

photoelectrochemical measurements. As shown in Figure 1, the photoinduced oxidation of acetic acid (presumably as the acetate ion) on an illuminated n-type TiO₂ rutile single-crystal electrode takes place at more negative potentials than the reduction of acetic acid protons on the same material and even more negative than the reduction of platinum. Thus, the reduction of acetic acid on platinum and the photooxidation of acetate ion on n-type TiO₂ can easily take place simultaneously at the two electrodes under short circuit conditions, i.e., without applied potential. The curves also indicate that this occurs at a common potential of about -0.6 V vs. the Hg/Hg₂Ac₂ reference electrode¹⁰ and with an estimated quantum yield of ~3–5%. Thus the apparent ease of photocatalytic decomposition of acetic acid on platinized n-type TiO₂⁷ can be rationalized, since this powder can be thought to act as a multitude of small, short-circuited Pt-TiO₂ electrode systems, where the partial coverage with Pt essentially boosts the yield by lowering the otherwise significant overpotential of the hydrogen reduction.¹¹ Light of energy greater than band gap ($\geq \sim 3.0\text{--}3.2$ eV¹²) causes the formation of an electron-hole pair, whose recombination is partially prevented (presumably due to bending of bands caused by the equilibria $\text{H}^+ + \text{e}^- \rightleftharpoons \text{H}(\text{ads})$ or $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$ on the Pt). The low-lying holes thereby created lead to the oxidation of acetate, thus initiating the Kolbe process. The rapid decomposition of the CH₃CO₂· radical, leading to the CH₃· radical and CO₂, prevents any reverse reaction. Hypothetical at the moment are the further follow-up processes, but the observed formation of methane indicates that they are reductive. While the reduction potential of methyl radicals (in aqueous surroundings) is not known, it seems reasonable to assume the sequence reduction and protonation, especially in view of the fairly negative short circuit potential of the Pt-illuminated TiO₂ pair in the electrochemical measurements (~-0.6 V). Such a sequence, at any rate, is in full accord with the following experiment with partially monodeuterated acetic acid produced by addition of 99.7% D₂O as cosolvent in the initially described experiment which theoretically produced a mixture CH₃CO₂D and CH₃CO₂H in the ratio 49:1 by exchange of the carboxylate protons.¹³ Irradiation of this solution with a suspension of platinized TiO₂ photocatalyst⁷ under inert atmosphere again led to gas evolution, with a slightly lower yield (5.5 mL/h), presumably as a consequence of the isotopic substitution. The mass spectral analysis revealed these gases to again consist of CO₂, CH₃CH₃ (undeuterated), methane (73% CH₃D, 27% CH₄), and hydrogen (H₂:HD:D₂ = 2:1:masked by He). This isotopic labeling pattern eliminates a mechanism involving hydrogen abstraction from the acetic acid methyl and supports the postulated origin of one of the methane hydrogens to be an acidic solution proton or deuteron.

Apparently the TiO₂ powder acts in a dual function causing the photooxidation of acetate and the reduction of intermediately formed methyl radicals, a property not found at metal electrodes under the usual Kolbe conditions where the electrode potential is maintained at a very positive value. Several unique properties of these partially metallized large-band-gap semiconductor powder photocatalysts emerge: (1) they are potentially strong photooxidizing agents, since the quasi-Fermi level of holes under irradiation lies near the valence band edge at very positive potentials;¹⁴ (2) their large surface area¹⁵ allows a low (surface) concentration of radical intermediates, thus suppressing radical-radical reactions (dimerization, disproportionation); (3) under proper conditions the intermediates are formed near reducing sites, since the quasi-Fermi level of electrons lies near the conduction band.¹⁴ These properties allow this heterogeneous photocatalytic Kolbe reaction to branch off from the normal paths (to ethane or methanol) with channeling of the intermediate methyl radicals into a reductive route to methane. The possible extension of

this reaction to other synthetically as well as mechanistically more interesting aliphatic or alicyclic carboxylic acids will hopefully clarify the mechanistic and synthetic scope of this alternate photo-Kolbe reaction. The effect of changes in experimental variables, the flux of light, and the dark rest potential of the semiconductor on the distribution of reaction products will also be subjects of upcoming investigations in this laboratory.¹⁶

