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SOME REACTIONS OF 3,7-DIMETHYL-2,3-EPOXYOCTANAL AND ITS DERIVATIVES

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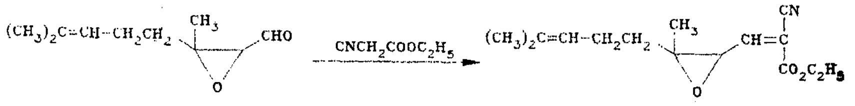
UDC 547.382.2'39.84:542.422.25:541.128

The oxide of citral (3,7-dimethyl-2,3-epoxioctanal) readily enters into the Knoevenagel condensation with the formation of the corresponding epoxydienecarboxylic acid. The epoxidation and addition of dichlorocarbene to similar epoxydienes proceeds at the double bond which does not adjoin the epoxide ring. The condensation of the acetal of citral oxide with ketones with the formation of 1,3-dioxolanes proceeds with the participation of the epoxide ring.

We have previously studied several reactions of citral oxide: the Darzan reaction, the Wittig reaction, acetalization, etc. [1]. Continuing the work in this field, we accomplished the Knoevenagel condensation of citral oxide (I) with ethyl cyanoacetate in the presence of catalytic amounts of piperidine; the condensation only affects the carbonyl group. An attempt to perform this reaction under the conditions of interphase catalysis (50% aqueous solution of NaOH, TEBA) proved to be unsuccessful.



I

II

Absorption bands in the region of 1610 (C=C), 860, 1240 (epoxide ring), 2180 (CN), and 1730 cm^{-1} (COOEt) were present in the IR spectrum of the resulting epoxydienic compound II. In the PMR spectrum, the signal of the aldehyde proton disappears, and the signals of the ethyl group appear; all the remaining signals are retained (see the Experimental section).

We performed the epoxidation of 6,10-dimethyl-5,6-epoxy-3-ethoxycarbonylundeca-3,9-dien-2-one (III), an analog of the diene II, using monoperphthalic acid according to the method of [2]. We performed the addition of dichlorocarbene to III using dichlorocarbene generated under the conditions of interphase catalysis by the method of [2]. We previously synthesized III by the condensation of citral oxide with acetoacetic ester. In both cases, the attack only proceeds at the isolated double bond which does not adjoin the epoxide ring and the acceptor groupings, and possesses higher nucleophilicity. The formation of the respective compounds IV and V is indicated by the disappearance of the signals of the vinyl group in the PMR spectrum and the appearance of the signals of the new epoxide ring [2.16 ppm for IV] or the dichlorocyclopropane ring [2.3 ppm for V], while the signals of all the remaining protons are retained. (Formula, below table, following page.)

On the reaction of the acetal of citral oxide VI, which was obtained by the acetalization of citral oxide with orthoformic ester according to [1], with ketones in the presence of an acid catalyst, the opening of the epoxide ring occurs with the formation of the correspond-

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Dnepropetrovsk State University, Dnepropetrovsk 320625. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 453-455, April, 1986. Original article submitted November 27, 1984.

0009-3122/86/2204-0370$12.50

TABLE 1

Compound	bp,*, °C	n_D^{20}	Found, %		Empirical formula	Calculated, %		Yield, %
			C	H		C	H	
VIIa	123—125	1,4782	67,5	10,5	$C_{17}H_{32}O_4$	68,0	10,7	46
VIIb	126—130	1,4839	69,5	10,2	$C_{19}H_{34}O_4$	69,9	10,5	44
VIIc	132—136	1,4828	70,5	10,0	$C_{20}H_{36}O_4$	70,5	10,7	52

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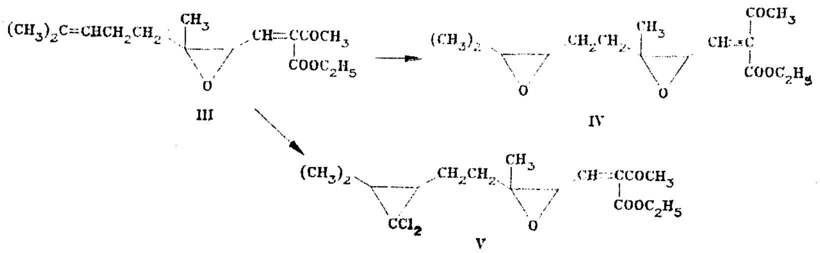
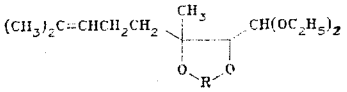
*Pressure 2 mm of Hg stem.



ing 1,3-dioxolanes VIIa-c. The absorption bands characteristic of the epoxide ring were absent from the IR spectra of (VIIa-c).



VIIa-c

VII a R=C(CH$_3$)$_2$; b R=C(CH$_2$)$_4$; c R=C(CH$_2$)$_5$

EXPERIMENTAL

The IR spectra were taken on a UR-20 instrument (in CCl_4). The PMR spectra were taken on a Varian HA-100 spectrophotometer (for solutions in CCl_4); the internal standard was HMDS. The UV spectra were taken on a Specord UV-vis instrument (in alcohol). The individuality of the substance was verified by the method of thin layer chromatography on plates of Silufol UV-254.

