

not react with olefins).¹⁷ The borolanes **1a,b** were found to undergo the same type of isomerization only slowly (half-life times of several days, 0.5 M solution, 25 °C),¹⁸ and this stability of **1a,b** is extremely gratifying. Thus, a variety of olefins were successfully hydroborated with **1a** and converted to the corresponding alcohols **15** in the usual manner⁹ as summarized in Table I. With the exception of a type I olefin or olefins (entry 1) *all* hydroborations proceeded with excellent stereoselection, clearly meeting the criteria set above. The reagent **1a** is sufficiently reactive to hydroborate even type IV olefins as reflected by high yields (entries 6-9) and remedies the deficiencies of some of the known chiral boranes, e.g., **2**.

Brown's recent kinetic studies of hydroboration indicate that in general (mono)boranes rather than diboranes are the reacting species involved in the transition state.¹⁹ Coupled with these kinetic data, the extent and directionality of the observed asymmetric inductions lead to the proposal of a simple transition-state model shown in **16** for the reaction of olefins with **1a**.²⁰ The distance between an olefinic carbon terminus and the boron atom must be quite short, and the HC=C and RC=C groupings of type II-IV olefins are clearly distinguished and afford a high degree of asymmetric induction (**16a**). The low percent ee observed for the type I olefin is also understandable (**16b**). A set of trans-3,4-disubstituted borolanes **17**, e.g., R = Et, cyclohexyl, have been prepared in optically active form and they exhibit a uniformly marginal degree of asymmetric induction (4-23% ee) with type II-IV olefins. This result is again consistent with the view that the trajectory of the olefins toward the monomer of **17** is approximated by that shown in **16** and the sp³ hybridization of the boron atom has substantially developed in the transition state.

The major problems associated with hydroboration of type II-IV olefins are now essentially solved (except perhaps for the costliness of the reagent) but those with type I olefins remain. Indeed, highly enantioselective or diastereoselective hydroboration of type I olefins is almost without precedent.^{7,21} While work is under way to solve these problems, it should be pointed out that long after the first impressive asymmetric hydroboration was observed in 1961 for bis(isopinocampheyl)borane **2**,²² a systematic, logical step has now been taken toward the design of chiral boranes.

Acknowledgment. We thank Drs. S. Nakagawa and H. Tobita for their pioneering work which had laid the foundation of the work presented above and the National Institutes of Health

(GM33039) and Kao Corporation (funds donated to S.M.) for financial support. J.S.P. is a National Cancer Institute Trainee (NCI-5-T-32-CA-09112).

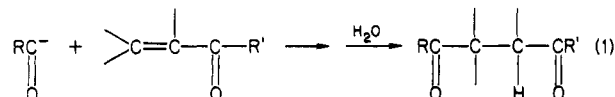
Supplementary Material Available: Full details of crucial experiments (12 pages). Ordering information is given on any current masthead page.

Direct Nucleophilic 1,4-Acylation of α,β -Unsaturated Ketones and Aldehydes via Acylcuprate Reagents

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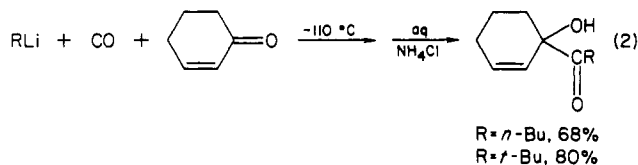
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Nucleophilic 1,4-addition of an acyl anion to α,β -unsaturated ketones and aldehydes (eq 1) is a reaction of great potential interest



to organic chemists. The resulting 1,4-diketones or 1,4-keto aldehydes are useful intermediates in the synthesis of either furan or cyclopentenone systems.¹ In the absence of a useful acyl anion reagent, previous workers have carried out extensive, only partially successful investigations of the applicability of "masked acyl anion equivalents" in 1,4-addition to α,β -unsaturated systems.² Noteworthy as a pioneering effort to effect direct nucleophilic acylation of conjugated enones was the reaction of Corey and Hegedus^{2e} in which an excess of the 1:1 RLi/Ni(CO)₄ reagent was used at -50 °C. Although good yields of 1,4-dicarbonyl products were obtained, this procedure had limited appeal due to the high toxicity of Ni(CO)₄.