References and Notes

- (1) A. Heller, Ed., "Semiconductor Liquid-Junction Solar Cells", Proceedings of The Electrochemical Society, Vol. 77-3, Princeton, N.J., 1977, and references therein.
- (2) S. N. Frank and A. J. Bard, *J. Am. Chem. Soc.*, **99**, 4667 (1977); T. Freund and W. P. Gomes, *Catal. Rev.*, **3**, 1 (1969); H. Gerischer and H. Roessler, *Chem.-Ing. Tech.*, **42**, 176 (1970); K. Nakatani and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **50**, 783 (1977).
- (3) B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, **99**, 7729 (1977).
- (4) S. N. Frank and A. J. Bard, *J. Am. Chem. Soc.*, **99**, 303 (1977); S. N. Frank and A. J. Bard, *J. Phys. Chem.*, **81**, 1484 (1977); M. Miyake, H. Yoneyama, and H. Tamura, *Electrochim. Acta*, **22**, 319 (1977).
- (5) Reaction 1 actually is exoenergetic with a standard free-energy change $\Delta G_1^\circ = -12.5$ kcal/mol (data taken from "Handbook of Chemistry and Physics", 53rd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1972, p D-61).
- (6) See, e.g., J. H. P. Utley in "Technique of Electroorganic Synthesis", Vol. 1, N. L. Weissenberger, Ed., Wiley-Interscience, New York, N.Y., 1974, p. 793; L. Ebersohn in "Organic Electrochemistry", M. M. Baizer, Ed., Marcel Dekker, New York, N.Y., 1973.
- (7) Produced by illuminating for 4 h a deoxygenated suspension of 100 mg (white) of n-type TiO₂ powder (anatase, reagent grade, MCB, particle size 125–250 μm) in 20 mL of platinizing solution (H₂PtCl₆ in dilute HCl, corresponding to ~100 mg of Pt) with the white light of a 2500-W xenon lamp, operating at 1600 W, followed by neutralization of the acidic solution, addition of 100 mg of hydroquinone, and 12-h reaction of 50 °C under nitrogen. The now grayish powder was extensively washed with distilled water and dried for 1 h at 120 °C. The distribution of platinum on the TiO₂ particle surface was found by electron microscopy to be uniform down to a resolution of <1 μm .
- (8) Reference data for mass spectra (*m/e* (rel intensity)) (from "Selected Mass Spectral Data", American Petroleum Institute, 1972) of ethane, 30 (26), 29 (21), 28 (100), 27 (33), 26 (26); and methane, 16 (100), 15 (85), 14 (6).
- (9) The evolving gases were swept out of the reaction chamber by a slow stream of nitrogen and were led through a 1 N NaOH solution saturated with Ba(OH)₂; the precipitate, BaCO₃, was determined gravimetrically.
- (10) The reference electrode, Hg/mercurous acetate in acetic acid/0.05 M sodium acetate and 0.7 M sodium perchlorate, has a potential of roughly 0.45 V positive of an aqueous SCE.
- (11) Similarly the overpotential for reduction of water on a SrTiO₃ single-crystal electrode was found to be lowered by Pt coating; M. S. Wrighton, P. T. Wolczanski, and A. B. Ellis, *J. Solid State Chem.*, **22**, 17 (1977).
- (12) The band gap for the anatase form of TiO₂ was reported to be slightly larger than for rutile, 3.23 and 3.02 eV, respectively; V. N. Pak and N. G. Ventov, *Russ. J. Phys. Chem.*, **49**, 1489 (1975).
- (13) A routine mass spectrum of the reaction mixture after the experiment gave the much lower ratio CH₃CO₂D:CH₃CO₂H of ~3:1 (presumably because of exchange in the mass spectrometer), but clearly established on upper limit of $\leq 4\%$ monodeuteration of the acetic acid methyl group.
- (14) H. Gerischer, *J. Electroanal. Chem.*, **82**, 133 (1977).
- (15) The active surface area of the powder can be estimated from the particle size (diameter ~150 μm) and grain size (~0.2 μm) to be 10^4 to 2×10^5 mm².
- (16) The support of this research by the Schweizerische Nationalfonds zur Foerderung der wissenschaftlichen Forschung (to B.K.) and by the National Science Foundation and the Robert A. Welch Foundation is gratefully acknowledged.

