

THE REACTION OF GRIGNARD REAGENTS WITH 1,3-DIOXOLANES

III *. A NOVEL SYNTHETIC ROUTE TO β -HYDROXYALKYL ENOL ETHERS

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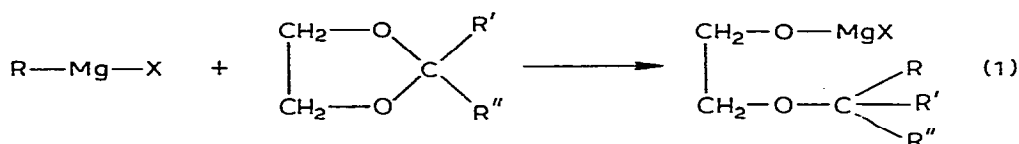
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Summary

The reaction of ethylmagnesium bromide, prepared in benzene with one or more molar equivalents of triethylamine, with 2-, 2,4- and 2,4,5-substituted 1,3-dioxolanes has been investigated. Besides β -hydroxyethyl sec-alkyl ethers, the normal products of the ring opening/addition reaction encountered with other Lewis bases, 2-hydroxyethyl enol ethers were formed as products of a ring opening/elimination reaction. Kinetic studies suggest an E_1 mechanism for this novel reaction.

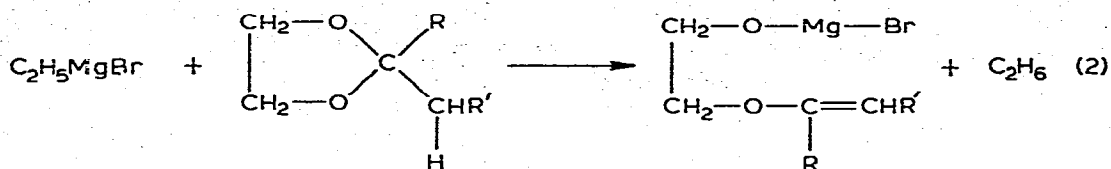
Introduction

So far, in the reaction of Grignard compounds with 2-substituted 1,3-dioxolanes only one product has been observed, viz. that resulting from ring cleavage and attack by the Grignard alkyl group on C(2) (eq. 1) [1]. We have now found



that, depending on the conditions, a 2-hydroxyalkyl enol ether can be formed as a side product, or even as the main product (eq. 2). Attack on β -hydrogen atoms in ethers by Grignard compounds has been reported in only a few cases:

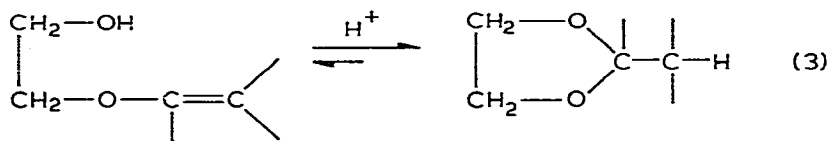
* For Part II: see ref. 10.



Cabiddu and coworkers observed this reaction, followed by elimination of a phenoxide ion, in reactions of Grignard compounds with dihydro-2,3-benzofuran [2] as well as with 1,3-dioxoles [3]. These reactions were carried out at elevated temperatures in benzene or toluene over long reaction times (13 h).

Common synthetic procedures for the preparation of enol ethers which are in principle suited for β -hydroxyalkyl enol ethers include the addition of alcohols to alkynes [4] and the elimination of alcohols from acetals or ketals [5] (see ref. 6 and 7 for a detailed discussion of these procedures). Both procedures have disadvantages. Thus, the addition of an alcohol to an alkyne requires higher pressures (10–20 atm) in the case of the lower alkynes. Furthermore, in the reaction of diols with alkynes a second reaction with the remaining alcohol function does take place to some extent

For the elimination reaction of acetals or ketals, simple heating sometimes suffices, in particular with ketals. However, acidic catalysts are usually required. In this case, an undesirable side reaction is the formation of the carbonyl compound from which the ketal is derived, by further cleavage of the intermediate enol ether. Furthermore, this method is not applicable to the synthesis of β -hydroxyalkyl enol ethers from 2-substituted 1,3-dioxolanes, since the reverse reaction is favoured under these conditions (eq. 3).



