SYNTHESIS AND PROPERTIES OF FURANYL 1,3-DIOXOLANES.
1. IMPROVED SYNTHESIS METHOD

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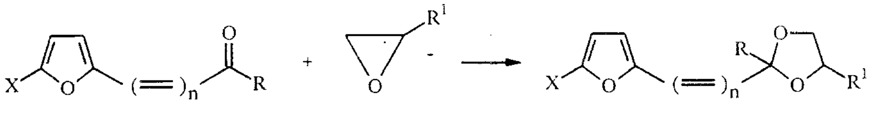
We obtained previously known and unknown furanyl 1,3-dioxolanes by the reaction of the corresponding oxiranes and the furanyl keto derivatives in the presence of Lewis acids by an improved method.

The present series of publications proposes the systematic presentation of the results of a study of the synthetic reactions and properties of 1,3-dioxolanes containing a furan ring and different functional groups in the substituted fragment. Generation of polysubstituted 1,3-dioxolanes of the indicated type allows access to new biologically-active materials and highly-reactive intermediates for organic synthesis. The literature describes a wide variety of furanyl 1,3-dioxolanes, chiefly obtained by the reaction of the corresponding diol with keto compounds in the presence of proton acids [1-6]; furyl-substituted α,β-unsaturated aldehydes with diols formed a mixture of reaction products which was difficult to separate [7]. The known synthesis of furanyl 1,3-dioxolanes from unsaturated aldehydes and silanyl glycol ethers [7] is limited in application by the difficult accessibility of the indicated ethers. The synthesis of 1,3-dioxolanes based on the reaction of methyl- and ethyl furyl ketones with epichlorohydrin in CCl_4 solution in the presence of tin tetrachloride is described [8], however, this reaction did not receive widespread use in the syntheses of furanyl 1,3-dioxolanes. At the same time, the use of commercially-available oxiranes in the synthesis of furanyl 1,3-dioxolanes presents considerable promise. In this regard, we established optimum conditions allowing the synthesis from oxiranes and furyl keto derivatives of a variety of substituted 1,3-dioxolanes containing furan fragments. In order to establish an optimal regime for the synthesis, we studied the influence on the furanyl 1,3-dioxolane yield of the addition of different Lewis acids, mole ratios of reagents, solvents, catalysts, and means of removal of the latter after completion of the reaction. It was established that low yields of dioxolanes were achieved in the presence of boron trichloride etherate (Table 1). The optimal mole ratio of oxirane, carbonyl compound, carbon tetrachloride and catalyst was 2:1:(8-10):0.05. The reaction was carried out at 40-45°C until complete consumption of the furanyl ketone, which was monitored by TLC. In contrast to the method of [8], all of the catalyst was introduced at the beginning of the process, and at the completion of the reaction it was removed by the addition of hydrated $Na_2CO_3 \cdot 10H_2O$ or diethyl ether, and the reaction products were isolated in vacuum, avoiding extraction. Introduction of the furanyl fragment in the 1,3-dioxolanes was accomplished by using either the corresponding furanyl carbonyl compound or the furfurylglycidyl ether. Compounds IIa-j were synthesized, of which IIa-c have not been described earlier. All the syntheses were based upon the easy accessibility of the commercial tin (IV) chloride in CCl_4 solution.



I a-j

II a-j

I, II a X = H, n = 1, R = CH_3, R^1 = CH_2Cl; b X = H, n = 0, R = H, R^1 = $CH_2OCC_6H_4CH_3$; c X = H, n = =0, R = H, R^1 = 2-furyl-CH_2OCH_2-; d X = H, n = 0, R = H, R^1 = CH_2Cl; e X = H, n = 1, R = H, R′ = =CH_2Cl; f X = CH_3, n = 0, R = H, R^1 = CH_2Cl; g X = Br, n = 0, R = H, R^1 = CH_2Cl; h X = Cl, n = 0, R = H, R′ = CH_2Cl; i X = NO_2, n = 0, R = H, R^1 = CH_2Cl; j X = CH_3, n = 0, R = CH_3, R^1 = CH_2Cl

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TABLE 1. Influence of Lewis Acid on the Yield of 1,3-Dioxolanes in the Reaction of Furanyl Carbonyl Compounds with Epichlorohydrin

Compound	Oxo-compound	Yield, %				
		$BF_3 \cdot Et_2O$	$SnCl_4$	$SnBr_4$	SnI_4	$ZnCl_2$
IId	Furfural	82	79	65	73	45
IIa	Methyl-2(2-furyl)ethenyl ketone	75	68	—	—	41

TABLE 2. Physicochemical Characteristics of Furyl 1,3-Dioxolanes IIa-c

Compound	Empirical formula	bp, °C (pressure, Pa)	n_D^{20}	d_{20}^{4}, g/cm^3	Yield, %
IIa	$C_{11}H_{13}ClO_3$	146...148 (798)	1,5295	1,1820	79
IIb	$C_{14}H_{16}O_3$	191...193 (665)	1,5400	1,2835	54
IIc	$C_{13}H_{14}O_5$	216...218 (798)	1,5000	1,5370	43

