SYNTHESIS OF 1,3-DIOXOLANES FROM ACETYLENIC 1,2,5-TRIOLS

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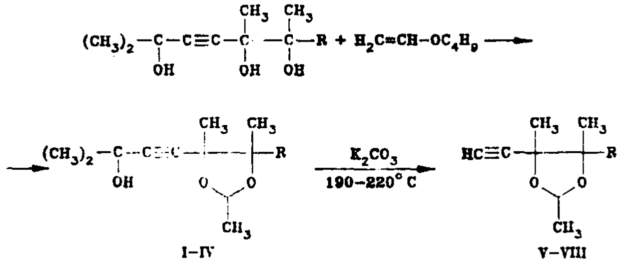
The reaction of acetylenic 1,2,5-triols with vinyl butyl ether in the presence of catalytic amounts of hydrochloric acid leads to the formation of 4-(3-hydroxy-1-alkynyl)-1,3-dioxolanes.

Until now ethynyl-substituted 1,3-dioxolanes have been little studied. It was shown [1, 2] that the reaction of acetylenyl-substituted α-oxides with carbonyl compounds leads to the formation of 4-ethynyl-1,3-dioxolanes. 4-Ethynyl-1,3-dioxolane was also obtained from 1,2-butynediol and benzaldehyde in the presence of p-toluene-sulfonic acid [3].



I, V R=CH_3; II, VI R=C_2H_5; III, VII R=C_3H_7; IV, VIII R=C_4H_9

A convenient method is proposed in the present work for the synthesis of alkynyl-1,3-dioxolanes, by which these compounds can be obtained with consistent and high yields (65... 85%) from acetylenic 1,2,5-triols and vinyl butyl ether in the presence of catalytic amounts of hydrochloric acid in toluene (Table 1).

The structure of the 1,3-dioxolanes I-IV obtained was confirmed by spectral data, and their purity by GLC. Dioxolanes I-IV were converted to 4-ethynyl-1,3-dioxolanes (V-VIII) by also be obtained in a 32...57% yield without isolation of the intermediate compounds I-IV. thermal alkaline splitting (Table 1). Dioxolanes V-VIII can also be obtained in a 32...57% yield without isolation of the intermediate compounds I-IV.

EXPERIMENTAL

The IR spectra were run on a UR-20 spectrophotometer in a thin layer. The purity of the dioxolanes was monitored by GLC on a Chrom-3 chromatograph, using a catharometer detector, a 2400 × 6 mm column (temperature 200°C), a polychromed solid carrier, 5% PMS-100 as the liquid stationary phase, and helium as carrier gas (80...85 ml/min).

General Method for the Preparation of 1,3-Dioxolanes I-IV. A mixture of 0.026 mole of the acetylenic 1,2,5-triol, 0.026 mole of vinyl butyl ether, 10 ml of toluene and 0.005 mole of concentrated hydrochloric acid is heated for 1 h 30 min at 110°C. The reaction mixture is distilled.

1-Ethynyl-1,3-dioxolanes (V-VIII). A mixture of 0.012 mole of dioxolane I-IV and 0.005 mole of potassium carbonate is rapidly heated to 190...220°C to the appearance of vapors of the splitting products. The mixture is then distilled dried over magnesium sulfate, and the 1,3-dioxolanes V-VIII are isolated by repeated distillation.

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TABLE 1. Characteristics of 1,3-Dioxolanes I-VIII