Our new synthetic procedure avoids the disadvantages. It can be performed with ordinary, all-glass laboratory equipment, and is carried out in a basic medium, in which the enol ether is stable. It is therefore the method of choice for the synthesis of compounds such as 2-hydroxyethyl vinyl ether, which were previously prepared by the addition of 1,2-ethanediol to ethyne [4,8].

Synthetic aspects

When $(\text{C}_2\text{H}_5\text{MgBr} \cdot \text{E})_2$ [9] ($\text{E} = i\text{-Pr}_2\text{O}$, Et_2O , THF or Et_3N) in benzene was allowed to react with 2-ethyl- or 2-ethyl-4-methyl-1,3-dioxolane, the normal 2-hydroxyethyl sec-alkyl ether (AE) [1] was the main product; only for $\text{E} = \text{Et}_3\text{N}$ were 2-hydroxyethyl enol ethers (EE) predominantly revealed by GLC (Table 1).

With more than one molar equivalent of Et_3N , the yields of the enol ether improved, but at the same time the rate decreased so much (cf. Table 4) that

TABLE 1

YIELDS OF PRODUCTS IN THE REACTION OF $(\text{EtMgBr} \cdot \text{E})_2^a$ WITH 2-ETHYL-1,3-DIOXOLANE (Et-D) AND WITH 2-ETHYL-4-METHYL-1,3-DIOXOLANE^e (EtMe-D) IN BENZENE

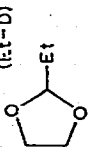
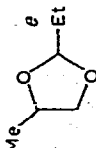
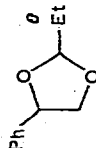
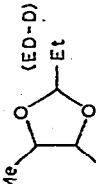
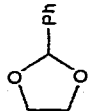
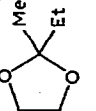
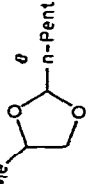
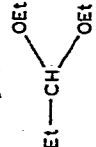
| E | D ₀ (mol/l) | EtMgBr ₀ (mol/l) | EE (%) ^b | AE (%) ^c | Total (%) ^d | Reaction time | Temperature (°C) |
|--------------------------|---------------------------|---------------------------------|------------------------|------------------------|---------------------------|------------------|---------------------|
| <i>Et-D</i> ^d | | | | | | | |
| i-Pr ₂ O | 0.39 | 0.13 | trace | >99 | quant. | 24 h | 40 |
| Et ₂ O | 0.11 | 0.10 | trace | >99 | quant. | 24 h | 40 |
| THF | 0.030 | 0.059 | 4 | 96 | quant. | 30 days | 40 |
| 1 eq. Et ₃ N | 0.15 | 0.15 | 1 | 10 | 11 | 2 h | 40 |
| 1 eq. Et ₃ N | 0.15 | 0.15 | 3 | 22 | 25 | 4 h | 40 |
| 1 eq. Et ₃ N | 0.15 | 0.15 | 8 | 42 | 48 | 7 h | 40 |
| 1 eq. Et ₃ N | 0.071 | 0.071 | 18 | 82 | quant. | 96 h | 40 |
| 5 equ. Et ₃ N | 0.246 | 0.230 | 59 | 41 | quant. | 72 h | 90 |
| <i>EtMe-D</i> | | | | | | | |
| i-Pr ₂ O | 0.30 | 0.34 | 5 | 95 | quant. | 72 h | 25 |
| Et ₂ O | 0.23 | 0.24 | 8 | 72 | quant. | 72 h | f |
| THF | 0.094 | 0.12 | 7 | 68 | 75 | 10 days | f |
| 1 equ. Et ₃ N | 0.15 | 0.17 | 56 | 20 | quant. | overnight | f |
| 4 equ. Et ₃ N | 0.15 | 0.17 | 95 | 5 | quant. | overnight | f |
| pure Et ₃ N | 0.09 | 0.08 | <5 | — | <5 | 48 h | f |
| | | (+0.12 M Et ₂ Mg) | | | | | |

