Table II. Comparison of Measured and Predicted Nitrogen Hyperfine Splittings (in Gauss) for Hydrazyl Radicals, $R_1N_{(1)}N_{(2)}R_2R_3$, in Solution

Radical	Measured		Predicted	
	$a^{N(1)}$	$a^{N(2)}$	$a^{N(1)}$	$a^{N(2)}$
1 HṄNH$_2$	11.7^{a,b}	8.8^{a,b}	11.5^c	8.9^d
2 HṄNHR			10.5^e	10.2^f
3 HṄNR$_2$	9.8^g	11.6^g		
4 RṄNR$_2$	11.8^h	10.3^h		
5 RṄNHR	12.7^{b,i}	9.1^{b,i}	12.8^j	9.1^j
6 RṄNH$_2$	13.8^{a,k}	7.9^{a,k}		

^{a} Reference 6. ^{b} Assigned to conform to predicted values. ^{c} Calculated from $a^{N(1)}$ values for 3, 4, and 6 by the relation $1 = 3 + 3[(6 - 4)/4]$. ^{d} Calculated from $a^{N(2)}$ values by the relation $1 = 6 + 6[(3 - 4)/4]$. ^{e} Calculated from $2 = 3 + 3[(5 - 4)/4]$. ^{f} Calculated from $2 = 5 + 5[(3 - 4)/4]$. ^{g} Average values for R = Me and i-Pr from ref 5, plus R = Et from ref 10. ^{h} This work. Average of values for acyclic trialkylhydrazyls, i.e., R_1 = Me and i-Pr with $R_2 = R_3$ = Me. ^{i} This work. R = i-Pr. ^{j} Linear interpolation in the series 3, 4, 5, and 6. ^{k} Average for R = Me and PhCH$_2$.

similar type of extrapolation to hydrazyl itself implies that $a^{N(1)} > a^{N(2)}$ as has also been concluded from theoretical consideration.[11,12]

Kinetic data on the decay of some of these radicals will be reported at a later date.

(11) R. Fantechi and G. A. Helcké, J. Chem. Soc., Faraday Trans. 2, 68, 924 (1972).

(12) D. E. Wood, C. A. Wood, and W. A. Latham, J. Amer. Chem. Soc., 94, 9278 (1972).

(13) N.R.C.C. Visiting scientists from the Istituto Chimica Organica, Università di Bologna, Bologna, Italy. A grant from 'Laboratorio CNR dei composti del carbonio' is gratefully acknowledged.
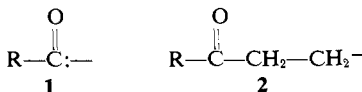
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Metalated Allylic Ethers as Homoenolate Anion Equivalents

Sir:

As a consequence of the central role which the carbonyl function has played in organic synthesis, chemists have endeavored to devise new synthetic methods centered around this functional group. One such area of investigation has been concerned with the design of "reversed polarity"[1,2] equivalents. An impressive number of synthetic methods have been developed in this area which provide access to useful "carbonyl anion" (1) equivalents.[3,4] The purpose of this com-

$$\underset{\textbf{1}}{R\!-\!\overset{\displaystyle O}{\overset{\|}{C}}:\!-} \qquad \underset{\textbf{2}}{R\!-\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!CH_2\!-\!CH_2^-}$$

munication is to describe a useful approach to a related

(1) For a general discussion of reversed polarity equivalents see D. A. Evans and G. C. Andrews, Accounts Chem. Res., 7, 147 (1974).

(2) E. J. Corey, Pure Appl. Chem., 14, 19 (1967).

(3) For a direct synthetic approach to 1 see L. S. Trzupek, T. L. Newirth, E. G. Kelly, M. E. Sbarbati, and G. M. Whitesides, J. Amer. Chem. Soc., 95, 8118 (1973), and references cited therein.

(4) D. Seebach, Angew Chem., Int. Ed. Engl., 8, 639 (1969); G. Stork and L. Maldonado, J. Amer. Chem. Soc., 93, 5286 (1971); J. E. McMurry and J. Melton, ibid., 93, 5309 (1971); J. P. Collman, S. R. Winter, and D. R. Clark, ibid., 94, 1788 (1972); K. Ogura and G. Tsuchihashi, Tetrahedron Lett., 3151 (1971); K. Oshima, K. Shimoji, H. Takahashi, H. Yamamoto, and H. Nozaki, J. Amer. Chem. Soc., 95, 2694 (1973).

reversed polarity equivalent which may be operationally equated to a homoenolate anion (2).[5]

We have found that allylic ethers, 3, may be rapidly metalated (10 min) at $-65°$ in tetrahydrofuran (THF)[6] with sec-butyllithium[7] in essentially quantitative yield. At these temperatures the allylic anion 4a[8] exhibited no tendency to undergo Wittig rearrangement, a reaction characteristic of these species at higher temperatures.[9] Our observation that these anions react regioselectively with electrophiles (E) γ to oxygen to give the adduct 5γ establishes the operational equivalency between the oxy allylic anion 4a and homoenolate anion 2 (R = H).

