Alkylation of Enol Ethers Obtained by Treatment of α,β-Unsaturated Acetals with Organopotassium Reagents: An Inverse Polarity Approach†

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The reaction of α,β-unsaturated acetals 1–4 with sec-butyllithium (2 equiv.) in the presence of potassium tert-butoxide in tetrahydrofuran at −95 °C gave, as a result of 1,4 elimination, α-metallated enol ethers. The latter react with alkyl halides and carbonyl compounds to afford substitution and addition products. In particular, for the reaction with the acetal 1 and D_2O as the electrophile, the α-deuteriated enol ether 5 cyclizes to [2-²H]-2-(prop-1-enyl)-1,3-dioxane.
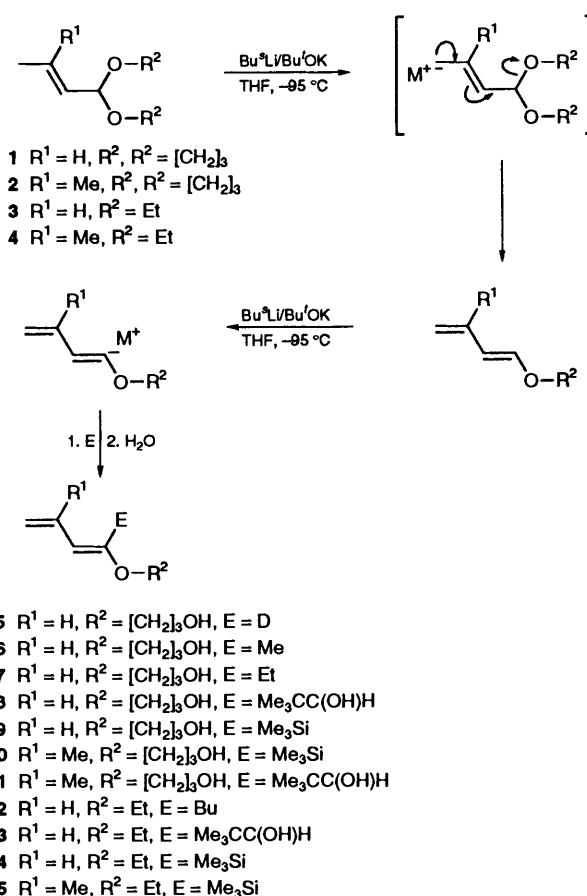
Reactions of allylic acetals with alkyllithium reagents have been much studied and various mechanistic pathways have been described for them. Of these reactions that of sec-butyllithium with acrolein dialkyl acetals in tetrahydrofuran (THF) at −95 °C has been reported to give gem-dialkoxyallyllithium reagents, Li[$CH_2CHC(OR)_2$] which react with organosilicon and organotin chlorides to afford ketene acetals.[1] The acid hydrolysis of these intermediates produces β-substituted propionic acid esters. Nucleophilic addition of alkyllithium reagents to the carbon–carbon double bond of 2-vinyl-1,3-dioxane has been studied in diethyl ether or pentane: the concomitant cleavage of the ring carbon–oxygen bond gives the enol ethers $RCH_2CH=CHO(CH_2)_3OH$.[2] Depending upon their structure and the reaction conditions, α,β-unsaturated acetals and ketals react with organolithium reagents in pentane by addition, elimination or proton abstraction.[3] A synthetically useful double alkylation of α,β-unsaturated acetals with allylzinc in the presence of nickel catalyst has been developed.[4] In previous works we reported that the change of counterion (carried out by using the Schlosser base: alkyllithium complexed with potassium tert-butoxide) modifies the regioselectivity of the reactions of 3,3-dichloroallyl metals with substituted benzaldehydes.[5]