In recent papers we have described how acyllithium reagents, generated in situ at low (-110 to -135 °C) temperatures by the RLi + CO reaction, may be used to effect direct nucleophilic acylation of diverse organic electrophiles.³⁻¹¹ In these reactions, a solution of the organic electrophile was cooled to the appropriate low temperature and saturated with carbon monoxide at atmospheric pressure, and then the organolithium reagent was added very slowly at a constant rate while the CO stream was continued. Such a procedure, when applied to the nucleophilic acylation of cyclohexen-2-one and cyclopenten-2-one, gave only products of 1,2-addition, e.g., eq 2. A similar reaction of the *t*-BuLi/CO



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Table I. Direct Nucleophilic Acylation of α,β -Unsaturated Carbonyl Compounds with Acylcuprate Reagents $R_2(CN)CuLi_2$

R	α,β -unsaturated carbonyl compd	product ^a (% yield) ^f
<i>n</i> -C ₄ H ₉	2-cyclohexenone	3-pentanoylcyclohexanone (86)
	2-cyclopentenone	3-pentanoylcyclopentanone (89)
	CH ₂ =CHC(O)CH ₃	<i>n</i> -C ₄ H ₉ C(O)CH ₂ CH ₂ C(O)CH ₃ (66)
	CH ₂ =CHC(O)C ₂ H ₅	<i>n</i> -C ₄ H ₉ C(O)CH ₂ CH ₂ C(O)C ₂ H ₅ (75)
	C ₂ H ₅ CH=CHCHO ^b	<i>n</i> -C ₄ H ₉ C(O)CH(C ₂ H ₅)CH ₂ CHO (63)
	<i>n</i> -C ₃ H ₇ CH=CHCHO	<i>n</i> -C ₄ H ₉ C(O)CH(<i>n</i> -C ₃ H ₇)CH ₂ CHO (70)
<i>sec</i> -C ₄ H ₉	2-cyclohexenone	3-(2-methylbutanoyl)cyclohexanone (75)
	CH ₂ =CHC(O)CH ₃	<i>sec</i> -C ₄ H ₉ C(O)CH ₂ CH ₂ C(O)CH ₃ (78)
	C ₂ H ₅ CH=CHCHO	<i>sec</i> -C ₄ H ₉ C(O)CH(C ₂ H ₅)CH ₂ CHO (76)
<i>t</i> -C ₄ H ₉	2-cyclohexenone	3-pivaloylcyclohexanone (78)
	2-cyclopentenone	3-pivaloylcyclopentanone (82)
	CH ₂ =CHC(O)CH ₃	<i>t</i> -C ₄ H ₉ C(O)CH ₂ CH ₂ C(O)CH ₃ ^c (66)
	CH ₂ =CHC(O)C ₂ H ₅	<i>t</i> -C ₄ H ₉ C(O)CH ₂ CH ₂ C(O)C ₂ H ₅ ^d (64)
	CH ₃ CH=CHCHO	<i>t</i> -C ₄ H ₉ C(O)CH(CH ₃)CH ₂ CHO ^e (52)
	C ₂ H ₅ CH=CHCHO	<i>t</i> -C ₄ H ₉ C(O)CH(C ₂ H ₅)CH ₂ CHO (72)
	<i>n</i> -C ₃ H ₇ CH=CHCHO	<i>t</i> -C ₄ H ₉ C(O)CH(<i>n</i> -C ₃ H ₇)CH ₂ CHO (64)

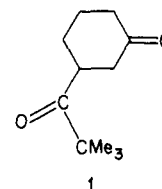
^a All new compounds were characterized by C/H analysis ($\pm 0.4\%$) and IR and ¹H NMR spectroscopy. ^b The reaction mixture was treated with the NH₄OH/NH₄Cl mixture at -40°C and the organic layer was washed with 0.1 N HCl and water. ^c *t*-C₄H₉CH₂CH₂C(O)CH₃ byproduct in 14% yield. ^d *t*-C₄H₉CH₂CH₂C(O)C₂H₅ byproduct in 24% yield. ^e *t*-C₄H₉CH(CH₃)CH₂CHO byproduct in 19% yield. ^f Yields based on utilization of one of the R groups of the $R_2(CN)CuLi_2$ reagent.