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Helium(I) Photoelectron Spectrum of Tropyli Radical

Sir:

There has been much recent discussion¹ of the structures and stabilities of C₇H₇ cations. We wish to report the initial results of our investigation of the photoelectron spectrum (pe) of tropyli radical which bear on the stability (heat of formation) of the tropylium ion and the structure of the tropyli radical. The spectrum (Figure 1, top) was obtained by flash vacuum pyrolysis² of bitropyl (Figure 1, bottom) in a manner similar to

Table I. Excited States of $C_7H_7^+$ (D_{7h})

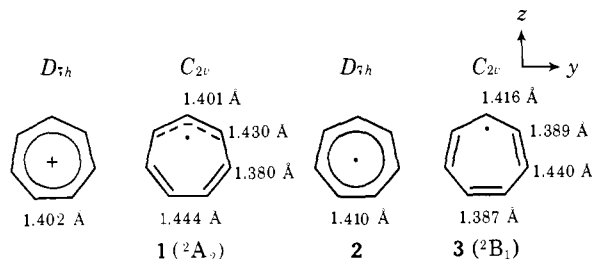
State symmetry (D_{7h})	GVB, ^a eV	Exptl, eV
1E_1	6.06	
1E_3	5.33	4.5 ^b
3E_3	4.29	3.4 (?)
3E_1	4.27	
1A_1	0.00	0.0

^a Reference 16. ^b Solution data: W. Doering and L. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954).

the previous electron impact studies of Lossing.³ The dimer dissociates to the extent of ~30% under the conditions of our experiment (400 °C at 0.1 Torr) as expected from the low bond dissociation energy measured previously.^{3,4} The only product isolated from the cold trap condensate of the pyrolysis stream was the starting dimer indicating that the flow gas was a simple two component (bitropyl-tropyl) system.

The first band in the observed spectrum shows a resolved vibrational structure with five components spaced at $1424 \pm 100 \text{ cm}^{-1}$. The position of the first member of this vibrational series occurs at $6.28 \pm 0.02 \text{ eV}$ in good agreement with the ionization potential estimated⁵ from the Rydberg series of this radical (6.24 eV). While the band shape does indicate a significant⁶ geometrical change on going from the radical to the cation, it rules out the possibility⁷ that the adiabatic ionization potential of the radical is appreciably lower than the first observed vibrational component. The heat of formation of the tropylium cation is thus bracketed at $210 \pm 2^8 \text{ kcal/mol}$. This value is in good agreement with that estimated by ab initio MO (4-31G) calculations (207.9 kcal/mol),⁹ though it is considerably above the MINDO/3 estimate (195.6 kcal/mol).⁷

Tropyl radical is subject to a Jahn-Teller distortion¹⁰ so that it is certain that the D_{7h} nuclear geometry is *not* at a classical (Born-Oppenheimer) energy minimum. Conversely, the carbonium ion structure is surely of D_{7h} symmetry.¹¹ The most interesting feature of the pe spectrum is the length of the vibrational series in the first band which implies a *large* structural change on ionization.¹² The frequency of this spacing is near the 1470-cm^{-1} mode (ν_{13}) observed¹¹ in the infrared spectrum of the cation in solution which was assigned as a ring stretch belonging to the E_1 species. Distortion along this mode is just what is predicted for the Jahn-Teller effect by empirical bond-order bond-length correlations.¹³ Our version¹⁴ gives 1.402 Å for the C-C bond length of tropylium ion in good agreement with the 1.405 Å derived⁷ by the MINDO/3 procedure.¹⁵ Structures **1** and **3** are suggested^{14,15} for the radical after Jahn-Teller distortion while **2** arises from the average bond order of the (orbitally degenerate) D_{7h} radical. The pe vibrational band intensities *and* the assignment of the observed 1424-cm^{-1} spacing as ν_{13} of the cation imply that structures **1** and/or **3** are energetically separated from **2** which is a ("forbidden"^{15a}) transition state for their interconversion.¹⁴



The third point of interest is the feature at 9.63 eV which is superimposed on the second gross band of the undissociated dimer. This band can be assigned to the lowest triplet excited state of the cation. Valence bond calculations on tropylium ion