^a The ratio $[\text{EtMgBr}]_0/[\text{Et}_3\text{N}]$ was 1.00/1.26 in Tables 1 and 2, and 1.00/1.10 in Table 3 unless otherwise stated; for E = i-Pr₂O, Et₂O and THF see ref. 1. ^b EE was the total yield of *cis* and *trans* β -hydroxyethyl sec-alkyl ether. When 4-substituted 1,3-dioxolanes are used, two products are possible of which one resulting from cleavage of the C(2)—O(3) bond always amounted to less than 4%. ^c By NMR-spectroscopy of the reaction mixture it was concluded that the conversion of 1,3-dioxolanes was mostly quantitative (>90%). However, the yields of EE and AE were determined by GLC-analysis: during this process some EE may rearrange back to the 1,3-dioxolane which explains that the sum of EE and AE does not amount to 100%. The rate of rearrangement depends on the structure of EE as well as on the temperatures in different parts of the gas-chromatograph, especially in the injection port. ^d $\text{HO}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}=\text{CHCH}_3$ could be determined by GLC, if the temperature was kept below 150°C: under these conditions no isomerization to the dioxolane occurred. ^e The $[\text{cis}]_0/[\text{trans}]_0$ ratio was about 6/5. ^f The reactions were mostly performed in closed glass apparatus. When the mixture is refluxed, the temperature depends on the temperature of the heating bath and the shape of the vessel and may vary from 40–60°C. In most cases it was probably close to 60°C. ^g In this case EE is structurally impossible. ^h In this case three enol ethers are possible; all three of them were observed by GCMS but their structure was not further identified. ⁱ This reaction was performed in the presence of 5 equivalents of Et₃N.

conversion was unsatisfactory. An example of a useful preparative procedure is given in the Experimental section.

From the dioxolanes with an ethyl or a n-pentyl group in the 2-position (see Table 2) *cis* and *trans* isomers of the enol ethers were expected, and were indeed observed by GLC analysis (15% SE 30 on Chromosorb W). In the case of the enol ethers formed from 2-ethyl-4-methyl-1,3-dioxolanes, the component with the shorter retention time was found to be the *cis* isomer: this component was isolated and the ¹H NMR spectrum compared with that of ethyl propenyl ether (Sadler Index nr 7448 M); the ethylenic protons show ³J(HH) = 6 Hz, which is consistent with a *cis* configuration. The *cis/trans* ratio was about 3/1. Assuming that for other cases also the *cis* isomer of the enol ether had the shorter retention time, we conclude from the relative peak heights of the two isomers that more of the *cis* than of the *trans* isomer was always formed. The results, presented

TABLE 2. YIELDS OF PRODUCTS IN THE REACTION OF EtMgBr IN THE PRESENCE OF Et_3N WITH SOME SUBSTITUTED 1,3-DIOXOLANES (D) IN BENZENE

| Dioxolane | [D] ₀ (mol/l) | [EtMgBr] ₀ (mol/l) | EE (%) ^b | AE (%) ^c | Total (%) ^c | Time | Temperature (°C) |
|--|-----------------------------|---|------------------------|------------------------|---------------------------|-----------|---------------------|
|  | 0.071 | 0.071 | 18 | 82 | quant. | overnight | 40 |
|  | 0.15 | 0.17 | 56 | 20 | quant. | overnight | <i>f</i> |
| <i>cis + trans</i>  | 0.17 | 0.17 | 53 | 18 | quant. | 24 h | 40 |
| <i>cis + trans</i>  | 0.15 | 0.17 | 29 | 60 | quant. | 11 days | <i>f</i> |
| <i>(+)-(4R, 5R)</i>  | 0.16 | 0.17 | <i>f</i> | quant. | quant. | 2 h | 23 |
|  | 0.15 | 0.17 | <i>h</i> 20 | 10 | quant. | 48 h | 40 |
|  | 0.16 | 0.17 | 71 | 11 | quant. | 3 days | <i>f</i> |
| <i>cis + trans</i> 4 eq. Et_3N  | 0.16 | 0.17 | 0 | 0 | 0 | 3 days | <i>f</i> |

a, b, c, e, f, g, h See footnotes to Table 1.