Here we report our study of the reaction of α,β-unsaturated acetals in the presence of organolithium–potassium reagents (2 equiv.). Acetals undergo first 1,4 elimination and, subsequently, metallation of the intermediate alkoxy dienes to give carbanions that react with electrophiles (Scheme 1); for the reaction with the acetal 1 and D_2O as electrophile, the α-deuteriated enol ether 5 cyclizes to [2-²H]-2-prop-1-enyl-1,3-dioxane (Scheme 2).[6] Further, since the substituted enol ethers obtained would be expected to lead to ketones,[7] the α,β-unsaturated acetals 1–4 may be considered as an acyl carbanion equivalent.[7a,8]
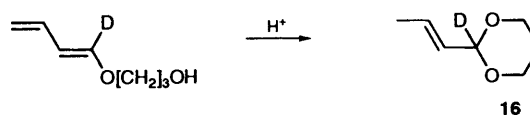
Results and Discussion

Treatment of crotonaldehyde (or 3-methylbut-2-enal) with an equivalent amount of propane-1,3-diol in the presence of pyridinium toluene-p-sulfonate (PPTS) yielded the cyclic acetal 1 (or 2). Reaction of the magnesium derivative of 1-bromoprop-1-ene (or 1-bromo-2-methylpropene) with diethyl phenyl orthoformate afforded the diethyl acetal 3 (or 4).

The acetals 1–4 react with electrophiles in the presence of 2 equiv. of sec-butyllithium complexed with potassium tert-butoxide in THF at −95 °C by a three-step mechanism (Scheme 1): (i) 1,4 elimination promoted by deprotonation at the γ site of the acetal; (ii) abstraction of the proton at the α

1 R^1 = H, R^2, R^2 = [CH_2]₃
2 R^1 = Me, R^2, R^2 = [CH_2]₃
3 R^1 = H, R^2 = Et
4 R^1 = Me, R^2 = Et

5 R^1 = H, R^2 = [CH_2]₃OH, E = D
6 R^1 = H, R^2 = [CH_2]₃OH, E = Me
7 R^1 = H, R^2 = [CH_2]₃OH, E = Et
8 R^1 = H, R^2 = [CH_2]₃OH, E = $Me_3CC(OH)H$
9 R^1 = H, R^2 = [CH_2]₃OH, E = Me_3Si
10 R^1 = Me, R^2 = [CH_2]₃OH, E = Me_3Si
11 R^1 = Me, R^2 = [CH_2]₃OH, E = $Me_3CC(OH)H$
12 R^1 = H, R^2 = Et, E = Bu
13 R^1 = H, R^2 = Et, E = $Me_3CC(OH)H$
14 R^1 = H, R^2 = Et, E = Me_3Si
15 R^1 = Me, R^2 = Et, E = Me_3Si

Scheme 1

Scheme 2

terminus of the produced vinyl ether; (iii) electrophilic attack that gives the substituted enol ethers. Elimination from the acetals to the intermediate alkoxy dienes occurs to give exclusively the E products, as can be inferred from the coupling constant (J 15 Hz), between the vinyl hydrogens at the α and β positions in the ¹H NMR spectrum of the enol ether obtained in the case in which the reaction is quenched with water without adding any electrophile. The results obtained with different electrophiles are reported in Table 1.

Table 1 Reaction of the α,β-unsaturated acetals 1, 2, 3 and 4 with different electrophiles, in the presence of 2 equiv. of Bu^{s}Li complexed with Bu^{t}OK ^{a}

Entry	Electrophile	Substrate	Product	Yield (%)^b
1	D$_2$O	1	5	95^c
2	MeI	1	6	80
3	EtI	1	7	80
4	Me$_3$CCHO	1	8	95
5	Me$_3$SiCl	1	9	85
6	Me$_3$SiCl	2	10	80
7	Me$_3$CCHO	2	11	75
8	BuI	3	12	60
9	Me$_3$CCHO	3	13	70
10	Me$_3$SiCl	3	14	80
11	Me$_3$SiCl	4	15	60

^{a} Substrate (2.5 mmol), Bu^{s}Li (5.0 mmol), Bu^{t}OK (5.0 mmol), electrophile (2.7 mmol), THF (10 ml), $T = -95$ °C. ^{b} Isolated yield of purified product, unless indicated otherwise. ^{c} Determined from the weight of the collected product on the basis of the ^{1}H NMR spectrum.

