RESEARCH ON POLYFUNCTIONAL OXIDES

VIII.* PREPARATION, PMR SPECTRA, CONFIGURATIONS, AND CONFORMATIONS OF SOME 1,3-DIOXOLANES

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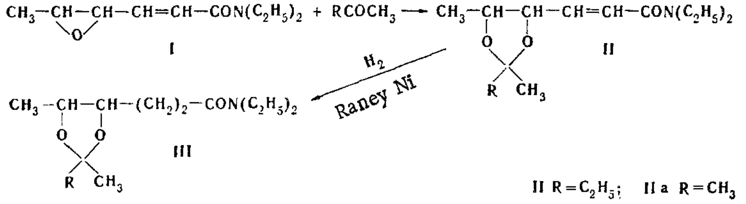
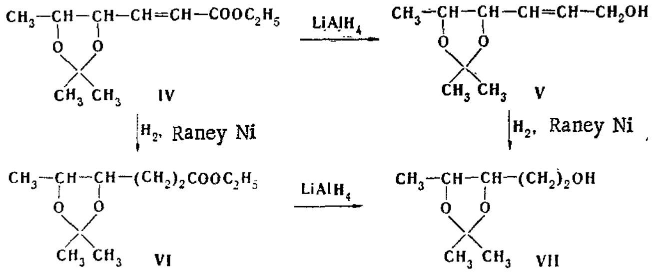
N,N-Diethylcarbamoyl-4,5-epoxy-2-hexenoic acid reacts with ketones in the presence of anhydrous $FeCl_3$ to give 2,2,4-trialkyl-5-[2-N,N-diethylcarbamoyl(vinylene)]-1,3-dioxolane. 2,2,4-Trimethyl-5-(1-propenyl-3-hydroxy)-1,3-dioxolane is formed in the reduction of 2,2,4-trimethyl-5-[2-carbethoxy(vinylene)]-1,3-dioxolane withlithium aluminum hydride.

Esters of 4,5-epoxy-2-hexenoic acid react with ketones in the presence of acid catalysts to give 2,2,4-trialkyl-5-[2-carbalkoxy(vinylene)]-1,3-dioxolanes [2]. In contrast to the esters, substituted amides of 4,5-epoxy-2-hexenoic acid react with ketones in the presence of a large excess of $FeCl_3$. We have carried out the reaction of N,N-diethylcarbamoyl-4,5-epoxy-2-hexenoic acid with acetone and methyl ethyl ketone:



II $R=C_2H_5$; IIa $R=CH_3$

The IR spectra of II contain absorption bands at 1025-1055 cm^{-1}, which are due to vibrations of C—O—C bonds, but do not contain the absorption bands of the epoxide ring (840 cm^{-1}). Compounds II are readily hydrogenated by hydrogen in the presence of Raney Ni to 2,2,4-trialkyl-5-[2-N,N-diethylcarbamoyl-(ethyl)]-1,3-dioxolanes (III).



The reduction of 2,2,4-trimethyl-5-[2-carbethoxy(vinylene)]-1,3-dioxolane (IV) with lithium aluminum hydride gave 2,2,4-trimethyl-5-(1-propenyl-3-hydroxy)-1,3-dioxolane (V), which is hydrogenated by hydrogen over Raney Nickel to saturated alcohol VII, which is also obtained by alternative synthesis from ester VI.

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*See [1] for communication VII.

