2-DICHLOROMETHYLENE-1,3-DIOXOLANE IN THE DIELS–ALDER REACTION WITH α,β-UNSATURATED ALDEHYDES

A. N. Mirskova, T. S. Proskurina,
V. K. Voronov, and A. S. Atavin

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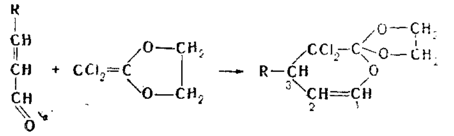
1,4,9-Trioxa-5,5-dichlorospiro[4,5]-7-decene and 1,4,9-trioxa-6-methyl-5,5-dichlorospiro-[4,5]-7-decene were synthesized by condensation of 2-dichloromethylene-1,3-dioxolane with acrolein and crotonic aldehyde.

Cyclic acetals of dichloroketene display a dual reactivity that is due to polarization of molecules with the formation of a heteroenoid system of conjugated bonds. Depending on the attacking agent, they react with retention of the dioxolane ring [1] or with cleavage of it at the C–O bond [2].

In the present research we have investigated the condensation of 2-dichloromethylene-1,3-dioxolane (I) with acrolein and crotonic aldehyde. The reaction proceeds on heating to 100-150°C to give dihydropyran derivatives with retention of the 1,3-dioxolane ring:



I

II, III

II R=H; III R=CH_3

Condensation with acrolein proceeds more readily than with ketene dimethylacetal [3]. In the case of crotonic aldehyde, more severe conditions are required to obtain a high yield of the adducts, but an increase in the heating time and temperature leads to partial decomposition and resinification.

The stretching vibrations of the cis-ethylene bond in the IR spectra of II and III lie at 1647 and 1662 cm^{-1}. A series of bands at 1080-1252 cm^{-1} characterizes the acetal grouping of the dioxolane ring. The absence of a carbonyl group band in the spectrum is evidence for 1,4-addition.

Allylic constant $J_{13} > J_{23}$ in the PMR spectrum of III. It is known [4] that J_{all} ranges from 1.3 to 3.1 Hz if $\theta \simeq 60$-110° (Scheme 1). At the same time, according to the Karplus equation, $J_{23} = 1.8$ Hz if $\varphi = 65°$

TABLE 1. Parameters of the PMR Spectra of 1,4,9-Trioxa-5,5-spiro-[4,5]-7-decenes

Compound	Chemical shift, δ, ppm					Spin–spin coupling constant, Hz (absolute values)
	1-H	2-H	3-H	4-H	CH_2—CH_2	
II	6,13 m*	4,72 m	3,02 g		4,25 m	$J_{12}=6{,}0$; $J_{13}=1{,}7$; $J_{23}=3{,}6$
III	5,99 m	4,41 g	3,08 m	1,24 d	4,19 m	$J_{12}=6{,}2$; $J_{13}=2{,}8$; $J_{23}=1{,}8$; $J_{34}=7{,}0$

*Abbreviations: m, multiplet; q, quartet; d, doublet.

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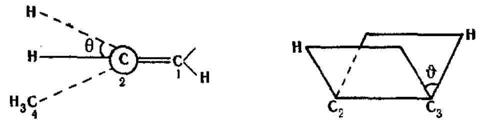
(Scheme 2). Analysis of the structure of the molecule with Briegleb–Stuart models showed that the hexene and dioxolane rings are in mutually perpendicular planes. Moreover, free rotation of the CH_3 group occurs if θ proves to be greater than half the angle for the sp^3-hybridized carbon atom (about 60-65°).



EXPERIMENTAL

The PMR spectra of CCl_4 solutions of the compounds were recorded with a BS487B spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The integral intensities of the signals were calculated with an accuracy up to 2%. The IR spectra were recorded with a UR-10 spectrometer.

Anhydrous and freshly distilled acrolein [bp 51-52° (720 mm), n_D^{20} 1.3990] and crotonic aldehyde [bp 101-102° (720 mm), n_D^{20} 1.4380] were used. The 2-dichloromethylene-1,3-dioxolane (I) was obtained by the method in [5] and had the following constants: bp 72-73° (2 mm) and mp 55-56° (mp 55.5-57° [5]). IR spectrum: 1710, 1104, 1103, and 1150 cm^{-1}.

1,4,9-Trioxa-5,5-dichlorospiro[4,5]-7-decene (II). A mixture of 11.65 g (0.07 mole) of I and 4.8 g (0.07 mole) of acrolein was heated in a sealed ampule at 100° for 8 h. Distillation of the contents yielded 11 g (68%) of II with bp 104-105° (6 mm), d_4^{20} 1.4100, and n_D^{20} 1.5020. Found, %: C 39.8; H 3.8; Cl 33.7; MR_D 44.17. $C_7H_8Cl_2O_3$. Calculated, %: C 39.9; H 3.8; Cl 33.7; MR_D 44.54. Chromatography in a thin layer on activity II aluminum oxide gave one spot with R_f 0.5 [benzene–hexane (5 : 1), development with iodine].

1,4,9-Trioxa-6-methyl-5,5-dichlorospiro[4,5]-7-decene (III). A 4 g (0.05 mole) sample of crotonic aldehyde was added to 8 g (0.05 mole) of I, and the mixture was heated in a sealed ampule at 150° for 12 h. Distillation yielded 8.1 g (70%) of III with mp 65° (from benzene) and bp 125° (3 mm). Found, %: C 42.6; H 4.3; Cl 31.5. $C_8H_{10}Cl_2O_3$. Calculated, %: C 42.7; H 4.4; Cl 31.5.

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