In no case were products obtained as a result of addition and/or substitution of the organometallic reagent to the α,β-unsaturated acetal. Earlier, Mioskowski, Manna and Falk[3] reported that β-disubstituted acetals such as 4 undergo elimination to 1,4-dienes with no evidence of addition products; in contrast, the authors reported that, under comparable experimental conditions, β-unsubstituted reagents like 3 give exclusively 1,4-addition products in high yield. The differences between our results and those reported by Bailey and Zartun,[2] and by Mioskowky, Manna and Falk,[3] can be attributed to the different nature of the base: an alkyllithium and a mixed lithium–potassium one. In this context, Schlosser and co-workers have studied reactions carried out using organometallic compounds generated through metallation with alkyllithium in the presence of potassium *tert*-butoxide, focusing their attention on the stereoselective and regioselective behaviour.[9] Accordingly to their results, in our case the acting base is a combination of lithium and potassium organometals, in which the lighter and more electrophilic alkali cation could favour elimination of the alkoxide group, while potassium metal would enhance basicity of its anionic counterpart thus facilitating deprotonation at the vinylic site, as shown in Fig. 1.[10,*]
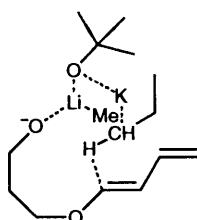

Fig. 1 Proposed transition structure with a chelation model that considers the interaction between Bu^{t}OLi and Bu^{s}K that facilitates proton abstraction at the α site of the vinylic ether.

When the acetals 2 and 4 undergo the reaction reported in Scheme 1 proton abstraction as in the second step of the

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* The preparation of carbanions derived from vinyl ethers has been described (see ref. 9*f* and R. K. Boeckman Jr. and K. J. Bruza, *Tetrahedron Lett.*, 1977, 4187), using Bu^{t}Li at −78 to 5 °C.

† The computations have been performed using the GAUSSIAN92 series of programs (M. J. Frish, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzales, R. I. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, J. A. Pople) on an IBM RISC 6000/550 computer at the Istituto di Chimica Organica.

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proposed mechanism might occur at either of two different sites: *i.e.*, either the vinylic hydrogen α to the oxygen or the δ methyl hydrogens. In the first case, a σ-localised carbanion stabilised by the adjacent oxygen, should be obtained; in the second case, an allylic carbanion should be generated. Notwithstanding, the presence of two nucleophilic termini the electrophiles used in this work react exclusively at the vinylic site. In connection with this regioselective behaviour, theoretical *ab initio* computations have been carried out at the CISD/3-21G//RHF/3-21G level, with size–consistency corrections, on four metallated model compounds.† The computational results reported in Fig. 2 show
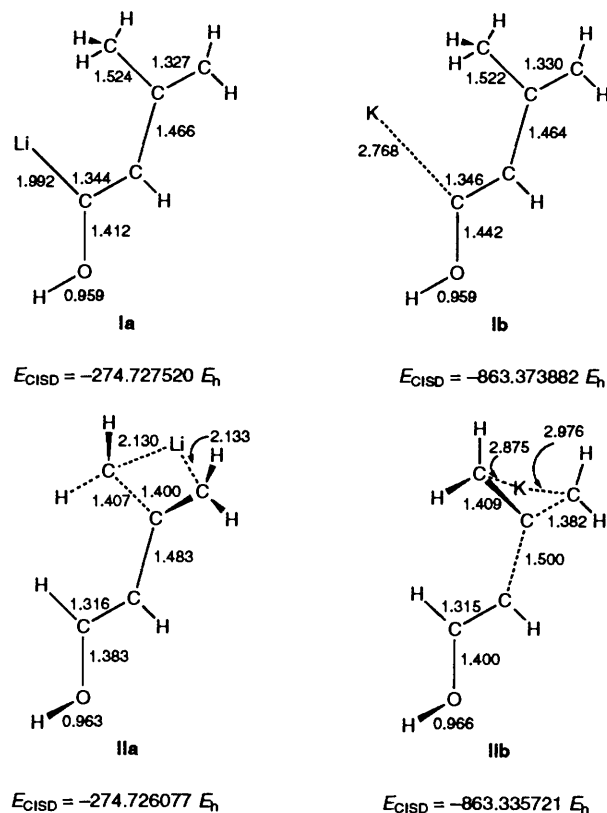