reagent with methyl vinyl ketone gave a mixture of 1,2 and 1,4 products: *t*-BuC(O)C(OH)(Me)(CH=CH₂) (52%) and *t*-BuC(O)CH₂CH₂C(O)Me (25%). In view of these results, we decided to investigate the possibility of the carbonylation of cuprate reagents, one of whose principal applications in synthesis is in their conjugate addition to α,β -unsaturated carbonyl compounds.¹²

The reaction of lithium di-*n*-butylcuprate with CO in diethyl ether at -22°C to give 5-nonanone in 70% yield was described some years ago by Schwartz.¹³ No further development of this chemistry was reported. In view of the excellent results obtained by Lipshutz and his co-workers in their studies of "higher order cuprates", soluble reagents of formal stoichiometry $R_2(CN)CuLi_2$, in conjugate additions to α,β -unsaturated carbonyl compounds,¹⁴ we chose cuprate reagents of this type for our investigations. Initially, we used the usual in situ procedure,¹¹ but we soon discovered that the carbonylation products of the $R_2(CN)CuLi_2$ reagents (R = *n*-, *sec*-, *t*-Bu) are stable in solution for short times at -110°C . Therefore, the nucleophilic acylation of α,β -unsaturated aldehydes and ketones could be carried out in a two-step procedure. A typical reaction is described.

A 500-mL three-necked flask equipped with a mechanical stirrer, a Claisen adapter (fitted with low-temperature thermometer and a gas outlet tube), and a no-air stopper which held a gas dispersion tube (which was connected to a carbon monoxide cylinder) was charged with 225 mL of the usual solvent mixture (4:4:1 by volume THF, diethyl ether, and pentane). The solvent was cooled to -110°C while a stream of carbon monoxide was bubbled through it. Meanwhile, the cuprate reagent, *t*-Bu₂(CN)CuLi₂ (7.18 mmol), was prepared under nitrogen by adding 14.36 mmol of *t*-BuLi in pentane to 7.26 mmol of copper(I) cyanide in degassed THF at -78°C .¹⁴ The resulting reagent was warmed briefly to 0°C and then was kept under nitrogen at -78°C . After carbon monoxide had been bubbled through the THF/Et₂O/pentane mixture for 20 min at -110°C , the cooled *t*-Bu₂(CN)CuLi₂ solution was added slowly, dropwise over 15 min, to the solvent mixture (by cannula) while the CO stream was continued. The resulting orange solution was kept at -110°C for 20 min under CO and then 7.02 mmol of cyclohexen-2-one was added by syringe while the admission of CO was continued. The now deep orange solution was stirred at -110°C for 1.5 h under CO and then was allowed to warm to room temperature. The resulting yellow-green solution was treated with 75 mL of a 1:10 by volume mixture of concentrated NH₄OH and saturated

aqueous NH₄Cl. The dark blue aqueous phase was extracted with ether and the combined organic layers were dried and concentrated at reduced pressure. GLC analysis of the high-boiling liquid residue showed the presence of the 1,4-diketone **1** in 78% yield



based on utilization of one *t*-BuLi. Similar reactions were carried out with *n*-Bu₂(CN)CuLi₂ and *sec*-Bu₂(CN)CuLi₂, both of which gave yellow solutions on carbonylation. The results of our experiments carried out in this preliminary investigation are summarized in Table I. Especially noteworthy is the fact that the conjugate nucleophilic acylation of α,β -unsaturated aldehydes, RCH=CHCHO, was quite successful in spite of the normally high reactivity of the aldehydic C=O group. The conjugate acylation of cyclic α,β -unsaturated ketones proceeded especially well, giving high yields of the expected 1,4-diketones in the case of all three alkyl lithium-derived acylcuprate reagents. Only in the case of the *t*-Bu₂(CN)CuLi₂/CO reagent were 1,4-alkylated (rather than acylated) byproducts formed (footnotes c–e in Table I) and this only with the more reactive α,β -unsaturated substrates. The use of a lower (-135°C) reaction temperature did not give cleaner reactions in these cases. In this connection we note that the exact constitution of higher order cuprates is still unclear¹⁴ and so the nature of the carbonylation product of the $R_2(CN)CuLi_2$ reagents remains to be defined. Since we have in a few cases seen alkylated byproducts, it is possible that the carbonylated cuprates are of composition [(RC(=O))(R)(CN)CuLi₂]. If this is the case, we were fortunate in most experiments that the acyl group was the more labile one. Assuming the [(RC(=O))(R)(CN)CuLi₂] formulation, we suggest that this selectivity is diminished when R = *t*-C₄H₉ because of steric and/or electronic factors.

