SYNTHESIS OF 1,3-DIOXOLANIUM SALTS FROM 1,3-DIOXOLANES

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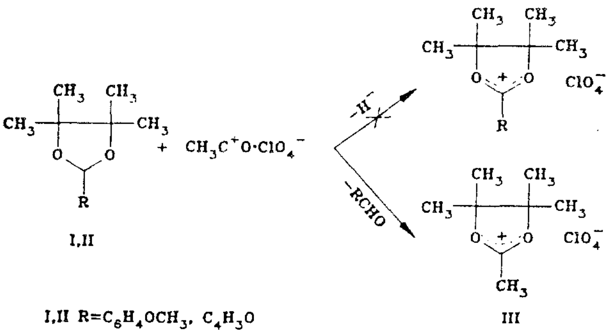
It was found that 2-(4-methoxyphenyl)- and 2-(2-furyl)-1,3-dioxolanes I, II are converted by the action of acetic anhydride in the presence of a 70% perchloric acid into 2,4,4,5,5-pentamethyl-1,3-dioxolanium perchlorate (III).

$$(CH_3CO)_2O + HClO_4 \rightleftharpoons CH_3\overset{+}{C}O\cdot ClO_4^- + CH_3COOH$$



I,II

III

I,II R=$C_6H_4OCH_3$, C_4H_3O

The proton signals of the substituent R are absent in the PMR spectra of salts obtained from compounds I and II, but in both cases a singlet appears at 2.33 ppm, which is characteristic for the methyl group of the acyloxonium fragment [1]. The IR spectra and the melting point of salt III correspond to the known [2] 2,4,4,5,5-pentamethyl-1,3-dioxolanium perchlorate.

Thus, the reaction of acetylium perchlorate with dioxolane, like that with 1,3-dioxane [1], does not lead to the splitting off of a hydride ion, as was previously shown in [3, 4], since ring opening and splitting of RCHO take place. Instead of this the CH_3C^+O fragment enters the molecule and, as a result, the 2,4,4,5,5-pentamethyl-1,3-dioxolanium cation is formed. The presence of aldehyde RCHO in the reaction mixture was confirmed by GLC and UV spectroscopy methods, on the example of dioxolane II.

4,4,5,5-Tetramethyl-2-(4-methoxyphenyl)-1,3-dioxolane (I) was obtained by the method described in [5], bp 160°C (15 mm Hg). PMR spectrum (CCl_4): 7.2 (2H, d, ^3J = 9.0 Hz), and 6.6 (2H, d, ^3J = 9.0 Hz, the C_6H_4 protons); 5.76 (1H, s, 2-H); 3.66 (3H, s, O-CH_3); 1.18 and 1.10 ppm (12H, s.s, CH_3).

4,4,5,5-Tetramethyl-2-(2-furyl)-1,3-dioxolane (II) was obtained by the method described in [5], bp 112°C (16 mm Hg). PMR spectrum (CCl_4): 7.28 (1H, d, 5-H); 6.23 (1H, d, 3-H); 6.1 (1H, d, 4-H); 5.76 (1H, s, 2-H); 1.18 and 1.12 m (12H, s.s, CH_3).

2,4,4,5,5-Pentamethyl-1,3-dioxolanium Perchlorate (III). A mixture of 1.18 g (5 mmoles) of dioxolane II and 3 ml of acetic anhydride was cooled to –10°C. Then a cooled mixture of 0.5 ml (0.5 mmoles) of a 70% perchloric acid and 2 ml of acetic anhydride were slowly added dropwise and with stirring. The mixture was then allowed to stand for 10 min at –10°C, and 10 ml of ether was added. The light crystals formed were washed thoroughly with ether. Yield 1 g (86%), mp 138°C. IR spectrum: 1537, 1510, 1460, 1400, 1380, 1200, 1180, 1130, 1100, 1035, 960, 830 cm^{-1}. PMR spectrum (CF_3COOH): 2.23 (3H, s, 2-CH_3); 1.38 ppm (12H, s, CH_3). Salt III was obtained in a similar way from dioxolane I.

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REVERSE INDUCTIVE EFFECT IN THE SERIES OF trans-3,4-DISUBSTITUTED THIOLANE 1,1-DIOXIDES

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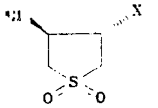
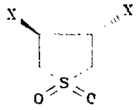
Series of trans-4-substituted 3-chlorothiolane 1,1-dioxides (Ia-h) and trans-3,4-disubstituted thiolane 1,1-dioxides (IIa-j) were studied by ^{33}S NMR spectroscopy (solutions in acetone-D_6 and DMSO-D_6, respectively).



Ia-b



IIa-j

I a X=H, b X=OH, c X=OCH_3, d X=$OCOCH_3$, e X=SC_4H_9, f X=SO_2Cl, g X=Cl, h X=Br; II a X=H, b X=$N(CH_3)_2$, c X=$N^+H(CH_3)_2$, d X=OH, e X=OCH_3, f X=$OCOCH_3$, g X=$OSO_2C_6H_5$, h X=F, i X=Cl, j X=Br

It was found that increase in the inductive acceptor power of the substituent X is accompanied by increase in screening of the ^{33}S nuclei, and not descreening, as should have been expected according to the classical concepts on the inductive effect of substituent X.

Statistically reliable correlational dependences of δ_S in compounds Ia-h and IIa-j [Eqs. (1) and (2), respectively] on σ_I (without taking into account δ_S in compounds Ie and IIb) were observed:

$$\delta_S = -23{,}40(\pm 0{,}99)\sigma_I + 361{,}03(\pm 0{,}42),\quad r = 0{,}996,\quad s_0 = 0{,}604,\quad n = 7; \tag{1}$$

$$\delta_S = -41{,}70(\pm 3{,}96)\sigma_I + 368{,}99(\pm 1{,}68),\quad r = 0{,}970,\quad s_0 = 2{,}282,\quad n = 9. \tag{2}$$

We believe that the character of the dependences indicates the influence of a field factor of substituent X on the screening of the ^{33}S nuclei, consisting in a dipole–dipole interaction of the C–X and S=O bonds with the resulting polarization of the latter in the direction of the sulfur atom.

TABLE 1. Characteristics of Compounds Ia-h and IIa-j*

Compound	δ_S	$\nu_{1/2}$, Hz	σ_I	Compound	δ_S	$\nu_{1/2}$, Hz	σ_I	Compound	δ_S	$\nu_{1/2}$, Hz	σ_I
Ia	361,5	10	0,00	Ig	349,8	50	0,46	IIe	357,2	5	0,25
Ib	354,8	25	0,25	Ih	351,4	15	0,44	IIf	353,6	9	0,27
Ic	355,5	28	0,25	IIa	370,6	5	0,00	IIg	344,2	240	0,58
Id	353,9	65	0,27	IIb	345,8	38	0,17	IIh	345,8	30	0,52
Ie	351,8	40	0,13	IIc	344,0	300	0,65	IIi	350,2	40	0,46
If	342,5	60	0,80	IId	361,2	7	0,25	IIj	351,5	15	0,44

*δ_S are NMR chemical shifts of the ^{33}S nuclei relative to δ_S in CS_2; $\nu_{1/2}$ is the width of the signals at half height; σ_I are the Taft inductive constants of substituent X.

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