TABLE 3

PRODUCT DISTRIBUTION ^a IN THE REACTION OF EtMgBr IN THE PRESENCE OF Et₃N ^a WITH 2-ETHYL-3,3-DIOXOLANE (Et-D) IN BENZENE, AT VARIOUS RATIOS [Et-D]₀/[EtMgBr]₀; THE REACTION TEMPERATURE WAS 40°C; THE YIELD WAS ALWAYS QUANTITATIVE (>90%)

| [Et-D] ₀ | [EtMgBr] ₀ | [Et-D] ₀ /[EtMgBr] ₀ | EE (%) | AE (%) |
|---------------------|-----------------------|--|--------|--------|
| 2.015 | 0.301 | 6.7/1.0 | 35 | 65 |
| 1.062 | 0.211 | 5.0/1.0 ⁱ | 56 | 44 |
| 0.530 | 0.195 | 2.7/1.0 | 40 | 60 |
| 0.688 | 0.349 | 2.0/1.0 | 38 | 62 |
| 0.278 | 0.287 | 1.0/1.0 | 42 | 58 |
| 0.071 | 0.071 | 1.0/1.0 | 18 | 82 |
| 0.246 | 0.230 | 1.0/1.0 ⁱ | 59 | 41 |
| 0.056 | 0.238 | 1.0/4.0 | 11 | 89 |
| 0.054 | 0.242 | 1.0/4.4 | 2 | 98 |
| 0.032 | 0.213 | 1.0/6.5 | 5 | 95 |

^{a,d,i} See footnotes to Table 1.

in Tables 1–3, give rise to the following comments:

a. no elimination is observed with the open acetal, 1,1-diethoxypropane (Table 2);

b. no major influence is observed when n-pentyl replaces ethyl in the 2-position (Table 2);

c. substitution in the 4-position of the dioxolane seems to favour the formation of the enol ether (Tables 1, 2);

d. since proton abstraction by THF, Et₂O or i-Pr₂O is rather unlikely, it seems that in these cases the formation of elimination products is largely caused by attack of the ethyl group of the Grignard reagent (Table 1). Thus the unique combination of properties of Et₃N, which is a strong base towards protons and a relatively weak base towards EtMgBr (comparable to Et₂O [9] which facilitates complexation and reaction between Grignard reagent and dioxolane) and makes the synthesis of the β-hydroxyethyl enol ether possible.

e. the ratio EE/AE does not change very much during the first half of the reaction; towards the end of the reaction relatively more EE is formed (Table 1);

f. with an excess of 2-ethyl-1,3-dioxolane, relatively more EE is formed than with an excess of EtMgBr (Table 3).


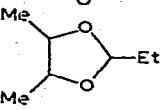
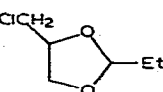
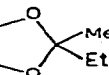
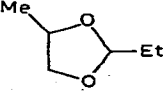
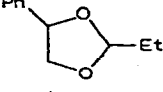
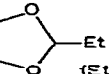
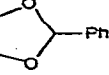
Kinetic measurements


For several dioxolanes (D) the rate of the reaction with (EtMgBr · Et₃N)₂ in benzene was measured to give information on the influence of substituents on the reactivity of dioxolanes with Grignard reagents. The yields of the reactions are given in Tables 1–3 (except that for 2-ethyl-4-chloromethyl-1,3-dioxolane, which is given in Table 4). A plot of ln c against time (c being the concentration of the reagent which is not in excess) gave a first order rate constant, *k*_{exp} (Table 4). Since, as we have shown earlier [1,10] at least part of the addition reaction proceeds via a second order mechanism, *k*_{exp} must be a complex quantity. The following comments can be made:

a. Increasing the Et₃N concentration does not increase the rate (reaction

TABLE 4

EXPERIMENTAL FIRST ORDER RATE CONSTANTS FOR THE REACTION OF $(\text{EtMgBr} \cdot \text{Et}_3\text{N})_2^a$ WITH SEVERAL DIOXOLANES (D) AT 40.5°C IN BENZENE