Fig. 2 Some optimized geometrical parameters of the structures of the metallated anionic allylic and vinylic species.

energy differences between the allylic **I a, b** and vinylic **II a, b** structures (0.90 and −23.95 kcal mol^{-1} for Li and K, respectively), that agree with the experimental results, potassium being expected to be the counterion of the obtained carbanions in the reactions reported.[9] Moreover, the possibility that potassiated species are formed is amply justified, the intermediate structure formed being like that proposed in Fig. 1. In such a situation the interactions between the lithium alkoxide and the organopotassium reagent could bring the base close to the vinylic hydrogen, thus favouring the formation of the corresponding σ-localised carbanion.

Experimental

All the reactions involving organometallic compounds have been performed under argon atmosphere in flame-dried glassware. THF was dried by distillation from benzophenone ketyl. Bu^{s}Li (1.4 mol dm^{-3} solution in cyclohexane) was purchased from Aldrich, Bu^{t}OK from Merck, and was sublimated *in vacuo* (0.1 mmHg) prior to the reaction. All chemicals commercially available were reagent grade and were used without further purification. ^{1}H NMR spectra were recorded on a Hitachi Perkin-Elmer R-24B 60 MHz high

resolution spectrometer in CDCl₃, using TMS as internal standard. J Values are given in Hz; ov = overlapped. Mass spectra were recorded at 70 eV with HP 5970 B mass selective detector connected to a HP 5890 GC, cross linked methyl silicone capillary column. Preparative column chromatography was carried out on silica gel Merck Kieselgel 60 with diethyl ether–light petroleum (b.p. 40–70) as an eluent. The reaction temperatures are uncorrected: they were measured using a pentane thermometer immersed to a depth of *ca.* 10 cm into the refrigerating bath (acetone frozen with liquid nitrogen).

*Prop-2-enyl-*1,3-*dioxane* **1**.—A solution of crotonaldehyde (7.0 g, 0.1 mol) and propane-1,3-diol (7.6 g, 0.1 mol) was refluxed for 2 h in anhydrous benzene (100 cm³) in a Dean-Stark trap in the presence of PPTS (0.25 g, 1.0 mmol). The mixture was washed with aqueous NaHCO₃ and brine, dried (K₂CO₃), filtered and concentrated under reduced pressure to give the acetal **1** (10.5 g, 82%) as a colourless oil; b.p. 80 °C (17 mmHg); δ_H(60 MHz CDCl₃; Me₄Si) 1.20–2.45 (2 H, m, CH₂C*H*₂CH₂), 1.68 (3 H, d, *J* 6, Me), 3.45–4.40 (4 H, m, C*H*₂CH₂C*H*₂), 4.80 (1 H, d, *J* 6 = CHC*H*), 5.35 (1 H, dd, *J* 16, 6, CH=C*H*CH), 5.77 (1 H, dq, *J* 16, 6, MeC*H*=CH).

2-(2-*Methylprop-*1-*enyl*)-1,3-*dioxane* **2**.—A solution of 3-methylbut-2-enal (8.4 g, 0.1 mol) was allowed to react according to the procedure described for **1** to afford the acetal **2** (10.6 g, 75%) as a colourless oil; b.p. 100 °C (17 mmHg); δ_H(60 MHz; CDCl₃; Me₄Si) 1.10–2.50 (2 H, m, CH₂C*H*₂CH₂), 1.65 (3 H, s, Me), 1.70 (3 H, s, Me), 3.45–4.40 (4 H, m, C*H*₂CH₂C*H*₂), 4.85 (1 H, d, *J* 6, =CHC*H*), 5.10 (1 H, d, *J* 6, =CHCH).

