similar type of extrapolation to hydrazyl itself implies that \( \alpha^{(n)} > \beta^{(n)} \) 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.

(3) R. K. N. C. C. Visiting scientists from the Istituto Chimica Organica, Universita di Bologna, Bologna, Italy. A grant from 'Laboratorio CNR dei composti del carbonio' is gratefully acknowledged.

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Metalled 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" 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 communication is to describe a useful approach to a related reversed polarity equivalent which may be operationally equated to a homoenolate anion (2).\(^5\)

We have found that allylic ethers, \(\mathbf{3}\), may be rapidly metallated (10 min) at \(-65^\circ\)C in tetrahydrofurran (THF)\(^6\) with sec-butyllithium\(^7\) in essentially quantitative yield. At these temperatures the allylic anion \(\mathbf{4a}\) 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) to oxygen to give the adduct \(\mathbf{5}\) establishes the operational equivalency between the oxy allylic anion \(\mathbf{4a}\) and homoenolate anion \(\mathbf{2}\) (R = H).

In alkylation reactions of \(\mathbf{4a}\) (E = \(n\)-C\(_5\)H\(_{11}\)), we have found the product ratio, \(\mathbf{5f}:\mathbf{5o}\), 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\(_6\)H\(_5\), \(\gamma:\alpha = 75:25\); R = i-Bu, \(\gamma:\alpha = 89:11\).\(^{10}\) The observation that such substrate steric factors are important in controlling site-reactivity in the reactions of ambient anions \(\mathbf{4a}\) with electrophiles is now well preceident.\(^{1,5a,12}\) It appears that the product ratio, \(\mathbf{5f}:\mathbf{5o}\), for alkylation reactions is rather insensitive to other reaction conditions involving a change in solvent,\(^4\) or temperature.

In the reactions of the oxy allylic anion \(\mathbf{4a}\) with carbonyl electrophiles (E = cyclohexanone), we have observed that the product ratio \(\mathbf{5f}:\mathbf{5o}\) is opposite to what one would predict based upon the above alkylation study: R = i-Bu, \(\gamma:\alpha = 27:73\); R = Ph, \(\gamma:\alpha = 24:76\); R = C\(_6\)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 allyl halides in contrast to ketones has been observed elsewhere.\(^{13}\) Furthermore,

(4) In alkylation reactions \(\mathbf{4a}\) may be also carried out in ether or in pentane with added tetramethylmethylenediamine (TMEDA).
(5) No appreciable ether fission was observed with this base; cf. G. Kobrich and A. Baumann, *Angew. Chem., Int. Ed. Engl.*, 12, 856 (1973). Other bases such as \(n\)-butyllithium are ineffective metatilating agents.
(8) In a number of experiments the average yields of \(\mathbf{5a} + \mathbf{5b}\) ranged from 75 to 95%.

Journal of the American Chemical Society | 96:17 | August 21, 1974
Table I. Reactions of Metalated Ethers with Electrophiles 31

<table>
<thead>
<tr>
<th>Anion (R = t-Bu)</th>
<th>Electrophile, E</th>
<th>Ratio ( \frac{Y}{\gamma} )</th>
<th>Yield, % ( \frac{\gamma + \alpha}{\gamma} )</th>
<th>Product</th>
<th>% yield isolated</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 4a )</td>
<td>( n-CsH_{11}I )</td>
<td>89:11</td>
<td>93</td>
<td>5( \gamma )</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>( \text{Br(CH}_2)_2\text{Br} )</td>
<td>80:20</td>
<td>90</td>
<td>5( \gamma )</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>( \text{sec-CsH}_{2}I )</td>
<td>64:36</td>
<td>65</td>
<td>5( \gamma )</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>( \text{Cyclohexanone} )</td>
<td>27:73</td>
<td>72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 4a ) (R = CH\text{I})</td>
<td>Cyclohexanone</td>
<td>72:28</td>
<td>93</td>
<td>6( \alpha )</td>
<td>72</td>
</tr>
<tr>
<td>( 4b ) (R = CH\text{I})</td>
<td>Cyclohexanone</td>
<td>68:32</td>
<td>99</td>
<td>5( \gamma )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{Cyclohexanone} )</td>
<td>0:10c</td>
<td>97</td>
<td>7( \alpha )</td>
<td>92</td>
</tr>
<tr>
<td>( 9a ) (R = C\text{H}_6)</td>
<td>( n-CsH_{11}I )</td>
<td>&gt;90:10</td>
<td>&gt;90:10</td>
<td>12( \gamma )</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}_2\text{SCCH}_2\text{Br} )</td>
<td>63:37</td>
<td>41</td>
<td>12( \gamma )</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>( \text{Cyclohexanone} )</td>
<td>90:10</td>
<td>93</td>
<td>12( \gamma ) + 12( \alpha )</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>( \text{Cyclohexanone} )</td>
<td>50:50</td>
<td>93</td>
<td>12( \gamma ) + 12( \alpha )</td>
<td>97</td>
</tr>
</tbody>
</table>

* All reactions were carried out at \(-65^\circ\). 3 Both products have been isolated and fully characterized. 4 Determined by nmr relative to an internal standard. 5 Produced by acid hydrolysis (10% HCl-THF) of the enol ether.

The product ratio is highly counterion dependent. The allyl zinc reagent \( 4b \) (R = CH\text{I}), prepared by the addition of 1 equiv of zinc chloride to \( 4a \), reacts with aldehydes and ketones exclusively \( \gamma \) 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 = CH\text{I}) with cyclohexanone. The results of other carbonyl addition reactions are included in Table I.11

As with anion \( 4a \), \( 9a \) (R = C\text{H}_6) reacts regioselectively \( \gamma \) to oxygen in substitution reactions (E = \( n-CSH_{11}I \), \( 12\gamma \):12\( \alpha \) = 90:10). No selectivity was observed in carbonyl addition (E = cyclohexanone, \( 12\gamma \):12\( \alpha \) = 50:50); however, the organozinc reagent \( 9b \) shows exclusive reaction \( \alpha \) 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 carbamions with electrophiles.

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Allyloxy Carbanions. A New Synthesis of Aldehydes via \( \beta \)-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-