4a, M = Li$^+$
b, M = Zn^{2+}

5γ 5α
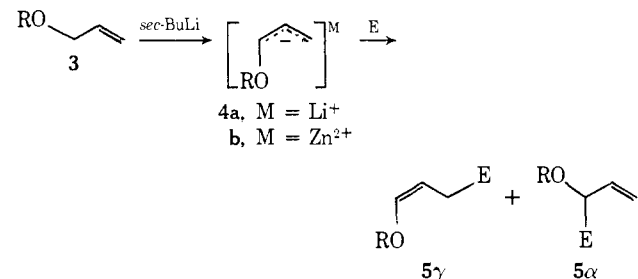
In alkylation reactions of 4a (E = n-C$_6$H$_{13}$I), we have found the product ratio, 5γ:5α, to be controlled by the oxygen ligand R; typical results being: R = THP, $\gamma:\alpha$ = 54:46; R = Ph, $\gamma:\alpha$ = 63:37; R = C$_2$H$_5$, $\gamma:\alpha$ = 75:25; R = t-Bu, $\gamma:\alpha$ = 89:11.[10,11] The observation that such substrate steric factors are important in controlling site-reactivity in the reactions of ambident anions 4a with electrophiles is now well precedented.[1,5a,12] It appears that the product ratio, 5γ:5α, for alkylation reactions is rather insensitive to other reaction conditions involving a change in solvent,[6] or temperature.

In the reactions of the oxy allylic anion 4a with carbonyl electrophiles (E = cyclohexanone), we have observed that the product ratio 5γ:5α is opposite to what one would predict based upon the above alkylation study: R = t-Bu, $\gamma:\alpha$ = 27:73; R = Ph, $\gamma:\alpha$ = 24:76; R = C$_2$H$_5$, $\gamma:\alpha$ = 70:30; R = CH$_3$, $\gamma:\alpha$ = 72:28.[10,11] This change in $\alpha:\gamma$ regioselectivity in the reactions of allylic carbanions with alkyl halides in contrast to ketones has been observed elsewhere.[13] Furthermore,

(5) For other examples of homoenolate anion equivalents see (a) E. J. Corey and D. E. Cane, J. Org. Chem., 35, 3405 (1970); (b) E. J. Corey, B. W. Erikson, and R. Noyori, J. Amer. Chem. Soc., 93, 1724 (1971); (c) Y. Leroux and C. Roman, Tetrahedron Lett., 2585 (1973); (d) K. Oshima, H. Yamamoto, and H. Nozaki, J. Amer. Chem. Soc., 95, 7926 (1973); (e) H. Ahlbrecht and G. Rauchschwalbe, Synthesis, 417 (1973); (f) G. Sturtz, B. Corbel, and H. Normant, C. R. Acad Sci., Ser. C., 277, 395 (1973).

(6) Metalation may be also carried out in ether or in pentane with added tetramethylethylenediamine (TMEDA).

(7) No appreciable ether fission was observed with this base; cf. G. Köbrich and A. Baumann, Angew. Chem., Int. Ed. Engl., 12, 856 (1973). Other bases such as n-butyllithium are ineffective metalating agents.

(8) For H nmr data on isomeric methoxy-substituted allylic anions see H. Kloosterziel and J. A. A. VanDrunen, Recueil, 89, 32 (1970).

(9) (a) H. Felkin and A. Tambuté, Tetrahedron Lett., 821 (1969); (b) D. R. Dimmel and S. B. Gharpure, J. Amer. Chem. Soc., 93, 3991 (1971); (c) D. R. Dimmel and S. Huang, J. Org. Chem., 38, 2756 (1973); (d) G. Courtois and L. Miginiac, Tetrahedron Lett., 2411 (1972); (e) V. Rautenstrauch, Helv. Chim. Acta, 55, 594 (1972); see correction, ibid., 55, 3064 (1972).

(10) In a number of experiments the average yields of 5α + 5γ ranged from 75 to 95 %.

(11) Satisfactory spectra and elemental analyses were obtained on all compounds reported herein.

(12) (a) E. J. Corey and D. E. Cane, J. Org. Chem., 34, 3053 (1969); (b) E. J. Corey and H. A. Kirst, Tetrahedron Lett., 5041 (1968).

(13) R. Kow and M. W. Rathke, J. Amer. Chem. Soc., 95, 2715 (1973); P. E. Pfeffer, L. S. Silbert, and E. Kinsel, Tetrahedron Lett., 1163 (1973).

