring.

With regard to addition of amines to the dioxide, it was not ascertained whether structure IV had a primary or secondary alcohol group. Krasuskii's rule [8] leads to assignment of a secondary alcohol structure.

The spectrograms were observed with a UR-10 spectrophotometer. Slit program 4 was used, the scanning rate was 50 cm^{-1}/min, the complete oscillation cycle time 32 sec, amplifier transmission band width 2. The material was put between two KBr plates, and the layer thickness was not fixed.

Experimental

1-Vinylcyclohexene-3 dioxide was prepared by oxidizing 1-vinylcyclohexene-3 by B. A. Arbuzov's method [9], with acetyl hydroperoxide. It had bp 97-99° (9 mm), n_D^{20} 1.4782, d_4^{20} 1.0967.

Reaction of chloroethers with 1-vinylcyclohexene-3 dioxide.

Reaction with chlorodimethyl ether. 8.6 g (0.107 mole) chlorodimethyl ether was added to 10 g (0.071 mole) of the dioxide dissolved in 40 ml dry ether, followed by 0.08 g zinc chloride. A strong evolution of heat occurred, the mixture was cooled with water, and then refluxed for 2 hr 45 min. The precipitate (zinc chloride) was filtered off, and the ether distilled off from the filtrate. The excess chloroether was evaporated off under a water pump vacuum, and the residue twice distilled in a high vacuum. Yield 4.8 g material, bp 89-90° (0.015 mm); d_4^{20} 1.1704; n_D^{20} 1.4828. Found: C 54.68, 54.58; H 7.72, 7.73%, MR_D 53.83. Calculated for $C_{10}H_{17}O_3Cl$: C 54.42; H 7.76%; MR_D 53.78. 0.8 g of a fraction, bp 100-105° (0.012 mm), n_D^{20} 1.4860 was obtained, but it was not further investigated as the quantity was too small.

Reaction with chloromethylethyl ether. A mixture of 15 g (0.107 mole) dioxide and 17.4 g (0.184 mole) chloromethylethyl ether was cooled to +5°, and 0.1 g zinc chloride added. There was marked heating, and by cooling the temperature was kept below 40°. Then the reactants were heated at 40-45° for 1 hr 45 min, the precipitate filtered off, and the excess chloroether taken off as before. The residue was twice vacuum-distilled, to give 12.7 g substance bp 93-95° (0.01 mm); d_4^{20} 1.1275; n_D^{20} 1.4749. Found: C 56.62, 56.45; H 8.10, 8.32%; MR_D 58.61. Calculated for $C_{11}H_{19}O_3Cl$: C 56.28; H 8.16%; MR_D 58.39. 2.3 g of a high-boiling fraction [122-155° (0.012 mm)] was also separated, but the product of addition at both epoxide rings could not be isolated from it.

Reaction with chloromethylpropyl ether. 12 g (0.086 mole) dioxide was added dropwise to 14 g (0.129 mole) chloroether containing 0.1 g of anhydrous zinc chloride, the temperature being maintained at 5-10°, after which reaction was effected as described in the previous experiment. Two substances were isolated: 1) 2.6 g, bp 103-105° (0.009 mm); d_4^{20} 1.1241; n_D^{20} 1.4803. Found: C 57.94, 57.81; H 8.32, 8.29%; MR_D 62.94. Calculated for $C_{12}H_{21}O_3Cl$: 57.94; H 8.51%; MR_D 63.01; 2) 7.4 g, bp 125-126.5° (0.009 mm); d_4^{20} 1.1172; n_D^{20} 1.4747. Found: C 54.08, 54.11; H 8.23, 8.17%; MR_D 90.05. Calculated for $C_{16}H_{30}O_4Cl_2$: C 53.78; H 8.46%; MR_D 90.20.

Reaction with diethylphosphorous chloroanhydride. 16 g (0.102 mole) chloroanhydride was added dropwise to 16 g (0.114 mole) dioxide in 70 ml dry toluene, the temperature being kept, by cooling, at 27° or less, after which the mixture was heated for about 1 hr 30 min at 45-50°. The solvent was distilled off, and the reaction products twice distilled in a vacuum, to give 18.5 g substance, bp 103-104° (0.012 mm); d_4^{20} 1.1491; n_D^{20} 1.4790. Found: P 10.50, 10.33; Cl 11.91, 11.95%; MR_D 73.23. Calculated for $C_{12}H_{22}O_4PCl$: P 10.44; Cl 11.95%; MR_D 72.80.

Reaction with dipropylphosphorous chloroanhydride. 10.9 g (0.059 mole) chloroanhydride was added to 13 g (0.093 mole) dioxide in 60 ml dry toluene, and the reaction run under the conditions stated above. Yield 4.3 g substance, bp 110-112° (0.007 mm); d_4^{20} 1.1112; n_D^{20} 1.4764. Found: P 10.00, 9.77; Cl 10.50, 10.75%; MR_D 82.50. Calculated for $C_{14}H_{26}O_4PCl$: P 9.54; Cl 10.92%; MR_D 82.01.

In both experiments the reaction products were viscous liquids, soluble in organic solvents.

Reaction of amines with 1-vinylcyclohexene-3 dioxide.

Reaction with propylamine. Two drops of water were added to a mixture of 10 g (0.071 mole) dioxide and 8.4 g (0.142 mole) propylamine, and the mixture was heated at 60-70° for 4 hr 30 min. Excess amine was distilled off under a water pump vacuum, and the residue twice distilled in a vacuum. Yield 4.3 g substance, bp 121-122° (0.02 mm); n_D^{70} 1.5150. Found: N 7.23, 7.21%. Calculated for $C_{11}H_{21}O_2N$: N 7.03%.

Reaction with butylamine. Two drops of water were added to a mixture of 10.4 g (0.142 mole) butylamine and 10 g (0.071 mole) dioxide, and the whole heated for 45 min at 70-85°. Excess amine was removed in the way previously described, and the residue twice distilled in a vacuum. Yield 5.9 g substance, bp 125-127° (0.03 mm); n_D^{50} 1.5102. Found: N 6.21, 6.38%. Calculated for $C_{12}H_{23}O_2N$: N 6.57%.

Reaction with ethanolamine. Three drops of water were added to a mixture of 10 g (0.071 mole) dioxide and 8.6 g (0.141 mole) ethanolamine, and the whole heated for 1 hr 30 min at 70-80°, after which the ethanolamine was removed in the way previously described, and the residue distilled in a vacuum. Yield 6.5 g substance, bp 182-183.5° (0.05 mm); n_D^{50} 1.5245. Found: N 6.78, 6.70%. Calculated for $C_{11}H_{19}O_3N$: N 6.96%.

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Institute of Organic Chemistry
AS USSR, Kazan