Ethyl 5,9-Dimethyl-4,5-epoxy-2-cyanodeca-2,8-dienoate (II). To 1.68 g (0.01 mole) of citral oxide I are added 1.13 g (0.01 mole) of ethyl cyanoacetate and 3 drops of freshly distilled piperidine. The reaction mixture is left to stand for 5-6 days at room temperature. It is dried with $MgSO_4$. Compound II is isolated with a yield of 1.55 g (59%) by distillation; it has bp 136.5°C (1 mm) and n_D^{20} = 1.4850. The UV spectrum, λ_{max} (log ε) is as follows: 245 nm (3.78). The PMR spectrum is as follows: 1.3 (6H, multiplet, 5-CH_3, OCH_2CH_3), 1.54-1.60 (6H, double doublet, 9,10-CH_3), 1.77-2.15 (4H, multiplet, 6,7-H), 2.67-3.09 (1H, multiplet, 4-H, J = 8 Hz), 4.15-4.23 (2H, multiplet, OCH_2CH_3), 5.03 (1H, multiplet, 8-H), and 7.21 ppm (1H, doublet, 3-H, J = 8 Hz). Found: C 68.4, H 8.0, and N 6.5%. $C_{15}H_{21}NO_3$. Calculated: C 68.5, H 8.0, and N 5.8%.

6,10-Dimethyl-5,6,9,10-diepoxy-3-ethoxycarbonylundec-3-en-2-one (IV). To the mixture of 5.6 g (0.02 mole) of 6,10-dimethyl-5,6-epoxy-3-ethoxycarbonylundeca-3,9-dien-2-one (III), 5.92 g (0.04 mole) of phthalic anhydride, and 0.06 g (0.01 mole) of urea in 20 ml of absolute ether are added 1.36 g (0.04 mole) of 87-90% hydrogen peroxide dropwise, maintaining the temperature at not greater than 20°C and with stirring. The reaction mixture is stirred at room temperature; control of the course of the reaction is by thin layer chromatography. The residue of phthalic acid is washed with ether and chloroform; the organic layer is washed with a solution of $NaHCO_3$ and water, and is dried. Compound IV is isolated with a yield of 2.08 g (50%); it has bp 142-145°C (1 mm) and n_D^{20} 1.4850. The UV spectrum, λ_{max} (log ε), is as follows: 220 (3.59) and 250 (3.52). The PMR spectrum is as follows: 0.9-1.44 (12H, multiplet, 6,10,11-CH_3, OCH_2CH_3), 1.53-1.89 (4H, multiplet, 7,8-H), 2.16 (1H, multiplet, 9-H), 2.47 (3H, singlet, 1-H), 2.89-9.23 (1H, multiplet, 5-H), 4.05-4.26 (2H, multiplet, OCH_2CH_3), and 6.25 ppm (1H, doublet, 4-H). Found: C 64.2 and H 8.0%. $C_{16}H_{24}O_5$. Calculated: C 64.7 and H 8.7%.

6,10-Dimethyl-5,6-epoxy-3-ethoxycarbonyl-9,10-dichloromethyleneundec-3-en-2-one (V). The solution of 5.6 g (0.02 mole) of compound III and 0.4 g of TEBA in 12.8 ml (0.16 mole) of chloroform is cooled to 10°C, and 24 ml of a 50% solution of NaOH together with 7 ml of methylene chloride are added with intense stirring. The mixture is kept for 3 h. It is extracted with ether and chloroform and then dried. Compound V is isolated with a yield of 3.04 g (42%); it has bp 144-147°C (1 mm) and n_D^{20} 1.5293. The UV spectrum, λ_{max} (log ε), is as follows: 207 (4.32) and 265 nm (4.30). The PMR spectrum is as follows: 1.08-1.30 (12H, multiplet, 6,10, 11-CH_3, OCH_2CH_3), 1.84-2.30 (5H, multiplet, 7,8-H, 9-H), 2.52 (3H, singlet, 1-H), 3.12 (1H, multiplet, 5-H), 4.04-4.26 (2H, multiplet, OCH_2CH_3), and 6.28-6.40 ppm (1H, multiplet, 4-H). Found: C 57.0, H 6.5, and Cl 20.0%. $C_{17}H_{24}Cl_2O_4$. Calculated: C 56.2, H 6.7, and Cl 19.5%.

Dioxolanes VIIa-c. To the mixture of 0.6 g of anhydrous ferric chloride and 15 ml of the ketone are added, with stirring, 5 g (0.021 mole) of the acetal of citral oxide VI. The mixture is heated for 5 h at 45-50°C, washed with a saturated solution of K_2CO_3, extracted, and dried. The dioxolanes VIIa-c are isolated by distillation. The constants of the dioxolanes are presented in Table 1.

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SYNTHESIS OF THE DIASTEREOMERIC 2-ARYL-1-CYCLOHEXYL-3-(2,3-EPOXYPROPIONYL)AZIRIDINES

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UDC 547.717.07

The reaction of cinnamoyloxiranes with an iodine–cyclohexylamine complex in the presence of an excess of amine led to a mixture of the four diastereomeric epoxypropionylaziridines the ratio of which depended on steric and electronic factors in the substrate and reactants.

The interaction of 2-methyl-2-cinnamoyloxiranes with iodine–methyl- or iodine–ethylamine complexes in aprotic solvents led to a mixture of the two diastereomeric trans-epoxypropionylaziridines differing in configuration at the chiral center of the epoxide ring [1]. In a continuation of the study of the influence of steric and electronic factors on the stereochemistry of the resulting epoxypropionylaziridines and with the aim of synthesizing new compounds in this series, the interaction of substituted cinnamoyloxiranes with an iodine–cyclohexylamine complex has been studied in the present work.

It has been established that in difference to the iodine–methyl- and iodine–ethylamine complexes the reaction of epoxyenes Ia-g with the iodine–cyclohexylamine complex in benzene orether led to a mixture of four or three diastereomeric 1-cyclohexyl-2-aryl-3-(2,3-epoxypropionyl)aziridines two of which had trans (IIa, b-VIIIa, b) and two (or one) cis configuration of the aziridine ring (IXa, b-XIIIa, b, XIVb, XVb).

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0009-3122/86/2204-0372$12.50