STUDIES IN THE FIELD OF REACTIONS OF CYCLENE α-OXIDES

IV. Reaction of 1-Methylcyclopentene Oxide with Alcohols*

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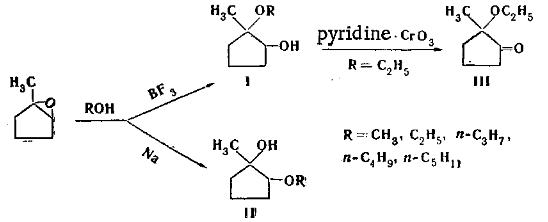
The reaction of 1-methylcyclopentene oxide with alcohols (methanol, ethanol, n-propanol and isopropanol, n-butanol, and n-pentanol) in the presence of Na and of BF_3 etherate has been described. The addition of alcohols in an alkaline medium takes place with the formation of secondary ethers of 1-methylcyclopentane-1,2-diol. In an acid medium, tertiary ethers of 1-methylcyclopentane-1,2-diol possibly contaminated with the secondary ethers are formed. In an acid medium, not only does addition take place but the initial oxide isomerizes into a carbonyl compound and to some extent forms trans-1-methylcyclopentane-1,2-diol. With isopropanol, in an alkaline medium the initial oxide is recovered and in an acid medium only the isomerization product is formed.

The order of addition of alcohols to α-oxides of unsymmetrical olefins has been studied in detail [2–6]. The reaction of unsymmetrical cyclene oxides with alcohols has been studied little [2, 3]. In a lecture at an All-Union Conference on Chemical Kinetics and Reactivity, A. A. Petrov reported the addition of methanol to methylcyclopentene and methylcyclohexene oxides in the presence of sodium methoxide and BF_3 etherate. In the presence of sodium methoxide, secondary ethers are formed and in the presence of BF_3 tertiary ethers [7]. However, we have not found an original paper in this question with a description of the experimental data and a discussion of the results. Earlier, one of us studied the reaction of methyl 4-methyl-Δ^3-cyclohexenecarboxylate oxide with alcohols in acid and alkaline media. The same characteristic was observed as in the case of oxides of unsymmetrical olefins. In an acid medium, as well as addition, isomerization of the oxide into a ketone took place [8].

In developing this work [8] we have studied the reaction of 1-methylcyclopentene oxide with methanol, ethanol, n-propanol and isopropanol, butanol, and pentanol in the presence of sodium alkoxides and of BF_3 etherate. Under these conditions the formation of the two addition products I and II (see table) might have been expected.



The order of addition of alcohols to 1-methylcyclopentene oxide has been studied in more detail in the case of ethanol. In this case, the reactions were carried out with larger amounts of reactants. The reaction of ethanol with 1-methylcyclopentene oxide in the presence of sodium ethoxide formed a substance with the structure II having mp 48.8° C. Under these conditions, all the other alcohols formed liquid products.

The reaction in the presence of BF_3 etherate took place in a more complex manner. As well as the addition product—the tertiary ether I, the constants of which are given in the table—2-methylcyclopentanone and, in an amount of 2.3–10.9% of the total weight of products obtained, trans-1-methylcyclopentane-1,2-diol were formed as by-products. The oxidation of the products of the addition of ethanol in the presence of BF_3 with the pyridine · CrO_3 complex [11] gave 2-ethoxy-2-methylcyclopentanone (III).

Tertiary and Secondary Ethers of 1-Methylcyclopentane-1, 2-diol

Initial alcohol	Structure of the ether	Bp, °C (mm)	d_4^{20}	n_D^{20}	Empirical formula	Found			Calculated			Yield, %
						C, %	H, %	MR_D	C, %	H, %	MR_D	
Methanol	I	87.2 (16)	1.0125	1.4606	$C_7H_{14}O_2$	64.25	10.80	35.26	64.56	10.84	35.69	83.7
	II	66–67 (9.5)	0.9967	1.4549		64.57	11.04	35.42				18.9
Ethanol	I	80–81 (8.5)	0.9798	1.4559	$C_8H_{16}O_2$	66.59	11.16	39.99	66.62	11.18	40.31	63.3
	II	72–74 (11)*	0.9505	1.4505		66.80	11.08	40.82				14.0
Propanol	I	94–95 (11)	0.9639	1.4555	$C_9H_{18}O_2$	68.27	11.52	44.59	68.31	11.46	44.73	62.7
	II	85–86 (11)	0.9405	1.4470		68.10	11.52	44.95				23.0
Butanol	I	108–110 (14)	0.9576	1.4569	$C_{10}H_{20}O_2$	69.31	11.85	48.96	69.72	11.70	49.35	61.2
	II	96–97 (10)	0.9355	1.4497		69.79	11.70	49.56				26.3
Pentanol	I	115–117 (9)	0.9455	1.4572	$C_{11}H_{22}O_2$	70.50	11.84	53.69	70.91	11.90	53.97	56.1
	II	70 (0.1)	0.9257	1.4500		70.81	11.75	54.09				15.0

*Mp 48.8° C

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*For part III, see [1].

