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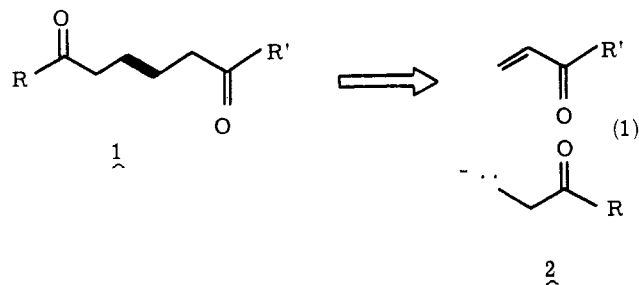
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A General Approach to the Synthesis of 1,6-Dicarbonyl Substrates. New Applications of Base-Accelerated Oxy-Cope Rearrangements

Sir:

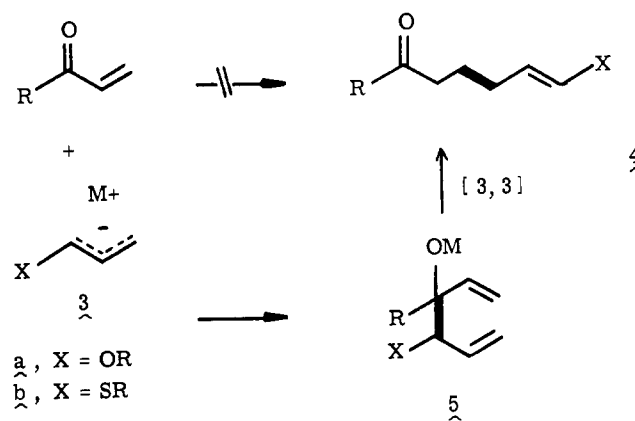
The synthesis of 1,6-dicarbonyl compounds from mono-functionalized three-carbon precursors embodies a problem comparable with those encountered in the construction of 1,4-dicarbonyl derivatives.¹ Symmetrical 1,6 diketones and related derivatives are readily accessible via the reductive coupling of α,β -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-

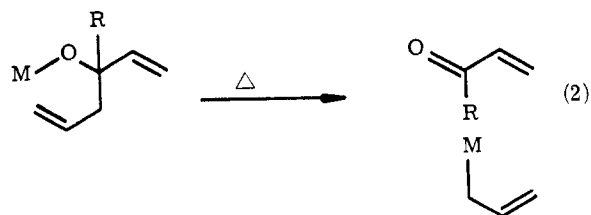
Scheme I



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 °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 ZnCl₂ or CdCl₂ (-65 °C). Addition of 1 equiv of enone at ca. -25 °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

Table I. Cope Rearrangements of Substituted 1,5-Hexadien-3-ols⁸

Entry	Alcohol 5 ^a	Conditions ^b	Yield, %	Product 4 ^d
1		R=H; KH, THF 66°C, 9.5h R=Me; KH, 85°C, 6h R=Me; Δ 230°C, 8h	85 79 93	
2		R=H; KH, 85°C, 10.5h R=Me; KH, 85°C, 12.5h	81 81	
3		KH, 85°C, 24h	11	
4		R=H; KH, 85°C, 30h R=H; Δ, 270°C, 8h R=Me; KH, 85°C, 30h	70 24 10	
5		KH, 85°C, 9h	64	
6		KH, 25°C THF, 1h	42	
7		NaH, 25°C Et ₂ O, 6h	71	

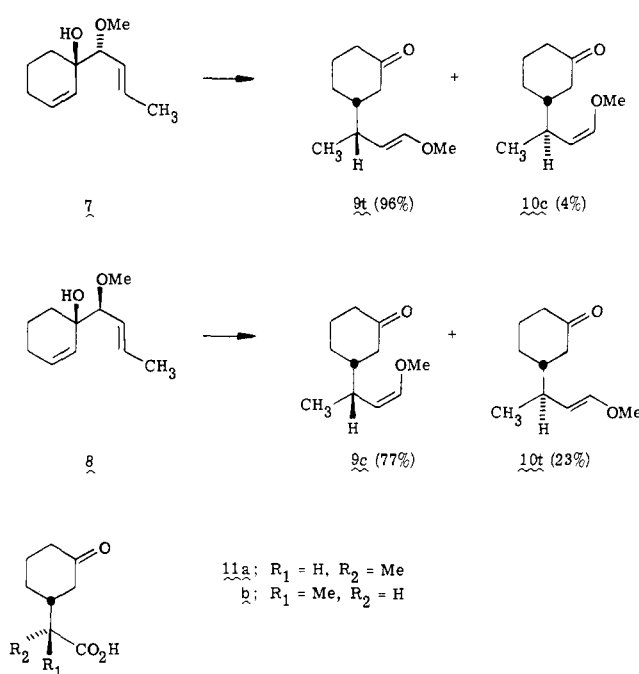
^a All alcohols were prepared as a mixture of diastereoisomers and rearranged as such. ^b Unless specified all rearrangements were carried out in dimethoxyethane (DME) under argon. ^c Values refer to isolated yields. ^d The products exist as a mixture of *E* and *Z* olefin isomers. ^e The Δ⁵ olefin exists as a mixture of *E* and *Z* olefin isomers.

can be suppressed by an alteration of reaction variables which will decrease the ionic 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 **9t** 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 **9t** 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

Scheme II



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**.