Some experiments were carried out to examine the stability of the *n*-Bu₂(CN)CuLi₂/CO reagent. In a reaction in which the cyclohexen-2-one was added 90 min after the addition of the cuprate reagent to the CO-saturated solvent mixture (at -110°C) had been completed, the 1,4-diketone yield was 82%. When this time under CO at -110°C was extended to 2 h, the 1,4-diketone yield fell to 60%; when it was extended further to 3 h, the 1,4-diketone was obtained in only 20% yield. In other reactions the *n*-Bu₂(CN)CuLi₂ carbonylation was carried out at -78°C . When the elapsed time at this temperature (under CO) was 25 min, the 1,4-diketone was obtained in only 10% yield, but when this time between completion of the reagent preparation and cyclohexen-

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2-one addition was reduced to 5 min, the 1,4-diketone yield was 73%. Thus at -78°C the acylcuprate reagent has only minimal stability but its reactions may be carried out at this higher temperature. This may be of advantage when less reactive organic electrophiles are to be acylated. Other experiments showed that there is no advantage to going to temperatures lower than -110°C .

A procedure for the *direct* nucleophilic conjugate acylation of α,β -unsaturated carbonyl compounds is a useful new synthetic method for the organic chemist. It is clear that the scope and limitations of this procedure remain to be defined. Furthermore, this new class of nucleophilic acylating reagents presents interesting possibilities for applications in synthesis other than that reported here and we are investigating such possibilities both in the organic and organometallic direction.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this work.

Registry No. $\text{CH}_2=\text{CHAc}$, 78-94-4; $\text{CH}_2=\text{CHC(O)Et}$, 1629-58-9; $\text{CH}_3\text{CH}=\text{CHCHO}$, 4170-30-3; $\text{C}_2\text{H}_5\text{CH}=\text{CHCHO}$, 764-39-6; $\text{PrCH}=\text{CHCHO}$, 505-57-7; $\text{Bu}_2(\text{CN})\text{CuLi}$, 80473-69-4; (*sec*-Bu) $_2(\text{CN})\text{CuLi}$, 86646-53-9; (*t*-Bu) $_2(\text{CN})\text{CuLi}$, 87263-84-1; $\text{BuC(O)(CH}_2)_2\text{Ac}$, 25234-82-6; $\text{BuC(O)(CH}_2)_2\text{C(O)Et}$, 96948-54-8; $\text{BuC(O)CH(Et)CH}_2\text{CHO}$, 96948-55-9; $\text{BuC(O)CH(Pr)CH}_2\text{CHO}$, 92803-30-0; (*sec*-Bu) $\text{C(O)(CH}_2)_2\text{Ac}$, 96948-57-1; (*sec*-Bu) $\text{C(O)CH(Et)CH}_2\text{CHO}$, 96948-58-2; (*t*-Bu) $\text{C(O)(CH}_2)_2\text{Ac}$, 38453-95-1; (*t*-Bu) $\text{C(O)(CH}_2)_2\text{C(O)Et}$, 65199-78-2; (*t*-Bu) $\text{C(O)CH(Me)CH}_2\text{CHO}$, 96948-60-6; (*t*-Bu) $\text{C(O)CH(Et)CH}_2\text{CHO}$, 96948-61-7; (*t*-Bu) $\text{C(O)CH(Pr)CH}_2\text{CHO}$, 96948-62-8; (*t*-Bu) $(\text{CH}_2)_2\text{Ac}$, 14272-73-2; (*t*-Bu) $(\text{CH}_2)_2\text{C(O)Et}$, 5054-71-7; (*t*-Bu) $\text{CH(Me)CH}_2\text{CHO}$, 37179-52-5; 2-cyclohexenone, 930-68-7; 2-cyclopentenone, 930-30-3; 3-pentanoylcyclohexanone, 25234-78-0; 3-pentanoylcyclopentanone, 64277-97-0; 3-(2-methylbutanoyl)cyclohexanone, 96948-56-0; 3-pivaloylcyclohexanone, 62687-29-0; 3-pivaloylcyclopentanone, 96948-59-3.