Compound	bp, °C (mm Hg)	d_4^t	n_D^t	IR spectrum, ν, cm⁻¹	Found, %		Empirical formula	Calculated, %		Yield, %
					C	H		C	H	
I	112 ... 115 (5)	$0{,}9809^{26}$	$1{,}4553^{26}$	2220 (C≡C), 3400 (OH), 1060 ... 1240 (C—O—C)	67,4	9,7	$C_{12}H_{20}O_3$	67,9	9,4	77
II	110 ... 112 (7)	$0{,}9962^{20}$	$1{,}4625^{20}$	2210 (C≡C), 3400 (OH), 950 ... 1200 (C—O—C)	69,3	9,9	$C_{13}H_{22}O_3$	69,0	9,7	88
III	110 ... 115 (5)	$0{,}9981^{18}$	$1{,}4600^{18}$	2220 (C≡C), 3410 (OH), 910 ... 1200 (C—O—C)	70,3	9,7	$C_{14}H_{24}O_3$	70,0	10,2	65
IV	125 ... 128 (6)	$0{,}9890^{18}$	$1{,}4580^{18}$	2200 (C≡C), 3400 (OH), 950 ... 1200 (C—O—C)	70,8	10,0	$C_{15}H_{26}O_3$	71,1	9,8	71
V	115 ... 120	$0{,}9463^{17}$	$1{,}4280^{17}$	3270, 2220 (HC≡C), 950 ... 1200 (C—O—C)	70,1	9,1	$C_9H_{14}O_2$	70,4	9,1	80
VI	178	$0{,}9416^{18}$	$1{,}4370^{18}$	3200, 2210 (HC≡C), 1010 ... 1220 (C—O—C)	71,4	9,5	$C_{10}H_{16}O_2$	71,2	9,5	79
VII	64 ... 67 (6)	$0{,}9348^{25}$	$1{,}4421^{25}$	3200, 2200 (HC≡C), 1010 ... 1220 (C—O—C)	72,5	9,9	$C_{11}H_{18}O_2$	72,4	9,7	75
VIII	65 ... 68 (6)	$0{,}9342^{18}$	$1{,}4441^{18}$	3200, 2200 (HC≡C), 950 ... 1200 (C—O—C)	73,5	10,2	$C_{12}H_{20}O_2$	72,9	10,5	87

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^{15}N CHEMICAL SHIFTS IN AZIRIDINES

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For a number of 1-substituted aziridines and also some 1,2-disubstituted aziridines it has been shown that electron-donating substituents on the nitrogen atom produce a downfield shift of the ^{15}N resonance. The ^{15}N chemical shifts of aziridines correlate with the ^{15}N shifts in N,N-dimethylamines and primary amines as well as with the ^{17}O shifts in oxiranes. A correlation is also observed between the ^{15}N chemical shifts and the electronegativity of the substituents on the nitrogen atom.

The ^{15}N NMR spectra of 1-substituted aziridines have received very little study. The chemical shifts of 1-alkyl-substituted aziridines [1], 1-arylaziridines [2], and certain aziridinephosphamides [3] have been reported. However, there has been no data up to now on aziridines that contain alkyl radicals with acceptor substituents on the nitrogen atom. In this connection we have obtained the ^{15}N NMR spectra of a number of 1-substituted aziridines synthesized at the Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, as well as those of some previously unstudied 1,2-disubstituted aziridines (Table 1).

The ^{15}N chemical shifts of 1-substituted aziridines, as in the case of the 2-substituted aziridines that we previously studied [4], give a satisfactory correlation with the E_S steric and σ^* induction constants of Taft.* Based on the data of [1]:

$$\delta_N = -378.9 - 14.0\sigma^* - 9.4E_s \quad (r = 0.942;\ s = 3;\ n = 15). \qquad (1)$$

For 2-substituted aziridines (including the data of [4]):

$$\delta_N = -379.7 + 1.9\sigma^* - 5.5E_s \quad (r = 0.926;\ s = 4.5;\ n = 13). \qquad (2)$$

The larger steric effect on the shielding of nitrogen atoms in 1-substituted aziridines in comparison with 2-substituted derivatives is evidently due to the fact that in the latter the substituent is remote from the center in question. The difference in sign of the angular coefficient for the inductive effect in the two correlations is worthy of note. Substituents that are joined directly to a nitrogen atom shift the ^{15}N resonance signal upfield as their electron-acceptor properties increase [equation (1)], while substituents separated by one bond, on the other hand, cause deshielding [equation (2)]. This is due to the alternation in substituent effect on the electron density in the vicinity of the nitrogen atom in relation to the number of bonds. In order to compare the inductive effects at both positions of the heterocycle we took a number of 1-methyleneaziridines $(CH_2)_2NCH_2R$ in which the substituent acts through the methylene bridge. In this case

$$\delta_N = -370.4 + 2.0\sigma^* - 1.0E_s \quad (r = 0.965;\ s = 6.1;\ n = 14). \qquad (3)$$

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*Here and subsequently the data of [1-4] are also used in the correlations. The value of σ^* and E_S are taken from [5, 6].

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