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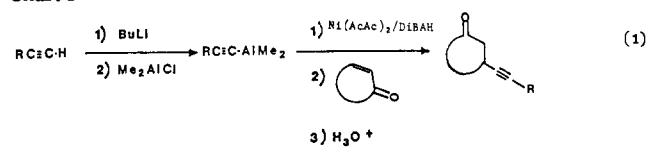
Nickel-Catalyzed Conjugate Addition of Organoaluminum Acetylides to α,β -Enones

Sir:

Conjugate addition of organometallic compounds to α,β -unsaturated ketones is a widely employed reaction in organic synthesis. Organocuprates are commonly employed for 1,4 addition of alkyl and alkenyl groups to α,β -unsaturated ketones;¹ however, cuprates cannot be used in *alkynylation* reactions owing presumably to the strength of the alkynyl-copper(I) ligand bond.² Several sequences have been reported, however, which do achieve conjugate addition of alkynyl units, but each suffers severe limitations. Both acetylenic alanes³ and boranes⁴ conjugately add to α,β -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^{4a} requires a convenient hydroxyl functional group for direction of *intramolecular* attack by an alane; the other⁵ is indirect and involves addition of di(*tri-n*-butylstannyl)ethylene by cuprate addition and subsequent oxidative elimination of a stannyl 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 noted⁶ that a catalyst prepared from Ni(acac)₂ and diisobutylaluminum hydride (1:1) would catalyze the conjugate addition of (alkenyl)zirconium complexes to α,β -enones. We wish to report herein that this catalyst will, as well, catalyze conjugate addition of terminal alkynyl units to α,β -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 °C is added Dibah in toluene solution. The reaction mixture rapidly turns dark red-brown. To this red-brown solution is then added a dialkylaluminum acetylide (prepared in the usual manner from the lithium acetylide and dialkylaluminum chloride)⁷ as a solution in ether. The reaction mixture is cooled to -5 °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 °C for several hours. Hydrolysis at 0 °C with saturated KH₂PO₄ (aqueous) solution is then followed by addition of just enough of 10% H₂SO₄ (aqueous) to dissolve aluminum salts. The organic layer is washed with saturated NaHCO₃ 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.^{8,9} For each case investigated involving the alkoxy-substituted cyclopentenone, the product formed possessed the anti stereochemistry as shown by NMR.¹⁰ 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.⁸

Chart I



Acetylene	α,β -enone	Product	$\nu(C\equiv C)$ Raman cm^{-1}	Yield % ^a
H-≡-+			2238	60
H-≡-+			2236	72
H-≡-C ₄ H ₉ ^b			2231	71
H-≡-SiMe ₃			2175	80 (vpc)
H-≡-H			2060	15 ^b
H-≡-+			2231	67 ^c
H-≡-+			2234	49 ^d
H-≡-+			2238	85
H-≡-SiMe ₃			2160	70 ^c
H-≡-SiMe ₃			2170	50

^a Yields are isolated except where noted and have *not* been maximized except for that of 8. ^b 5 can be prepared approximately quantitatively from 4;¹⁵ $\nu_{C\equiv C-H} = 3313 \text{ cm}^{-1}$. ^c Cis ring fusion was assigned by conversion of 9 to the terminal acetylene by cleavage with (CH₃CH₂)₄NF and by subsequent reduction of the terminal acetylene (5% Pd/C, H₂ (1 atm)). The resulting ketone was found to be identical by NMR, IR, and gas chromatographic analysis with 9-ethyl-*cis*-2-decalone, prepared by the copper acetate catalyzed addition of ethyl Grignard reagent to $\Delta^1,9$ -octalone, a sequence which has been shown to afford *cis* ring fusion (R. F. Church, R. B. Ireland, and D. R. Shredar, *J. Org. Chem.*, **27**, 707 (1962); S. Boatman, T. M. Harris, and C. R. Hauser, *J. Am. Chem. Soc.*, **87**, 82 (1965)). ^d Cis ring fusion is based on ¹H NMR (K. L. Williamson, T. Howell, and T. A. Spencer, *J. Am. Chem. Soc.*, **88**, 325 (1966); M. J. T. Robinson, *Tetrahedron Lett.*, 1685 (1965)).

We find that optimal yields of conjugate adduct are obtained when an excess of dialkylaluminum acetylide is employed. For example, using 0.22 equiv of Ni(acac)₂, 0.20 equiv of Dibah, 2.2 equiv of dimethylaluminum(*t*-butylacetylide) and 1 equiv of cumyloxycyclopentenone gave compound 8 (after 1.5-h reaction) in 85% 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