SYNTHESIS OF 1,3-DIOXANES FROM FURAN ALDEHYDES

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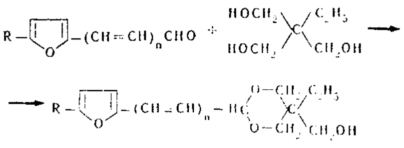
Six new cyclic acetals have been synthesized by the reaction of furfural and its 5-methyl, 5-bromo, 5-chloro, and 5-nitro derivatives and furyl-acrolein with 1,1,1-tris(hydroxymethyl)propane. Their UV and IR spectra are given.

We have previously shown the possibility of the acetalation of furfural with aliphatic [1] and aromatic [2] alcohols in the presence of an ion-exchange resin. In the present work we have studied the reaction of furfural and its derivatives, and also furylacrolein, with 1,1,1-tris(hydroxymethyl)propane using KU-2 ion-exchange resin as catalyst.



n = 0,1; R = H, CH_3, Cl, Br, NO_2

As a result, we have obtained previously unreported 5-ethyl-5-hydroxymethyl-1,3-dioxanes substituted in position 2 (table). All the acetals are white crystalline substances readily soluble in ethanol and hot benzene but insoluble in heptane and water. The UV spectra of the acetals (apart from **V**) have a single absorption maximum, in contrast to the spectra of the initial aldehydes, which are characterized by two absorption maxima (table). Similarity of the UV spectra of compounds **I–IV** to the spectra of the acetals of furfural with aliphatic [1] and aromatic [2] alcohols (λ_{max} 216 nm) is one of the proofs of the acetal structure of the products obtained.

The IR spectra of the acetals obtained, which were recorded on an IKS-14 spectrograph, show absorption bands characteristic of a hydroxyl (3480–3500 cm^{-1}), a furan ring (3109–3112 cm^{-1}), and of monosubstituted furans in the case of I and VI (885–889 cm^{-1}), which correspond to the literature [4], of 2,5-disubstituted furans for II–IV (726–776 cm^{-1}), which corresponds to the literature [5], and of ethylene bonds for VI (1634, 1655 cm^{-1}), of a nitro group for V (1560 and 1345 cm^{-1}), and of acetals (1200–1040 cm^{-1}), which again corresponds to the literature [4, 6].

EXPERIMENTAL

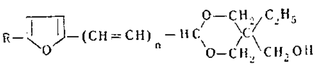
2-Substituted 5-ethyl-5-hydroxymethyl-1,3-dioxanes. A mixture of 0.1 mole of the aldehyde, 0.1 mole of the alcohol, 50 ml of dry benzene, and KU-2 cation-exchange resin, converted into the H-form by a published method [7] (10% on the initial aldehyde) was boiled in a flask fitted with a Dean-Stark trap until the evolution of water of reaction ceased. The hot mixture was filtered, and the catalyst was washed with a small amount of benzene. The solvent was distilled off from the filtrate, and the product was isolated from the residue either by crystallization or by distillation at 180–210° C (3–5 mm).

REFERENCES

1. Z. I. Zelikman, Izv. VUZ SSSR, Pishchev., tekhnol., 5, 116, 1967.

2. Z. I. Zelikman and V. G. Kul'nevich, Sb. trudov Krasnodarsk. politekhn. inst., 23, 788, 1968.

3. S. A. Hiller and Ya. I. Eidus, Izv. AN Latv. SSR, 8, 1223, 1951.



Compound	n	R	Mp, °C	Empirical formula	Found, %		Calculated, %		UV spectra (in 30% ethanol)				Yield, %
									1,3-dioxane		initial aldehyde		
					C	H	C	H	λ_{max}, nm	log ε	λ_{max}, nm	log ε	
I	0	H	70[b]	$C_{11}H_{16}O_4$	62.33	7.22	62,26	7.54	214	4.03	227 272	3.39[a] 4.14	53
II	0	CH_3	81–83[c]	$C_{12}H_{18}O_4$	63.87	7.80	63.71	7.96	220	3.97	228 292	 4.23	90
III	0	Br	88[c]	$C_{11}H_{15}BrO_4$	45.30	5.54	45.37	5.15	220	4.07	220 290	3.52 4.20	47
IV	0	Cl	54[d]	$C_{11}H_{15}ClO_4$	54.01	6.08	53.54	6.08	224	4.04	225 288	3.46 4,17	63
V	0	NO_2	70–71[d]	$C_{11}H_{15}NO_6$	51.81	6.29	51.36	5.85	224 310	3.40 3.78	226 310	3.92[e] 4.06	94
VI	1	H	88–90[d]	$C_{13}H_{18}O_4$	65.52	7.41	65.54	7.56	268	4.22	236 322	3.37 4.26	71

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[a] According to [8]. [b] From benzene. [c] From ether. [d] From a mixture of benzene and heptane. [e] According to [3].