TABLE 3. Spectral Characteristics of Compounds IIa-c

Compound	IR spectrum, cm^{-1}	^{1}H NMR spectrum, ppm						
		dioxolane			furan			other substituents
		2-H,	4-H,	5-H,	5-H, s	4-H, s	3-H, s	
IIa	1250, 1520, 1430, 720 (furan), 1150, 1080, 1090, 1020 (dioxolane), 1650	—	4,0	3,9	7,25	6,21	6,23	3,8 (d, CH_2Cl); 5,95 d, 6,31 (CH=CH); 1,9 (2 s, CH_3, E+Z)
IIb	1600, 1510, 1360, 935, 890 (furan), 1155, 1100, 1090, 1000 (dioxolane, 3080, 1600, 1580, 1450 (Ar)	5,8	4,0	3,9	7,24	6,19	6,22	7,1 (m, Ph); 3,8 (d, CH_2O); 2,1 s, CH_3)
IIc	1440, 1255, 980, 720 (furan), 1155, 1080, 1020, 1010 (dioxolane)	5,9	4,1	3,92	7,3	6,22	6,24	3,36 (d, 4H), 7,22 s, 6,1 s, 6,14 s (furan)

The characteristics of the new compounds IIa-c are presented in Table 2. Their homogeneity and structure was confirmed chromatographically and spectrally (Table 3). The yields of the earlier-described 1,3-dioxolanes IId-j ranged between 50 and 95%: their physicochemical constants and spectral characteristics corresponded with literature data [1-3, 6].

The IR spectra of all the synthesized compounds did not show an absorption band for the C=O group in the 1660 cm^{-1} region belonging to the starting carbonyl compound. The spectra of compounds IIa and IId retained the signal for the C=C in the 1645 cm^{-1} region, and all spectra showed characteristic bands for the furan and dioxolane rings (Table 3). The ^{1}H NMR spectra had signals for the furanyl protons in the 7.3-7.21 ppm and 6.8-6.21 ppm regions, and signals for the 1,3-dioxolane ring in the 3.8-6 ppm region. The protons and methyl groups for the secondary carbon atoms of the dioxolane rings of compounds IIa-k were two signals with splitting of 4 Hz and 2 Hz, resulting from the presence of the cis- and trans-isomers, which correlates with the literature data for 1,3-dioxolanes of other series [9].

EXPERIMENTAL

IR spectra were obtained with a Specord IR-71 instrument. The ^{1}H NMR spectra were recorded as 10% solutions in CCl_4 with a Tesla BS-467 (60 MHz) instrument, using TMS as internal standard. The course of the reactions and the purity of the products was monitored on Silufol UV-254 plates in the systems toluene–ethanol = 20:3 and hexane–ethyl acetate = 6:1, with visualization by iodine vapor.

Elemental analysis data for C, H, and Cl corresponded with the calculated values.

2-Methyl-2-(2-furyl-2-ethenyl)-4-chloromethyl-1,3-dioxolane(IIa), 2-(2-Furyl)-4-(4-methylphenoxymethyl)-1,3-dioxolane(IIb), and 2-(2-Furyl-4-(2-furylmethoxymethyl)-1,3-dioxolane (IIc). To a mixture of 0.1 mole of carbonyl compound, 15.7 ml (0.2 mole) of oxirane, 100 ml (1.06 moles) of CCl_4 was added dropwise a 12% solution of $SnCl_4$ in CCl_4 [1.2 g (0.005 mole) of $SnCl_4$ in 8.8 g of CCl_4] at such a rate that the temperature of the reaction mixture did not exceed 40°C. After the addition of the catalyst, the reaction mixture was heated for 20 min at 40-45°C and kept for 1-2 h.

After completion of the reaction, and cooling of the reaction mixture, 2 g of finely-powdered $Na_2CO_3 \cdot 10H_2O$ (or 200-300 ml of diethyl ether) was added to the reaction mixture, which was carefully stirred, passed through a filter, and after removal of the solvent, the product was isolated by vacuum distillation.

The products IId-j were obtained by the earlier-described methods with the following yields; 4-chloromethyl-2-(2-furyl)-1,3-dioxolane (IId), 95%; 4-chloromethyl-2-(2-furyl)ethenyl-1,3-dioxolane (IIe), 50%; 4-chloromethyl-2-(5-methyl-2-furyl)-1,3-dioxolane (IIf), 80%; 4-chloromethyl-2-(5-bromo-2-furyl)-1,3-dioxolane (IIg), 65%; 4-chloromethyl-2-(5-chloro-2-furyl)-1,3-dioxolane (IIh), 60%; 4-chloromethyl-2-(5-nitro-2-furyl)-1,3-dioxolane (IIi), 63%; 4-chloromethyl-2-methyl-2-(5-methyl-2-furyl)-1,3-dioxolane (IIj), 78%.

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