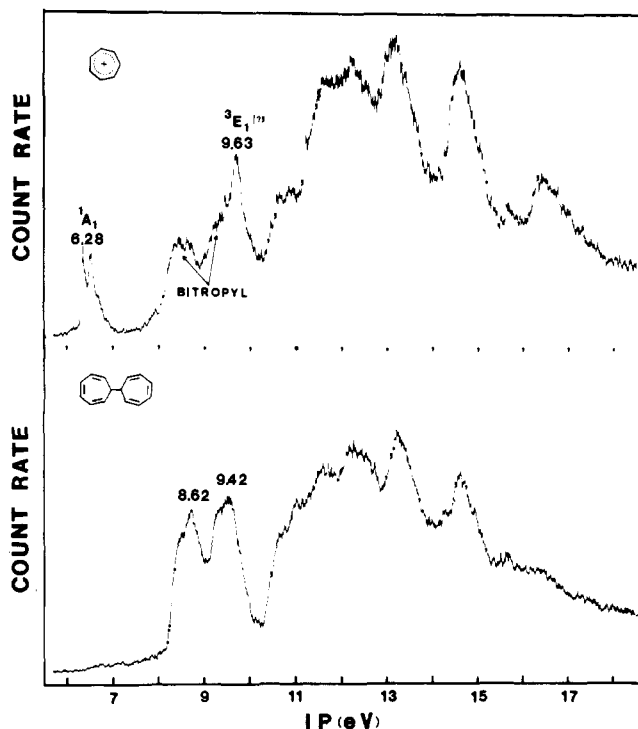


Figure 1. Helium(I) photoelectron spectrum of tropyli at 400 °C (top) and bitropyl (bottom).

predict¹⁶ 3E_1 as the lowest triplet although 3E_3 is only slightly higher. The intensity of the observed band does not appear large enough to be assigned as a superposition of both. Table I compares the GVB calculations with observed transitions.

In summary we believe our data remove any uncertainty concerning the heat of formation of tropyli cation due to geometrical reorganization. At the same time the pe spectrum does suggest a significantly large Jahn-Teller distortion of the radical. The position of the lowest triplet state of the cation is indicated to be 3.4 eV above its ground state. It is our hope that these results will stimulate the application of good theoretical methods to the problems of the geometry of tropyli radical and the electronic excited states of the cation. We are continuing the investigation of the spectra of deuterated and substituted derivatives which should allow a distinction between structure **1** and **3** for the radical.¹⁷

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References and Notes

- (1) F. W. McLafferty and J. Winkler, *J. Am. Chem. Soc.*, **96**, 5182 (1974); J. Shen, R. C. Dunbar, and G. A. Olah, *ibid.*, **96**, 6227 (1974); R. C. Dunbar, *ibid.*, **97**, 1382 (1975).
- (2) T. Koenig, T. Balle, and W. Snell, *J. Am. Chem. Soc.*, **97**, 662 (1975); T. Koenig, R. Wlelessek, T. Balle, and W. Snell, *ibid.*, **97**, 3225 (1975).
- (3) A. G. Harrison, L. R. Honnen, H. J. Dauben, and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960).
- (4) G. Vincow, H. J. Dauben, F. R. Hunter, and W. V. Volland, *J. Am. Chem. Soc.*, **91**, 2823 (1969).
- (5) B. A. Thrush and J. J. Zwolenik, *Discuss. Faraday Soc.*, **35**, 196 (1963). The photoionization value is the same (6.24 eV, F. Elder and A. Parr, *J. Chem. Phys.*, **50**, 1027 (1969)).
- (6) This degree of geometrical reorganization does not suggest isomerization, for example, to benzyl cation which shows a very different pe spectrum,¹⁸ from that of Figure 1.
- (7) C. Cone, M. Dewar, and D. Landman, *J. Am. Chem. Soc.*, **99**, 372 (1977).
- (8) This value assumes a heat of formation for tropyli radical of +64.80 kcal/mol.⁴ Rosenstock and coworkers^{9a} have recently estimated this value as 71.3 kcal/mol. Since submission of this manuscript, Traeger and McLoughlin^{9b} have provided an independent experimental estimate of the heat of formation of tropyli cation of 207 kcal/mol. (a) H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem., Ref. Data Suppl.*, **1**, 6 (1977). (b) J. C. Traeger and R. G. McLoughlin, *J. Am. Chem. Soc.*, **99**, 7351 (1977).
- (9) J. Abboud, W. Hehre, and R. Taft, *J. Am. Chem. Soc.*, **98**, 6072 (1976).
- (10) H. A. Jahn and E. Teller, *Proc. R. Soc. (London)*, *Ser. A*, **161**, 220

