SYNTHESIS OF AROMATIC 4,4,5,5-TETRAMETHYL-1,3-DIOXOLANES SUBSTITUTED IN POSITION 2 AND THEIR SALTS

Z. I. Zelikman, L. A. Falina,
L. V. Mezheritskaya, G. N. Dorofeenko,
and V. G. Kul'nevich

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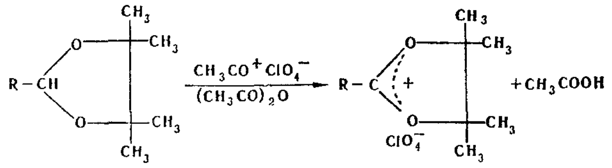
A method for the synthesis of 2-aryl-4,4,5,5-tetramethyl-1,3-dioxolanium salts from cyclic acetals has been developed. The IR spectra of the compounds obtained are discussed.

In the search for new physiologically active substances among cyclic acetal compounds [1, 2] in the present work we have performed the condensation of aromatic aldehydes with pinacone hydrate and have obtained a series of 1,3-dioxolanes (Table 1). We then studied the reaction involving the elimination of a hydride ion with the formation of 2-aryl-1,3-dioxolanium salts.



I – IV V – VIII

In the IR spectra of compounds (I-IV) there are the bands of a dioxolane ring in the 1200-1040-cm^{-1} region. Another confirmation of the structure given is the absence of the absorption of hydroxy and carbonyl groups in the 3600- and 1700-cm^{-1} regions, respectively. The UV spectra of the acetals (I), (II), and (IV) each have a single absorption maximum in the 253-268-nm region (log ε 2.71-4.89). The observed bathochromic shift with the introduction of an electron-donating substituent into the aromatic ring is in harmony with the literature [3, 4]. An exception is formed by (III) the UV spectrum of which has, in addition to the main peak at 253 nm (log ε 2.82) a second peak at 281 nm (log ε 2.29).

When the 1,3-dioxolanes (I-IV) were treated with an equimolecular amount of 70% perchloric acid in an excess of acetic anhydride [5], the salts (V-VIII) were formed (see Table 1). Their IR spectra each have a strong band of $\nu_{ClO_4^-}$ at 1090 cm^{-1}, and also strong absorption bands in the 1520-1537-cm^{-1} region due to the vibrations of the O–C–O fragment [5].

A characteristic feature of all the salts synthesized is a decrease in the intensity of the 1600-cm^{-1} band and an increase in the absorption in the 1537-1510-cm^{-1} region as compared with the initial 1,3-dioxolanes, which shows the existence of a system of conjugation of the carbocation formed with the aromatic ring. This conjugation leads to a shift of the absorption maximum in the short-wave region of the UV spectrum, and the spectrum acquires the nature of a descending curve in the near-ultraviolet region.

A confirmation of the structure of the perchlorates obtained is the formation of esters on their acid alcoholysis. In the case of (VIII), for example, this process yielded ethyl p-methoxybenzoate, the IR spectrum of which clearly showed strong bands of an ester group (1720 cm^{-1}).

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TABLE 1. Properties of the Compounds (I-VIII) Obtained

Compound	R	Mp, °C	n_D^{20}	Empirical formula	Found, %		
					C	H	Cl
I	C_6H_5	110(12)*	1,4999	$C_{13}H_{18}O_2$	76,5	9,2	—
II	o-HO—C_6H_4	128	—	$C_{13}H_{18}O_3$	70,8	8,4	—
III	C_6H_5—CH=CH—	184(760)*	1,5315	$C_{15}H_{20}O_2$	77,7	8,6	—
IV	p-H_3CO—C_6H_4	155(11)*	1,5145	$C_{14}H_{20}O_3$	70,6	8,6	—
V	C_6H_5	138—139	—	$C_{13}H_{17}ClO_6$	50,8	6,0	10,9
VI	o-HO—C_6H_4	138—139	—	$C_{13}H_{17}ClO_7$	49,0	5,6	11,2
VII	C_6H_5—CH=CH	140—141	—	$C_{15}H_{10}ClO_6$	53,7	5,3	11,1
VIII	p-H_3CO—C_6H_4	137—138	—	$C_{14}H_{19}ClO_7$	50,6	6,0	11,0

Compound	Calculated, %			IR spectrum cm^{-1}			Yield, %
	C	H	Cl	ν_{arom}	ν_{O-C-O}	$\nu_{ClO_4^-}$	
I	75,7	8,8	—	1600, 1575 1490	—	—	70
II	70,2	8,2	—	1600, 1580 1502	—	—	60
III	77,5	8,6	—	1674, 1628 1600, 1580	—	—	65
IV	70,2	8,7	—	1608, 1584 1506, 1459	—	—	62
V	51,2	5,6	11,3	1600 сл	1502 1537	1092 1082	50
VI	48,7	5,3	11,8	1600 сл 1643 ср	1537	1100 1075	52
VII	54,1	5,8	10,7	1600 сл 1666 ср	1537 1510	1100 1078	58
VIII	50,2	5,7	10,6	1610 сл	1537 1514	1100 1085	56

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* Bp, °C (mm).

EXPERIMENTAL

The UV spectra were taken on an SF-4A spectrophotometer using ethanol as solvent for the 1,3-dioxolanes and glacial acetic acid for the 1,3-dioxolanium salts. The IR spectra were taken on an IKS-14 instrument in paraffin oil.

2-(p-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3-dioxolane (IV). A mixture of 11.3 g (0.05 mole) of pinacone hydrate in 100 ml of absolute benzene was boiled with a Dean–Stark trap for 1 h 30 min. Then, with careful stirring, 0.22 g of p-toluenesulfonic acid and 6.80 g (0.05 mole) of anisaldehyde were added. Boiling was continued until the separation of the water of reaction in the trap ceased. Then the mixture was cooled and was washed with 5% sodium bicarbonate solution and with water and was dried with sodium sulfate. The solvent was distilled off, giving 7.3 g (62%) of (IV) and with bp 155°C (11 mm). Compounds (I) and (III) were obtained similarly. Compound (II) was recrystallized from heptane with the addition of benzene.

2-(p-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3-dioxolanium Perchlorate (VIII). In drops, 0.75 ml (8.6 mmoles) of 70% perchloric acid was added to a cooled solution of 2.2 g (8.6 mmoles) of (IV) in 9 ml of acetic anhydride. After 10-15 min, about 1 ml of ether was added to the mixture and the resulting crystalline precipitate of (VIII) was separated off and carefully washed with ether. It was recrystallized from acetic acid. Yield 1.5 g (56%). Compounds (V-VII) were obtained similarly.

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