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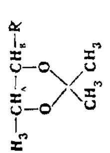
TABLE 1. PMR Spectra of 1,3-Dioxolanes


$CH_3-CH_A-CH_B-R$ (1,3-dioxolane ring with $C(CH_3)_2$)

Compound	R	δ, ppm					δ, ppm				J, Hz					
		$C\langle^{CH_3}_{CH_3}$	CH_3CH	H_A	H_B	H_C	H_D	CH_3	CH_2	OH	CH_3H_A	H_AH_B	H_BH_C	H_CH_D	H_BH_D	CH_3CH_2
IIa	$H_CC{=}CH_D-CON(C_2H_5)_2$	1,35 1,48	1,18	4,38	4,69	6,61	6,34	1,26	3,43	—	6,3	6,3	4,0	15,0	1,4	6,5
IIIa	$CH_{2C}CH_{2D}-CON(C_2H_5)_2$	1,25 1,34	1,15	4,25	3,96	1,71	2,39	1,20	3,35	—	6,6	6,0	4,0	M	M	6,6
V	$CH_C{=}CH_D-CH_2OH$	1,30 1,45	1,05	3,54	4,22	4,70	4,60	—	4,00	2,58	6,3	6,3	6,0	M*	M	—
VII	$CH_{2C}CH_{2D}CH_2OH$	1,30 1,41	1,05	4,12	3,96	1,50	1,50	—	3,54	3,15	6,5	6,5	M	M	M	—

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* The abbreviation "M" indicates a complex multiplet.

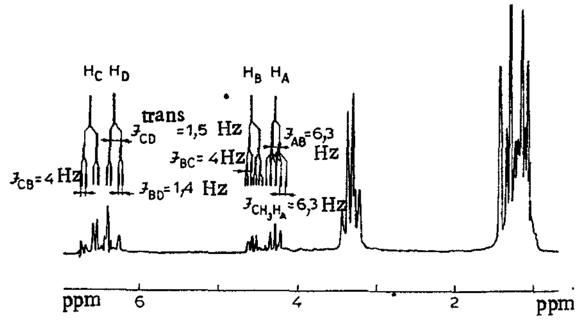

Fig. 1. PMR spectrum of IIa.

The PMR spectra (Table 1) confirm the assigned structure for all of the 1,3-dioxolanes obtained. The spectrum of IIa is presented in Fig. 1 as an example. The magnitude of the J_{CD} vicinal constant (15 Hz) in the spectrum of IIa indicates trans orientation of the coupling protons attached to the double bond. According to the Karplus–Conroy angular correlation [3], a J_{CB} constant of 4 Hz corresponds to the gauche conformation between the two coupling H_B and H_C protons.

The configuration of substituents relative to the 1,3-dioxolane ring is usually established from the coupling constants of the H_A and H_B vicinal protons. It is seen from Table 1 that these protons couple with a constant of 6.3 Hz. It is known [4] that the trans constant is lower than the cis constant for small rings, including five-membered rings. We therefore assume that the J_{AB} constant of 6.3 Hz indicates trans orientation of the substituents.

Let us consider the conformation of the diethylcarbamoyl group relative to the unsaturated bond. The H_C and H_D protons are nonequivalent ($\Delta\delta_{CD}$ = 0.27 ppm), and the H_C proton (Fig. 1) is shifted to weak field as a consequence of the paramagnetic anisotropic effect of the carbonyl group; this is possible if it is not in conjugation with the double bond. A consequence of this is the s-cis conformation of the unsaturated fragment.

The structure of the saturated 1,3-dioxolanes (IIIa) was also established by means of the PMR spectra. It can be seen from Table 1 that the position of the substituents relative to the 1,3-dioxolane ring is retained during reduction, as indicated by the almost equal J_{AB} values, but the chemical shifts of the H_A and H_B protons are inverted because of removal of the paramagnetic effect of the double bond.

EXPERIMENTAL

The PMR spectra* of 1% solutions of the compounds in CCl_4 were recorded with a Varian HA-100D spectrometer at 100 MHz and with a Varian T-60 spectrometer at 60 MHz at room temperature. Stabilization of the resonance conditions was accomplished from the line of tetramethylsilane. The IR spectra of solutions of the compound in CCl_4 were recorded with a UR-10 spectrometer. Gas–liquid-chromatographic analysis was performed with an LKhM-7a chromatograph with a 1-m long

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column filled with Chromosorb W, 18% Apiezon L, and 5% polyethylene glycol distearate; the column temperature was 120-140°, and the carrier gas was N_2.