- (1937).
- (11) W. Fateley, B. Curnutte, and E. Lippincott, *J. Chem. Phys.*, **26**, 1471 (1957).
- (12) The structural change implied by the spectrum of tropyli is at least superficially greater than that indicated by the related pe spectrum of $C_8H_5^+$ to the Jahn-Teller $C_8H_5^+$ radical: P. C. Engelking and W. C. Lineberger, *J. Chem. Phys.*, **67**, 1412 (1977).
- (13) The conclusion of a strong Jahn-Teller distortion for tropyli might seem to be at odds with the observations^{13a} of 7 equiv ESR proton hyperfine couplings. This is not necessarily true since both **1** and **3** may rapidly permute carbon positions through (antisymmetric) ring modes without involving the D_{7h} transition state (2) or interconverting a member of the **1** series with a member of the **3** series. Such motions would average the ESR observables even if the Jahn-Teller energy gain is very large. (a) H. J. Silverstone, D. Wood, and H. McConnell, *J. Chem. Phys.*, **41**, 2311 (1964); W. Volland and G. Vincow, *J. Chem. Phys.*, **48**, 5589 (1968).
- (14) T. Koenig and R. Wolfe, *J. Am. Chem. Soc.*, **91**, 2569 (1969); $r_{ij} = 1.69 - 0.360 (P_{ij})^{1/2}$ where r_{ij} is C_i-C_j bond distance and P_{ij} is the corresponding total π bond order between C_i and C_j .
- (15) Since submission of this article MINDO/3 structures for tropyli radical which are very similar to **1** and **3** have been published.^{15a} An ab initio structure for the cation also appeared^{15b} which gives the C-C bond length at 1.398 Å. (a) P. Bishof, *J. Am. Chem. Soc.*, **99**, 8145 (1977). (b) L. Radom and H. F. Schaefer, *J. Am. Chem. Soc.*, **99**, 7522 (1977).
- (16) G. A. Gallup and J. M. Nabeck, *J. Am. Chem. Soc.*, **97**, 970 (1975).
- (17) Nonplanar structures must and will also be considered the complete Frank Condon analysis.
- (18) T. Koenig, W. Snell, and J. C. Chang, *Tetrahedron Lett.*, **No. 50**, 4569 (1976).

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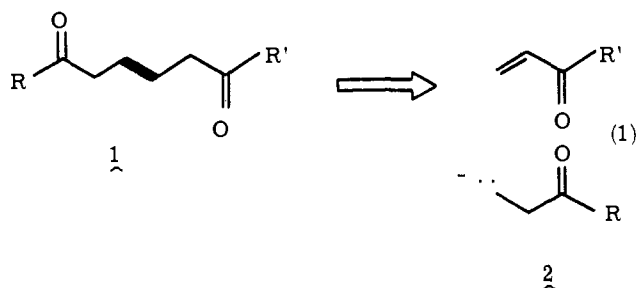
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A General Approach to the Synthesis of 1,6-Dicarbonyl Substrates. New Applications of Base-Accelerated Oxy-Cope Rearrangements

Sir:

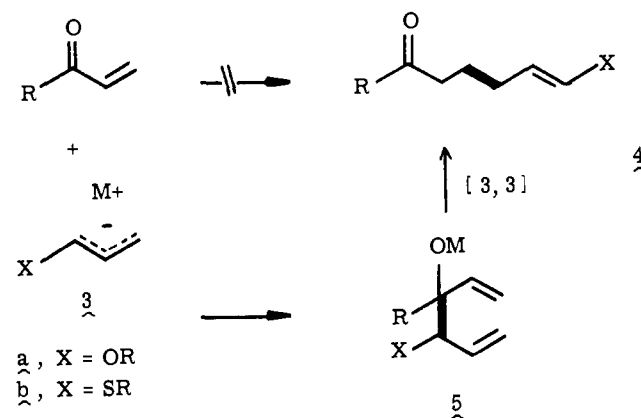
The synthesis of 1,6-dicarbonyl compounds from mono-functionalized three-carbon precursors embodies a problem comparable with those encountered in the construction of 1,4-dicarbonyl derivatives.¹ Symmetrical 1,6 diketones and related derivatives are readily accessible via the reductive coupling of α,β -unsaturated ketones with active metals² and by electrolysis.^{3,4} Such methods, however, have thus far proven unsatisfactory for the synthesis of *unsymmetrical* dicarbonyl substrates.

