NEW ACID CATALYZED CONVERSION OF 2-ALKOXY-4,5-BENZO-1,3-DIOXOLANES

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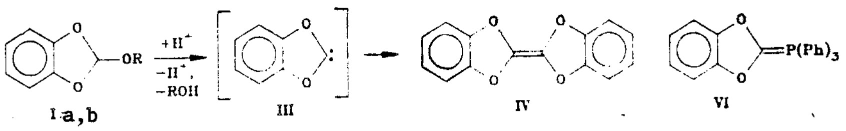
Formation of dialkoxycarbenes as intermediates in a number of reactions has been proposed in [1-4]. Hence it has been shown [1-3] that acyclic dialkoxycarbenes $RO\ddot{C}OR$ (R = CH_3, C_2H_5) dimerize to the corresponding tetraalkoxyethenes whereas cyclic dialkoxycarbenes of the type $\underline{>C-O}-\ddot{C}-O-C<$ are unstable and lose CO_2 to form alkenes in the Corey-Winter synthesis [4].

For the first time we have found that treatment of 2-alkoxy-4,5-benzo-1,3-dioxolanes (Ia, b) with trace amounts of trifluoro- (IIa) or trichloroacetic acid (IIb) leads to formation of the alkene 2,2'-bi(4,5-benzo-1,3-dioxolan-2-ylidene) (IV) and the corresponding alcohol. Apparently reaction of esters Ia, b to give alkene IV takes place via formation of the cyclic dialkoxycarbene III:



Evidently carbene III is thermodynamically more stable than a cyclic dialkoxycarbene because its conversion analogously to synthesis [4] should lead to an arene. This process is undoubtedly more favored than alkene formation via dissociation of a cyclic dialkoxycarbene. Hence the presence of the aromatic ring basically changes the reaction course towards formation of dimer IV.

Carrying out the reaction in the presence of the carbene trap triphenylphosphine [5, 6] captures carbene III as the adduct VI.

The reaction was carried out in an argon atmosphere with distillation of the corresponding alcohol evolved during its course. The yield of IV upon catalysis by acid IIa was 38-40% and 30-32% for acid IIb, the degree of conversion from the starting compound being 50-60%. Analogously, distillation of ethanol from an equimolar mixture of Ia and triphenylphosphine gave V in 7% yield (conversion of Ia = 60%). The products IV and V were separated by TLC on silica gel (20-60 micron) using chloroform-hexane (1:5) eluant.

<u>2,2'-Bi(4,5-benzo-1,3-dioxolan-2-ylidene) (IV)</u> had mp 84°C. ^1H NMR spectrum ($(CD_3)_2CO$): 6.78 ppm (8H, m, arom.). ^{13}C NMR spectrum ($CDCl_3$): 107.4 (4C, d); 120.5 (4C, d); 142.7 (2H, s); 143.4 ppm (4C, s).

<u>2-(Triphenylphosphinylidene)-4,5-benzo-1,3-dioxolane (V)</u> had mp 104-105°C. ^1H NMR spectrum ($(CD_3)_2CO$): 7.42 (15H, m, arom.); 7.50 ppm (4H, m, arom.). ^{13}C NMR spectrum ($CDCl_3$): 141.9 (1C, d); 145.7 (2C, s); 129.9 (2C, d); 120.6 (2C, d); 123.9-131.0 ppm (18C, m). ^{31}P NMR spectrum ($(CD_3)_2CO$): 24.7 ppm (s).

LITERATURE CITED

1. R. W. Hoffmann and H. Häuser, Tetrahedron Lett., No. 3, 197 (1964).
2. R. J. Crawford and R. Raap, Proc. Chem. Soc., No. 5, 370 (1963).
3. R. Olfson, S. Walinski, J. Marino, and J. Lerua, J. Am. Chem. Soc., 90, 6554 (1968).
4. E. J. Corey and R. A. E. Winter, J. Am. Chem. Soc., 85, 2677 (1963).
5. A. J. Speziale, G. J. Marco, and K. W. Ratts, J. Am. Chem. Soc., 82, 1260 (1960).
6. D. Sevferth, S. O. Grim, and T. O. Read, J. Am. Chem. Soc., 82, 1510 (1960).

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