| No | D | [D] ₀ | [EtMgBr] ₀ | k_{exp} (sec ⁻¹) ± σ ^b |
|----|---|----------------------|-----------------------|--|
| 1 |  ^c | no reaction observed | | |
| 2 |  (±)-(4 <i>R</i> , 5 <i>R</i>) | 0.199 | 0.170 | $(3.95 \pm 0.33) \times 10^{-7}$ |
| 3 |  <i>trans</i> | 0.082 | 0.170 | $(8.50 \pm 2.26) \times 10^{-7}$ |
| 4 | <i>idem, cis</i> ^e | 0.113 | 0.170 | $(1.77 \pm 0.094) \times 10^{-6}$ |
| 5 |  | 0.182 | 0.171 | $(1.90 \pm 0.044) \times 10^{-5}$ |
| 6 |  <i>trans</i> ^f | 0.105 | 0.113 | $(1.33 \pm 0.13) \times 10^{-5}$ |
| 7 | <i>idem, cis</i> ^g | 0.142 | 0.140 | $(3.81 \pm 0.32) \times 10^{-5}$ |
| 8 |  <i>trans</i> ^d | 0.073 | 0.170 | $(3.72 \pm 0.40) \times 10^{-5}$ |
| 9 | <i>idem, cis</i> | 0.093 | 0.170 | $(4.50 \pm 0.26) \times 10^{-5}$ |
| 10 |  a (Et-D) | 0.278 | 0.287 | $(4.61 \pm 0.33) \times 10^{-5}$ |
| | b 5 eq. Et ₃ N | 0.246 | 0.230 | $(1.02 \pm 0.07) \times 10^{-5}$ |
| | c Et-D | 0.530 | 0.195 | $(3.20 \pm 0.66) \times 10^{-5}$ |
| | d 5 eq. Et ₃ N | 1.062 | 0.211 | $(1.55 \pm 0.07) \times 10^{-5}$ |
| 11 |  | 0.156 | 0.172 | $(8.59 \pm 0.10) \times 10^{-4}$ ^h |

^a The ratio $[\text{EtMgBr}]_0/[\text{Et}_3\text{N}]$ was 1.0/1.26, except when otherwise stated. ^b σ is the standard deviationof the mean. ^c  is known to precipitate MgBr₂. However, the lack of reactivity is not necessarily due to the fact that only Et₂Mg is left in solution because the formation of a precipitate can also beobserved for , which nevertheless reacts with a rate, comparable with that of Et-D. ^d Thereaction was performed with the equilibrium mixture of the *cis* and *trans* compound: the $[\text{cis}]_0/[\text{trans}]_0$ ratio was about 6/5. ^e By GCMS the following products were found: EE (43%), AE (26%), EtCH₂CHOCH₂OCH-(Et)₂ (17%), and trace amounts of EtCH₂CHOHCH₂OCH=CHCH₃, BrCH₂CH(OH)CH₂OCH(Et)₂ and BrCH₂CH(CH₂OH)OCH(Et)₂. The last 3 products result from exchange of a Cl-atom with the Et-group or the Br-atom of EtMgBr. ^f This compound contained 7.5% of the *cis*-isomer. ^g This compound contained 12.5% of the *trans*-isomer. ^h The rate constant was determined at 23°C.

10, Table 4), although the relative yield of EE is increased under those conditions (Tables 1 and 3). Thus Et_3N is not directly involved in the rate-determining step of the reaction: the normal addition reaction and the elimination proceed via a common intermediate, and thus the overall rate constants may be used to compare the reactivities of the dioxolanes towards the Grignard reagent (Table 1 and ref. 10). This conclusion is reinforced by the observation that in the reaction with one equivalent of Et_3N (Table 1), AE and EE were formed initially in an approximately constant ratio; at longer reaction times, the relative yield of EE increases, presumably because increasing amounts of Et_3N are released as the reaction proceeds.

b. The protons at C(2) of *cis*- and *trans*-2,4-disubstituted 1,3-dioxolanes give separate NMR signals and so it was easy to observe that no *cis*-*trans* isomerization, leading to an equilibrium, occurred; because of the faster reaction of the *cis* isomer, the *cis*-*trans* ratio decreased in all cases.

