Tetrahedron Letters,Vol.29,No.29,pp 3597-3598,1988 0040-4039/88 $3.00 + .00
Printed in Great Britain Pergamon Press plc

SYNTHESIS OF 2-(2-ALKOXYETHYLIDENE)-1,3-DIOXOLANES BY USING THE 1,3-DIOXOLANE RING AS A DOUBLE BOND DIRECTING GROUP

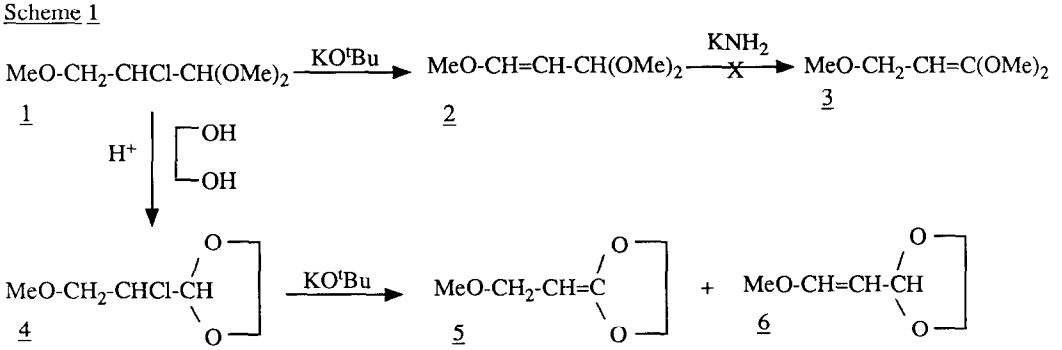
R.W.M. Aben and J.W. Scheeren*
Department of Organic Chemistry, Catholic University Nijmegen
Toernooiveld, 6525 ED Nijmegen, The Netherlands

Summary:The title compounds could be synthesized from 2-chloro-acetal precursors having a dioxolan ring as acetal function so that the double bond is directed towards the dioxolan ring.

Ketene acetals $R^1R^2C=C(OR)_2$ have shown to be highly reactive reaction partners in a variety of cycloadditions[1,2,3]. Especially the ketene acetal $MeCH=C(OMe)_2$, as a propionate equivalent, appeared to be very useful in the synthesis of esters and lactones[3].

In an analogous way it can be envisaged that 1,1,3-trimethoxy propene (3) can be used in cycloadditions as a reactive masked acrylate which is an important structural part of several natural products (e.g. α-methylenelactones[4]). For that reason we tried to prepare 3 via elimination of hydrogen chloride from the easily available 2-chloro-1,1,3-trimethoxy propane (1) as outlined in scheme 1. The elimination yields however exclusively 1,3,3-trimethoxypropene (2)[5]. Furthermore it was not possible to shift the double bond of 2 to the acetal side in the presence of potassium amide[6] (scheme 1).

Scheme 1

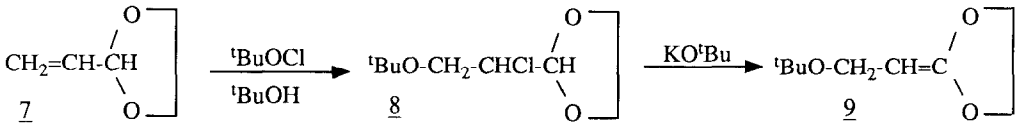


We rationalized that for steric reasons formation of an exo-double bond at the 2-position of a 1,3-dioxolan ring will be more advantageous than in the dimethoxy ketene acetal 3. Besides the lone pairs at the oxygen atoms in the 5-membered dioxolan ring are in a favourable position for overlap with the double bond.

Indeed elimination of hydrogen chloride from the 2-chloro-acetal 4 delivered a mixture of the ketene acetal 5 and the enol ether 6 in nearly equimolar amounts (scheme 1). The amount of ketene acetal could be increased by making the 3-alkoxy group in the 2-chloro-acetal more bulky. So elimination of hydrogen chloride from 8, which can easily be prepared from 7, yielded exclusivily the ketene acetal 9 as described in scheme 2[7].

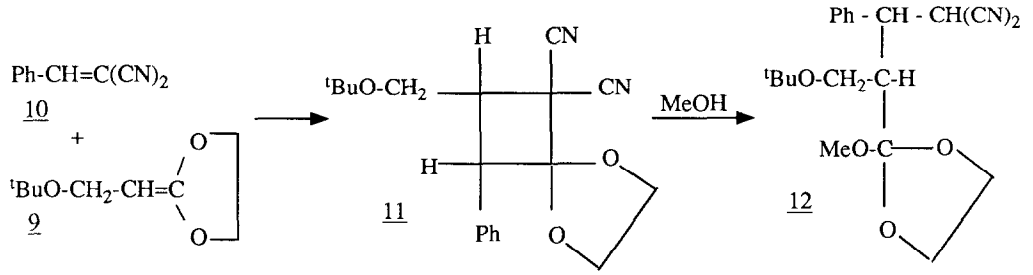
The regioselective addition of ^{t}BuOCl to 7 was carried out in an analogous way as described in the literature for some other alkenes[8].

Scheme 2



We believed that 9 is a promising synthon for the introduction of β-oxy-propionic- or acrylic acid equivalents. This application is now explored by us in [2+2] and [4+2] cycloadditions. The reactivity of 9 appears from the [2+2] cycloaddition reaction given below in scheme 3.

Scheme 3



Ketene acetal 9 showed about the same reactivity as the very reactive 1,1-dimethoxy propene[9]. Compound 11 was formed in acetonitrile within 10 minutes at roomtemperature. Only the trans isomer was isolated as could be deducted from NMR*. Further conversion into the more stable orthoester 12 occurrred in high yield after treatment of 11 with methanol at roomtemperature.

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5. Elimination of hydrogen bromide from the more difficult available 2-bromo-1,1,3-trimethoxypropane yielded also exclusively 2.
6. The ketene acetal MeCH=C(OMe)$_2$ can be easily prepared from 3,3-dimethoxypropene by shifting the double bond with a strong base. See reference 3.
7. The distilled compound 8 (b.p. 55°/0,5mm) still contains an impurity which deactivates the KO^{t}Bu. Therefore in the preparation of 9 compound 8 is two times treated with KO^{t}Bu by the following procedure: 10 g (48 mmol) of the impure 8, dissolved in 75 ml of THF was treated with 6,5 g KO^{t}Bu (58 mmol) for twenty minutes. The mixture is concentrated in vacuo and the residu is extracted with dichloromethane. After evaporation of the solvant the residu is treated again with KO^{t}Bu for two hours as described above. After work up as discribed above the residu is distilled in vacuo (bulb to bulb distillation) yielding 3.8 g (46%) of the pure ketene acetal b.p. 110°/15mm.
^{1}H N.M.R. ($CDCl_3$) δ[ppm]: 4.17 [br.s, 3H, CH_2 and HC=]; 3.88 [br.s, 4H, -$(CH_2)_2$-]; 1.22 [9H, ^{t}Bu].
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(Received in UK 7 June 1988)