N,N-Diethylcarbamoyl-4,5-epoxy-2-hexenoic acid (I) and 2,2,4-trimethyl-5-[2-carbethoxy(vinylene)]-1,3-dioxolanes (IV) were obtained by the method in [2, 5].

2,4-Dimethyl-2-ethyl-5-[2-N,N-diethylcarbamoyl(vinylene)]-1,3-dioxolane (II). This compound was obtained from 23.6 g (0.032 mole) of methyl ethyl ketone and 4 g (0.021 mole) of N,N-diethylcarbamoyl-4,5-epoxy-2-hexenoic acid in the presence of 3.85 g (0.023 mole) of anhydrous ferric chloride by heating to 45-50° for 12 h. The mixture was treated with potassium carbonate and worked up to give 1.72 g (31%) of the dioxolane with bp 147-150° (2 mm) and n_D^{20} 1.4857. Found %: C 64.1; H 9.8; N 5.5. $C_{14}H_{25}NO_3$. Calculated %: C 63.9; H 9.5; N 5.2.

2,4-Dimethyl-2-ethyl-5-[2-N,N-diethylcarbamoyl(ethyl)]-1,3-dioxolane (III). This compound was obtained by reduction of 1 g (0.030 mole) of II with hydrogen over Raney nickel under standard conditions. The yield of product with bp 118-120° (2 mm) and n_D^{20} 1.4511 was 0.6 g (61%). Found %: C 67.1; H 11.3; N 5.2. $C_{14}H_{27}NO_3$. Calculated %: C 66.4; H 9.0; N 5.4.

2,2,4-Trimethyl-5-[2-N,N-diethylcarbamoyl(vinylene)]-1,3-dioxolanes (IIa and IIIa). These compounds were obtained by the method in [6].

2,2,4-Trimethyl-5-(1-propenyl-3-hydroxy)-1,3-dioxolane (V). A solution of 2.14 g (0.01 mole) of IV in 10 ml of ether was added dropwise to 0.4 g (0.01 mole) of $LiAlH_4$ in 40 ml of dry ether at such a rate that the ether refluxed gently. The mixture was heated up to the boiling point and treated with a small amount of water. The precipitate was removed by filtration and washed several times with ether and alcohol. The ether–alcohol extracts were dried with $MgSO_4$. The solvents were removed, and the residue was vacuum distilled to give 0.7 g (40%) of the dioxolane with bp 98-100° (3 mm), n_D^{20} 1.4540, and d_4^{20} 1.0231. Found %: C 62.5; H 10.2; MR_D 49.04. $C_9H_{16}O_3$. Calculated %: C 62.7; H 10.3; MR_D 47.04. IR spectrum: 1650 (C=C), 3450 (OH), and 1080-1090 (C–O–C) cm^{-1}.

2,2,4-Trimethyl-5-(3-propylhydroxy)-1,3-dioxolane (VII). A) A 2.16-g (0.01 mole) sample of VI was reduced with 0.4 g (0.01 mole) of $LiAlH_4$ by heating in 30 ml of dry ether. Workup of the mixture gave 1 g (60%) of dioxolane with bp 96° (5 mm), n_D^{20} 1.4430, and R_f 0.18 [ether–hexane (3:1)]. Found %: C 62.3; H 10.1. $C_9H_{18}O_3$. Calculated %: C 62.0; H 10.3.

B. A 1.72-g (0.01 mole) sample of V was reduced with hydrogen in the presence of 1.5 g of Raney nickel in 20 ml of alcohol under standard conditions until 225 ml of hydrogen had been absorbed. Distillation gave 1.4 g (80%) of the dioxolane with the physical constants presented above. Gas–liquid-chromatographic analysis of a mixture of the substances obtained by the two different methods gave one peak; this confirmed that they were identical. IR spectrum: 3450 (OH) and 1080-1090 (C–O–C) cm^{-1}.

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