c. Substitution on C(2) is essential for reaction to occur. The reaction is faster as a positive charge on C(2) is better stabilized (reaction 1, 10, 11, Table 4).

d. The introduction of a second substituent at C(2) does not influence the reactivity markedly (reactions 4 and 5 and 10 (Table 4)). The same holds for a methyl or phenyl group at C(4) (reactions 6 to 9 (Table 4)). Indeed the reaction is somewhat slower (as compared to reaction 10 (Table 4)), which is probably due to steric influences: the first step of the reaction is complexation of EtMgBr with the dioxolane, which is presumably rendered more difficult by di-substitution. In reactions (Table 4), this effect is expected to be very large; but it is partly compensated by the stabilizing influence of the methyl group on the transition state leading to the oxocarbenium ion.

e. When a CH_2Cl group is introduced at C(4) the rate drops remarkably. This must be due to electronic factors, electron withdrawal from the O(2)-C(3) bond retarding the reaction. The magnitude of the influence of the Cl atom is rather surprising in view of its relatively large distance from the site of reaction, but similar effects have been observed in complexation of dioxolanes with BF_3 [11].

f. In 2,4-disubstituted 1,3-dioxolanes the *cis*-compound always reacts faster than the *trans* compound (Table 4, reaction 3 vs. 4, 6 vs. 7, 8 vs. 9). This must be due to easier complexation, because the Grignard compound can approach the *cis*-dioxolane from the *trans* side without hindrance.

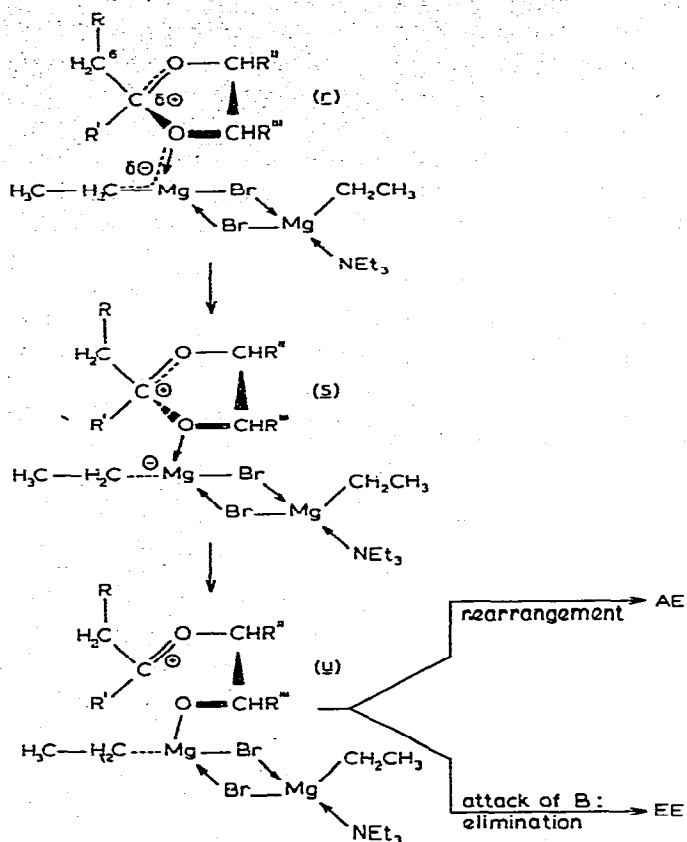
g. (+)(4*R*,5*R*)-2-Ethyl-4,5-dimethyl-1,3-dioxolane reacts very slowly (reaction 2 (Table 4)); apparently steric hindrance renders complexation with the Grignard reagent extremely difficult, as both sides of the dioxolane ring are hindered by alkyl groups. The presence of a substituent at C(4) of the dioxolane ring results in a higher ratio EE/AE; no explanation of this effect can be offered at present.

Mechanism

The results can be accounted for by an extension of the mechanism given in ref. 10.

