with the development of metalted allylic ethers and sulfides recently been able to achieve highly regioselective 1,2-carbonyl ones and allylic organometallic reagents. However, we have problems associated with the ambident reactivity of both en-
to effect regioselective conjugate addition of allylic cuprates 3 as viable precursors to monoprotected 1,6-dicarbonyl deriva-
coupling of aJ-unsaturated ketones with active metals2 and
Sir:
unsatisfactory for the synthesis of
by electr~lysis. Such methods, however, have thus far proven
lustrated in eq 1
comparable with those encountered in the construction of
liminary results in this area on the bond-path construction il-
functionalized three-carbon precursors embodies a problem
The synthesis of 1,6-dicarbonyl compounds from mono-
modified three-carbon precursors embodies a problem
The structural change implied by the spectrum of tropyli is at least super-
ordinately true since both 1 and 3 may rapidly permute carbon positions through (antisymmetric) ring modes without in-
volving the D1 transition state (2) or interconverting a member of the 3 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); (b) S. A. Vosloo and G. W. Linbarger, J. Chem. Phys., 48, 5589 (1968).
T. Koenig and R. Wolfe, J. Am. Chem. Soc., 91, 2559 (1969); r1 = 1.69±0.360 (P1)10 where r1 is C-C bond distance and P1 is the corre-
sphere. Such methods, however, have thus far proven unsatisfactory for the synthesis of un symmetrical dicarbonyl
Substitution that this protocol has led to side products (CF3CO2H, CF3CO2K, C6H5CO2H).
In the present communication we wish to report our pre-
ary results in this area on the bond-path construction il-
the ESR proton hyperfine coupling of the allylic cuprates 3a (M = Li) and related substrates from allylic ethers and sulfides via sec-
butyllithium metalation (THF, -65 °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 allylic substrates by subsequent treatment with 1.2 equiv of anhydrous ZnCl2 or CdCl2 (-65 °C). Addition of 1 equiv of enone at ca. -25 °C followed by warming to ambient tem-
perature 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);9,7 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 sus-
pension of excess potassium hydride and anhydrous, deoxygen-
ated, etheral 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 con-
sumption 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 homopropionic acids have been documented to undergo cleavage to ketones and allylic organometa
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-methylcyclohexaneone.
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

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-
functionalyzed three-carbon precursors embodies a problem comparable with those encountered in the construction of 1,4-dicarbonyl derivatives.1 Symmetrical 1,6 di ketones 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 pre-
liminary results in this area on the bond-path construction il-
}
Communications to the Editor

Table I. Cope Rearrangements of Substituted 1,5-Hexadien-3-ols

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alcohol 5a</th>
<th>Conditions b</th>
<th>Yield, %</th>
<th>Product 4c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R=H; KH, THF 66°C, 9.5h</td>
<td>85</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R=Me; KH, 85°C, 6h</td>
<td>75</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R=Me; o 230°C, 8h</td>
<td>92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>R=H; KH, 85°C, 10.5h</td>
<td>81</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R=Me; KH, 85°C, 12.5h</td>
<td>81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>KH, 85°C, 24h</td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>R=H; KH, 85°C, 30h</td>
<td>70</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R=H; o, 370°C, 8h</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R=Me; KH, 85°C, 30h</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>KH, 85°C, 8h</td>
<td>64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>HO PhS</td>
<td>25°C</td>
<td>THF, 1h</td>
<td>42</td>
</tr>
<tr>
<td>7</td>
<td>HO PhS</td>
<td>KH, 25°C</td>
<td>Et2O, 6h</td>
<td>71</td>
</tr>
</tbody>
</table>

a All alcohols were prepared as a mixture of diastereoisomers and rearranged as such. b Unless specified all rearrangements were carried out in dimethoxyethane (DME) under argon. c Values refer to isolated yields. The products exist as a mixture of E and Z olefin isomers. d The Δ3 olefin exists as a mixture of E and Z olefin isomers.

can be suppressed by an alteration of reaction variables which will decrease the ionogenic character of the metal alkoxide bond. This may be achieved by employing more electronegative alkali metals (Na⁺ vs. K⁺) or by selecting ethereal solvents which possess weaker cation solvating capacity (Et2O vs. THF). For example, dienol 6 (entry 7) undergoes rearrangement (NaH, Et2O, 25 °C) in 71% isolated yield; however, the same substrate undergoes predominant cleavage as the sodium salt in THF at the same temperature.

To gain further insight into the mechanism and possible transition state geometry of these sigmatropic processes, we have studied the rearrangement of the diastereoisomeric dienols 7 and 8 (KH, diglyme, 110 °C, 24 h). Dienol 7 (Scheme II) was found to rearrange in 78% yield to 9a and 10c (96:4), while 8 afforded 9c and 10t (77:23). The stereochemical assignments of 9 and 10 were made by oxidation (O3, CrO3)13 to the known keto acids 11a and 11b.14 It is thus concluded that the rearrangements of 7 and 8 proceed via chair transition states to give 9a and 9c and boat transition states to give 10c and 10t, respectively.