Norborna-2,5-dien-7-one: A Covalent Benzene–Carbon Monoxide Adduct. A New Point on the Cycloreversion Structure–Reactivity Correlation Curve

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We ask whether any hypothetical full-valence molecule can fail to exist because the activation energy for its thermal cycloreversion to stable fragments is zero. Previous discussions^{1,2} of a few experimental examples of cycloreversion have assumed³ a correlation between exothermicities and rates, which, if generally correct, could guide efforts to answer this question by the synthesis of substances of increasing thermodynamic instability.

A broader survey (Figure 1) shows a monotonic relationship between activation free energy (ΔG^\ddagger at 300 K) and reaction enthalpy change (ΔH_r) for 17 orbital symmetry-“allowed” fragmentations.⁴ The data correspond to rate and equilibrium constant ranges of 10^{27} and 10^{70} , respectively. In the present work, we have attempted to extend this curve toward lower ΔG^\ddagger values by the simultaneous synthesis of two substances of current the-

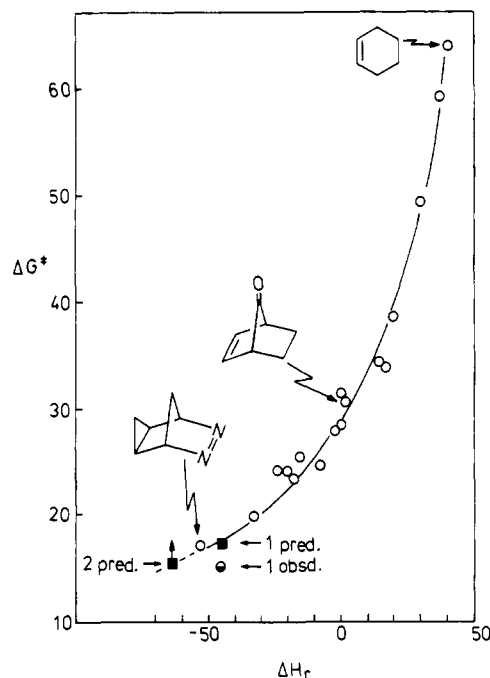
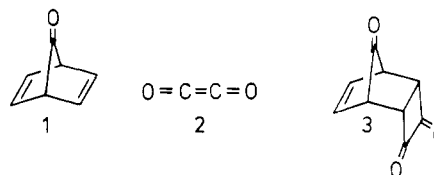


Figure 1. Dependence of ΔG^\ddagger (300 K) for fragmentation on reaction enthalpy. Values (kcal/mol) from the literature are shown as open circles. The actual ΔG^\ddagger value for triplet (ground state) **2** could be higher, since fragmentation of **2** is spin forbidden.^{6a,b}

oretical and preparative interest, norborna-2,5-dien-7-one (**1**)⁵ and ethylenedione (**2**),⁶ whose predicted approximate ΔG^\ddagger values,¹⁷



and 15 kcal/mol, for fragmentation (into benzene + CO and 2CO, respectively), are obtained by extrapolation (see Figure 1).

The synthesis of the pink, crystalline tricyclo[4.2.1.0^{2,5}]non-7-en-3,4,9-trione (**3**), mp 123–124 $^{\circ}\text{C}$ (dec), a potential precursor of both **1** and **2**, was achieved by a three-step sequence: Diels–Alder addition of 5,5-diethoxycyclopentadiene to diethyl maleate, acyloin condensation, and oxidation with Br_2 .⁷ Photolysis of CD_2Cl_2 solutions of **3** at 25 $^{\circ}\text{C}$ gave benzene as the only identified product, but photolysis of an argon matrix of **3** at 15 K with light of 313 nm, monitored by FT-IR, led to the disappearance of the bands of **3** (notably those of 1820 and 1772 cm^{-1}) and to the appearance of bands of CO at 2136 and 2121 cm^{-1} . Bands⁸ of an unstable intermediate also grew in at 1846 (s), 1795 (s), 1327, 1317, 1206, 809, and 716 (s) cm^{-1} . The latter band is tentatively assigned to an olefinic C–H out-of-plane deformation mode. Warming the sample or prolonged irradiation produced benzene.

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