4. K. Nakanishi, Infrared Absorption Spectroscopy [Russian translation], Mir, Moscow, p. 61, 1965.

5. M. Fetizon and S. Guy, C. r., **247**, 1182, 1958.

6. W. West, ed., Chemical Applications of Spectroscopy [Russian translation], IL, Moscow, p. 354, 1959.

7. K. M. Saldadze, A. B. Pashkov, and V. S. Titov, High-Molecular-Weight Ion-Exchange Compounds [in Russian], Izd-vo AN SSSR, Moscow, p. 85, 1960.

8. Organic Electronic Spectral Data, **11**, 27, 1960.

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PYRANYLTRIPHENYLPHOSPHONIUM SALTS

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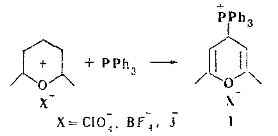
The reaction of pyrylium salts having a free α or γ position with triphenylphosphine has given pyranylphosphonium salts. 2, 4, 6-Trisubstituted pyrylium salts do not react with triphenylphosphine. The properties and IR spectra of the compounds synthesized are discussed.

The phosphonium salts that are finding wide use in the Wittig reaction are readily obtained by the reaction of alkyl halides, α-halogenoacids, or ketones having terminal halogen atoms with triphenylphosphine [1]. In a study of pyrylium salts with a free α or γ position we have found that the latter also react with triphenylphosphine giving high yields of pyranylphosphonium salts I according to the scheme:



The reaction takes place when a mixture of the reactants in a polar solvent (for example, nitromethane) is heated for a short time. When ethyl acetate is added to the hot reaction mixture, the crystalline final product separates out on cooling. The elementary analysis and the IR spectra and the frequently almost quantitative yields of the substances formed permit the statement with full certainty that the compounds obtained are the pyranylphosphonium salts I. They are colorless or faintly colored crystalline products which melt, as a rule, lower than the initial pyrylium salts and which have properties (solubility, stability, etc.) similar to those of ordinary phosphonium salts. Boiling in acetic acid does not change the phosphonium salts, nor does their prolonged boiling in ethanol with an aldehyde.

When bases are added to suspensions of the compounds under consideration in ether, a dark color appears which immediately disappears again. Treating a suspension of a phosphonium perchlorate in ether or in ethanol with an equimolecular amount of sodium ethoxide leads to the separation of triphenylphosphine from the mixture. It is likely that the normal product of the Wittig reaction—the colored phosphorane II—formed in this process decomposes under the usual conditions into triphenylphosphine and the carbene III by the reaction:

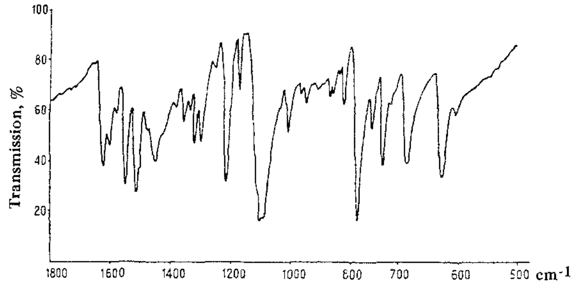
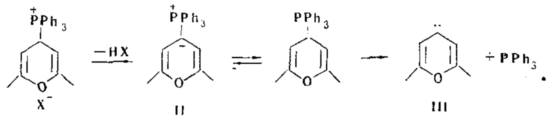


Fig. 1. IR spectrum of 2,6-diphenylpyrylium perchlorate.



Since trisubstituted pyrylium salts do not form phosphonium salts, this method can be used to establish the presence of a free α or γ position in a pyrylium salt.