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SYNTHESIS OF 1,1,4,4-TETRAALKOXY-1,3-BUTADIENES

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In view of the high reactivity of the electron-rich 1,1-dialkoxyalkenes (1)[1] and tetraalkoxyethenes (2)[2,3,4] towards electrophiles and electron-poor ethenes valuable applications in organic synthesis might also be expected for 1,1,4,4-tetraalkoxy-1,3-butadienes (3). Until now, however, compounds (3) have not been described in the literature. Treatment of the possible precursor 1,1,4,4-tetramethoxy-2,3-dibromobutane (5) with a base[5] yielded only 1,1,4,4-tetramethoxy-2-butyne (4) (from the racemic bromide[5]) and 1,1,4,4-tetramethoxy-2-bromobutene-2 (from the meso bromide). Apparently the desactivating effect of the alkoxy groups on proton abstraction at the α-carbon atoms[2,6] prevents formation of the thermodynamically more stable tetramethoxy-1,3-butadiene (6). We found a simple method to isomerise (4) into (6).

By refluxing the electrochemically easily available 2,5-dimethoxy-2,5-dihydrofuran[7] in methanol, containing 5% ammoniumbromide and a trace of formic acid, (5) was obtained in 50% yield. By bromination and subsequent elimination of HBr with KOH in methanol it was converted into (4) in 70% yield. Other tetraalkoxybutynes (ethyl, butyl, isobutyl e.o.) could be obtained from (4) by alcohol-exchange reactions using p-toluenesulphonic acid as a catalyst (60 to 80% yields). They could be converted into the isomeric 1,3-butadienes (3) by dropwise addition of a solution of 0.1 mole of an appropriate butyne in ether into a solution of 0.2 mole of potassium amide in liquid ammonia at -40°. Sodium amide or hydride could not be used in this isomerization. In some cases (methyl, ethyl) the butadienes (3) remaining after removal of the ammonia and the ether were about 90% pure. They could be further purified by distillation and were identified by NMR and mass spectra (Table 1).

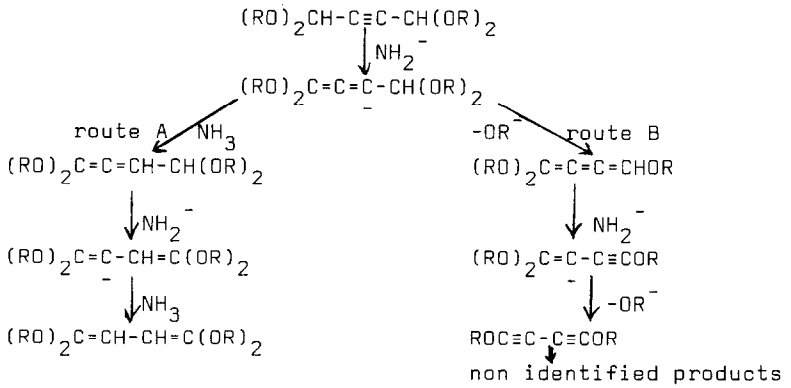
TABLE 1

$(RO)_2C{=}CH{-}CH{=}C(OR)_2$

R	B_p/mm	*δ H–C=	Yield	Remarks
methyl	110°/15	4.30 ppm	50%	
ethyl	78°/0.2	4.45 ppm	55%	
n-butyl	60°/0.001	4.35 ppm	40%	Molecular distillation
isobutyl	132°/0.2	4.40 ppm	60%	

* 10% solutions in CCl_4, TMS internal

Apparently the isomerization is accompanied by important side reactions yielding products which are poorly soluble in ether. In the cases of the methyl and ethyl compounds, less than 10% of the other products were present in the reaction mixture. Tetraalkoxybutynes with cyclic acetal residues ($\begin{smallmatrix}CH_2\text{-}O\\CH_2\text{-}O\end{smallmatrix}\!>C-$ or $H_2C\!<\!\begin{smallmatrix}CH_2\text{-}O\\CH_2\text{-}O\end{smallmatrix}\!>C-$) yielded only side products. We suggest the following reactionscheme:



In accordance with pathway A, Mantione[8] isolated allene derivatives $ROCH=C=CH-CH(OR)_2$ (R=t.butyl, phenyl) when trialkoxybutynes $ROCH_2\text{-}C\equiv C\text{-}CH(OC_2H_5)_2$ were treated with potassium t.butanolate in DMSO. Repeating this reaction we found the same results for R=methyl. The pathway B (see also ref. 9) may explain that amide is consumed during the reaction, and that the butynes disappear entirely during the reaction but do not isomerise quantitatively. Dialkoxybutadiynes could not be isolated. They are unknown in the literature but it is known that the related dialkoxyethynes are very unstable[10,11].

As expected, the 1,1,4,4-tetramethoxy-1,3-butadienes appeared to be very reactive. They dissolved in CCl_4 to give a yellow colouration probably due to charge-transfer complexation. The compound (6) gives dimethyl succinate with water and 1,1,1,4,4,4-hexamethoxybutane with methanol.

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