Table I. Reactions of Metalated Ethers with Electrophiles[11]

Anion	Electrophile, E[a]	Ratio[b] $\gamma:\alpha$	Yield, %[c] $\gamma + \alpha$	Product	% yield isolated
4a (R = t-Bu)	n-C₆H₁₃I	89:11	93	5γ	83
	Br(CH₂)₄Br	80:20	90	5γ	70
	sec-C₃H₇I	64:36	65	5γ	
	CH₃SSCH₃	>95:5		5γ	80
	Cyclohexanone	27:73	72		
4a (R = CH₃)	Cyclohexanone	72:28	93	6[d]	72
4a (R = CH₃)	(CH₃)₂CHCHO	68:32	99	5γ	
4b (R = CH₃)	Cyclohexanone	0:100	97	7	92
9a (R = C₂H₅)	n-C₆H₁₃I	>90:10		12γ	79
	(CH₃)₂C=CHCH₂Br	63:37	41	12γ	26
	CH₃SSCH₃	90:10		12γ + 12α	79
	Cyclohexanone	50:50	93	12γ + 12α	
9b (R = C₂H₅)	Cyclohexanone	0:100		12α	97

[a] All reactions were carried out at −65°. [b] Both products have been isolated and fully characterized. [c] Determined by nmr relative to an internal standard. [d] Produced by acid hydrolysis (10% HCl–THF) of the enol ether.

the product ratio is highly counterion dependent. The allyl zinc reagent **4b** (R = CH₃), prepared by the addition of 1 equiv of zinc chloride to **4a**, reacts with aldehydes and ketones *exclusively* α to oxygen.[14] This counterion effect is *independent* of the steric bulk of R in metalated ether anion **4b**. Such counterion dependence is illustrated below in the reaction of **4a** and **4b** (R = CH₃) with cyclohexanone. The results of other carbonyl addition reactions are included in Table I.[11]
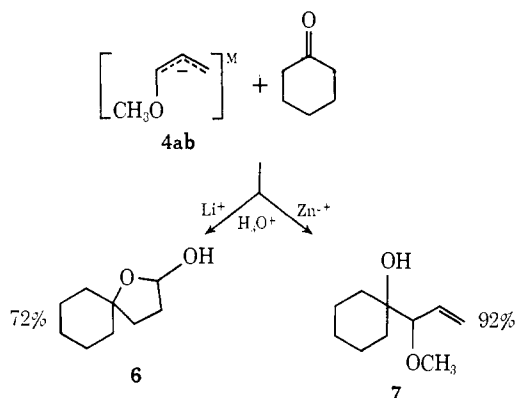
In the metalation of methyl-substituted ethers **8** and **10**, it is possible to form two different allylic anions resulting from proton abstraction from either the methyl or methylene positions. However, metalation of **8** and **10** with *sec*-butyllithium (THF, −65°) affords only the allylic anions **9a** and **11a**. The conclusion that, under
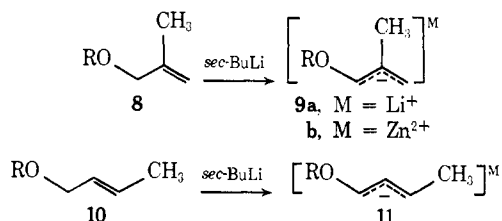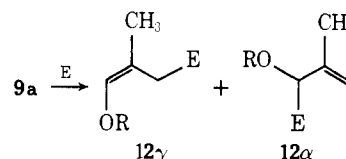

these conditions, the alkoxy substituent *enhances* the kinetic acidity of adjacent positions is interesting in light of other studies which show the opposite to be the case under different conditions.[15]

(14) For analogous counterion-dependent processes, see ref 5d and 12a.
(15) D. H. Hunter, Y. Lin, A. L. McIntyre, D. J. Shearing, and M. Zuagulis, *J. Amer. Chem. Soc.*, **95**, 8327 (1973), and references cited therein.

As with anion **4a**, **9a** (R = C₂H₅) reacts regioselectively γ to oxygen in substitution reactions (E = n-C₆H₁₃I, 12γ:12α = 90:10). No selectivity was observed in carbonyl addition (E = cyclohexanone,

12γ:12α = 50:50); however, the organozinc reagent **9b** shows exclusive reaction α to oxygen.

The conclusions of this preliminary study are that metalated allylic ethers may be effectively employed as homoenolate anion equivalents in substitution reactions. The present examples point to the fundamental differences in the relative directive effects that are observed in the reactions of oxygen and sulfur-substituted allylic carbanions with electrophiles.

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Allyloxy Carbanions. A New Synthesis of Aldehydes *via* a β-Acyl Carbanion Equivalent

Sir:

The central role of carbonyl compounds in organic chemistry makes new methods for their construction especially valuable. In this communication, we wish to report a new approach to the synthesis of these compounds and its application to a new synthesis of aldehydes.

The most useful carbonyl syntheses are generally those which incorporate carbon–carbon bond forma-