1,1-*Diethoxybut-*2-*ene* **3**.—1-Bromoprop-1-ene (12.1 g, 0.1 mol) was converted in THF into the corresponding Grignard reagent, and then treated with diethyl phenyl orthoformate (19.6 g, 0.1 mol), according to the procedure reported by Miginiac and co-workers,[11] to afford **3** (10.1 g, 70%) as a colourless oil; b.p. 50 °C (17 mmHg) (lit.,[11] 48 °C/15 mmHg); δ_H(60 MHz; CDCl₃; Me₄Si) 1.15 (6 H, t, *J* 6, OCH₂C*H*₃), 1.70 (3 H, d, *J* 6, Me), 3.05–3.50 (4 H, ov q, *J* 6, OC*H*₂CH₃), 4.65 (1 H, d, *J* 6, =CHC*H*), 5.25 (1 H, dd, *J* 16, 6, CH=C*H*CH), 5.65 (1 H, dq, *J* 16, 6, MeC*H*=CH).

1,1-*Diethoxy-*3-*methylbut-*2-*ene* **4**.—1-Bromo-2-methylpropene (13.5 g, 0.1 mol) was allowed to react according to the procedure described for **3**, to afford the acetal **4** (11.1 g, 70%) as a colourless oil; b.p. 132 °C (760 mmHg) (lit.,[11] 63 °C/67 mmHg). ¹H NMR, δ_H(60 MHz; CDCl₃; Me₄Si) 1.15 (6 H, t, *J* 6, OCH₂C*H*₃), 1.70 (6 H, ov s, Me), 3.05–3.50 (4 H, ov q, *J* 6 OC*H*₂CH₃), 4.70 (1 H, d, *J* 6, =CHC*H*), 4.90 (1 H, d, *J* 6, =C*H*CH).

General Procedure for the Reactions of Acetals with Organolithium–Potassium Reagents.—Under an atmosphere of argon, BuᵗOK (0.56 g, 5.0 mmol) was added to anhydrous THF (5.0 cm³) at room temperature.[12] The suspension was cooled to −95 °C and BuˢLi (1.4 mol dm⁻³ solution in cyclohexane; 3.57 cm³, 5.0 mmol) was added to it dropwise with stirring. After 15 min, 2.5 mmol of the appropriate acetal (**1**, 0.32 g; **2**, 0.35 g; **3**, 0.36 g; **4**, 0.40 g) was added to the resulting pale yellow solution. After a few seconds the solution turned purple and was stirred at −95 °C for 2 h. After the addition of the appropriate electrophile (2.7 mmol) the colour was discharged and the mixture was allowed to react for 2 h; it was then quenched by addition of aqueous THF (0.5 cm³). The mixture was poured into water, the organic phase was separated and the aqueous phase extracted twice with diethyl ether; the combined organic phases were washed with brine, dried (Na₂SO₄), and concentrated to give crude products. Further purification of the

products was carried out by means of chromatography on a SiO₂ column followed by Kugelrohr distillation. Some pertinent data for products **5-13** are reported below.

3-([1-²H]*Buta-*1,3-*dienyloxy*)*propan-*1-*ol* **5**. δ_H(60 MHz; CDCl₃; Me₄Si) 1.90 (2 H, quint., 6, CH₂C*H*₂CH₂), 3.10 (1 H, s, OH), 3.65 (4 H, ov t, 6, C*H*₂CH₂CH₂), 4.60 (1 H, dd, *J* 10, 2, =CH*H*-*cis*), 4.75 (1 H, dd, *J* 16, 2, =CH*H* *trans*), 5.50 (1 H, d, *J* 10, =CHC*H*=), 5.90–6.55 (1 H, m, *J* 16, 10, 10, =C*H*CH=); *m/z* (relative intensity) 129 (M⁺, 12), 71 (100) and 41 (22).

3-(1-*Methylbuta-*1,3-*dienyloxy*)*propan-*1-*ol* **6**. δ_H(60 MHz; CDCl₃; Me₄Si) 1.85 (3 H, s, Me), 1.90 (2 H, quint., 6, CH₂C*H*₂CH₂), 2.80 (1 H, s, OH), 3.65 (4 H, overlapped t, *J* 6, C*H*₂CH₂C*H*₂), 4.60 (1 H, dd, *J* 10, 2, =CH*H* *cis*), 4.75 (1 H, dd, *J* 16, 2, =CH*H* *trans*), 5.15 (1 H, d, *J* 10 =CHC*H*=), 5.90–6.55 (1 H, m, *J* 16, 10, 10, =C*H*CH=); *m/z* (relative intensity) 142 (M⁺, 17), 83 (100), 69 (12), 57 (7) and 41 (63). (Found: C, 67.2; H, 9.8 Calc. for C₈H₁₄O₂: C, 67.6; H, 9.9 %).