The isomers I and II were studied spectroscopically. The IR spectra of these compounds have strong absorption maximum at 1075 and 1087 cm^{-1}, respectively, which must be ascribed to the C—OH vibrations. It is known that the frequency of this vibration is sensitive to the degree of substitution of the carbon atom and rises from primary to secondary and tertiary groups [12]. The difference in the frequencies given in our case agrees with this rule, thus confirming the position of the hydroxy group. In addition to this, both bands are located below the usual range of apperance of secondary and tertiary C—OH groups, which is in agreement with the fact of the lowering of $\nu_{C—OH}$ for cyclic alcohols. Furthermore, I and II, recorded in dilute CCl_4 solution have the ν_{OH} maxima at 3639 and 3623 cm^{-1}, respectively, which also confirms the position of the hydroxyl [12]. In the spectrum of I the maximum has a shoulder on the low-value side which may indicate contamination with the isomer II containing a tertiary hydroxy group.

In contrast to the oxide of a methylcyclohexene derivative, 1-methylcyclopentene oxide does not react with secondary alcohols (isopropanol). In an alkaline medium the initial oxide was recovered unchanged from the reaction mixture, and in an acid medium the only reaction product was a product of the isomerization of the oxide with constants corresponding to 2-methylcyclopentanone [13].

EXPERIMENTAL

The 1-methylcyclopentene oxide, obtained by the oxidation of 1-methylcyclopentene with acetyl hydroperoxide [14], had the following constants: bp 109°-110° C (758 mm); d_4^{20} 0.9200; n_D^{20} 1.4285, which are close to literature data [15].

Action of alcohols on 1-methylcyclopentene oxide in the presence of boron trifluoride etherate. A flask was charged with 0.1-0.2 mole of the oxide and 0.5-1.0 mole of an alcohol and, with vigorous stirring, BF_3 etherate (0.5-0.6% of the weight of the oxide) was cautiously added. The temperature of the mixture rose to 60°-65° C. Then it was heated for from 6 to 14 hr at the boiling point of the corresponding alcohol. After the alcohol had been driven off, the product was distilled in vacuum. The characteristics of the products are given in the table.

Action of ethanol. Twenty grams (0.2 mole) of the oxide and 0.1 ml of BF_3 etherate were added to 56.4 g (1.2 mole) of ethanol that had been redistilled over Na. The reaction mixture was heated for 5 hr 30 min. On distillation, the initial fractions were found to be contaminated with 2-methylcyclopentanone. The main product (15.2 g) was 2-ethoxy-2-methylcyclopentanol with bp 80°-81° C (9 mm), its other constants being given in the table. The residue after distillation yielded 2.1 g of trans-1-methylcyclopentane-1, 2-diol with mp 65° C. Found, %: C 62.00; H 10.42. Calculated for $C_6H_{12}O_2$, %: C 60.04, H 10.41. The substance gave no depression of the melting point in admixture with the diol obtained by the addition of water to 1-methylcyclopentene oxide. The 3, 5-dinitrobenzoate of the product of the addition of ethanol to the oxide had mp 61.5°-62° C (from petroleum ether). Found, %: C 52.99, H 5.62. Calculated for $C_{15}H_{14}N_2O_7$,, %: C 53.22; H 5.36.

Oxidation by the CrO_3 · pyridine complex of the product of the addition of ethanol to 1-methylcyclopentene oxide. The reaction was carried out [11] with 7.9 g (55 mM) of compound I in 85 ml of pyridine and 16.4 g of CrO_3 (0.16 mole) in 165 ml of pyridine. Two distillations of the product yielded 4.4 g of a ketone with the following constants: bp 73.3°-74° C (29 mm); d_4^{20} 0.9637, n_D^{20} 1.4392. Found, %: C 67.59; H 10.02; MR_D 38.80. Calculated for $C_8H_{14}O_2$, %: C 67.57, H 9.92%, MR_D 38.60. The semicarbazone had mp 183° C. Found, %: N 21.11. Calculated for $C_9H_{17}N_3O_2$, %: N 21.09.

Action of isopropanol. A mixture of 10 g (0.1 mole) of the oxide, 42 g (0.7 mole) of 2-propanol, and 0.05 ml of BF_3 etherate was heated for 19 hr. Two distillations of the products yielded a substance with bp 51°-52° C (37-34 mm), d_4^{20} 0.9342, n_D^{20} 1.4355. Found: MR_D 27.45. Calculated for $C_6H_{10}O$: MR_D 27.72. The semicarbazone of the reaction product had mp 175° C. Found, %: C 54.65, H 8.65, N 26.78%. Calculated for $C_7H_{13}N_3O$, %: C 54.17, H 8.44, N 27.07%. The 2, 4-dinitrophenylhydrazone had mp 155°-156° C.

Action of alcohols on 1-methylcyclopentene oxide in the presence of metallic sodium. Metallic sodium was added to 0.4-4.3 mole of the alcohol in an amount of 3% of the weight of the oxide taken. Then the oxide (0.1-0.6 mole) was added to the solution of the alkoxide in the alcohol and the reaction mixture was heated for from 10 to 17 hr at the boiling point of the alcohol concerned. After this, it was treated with water with subsequent salting out and extraction with ether. The product was distilled in vacuum. The characteristics of the products are given in the table.

The 3, 5-dinitrobenzoate of the product of the addition of ethanol had mp 94°-95° C (from petroleum ether). Found, %: C 53.26, H 5.50%. Calculated for $C_{15}H_{18}N_2O_7$, %: C 53.22, H 5.36%.

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