The first step of the reaction (Scheme 1) is complexation of $(\text{EtMgBr} \cdot \text{Et}_3\text{N})_2$ with the dioxolane (D) with formation of a complex (r), which has oxonium ion character. In a second, rate-determining step, r is converted into the "normal"

SCHEME 1. The second order addition has been omitted for simplicity.



addition product either by a first order reaction via transition states and the oxocarbenium ion u, or via a second order reaction involving collision with another Grignard entity [10]. (The second order reaction has been omitted in Scheme 1 for simplicity).

In a competing reaction, free base (Et₃N or, less efficiently, the Grignard reagent) can attack a proton at C(6), thus giving the observed enol ethers. This reaction probably involves the same activated complex (s) in the rate-determining step and the same intermediate u as the first order reaction: the use of excess Et₃N does not accelerate the reaction but more EE is formed; moreover, under conditions where the first order reaction is known to be important (excess of 2-ethyl-1,3-dioxolane) the yield of EE is relatively high (Table 3), whereas under conditions in which the second order addition reaction is known to be important, only a small amount of EE is formed. This may also explain the low yield of EE from (+)(4*R*,5*R*)-2-ethyl-4,5-dimethyl-1,3-dioxolanes: this compound probably reacts predominantly via a second order process.

The intermediate u cannot have a very long lifetime in the presence of a Grignard reagent, and does not lead to *cis-trans* isomerization. Thus, its geometry will be close to that of the dioxolane, the group R attached to C(6) can be expected to be turned away from the magnesium atom with its bulky substituent.

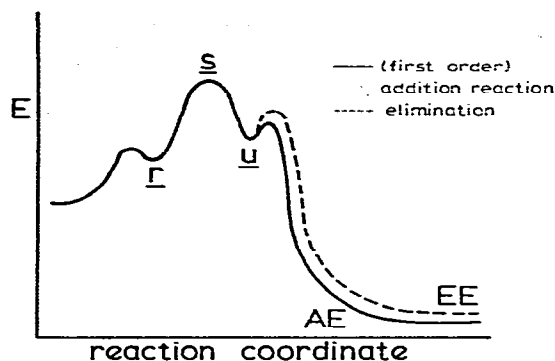


Fig. 1.

tents, and thus would explain the preferences for the formation of the *cis*-enol ether.

It is obvious that the addition of excess of Et_3N will shift competition between the two possible reactions of *u* in favour of the elimination. The rate of reaction is not affected by this E1 reaction, as it occurs after the rate-determining step. The energetics of the reaction may be visualised in a qualitative fashion by the energy diagram (Fig. 1).

Experimental

Experiments were performed using the vacuum-technique described earlier [12]. Some of the experiments mentioned in Table 1 were paralleled by experiments in ordinary laboratory equipment under nitrogen and these gave essentially identical results.

The rates of reaction were measured by following the disappearance of characteristic peaks in the NMR spectra, relative to the methylene proton of Et_3N as the internal standard. The NMR-spectrometers used were Varian models A-60, XL-100 or EM-360.

The dioxolanes were prepared from the corresponding glycols* and the carbonyl compound in benzene by the method of Salmi [13] with acid catalysis, the water formed during the reaction being removed by azeotropic distillation. The *cis/trans* ratios of the 2,4-disubstituted dioxolanes were calculated from the relative peak heights of the PMR spectra from the protons at carbon atom 2 (triplets at δ 4.8 and 4.9 ppm). The signal at high field is known to belong to the *cis*-compound [14]. *cis*- and *trans*-2-Ethyl-4-methyl-1,3-dioxolanes were separated by GLC on a 15% triethanolamine on Gaschrom R column of 4 meter length.

The following general procedure was applied for the preparation of enol ethers. A solution of 0.25 M EtMgBr was prepared in benzene with one equivalent of Et_3N [15]. An aliquot of this solution was decanted and 3 equivalents

* (—)(2*R*,3*R*)-2,3-Butanediol was kindly supplied, many years ago, by the National Research Council in Ottawa (Canada).

of Et_3N added. To this solution an equivalent amount of the dioxolane was added (to 0.25 M) and the mixture refluxed overnight, or longer, depending on the reactivity of the dioxolane. The mixture was hydrolyzed with as little as possible of saturated aqueous sodium chloride solution, after which the magnesium salts and most of the Et_3N were removed from the organic layer by centrifugation. If necessary, the enol ether can be extracted from the water layer by continuous extraction. When possible the solution of the enol ether given by the extraction is best used as such, since heating or treatment with acids may cause considerable reversion to the dioxolanes.