3-(1-*Ethylbuta-*1,3-*dienyloxy*)*propan-*1-*ol* **7** δ_H(60 MHz; CD-Cl₃; Me₄Si) 1.05 (3 H, t, *J* 7, CH₂CH₃), 1.90 (2 H, quint., *J* 6, CH₂C*H*₂CH₂), 2.25 (2 H, q, *J* 7, C*H*₂CH₃), 3.30 (1 H, s, OH), 3.65 (4 H, ov t, *J* 6, C*H*₂CH₂C*H*₂), 4.60 (1 H, dd, *J* 10, 2, =CH*H* *cis*), 4.75 (1 H, dd, *J* 16, 2, =CH*H* *trans*), 5.05 (1 H, d, *J* 10, =CHC*H*=), 5.90–6.55 (1 H, m, *J* 16, 10, 10, =C*H*CH=); *m/z* (relative intensity) 156 (M⁺, 12), 69 (100), 41 (22) and 39 (13) (Found: C, 68.9; H, 10.1. Calc. for C₉H₁₆O₂: C, 69.2; H, 10.3 %).

4-(3-*Hydroxypropoxy*)-2,2-*dimethylhepta-*4,6-*dien-*3-*ol* **8**. M.p. 43 °C; δ_H(60 MHz; CDCl₃; Me₄Si) 0.90 (9 H, s, Me₃), 1.90 (2 H, quint., *J* 6, CH₂C*H*₂CH₂), 3.10 (2 H, s, OH), 3.65 (4 H, q, *J* 6, C*H*₂CH₂C*H*₂), 4.20 (1 H, s, CH), 4.60 (1 H, dd, *J* 10, 2, =CH*H* *cis*), 4.75 (1 H, dd, *J* 16, 2, =CH*H* *trans*), 5.25 (1 H, d, *J* 10, =CHC*H*=), 5.90–6.55 (1 H, m, *J* 16, 10, 10, =C*H*CH=); *m/z* (relative intensity) 214 (M⁺, 5), 157 (32), 81 (98), 69 (42), 57 (91) and 41 (100) (Found: C, 66.8; H, 10.6. Calc. for C₁₂H₂₂O₃: C, 67.3; H 10.4 %).

3-(1-*Trimethylsilylbuta-*1,3-*dienyloxy*)*propan-*1-*ol* **9**. δ_H(60 MHz; CDCl₃; Me₄Si) 0.15 (9 H, s, SiMe₃), 1.90 (2 H, quint., *J* 6, CH₂C*H*₂CH₂), 2.10 (1 H, s, OH), 3.65 (4 H, q, *J* 6, C*H*₂CH₂C*H*₂), 4.60 (1 H, dd, *J* 10, 2, =CH*H* *cis*), 4.75 (1 H, dd, *J* 16, 2, =CH*H* *trans*), 5.75 (1 H, d, *J* 10, =CHC*H*=), 6.0–6.65 (1 H, m, *J* 16, 10, 10, =C*H*CH=); *m/z* (relative intensity) 200 (M⁺, 6), 127 (6), 75 (39), 73 (100) and 45 (21) (Found: C, 60.7; H, 9.8. Calc. for C₁₀H₂₀O₂Si: C, 60.0; H, 10.1 %).

3-(3-*Methyl-*1-*trimethylsilylbuta-*1,3-*dienyloxy*)*propan-*1-*ol* **10**. δ_H(60 MHz; CDCl₃; Me₄Si) 0.10 (9 H, s, SiMe₃), 1.70 (3 H, s, Me), 1.80 (2 H, quint., *J* 6, CH₂C*H*₂CH₂), 2.70 (1 H, s, OH), 3.65 (4 H, ov q, *J* 6, C*H*₂CH₂C*H*₂), 4.65 (2 H, br s, =CH₂), 5.55 (1 H, br s, C*H*=); *m/z* (relative intensity) 214 (M⁺, 2), 141 (5), 75 (80) and 73 (100) (Found: C, 61.8; H, 10.5. Calc. for C₁₁H₂₂O₂Si: C, 61.6; H, 10.3%).