The observed changes in stereoselectivity in the rearrangement of dienols 7 and 8 are in qualitative agreement with predictions based upon transition state conformational analysis.15 The smaller ΔΔG‡ in the “chair” vs. “boat” paths for dienol 8 is understandable in terms of destabilizing contribution of the axial methoxyl substituent in the chair transition state leading to 9c. In the diastereoisomeric chair transition state leading to 9t this substituent is equatorial.

Acknowledgment. Support from the National Science Foundation is gratefully acknowledged. We thank Professor J. Ficini for a sample of 11a.

References and Notes


(8) Satisfactory spectra and elemental analyses were obtained for all compounds reported herein.


(11) R. A. Berkeser and M. S. Siklosi, J. Org. Chem., 41, 3212 (1976); F. Barbot,
Nickel-Catalyzed Conjugate Addition of OrganoaIuminun Acetylides to $\alpha,\beta$-Enones

Sir:

Conjugate addition of organometallic compounds to $\alpha,\beta$-unsaturated ketones is a widely employed reaction in organic synthesis. Organocuprates are commonly employed for 1,4 addition of alkyl and alkenyl groups to $\alpha,\beta$-unsaturated ketones; however, cuprates cannot be used in alkynylation reactions owing presumably to the strength of the alkynyl-copper(I) ligand bond. Several sequences have been reported, however, which do achieve conjugate addition of alkynyl units, but each suffers severe limitations. Both acetylenic alanes and boranes conjugately add to $\alpha,\beta$-enones but only to those capable of achieving an $S$-cis conformation. Of the methods reported which can be applied to fixed $S$-trans enones (such as 2-cyclohexenone), one requires a convenient hydroxyl functional group for direction of intramolecular attack by an alane; the other is indirect and involves addition of di(tri-n-buty1stannyl)ethylene by cuprate addition and subsequent oxidative elimination of a stanny1 group to give, overall, conjugate addition of acetylide to the enone. Extension to alkyl acetylides by this latter method has not been reported. We recently noted that a catalyst prepared from Ni(acac)$_2$ and disobuty1aluminum hydride (1:1) would catalyze the conjugate addition of (alkenyl)zirconium complexes to $\alpha,\beta$-enones. We wish to report herein that this catalyst will, as well, catalyze conjugate addition of terminal alkynyl units to $\alpha,\beta$-unsaturated ketones. This procedure is the first one, to the best of our knowledge, which enables this addition to ordinary $S$-trans enones.

A typical procedure for effecting conjugate addition by this route is illustrated as follows. To Ni(acac)$_2$ in ether at 0 $^\circ$C is added Dibah in toluene solution. The reaction mixture rapidly turns dark red-brown. To this red-brown solution is then added a dialky1aluminum acetylide (prepared in the usual manner from the lithium acetylide and dialky1aluminum chloride) as a solution in ether. The reaction mixture is cooled to $-5$ $^\circ$C and the unsaturated ketone in ethereal solution is added dropwise over a period of 15 min. The reaction mixture is allowed to stir at $-5$ $^\circ$C for several hours. Hydrolysis at 0 $^\circ$C with saturated KH$_2$PO$_4$ (aqueous) solution is then followed by addition of just enough of 10% H$_2$SO$_4$ (aqueous) to dissolve aluminum salts. The organic layer is washed with saturated NaHCO$_3$ and NaCl solutions and is then dried. Removal of solvent and separation of products on silica gel gives the conjugate adduct. Results shown in Chart I demonstrate in part the scope of this reaction. For each case investigated involving the alkoxy-substituted cyclopentenone, the product formed possessed the anti stereochemistry as shown by NMR. Only the acetylide group of the mixed alane was transferred to the enone in a 1,4 manner, and no 1,2 addition was observed in each case examined herein.

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4 Yields are isolated except where noted and have not been maximized except for that of 8. 0.5 can be prepared approximately quantitatively from 4: $^{13}$C$_2$H$_4$ = 3123 cm$^{-1}$. Cis ring fusion was assigned by conversion of 9 to the terminal acetylene by cleavage with (CH$_3$CH$_2$)NF and by subsequent reduction of the terminal acetylene (5% Pd/C, H$_2$ (1 atm)). The resulting ketone was found to be identical by NMR, IR, and gas chromatographic analysis with 9-ethylis-2-decalone, which has been shown to afford cis ring fusion (R. F. Church, R. B. Ireland, and D. R. Shredar, J. Am. Chem. Soc., 87, 82 (1965)). Cis ring fusion is based on 'H NMR (K. L. Williamson, T. Howell, and T. A. Spencer, J. Am. Chem. Soc., 88, 325 (1966); M. J. T. Robertson, Tetrahedron Lett., 1685 (1965)).

We find that optimal yields of conjugate adduct are obtained when an excess of dialky1aluminum acetylide is employed. For example, using 0.22 equiv of Ni(acac)$_2$, 0.20 equiv of Dibah, 2.2 equiv of dimethylaluminum(1-buty1acetylide) and 1 equiv of cumyloxycyclopentenone gave compound 8 (after 1.5-h reaction) in 8% isolated yield. Using a smaller excess of the aluminum acetylide results in a decreased yield of the desired product. In each of these sequences we find that most of the unused aluminum acetylide is converted on workup back to the

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