In a typical example, 3.75 g of 2,2-dimethyl-4,5-tetramethylene-1,3-dioxolane, prepared from 1,2-cyclohexenediol and acetone, was treated as described above; after distillation (with a short path Vigreux column; bath temperature 80–100°C, 12 mmHg pressure) a yield of 3 g (80%) of a product was obtained which consisted of less than 20% addition product and more than 80% of enol ether. The enol ether was characterized by its NMR spectrum (multiplets from 3.8 to 4.2 ppm and from 1–2.2 ppm, relative intensities 1/3, and a methyl singlet at 1.68 ppm) and by GCMS ($M^+ = m/e = 156$ (0.05%), 141 (45%), 113 (0.5%), 109 (0.7%), 99 (35%), 98 (16%), 81 (100%), 59 (25%), 58 (18%), 55 (20%), 43 (55) *).

The "normal" reaction products, $\text{HOCH(R)CH(R')OCR''(Et)}_2$, were identified by their IR, PMR and mass spectra. Identification of the enol ethers was achieved by GCMS and, in the case of $\text{HOCH}_2\text{CH}(\text{CH}_3)\text{OCH}=\text{CHCH}_3$, by IR and PMR spectra. Their reconversion to the corresponding dioxolane upon treatment with acid was also a proof of their structure. For details see ref. 16.

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References

- 1 G. Westera, C. Blomberg and F. Bickelhaupt, *J. Organometal. Chem.*, **82** (1974) 291, and refs. cited therein.
- 2 S. Cabiddu, M. Secci and A. Maccioni, *J. Organometal. Chem.*, **88** (1975) 121.
- 3 S. Cabiddu, R. Pirisi and A. Plumitallo, *J. Organometal. Chem.*, **88** (1975) 129.
- 4 M.F. Shostakovskii and E.P. Gracheva, *Izv. Akad. Nauk SSSR*, **1** (1950) 144; *Chem. Abstr.*, **47** (1953) 8002.
- 5 M.Z. Yazal'man, Z.M. Muldahkmetov, R.D. Yakubov and G.A. Shitof, *Khim. Atsetilena Tekhnol. Karbida Kat'siya*, (1972), 270; *Chem. Abstr.*, **79** (1973) 137012.
- 6 H. Meerwein in Houben-Weyl *Methoden der Organischen Chemie*, 4. Aufl., Band VI/3, p. 92, Sauerstoff-Verbindungen, Georg Thieme Verlag, Stuttgart, 1965.
- 7 E. Schmitz and I. Eichhorn in S. Patai (Ed.), *The chemistry of the Ether Linkage*, Interscience Publ., London, 1967, p. 337.
- 8 M.F. Shostakovskii and E.P. Gracheva, *Z. Obshch. Khim.*, **19** (1949) 1250; *Chem. Abstr.*, **44** (1950) 3439.
- 9 G. Westera, G. Schat, C. Blomberg and F. Bickelhaupt, *J. Organometal. Chem.*, **144** (1978) 273.
- 10 G. Westera, C. Blomberg and F. Bickelhaupt, *J. Organometal. Chem.*, **144** (1978) 285.
- 11 D.P.N. Satchell and R.S. Satchell, *Chem. Rev.*, **69** (1969) 251, Table IX.

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- 12 A.D. Vreugdenhil and C. Blomberg, *Rec. Trav. Chim. Pays-Bas*, 82 (1963) 453 and 461.
- 13 E.J. Salmi, *Chem. Ber.*, 71 (1938) 1803.
- 14 F. Borremans, M. Anteunis and F. Anteunis-De Ketelaere, *Org. Magn. Res.*, 5 (1973) 299, and refs. cited therein.
- 15 E.C. Ashby and R. Reed, *J. Org. Chem.*, 31 (1966) 971.
- 16 G. Westera, Thesis, Vrije Universiteit, Amsterdam, 1976.