RESEARCH ON FURAN ACETAL COMPOUNDS

VI.* SYNTHESIS OF α'-SUBSTITUTED 2-(α-FURYL)-5,5-DIMETHYL-1,3-DIOXANES AND THEIR CARBINOL DERIVATIVES

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Furan 1,3-dioxanes were obtained by condensation of 2,2-dimethyl-1,3-propanediol with aldehydes of the furan series. The lithium derivatives of bromine-substituted 1,3-dioxanes were used for the synthesis of a number of alcohols.

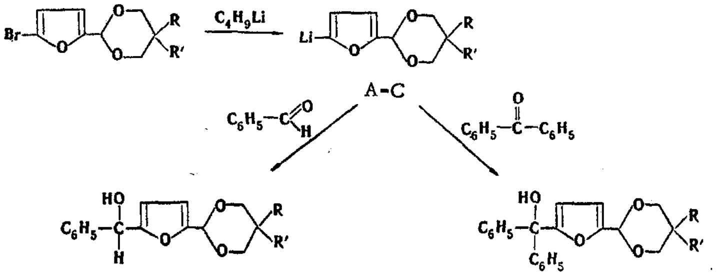
Continuing our search for physiologically active compounds [2, 3], we have synthesized α'-substituted 2-(α-furyl)-5,5-dimethyl-1,3-dioxanes and secondary and tertiary alcohols from them. The furan 1,3-dioxanes were obtained by condensation of 2,2-dimethyl-1,3-propanediol with furan aldehydes (Table 1).

Bands characterizing the valence vibrations of the furan ring (1592, 1500, and 1459 cm^{-1}), the pulsation vibrations of the ring (1020 cm^{-1}), the $=C-O-C=$ grouping of furan (1253 cm^{-1}), and a group of four to five bands of the dioxane ring (1194, 1151, 1100, and 1049 cm^{-1}) are observed in the IR spectra of products I-V, while bands are absent at 1650-1700 cm^{-1} (aldehyde $\nu_{C=O}$) and 3300-3600 cm^{-1} (ν_{OH}); this confirms the proposed structure.

Organic derivatives of alkali metals are distinguished by their high reactivities. The reaction of bromofuran acyclic acetals with butyllithium proceeds relatively easily and practically without side reactions [5], while lithiation of derivatives of dioxolanes proceeds less smoothly.

The formation of organolithium derivatives of 1,3-dioxanes proceeds to give products in satisfactory yields, and the subsequent transformations proceed with retention of the furan and dioxane rings [2]; this again confirms the previously noted [6] stability of these cyclic systems.

The reaction of 2-[α-(α'-lithio)furyl]-5,5-dimethyl-1,3-dioxanes (A-C) with benzophenone and benzaldehyde gave alcohols VI-XI, the structures of which were confirmed by physicochemical analyses (Table 1).



IX-XI VI-VIII

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* See [1] for communication V.

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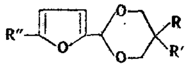
TABLE 1



Compound	R	R′	R″	mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %
						C	H	Hal	C	H	Hal	
I	CH_3	CH_3	H	20*	$C_{10}H_{14}O_3$	65,8	7,7	—	65,9	7,7	—	90
II	CH_3	CH_3	CH_3	68	$C_{11}H_{16}O_3$	67,2	8,2	—	67,4	8,2	—	81
III	CH_3	CH_3	Br	52	$C_{10}H_{13}BrO_3$	45,7	5,1	30,3	46,0	5,0	30,6	88
IV	CH_3	CH_3	I	111	$C_{10}H_{13}IO_3$	38,8	4,8	41,0	39,0	4,2	41,3	98
V	CH_3	CH_3	NO_2	109	$C_{10}H_{13}NO_5$ †	52,7	6,0	—	52,9	5,7	—	96
VI	CH_3	CH_3	$(C_6H_5)_2COH$	94	$C_{23}H_{24}O_4$	75,7	6,7	—	75,8	6,6	—	67
VII	C_2H_5	CH_2OH	$(C_6H_5)_2COH$	98	$C_{24}H_{26}O_5$	72,9	6,9	—	73,1	6,6	—	64
VIII	CH_2Cl	CH_2Cl	$(C_6H_5)_2COH$	128	$C_{23}H_{22}Cl_2O_4$	63,6	5,3	16,1	63,7	5,1	16,4	60
IX	CH_3	CH_3	C_6H_5CHOH	36	$C_{17}H_{20}O_4$	70,7	7,0	—	70,8	6,9	—	31
X	C_2H_5	CH_2OH	C_6H_5CHOH	38	$C_{18}H_{22}O_5$	67,7	7,4	—	67,9	6,9	—	32
XI	CH_2Cl	CH_2Cl	C_6H_5CHOH	40	$C_{17}H_{18}Cl_2O_4$	57,0	5,3	19,6	57,1	5,1	19,9	30

* This compound had bp 110° (13 mm) (bp 107-109° (12 mm) [4]).

† Found: N 6.6%. Calculated: N 6.2%.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with an IKS-14 spectrophotometer at 650-4000 cm^{-1} with LiF and NaCl prisms.

2-[α-(α′-Bromo)furyl]-5,5-dimethyl-1,3-dioxane (III). A mixture of 17.5 g (0.1 mole) of bromofurfural, 10.4 g (0.1 mole) of 2,2-dimethyl-1,3-propanediol, 3.5 g of KU-2 ion-exchange resin (in the H form) in 80 ml of absolute benzene was refluxed for 4-5 h. The end of the reaction was determined by spectrophotometry [7]. The benzene was removed by distillation, and the product was recrystallized from benzene–heptane (1:3) to give 23 g (88%) of a product with mp 52°. Compounds I, II, IV, and V were similarly obtained.

2-[α-(α′-Diphenylhydroxymethyl)furyl]-5,5-dimethyl-1,3-dioxane (VI). A solution of 3.9 g (0.021 mole) of benzophenone in 30 ml of absolute ether was added at −10° to 2-[α-(α′-lithiofuryl)]-5,5-dimethyl-1,3-dioxane (A), obtained from 0.51 g (0.072 g-atom) of lithium and 2.6 g (0.01 mole) of 2-[α-(α′-bromo)furyl]-5,5-dimethyl-1,3-dioxane in absolute ether. The mixture was held at this temperature for 30 min and at room temperature for 3 h. Water (80 ml) was then added, and the ether layer was separated and dried over calcined sodium sulfate. The ether was removed by distillation to give 3.62 g (67%, based on the starting bromofuryldioxane) of light-yellow crystals with mp 94°.

Similarly, VII and VIII were obtained from 2-[α-(α′-lithio)furyl]-5-ethyl-5-hydroxymethyl- and 2-[α-(α′-lithio)furyl]-5,5-bis(chloromethyl)-1,3-dioxanes (B and C), which were synthesized from the corresponding bromo derivatives [8].

2-[α-(α′-Phenylhydroxymethyl)furyl]-5,5-dimethyl-1,3-dioxane (IX). Organolithium compound A was cooled to −20°, and 2.5 g (0.023 mole) of benzaldehyde in 2.5 ml of dry ether was added. The mixture was stirred at this temperature for 2 h and at room temperature for 30 min. Water (10 ml) and 1 ml of acetic acid were then added, and the ether layer was separated, washed with water, and dried. The solvent was removed by distillation, and the resulting crystals of the carbinol were recrystallized from petroleum ether–benzene to give 1.3 g (31%, based on 2-[α-(α′-bromo)furyl]-5,5-dimethyl-1,3-dioxane) with mp 36°.

Similarly, alcohols X and XI were obtained from B and C.

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