LETTERS TO THE EDITOR

CLEAVAGE OF 1,3-DIOXOLANES BY ACETIC ANHYDRIDE TO GIVE ALLYLIC ALCOHOL ACETATE DERIVATIVES

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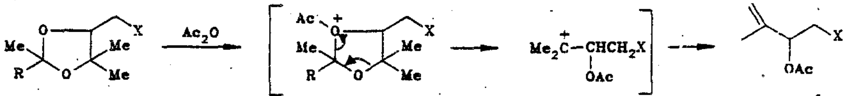
It is well known that reactions of cyclic acetals with acid anhydrides occur via a scheme involving cleavage and addition of the elements of the electrophilic reagent across the C–O bond [1].

We have found that high-temperature acid-catalyzed cleavage (p-toluenesulfonic acid, 140-150°C, 15-20 h) of several 1,3-dioxolanes Ia-c by acetic anhydride proceeds in a different manner: allylic alcohol acetates II are formed. We assume that these reactions occur via attack of an acylium cation at the O(4) atom and cleavage of the C–O bond [either acetone (Ia, b) or methyl ethyl ketone (Ic) was isolated as well], which forms a carbocationic intermediate and is subsequently deprotonated [2].



Ia-c

IIa,b

Ia R=Me, X=Cl; b R=Me, X=Br; c R=Et, X=Br; II a X=Cl; b X=Br

3-Acetoxy-2-methyl-4-chloro-1-butene (IIa). Yield 55%; bp 69-71°C (11 mm Hg); n_D^{20} 1.4470; d_4^{20} 1.0766. PMR spectrum, δ (CCl_4): 1.78 (3H, dd, J = 1 Hz, CH_3); 2.10 (3H, s, $CH_3C{=}O$), 3.63 (2H, d, J = 6.6 Hz, CH_2Cl), 5.10 (2H, m, $=CH_2$), 5.32 ppm (1H, t, J = 6.6 Hz, CH–O).

3-Acetoxy-4-bromo-2-methyl-1-butene (IIb). This was prepared via cleavage of 5-bromomethyl-2,2,4,4-tetramethyl-1,3-dioxolane (Ib) or 5-bromomethyl-2,4,4-trimethyl-2-ethyl-1,3-dioxolane (Ic) in 70-75% yield; bp 81-82°C (11 mm Hg); n_D^{20} 1.4680; d_4^{20} 1.3252. PMR spectrum, δ (CCl_4): 1.70 (3H, dd, J = 1.0 Hz, CH_3), 2.02 (3H, s, $CH_3C{=}O$), 3.45 (2H, d, J = 6.6 Hz, CH_2Br), 5.04 (1H, m, =CH), 5.37 ppm (1H, t, J = 6.6 Hz, CH–O).

Elemental analyses of compound IIa, b agreed with the calculated values.

LITERATURE CITED

1. Z. Summers, Chem. Rev., 55, 301 (1955).
2. A. A. Gevorkyan, Arm. Khim. Zh., 36, 81 (1983).

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