4-(3-*Hydroxypropoxy*)-2,2,6-*trimethylhepta-*4,6-*dien-*3-*ol* **11**. M.p. 69–71 °C; δ_H(60 MHz; CDCl₃; Me₄Si) 0.90 (9 H, s, Me₃), 1.70 (3 H, s, Me), 1.90 (2 H, quint., *J* 6, CH₂C*H*₂CH₂), 2.10 (2 H, s, OH), 3.65 (4 H, q, *J* 6, C*H*₂CH₂C*H*₂), 4.20 (1 H, s, CH), 4.85 (2 H, br s, =CH₂), 5.15 (1 H, br s, −CH=); *m/z* (relative intensity) 228 (M⁺, 5), 173 (3), 141 (100), 69 (5), 57 (19) and 55 (25) (Found: C, 68.8; H, 10.8. Calc. for C₁₃H₂₄O₃: C, 68.4; H 10.6%).

4-*Ethoxyocta-*1,3-*diene* **12**. δ_H(60 MHz; CDCl₃; Me₄Si) 0.70 (3 H, t, CH₂C*H*₃), 1.15 (3 H, t, *J* 7, OCH₂C*H*₃), 2.05 (2 H, t, *J* 7, C*H*₂CH₂−), 3.55 (2 H, q, *J* 7, OCH₂), 4.50 (2 H, dd, *J* 10, 2, =CH₂ *trans*), 4.70 (2 H, dd, *J* 16, 2, =CH₂ *cis*), 5.0 (1 H, d, *J* 10 =CHC*H*=), 5.90–6.55 (1 H, m, *J* 16, 10, 10, =C*H*CH=); *m/z* (relative intensity) 154 (M⁺, 19), 97 (46), 69 (100) and 57 (13). (Found: C, 78.4; H, 12.0. Calc. for C₁₀H₁₈O: C, 77.9; H, 11.8%).

4-*Ethoxy-*2,2-*dimethylhepta-*4,6-*dien-*3-*ol* **13**. δ_H(60 MHz; CD-Cl₃; Me₄Si) 0.85 (9 H, s, Me₃), 1.20 (3 H, t, *J* 7, OCH₂C*H*₃), 2.65 (1 H, s, OH), 3.65 (2 H, q, *J* 7, OCH₂), 4.05 (1 H, s, CH), 4.60

(2 H, dd, J 10, 2, =CH$_2$ *trans*), 4.80 (2 H, dd, J 16, 2, =CH$_2$ *cis*), 5.20 (1 H, d, J 10 =CHCH=), 6.0–6.65 (1 H, m, J 16, 10, 10, =CHCH=); m/z (relative intensity) 184 (M$^+$, 21), 127 (25), 81 (100) and 57 (73) (Found: C, 71.4; H, 11.0. Calc. for C$_{11}$H$_{20}$O$_2$: C, 71.7; H, 10.9%).

4-*Ethoxy*-4-*trimethylsilylbuta*-1,3-*diene* **14**. δ_H(60 MHz; CD-Cl$_3$; Me$_4$Si) 0.15 (9 H, s, SiMe$_3$), 1.15 (3 H, t, J 7, OCH$_2$CH_3), 3.55 (2 H, q, J 7, OCH$_2$), 4.60 (2 H, dd, J 10, 2, =CH$_2$ *trans*), 4.70 (2 H, dd, J 16, 2, =CH$_2$ *cis*), 5.55 (1 H, d, J 10, =CHCH=), 5.95–6.55 (1 H, m, J 16, 10, 10, =CHCH=); m/z (relative intensity) 170 (M$^+$, 53), 103 (22), 75 (24) and 73 (100). (Found: C, 63.0; H, 10.4. Calc. for C$_9$H$_{18}$OSi: C, 63.5; H, 10.6%).