In the present communication we wish to report our preliminary results in this area on the bond-path construction illustrated in eq 1.⁵ Earlier research in our laboratory has dealt



with the development of metalated allylic ethers and sulfides as homoenolate anion operational equivalents (cf. 2).⁶ Efforts to effect regioselective conjugate addition of allylic cuprates **3** ($M = Cu^I$) to enones to give adducts **4** directly (Scheme I) have proven unsatisfactory to date because of the intrinsic problems associated with the ambident reactivity of both enones and allylic organometallic reagents. However, we have recently been able to achieve highly regioselective 1,2-carbonyl additions with allylzinc reagents **3a** ($M = ZnCl$)⁶ and allylcadmium reagents **3b** ($M = CdCl$) to enones affording dienols **5** ($M = H$) in good yields. In turn, such dienols should serve as viable precursors to monoprotected 1,6-dicarbonyl deriva-

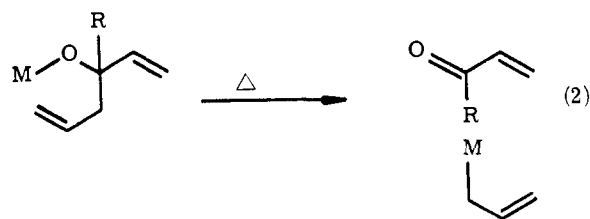
Scheme I



tives via an oxy-Cope rearrangement (cf. Scheme I).⁷

Preparation of allyllithium reagents **3a** and **3b** ($M = Li$) and related substrates from allylic ethers and sulfides via *sec*-butyllithium metalation (THF, $-65^\circ C$, 10 min) has been described by us.⁶ The organozinc and organocadmium reagents **3a** ($M = ZnCl$)⁶ and **3b** ($M = CdCl$) were prepared via the allyllithium substrates by subsequent treatment with 1.2 equiv of anhydrous $ZnCl_2$ or $CdCl_2$ ($-65^\circ C$). Addition of 1 equiv of enone at ca. $-25^\circ C$ followed by warming to ambient temperature and product isolation afforded the desired dienols **5** (cf. Table I) in 80–90% isolated yields.⁸

Numerous examples have been reported which document the oxy-Cope rearrangement of simple dienols such as **5** ($X = H$);^{7,9} however, the synthetic utility of these rearrangements is diminished by the competing retro-ene (β -hydroxy olefin) cleavage process (eq 2, $M = H$).^{9,10} Recently, we reported the



first substantial case of an apparent facile Cope rearrangement of 1,5-diene alkoxide (cf. **5**, $M = K$).⁷ The thermal rearrangements of the alkali metal salts of the dienols shown in Table I substantiate that this protocol for achieving dramatic rate enhancements is indeed a general phenomenon. Typical conditions for the rearrangement of the dienols illustrated in Table I involved the addition of the alcohol to a stirred suspension of excess potassium hydride and anhydrous, deoxygenated, ethereal solvent under argon. For rearrangements which required external heating for extended time periods, dimethoxyethane (DME) was found to be superior to THF. Under such conditions THF is degraded with attendant consumption of hydride. In general, the cited rearrangements proceed with little apparent dissociation-recombination (cf. eq 2, $M = K$) in spite of the fact metal alkoxides of homoallylic alcohols have been documented to undergo cleavage to ketones and allylic organometallics.^{11,12} Exceptions to the above observation are found in those cases where a quaternary center is generated as a consequence of the Cope process (entries 3 and 4, $R = Me$). In the latter case the predominant by-product (70%) was 3-methylcyclohexenone.

Further substituent effects have become apparent upon attempted rearrangement of the 4-thiophenyl dienols **5b** (entries 6, 7). It has been generally observed that the sulfur-substituted diene alkoxides **5b** undergo rearrangement under far milder conditions than the alkoxy-substituted counterparts **5a**. Attendant cleavage reactions appear to be competitive but