

FURAN ACETAL COMPOUNDS

III.* SYNTHESIS OF SUBSTITUTED 2-(2-FURYL)-1,3-DIOXANES

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A number of previously unreported 1,3-dioxanes were obtained by the condensation of α -substituted furan aldehydes with 3-methyl-1,3-butanediol and also via organolithium compounds.

In recent years great interest has been shown for 1,3-dioxanes, including furyl-substituted ones, in connection with their high physiological activity [2, 3].

In a continuation of our previous investigations [4], we have studied the interaction of α -substituted furan aldehydes with 3-methyl-1,3-butanediol.† Previously unreported dioxanes (I-V) (Table 1) were obtained in the process.

We also synthesized carboxyfuryldioxanes VI-VIII from the corresponding organolithium compounds, which were obtained from 2-(5-bromo-2-furyl)-1,3-dioxanes and butyllithium.

The UV spectra of the compounds obtained were similar to the spectra of the previously [4] synthesized cyclic acetals of furan series and have one absorption maximum. Dioxane I has a maximum at 207 nm. A considerable bathochromic shift due to conjugation between the furan ring and the donor-acceptor substituents in its α position is observed for II-VIII.

Bands characteristic for the valence vibrations of the furan ring (1600, 1498, and 1447 cm^{-1}), ring pulsation vibrations (1030 cm^{-1}), the furan $\text{C}-\text{O}-\text{C}=\text{C}$ grouping (1250 cm^{-1}), and a group from four to five bands of the dioxane ring (1194, 1150, 1090, and 1049 cm^{-1}) are observed in the IR spectra of I-VIII. Bands at 1650-1700 cm^{-1} (aldehyde $\text{C}=\text{O}$) and bands at 3300-3600 cm^{-1} (OH group) are absent in the spectra of I-V. A carboxyl absorption band at 1682 cm^{-1} ($\text{C}=\text{O}$ conjugated with the furan ring) is observed in the spectra of VI-VIII, and there is a group of bands in the high-frequency region at 2500-3000 cm^{-1} (acid group OH).

EXPERIMENTAL

2-(2-Furyl)-4,4-dimethyl-1,3-dioxane (I). Furfural [9.6 g (0.1 mole)] was added in small portions with stirring to a refluxing solution of 10.4 g (0.1 mole) of 3-methyl-1,3-butanediol in 80 ml of dry benzene containing 1.92 g of KU-2. The water was led off into a trap. The completion of the reaction was determined by spectrophotometry. The benzene was removed by distillation, and the reaction product was vacuum distilled.

Compounds II-V were similarly obtained. Dioxanes III-V were recrystallized from benzene-heptane (1:3).

2-(5-Carboxy-2-furyl)-4,4-dimethyl-1,3-dioxane (VI). 2-(5-Bromo-2-furyl)-4,4-dimethyl-1,3-dioxane (III) [1.8 g (0.008 mole)] in 30 ml of absolute ether was added with stirring under nitrogen to a solution

* See [1] for communication II.

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TABLE 1.

Compound	R	R'	R''	R'''	Mp °C	Empirical formula	Found %				Calculated %				λ_{\max} , nm	lg ϵ	Yield, %
							M	C, %	H, %	halogen, %	M	C, %	H, %	halogen, %			
I	H	H	H	CH ₃	143* (30)	C ₁₀ H ₁₄ O ₃	180	65,8	7,9	—	182	65,9	7,7	—	207	3,98	74
II	CH ₃	H	H	CH ₃	126* (10)	C ₁₁ H ₁₆ O ₃	194	67,1	8,2	—	196	67,3	8,1	—	216	3,98	56
III	Br	H	H	CH ₃	44—45	C ₁₀ H ₁₃ BrO ₃	262	45,8	5,2	30,4	261	46,0	5,0	30,6	217	4,02	70
IV	I	H	H	CH ₃	78—80	C ₁₀ H ₁₃ IO ₃	310	38,8	4,4	41,0	308	39,0	4,3	41,2	230	4,01	69
V	NO ₂	H	H	CH ₃	47—49	C ₁₀ H ₁₃ NO ₃ †	225	52,7	5,8	—	227	52,9	5,8	—	310	4,04	92
VI	COOH	H	H	CH ₃	151—153	C ₁₁ H ₁₄ O ₃	224	58,3	6,4	—	226	58,4	6,2	—	245	4,05	71
VII	COOH	CH ₂ Cl	CH ₂ Cl	H	200—202	C ₁₁ H ₁₂ Cl ₂ O ₅	293	44,8	4,3	24,0	294	44,9	4,1	24,1	244	4,06	50
VIII	COOH	C ₂ H ₅	CH ₂ OH	H	168—170	C ₁₂ H ₁₆ O ₆	255	56,1	6,4	—	256	56,2	6,2	—	244	4,06	58

*Bp (mm).

† Found %: N 6.09. Calculated %: N 6.16.

of butyllithium prepared from 0.4 g (0.058 g-atom) of lithium and 5.07 g (0.03 mole) of butyl bromide in 25 ml of absolute ether. The reaction was carried out at 0–5° for 15 min, after which the resulting organolithium compound was carbonated with dry ice. Water (10 ml) and 10 ml of 10% sodium hydroxide were added to the mixture. The alkaline extract was treated with 10% hydrochloric acid.

Compounds VI and VII were similarly obtained.

The UV spectra of ethanol solutions were measured with an SF-4A spectrophotometer. The IR spectra were obtained with an IKS-14 spectrometer from thin liquid layers (0.04 mm) for I, II, and from mineral oil pastes for III–VIII.

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