4-*Ethoxy*-2-*methyl*-4-*trimethylsilylbuta*-1,3-*diene* **15**. δ_H(60 MHz; CDCl$_3$; Me$_4$Si) 0.15 (9 H, s, SiMe$_3$), 1.15 (3 H, t, J 7, OCH$_2$CH_3), 1.65 (3 H, s, Me), 3.50 (2 H, q, J 7, OCH$_2$), 4.65 (2 H, br s, =CH$_2$), 5.55 (1 H, br s, –CH=); m/z (relative intensity) 184 (M$^+$, 1), 75 (23), 73 (100) and 45 (25) (Found: C, 65.7; H, 11.1. Calc. for C$_{10}$H$_{20}$OSi: C, 65.2; H, 10.9%).

Procedure for the Formation of [2-^{2}H] *Prop*-2-*enyl*-1,3-*dioxane* **16**.—A solution of **5** (0.32 g, 2.5 mmol) in anhydrous chloroform (25 cm^3) was vigorously stirred whilst being treated with a catalytic amount of methanesulfonic acid at room temperature. After 0.5 h the reaction mixture was washed with brine, dried (K$_2$CO$_3$), filtered and concentrated to give the acetal **16** (0.30 g, 94%): δ_H(60 MHz; CDCl$_3$; Me$_4$Si) 1.20–2.40 (2 H, m, CH$_2$CH_2CH$_2$), 1.70 (3 H, d, J 6, Me), 3.45–4.20 (4 H, m, CH_2CH$_2$CH_2), 5.25 (1 H, d, J 16, =CH) and 5.65 (1 H, dq, J 16, 6, =CHCH$_3$); m/z (relative intensity) 129 (M$^+$, 85).

Acknowledgements

References

1 D. Seyferth, R. E. Mammarella and H. A. Klein, *J. Organomet. Chem.*, 1980, **194**, 1.

2 W. F. Bailey and D. L. Zartun, *J. Chem. Soc., Chem. Commun.*, 1984, 34.

3 C. Mioskowski, S. Manna and J. R. Falck, *Tetrahedron Lett.*, 1984, **25**, 519.

4 A. Yanagisawa, S. Habaue and H. Yamamoto, *J. Am. Chem. Soc.*, 1989, **11**, 366.

5 C. Canepa, S. Cobianco, I. Degani, A. Gatti and P. Venturello, *Tetrahedron*, 1991, **47**, 1485; C. Canepa, G. Tonachini and P. Venturello, *Tetrahedron*, 1991, **47**, 8739.

6 Preliminary communication, P. Venturello, *J. Chem. Soc., Chem. Commun.*, 1992, 1032.

7 (*a*) W. C. Still and T. L. Macdonald, *J. Am. Chem. Soc.*, 1974, **96**, 5561; (*b*) H. Staudinger and L. Ruzicka, *Helv. Chim. Acta*, 1924, **7**, 377.

8 (*a*) E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 1075; (*b*) D. Seebach and M. Kolb, *Chem. Ind. (London)*, 1974, 687; (*c*) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 239; (*d*) W. S. Murphy and S. Wattanasin, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2678; (*e*) D. A. Evans, G. C. Andrews and B. Buckwalter, *J. Am. Chem. Soc.*, 1974, **96**, 5560; (*f*) J. E. Baldwin, G. A. Höfle and O. W. Lever, Jr., *J. Am. Chem. Soc.*, 1974, **96**, 7125; experiments are in course in our laboratory for converting the obtained enol ethers into carbonyl compounds.

9 M. Schlosser, *J. Organomet. Chem.*, 1967, **8**, 9; M. Schlosser and J. Hartmann, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 508; M. Schlosser, J. Hartmann and V. David, *Helv. Chim. Acta*, 1974, **57**, 1567.

10 A. Mordini, E. Ben Rayana, C. Margot and M. Schlosser, *Tetrahedron*, 1990, **46**, 2401.

11 F. Barbot, L. Poncini, B. Randrianoelina and P. Miginiac, *J. Chem. Research* 1981 (*S*), 343.

12 L. Brandsma and H. Verkruijsse, *Preparative Polar Organometallic Chemistry 1*, Springer-Verlag, Berlin, 1987, p. 18.