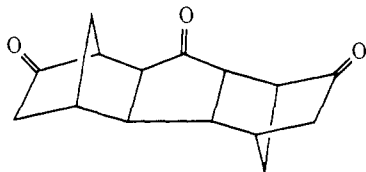


Table I. Nmr Spectra of the Adduct

	H-1	H-3x	H-3n	H-4	H-5	H-6	H-7s ^a	H-7a
Pmr (CDCl ₃ , δ ± 0.01 ppm) (J , ± 0.1 Hz)	2.87	2.14	1.96	2.77	2.23	2.48	1.69	1.50
	² J _{3x,3n} = 18; ² J _{5,7a} = 11.5 ³ J _{3x,4} = 4.5; ³ J _{5n,6n} = 7.5; ⁴ J _{3n,7a} = 4							
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
Cmr (CDCl ₃ , δ ± 0.1 ppm)	54.1	211.9	44.1	43.5 (or 48.9)	48.9 (or 43.5)	53.1	33.8	217.3

^a Syn to the C-2 carbonyl.

trum contains only eight carbon resonances (Table I). It should be noted here in passing that cmr with its resolution is an extremely powerful tool for the identification of symmetrical structures. In this case, it rules out *all* the off-diagonal stereoisomers. Analysis of the ¹H spectrum at 300 MHz is straightforward; exo-exo substitution is indicated by the lack of observable coupling between the endo 5- and 6-protons and the bridgehead 1- and 4-protons.⁴ A cis cyclopentanone is excluded because the vicinal ³J_{5,5'} (or ³J_{6,6'}) coupling constant has an upper limit of 2 Hz as shown by computer simulation of the AA'BB' system observed for the 5,5'- and 6,6'-protons.⁵ Finally, it is possible to choose between the remaining SXTXS and AXTXA structures from the dipole moment; the calculated values are 4.7 ± 0.7 and 1.5 ± 0.5 D, respectively, while the measured⁶ value is 4.6 ± 0.3 D. The adduct formed is thus the SXTXS stereoisomer.



Outside of starting material and polymers, it is the only organic material we could isolate by column chromatography from the reaction mixture. Since (*R,S*)-norbornen-5-one-2 was used, the finding of the single pair of enantiomers (SXTXS, SXTXS) is equivalent to the statement that the (*R*) enantiomer of norbornen-5-one-2 combines only with another (*R*) enantiomer, and that the (*S*) enantiomer likewise recognizes another (*S*) enantiomer. This rather unusual observation of asymmetric induction at the level of the first organometallic complex formed is an important clue to the mechanism of the reaction. Further experiments are now in progress to test our working hypothesis of a trigonal bipyramidal intermediate or transition state with the two olefins as equatorial ligands, and the inserted carbonyl originating from an axial position.

Acknowledgments. We are grateful to Professors Anteunis and Gelan for the 300-MHz spectrum. The

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FT Bruker HFX-90 nmr spectrometer was purchased with the help of a grant from "Fonds de la Recherche Fondamentale Collective."

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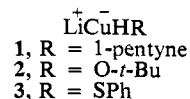
Reduction of α,β -Unsaturated Carbonyl Compounds by "ate" Complexes of Copper(I) Hydride

Sir:

We would like to report the results of our studies on the selective reduction of α,β -unsaturated carbonyl compounds by complexes of Cu^IH. Whitesides and SanFillippo's initial studies showed that solubilized Cu^IH is capable of functioning as a reducing agent.¹ More recently, Masamune and coworkers demonstrated that a complex of Cu^IH can cleanly effect the reductive removal of halide and tosylate groups. However, the presence of aluminum salts clouds the exact nature of the reducing species.²

As a part of our program aimed at generalizing the preparation of enolate species containing copper,³ we have prepared a series of "ate" complexes (1-3) analogous to the diorganocuprate alkyl transfer reagents prepared by Corey and Posner.^{4,5} We anticipated that selective transfer of hydride in the 1,4 sense would occur, and this has been realized.

The Cu^IH was prepared free of other salts¹ and then solubilized utilizing the lithio derivative of the nontransferable ligand. This eliminates the necessity of dealing with additional solubilizing ligands which may interfere with subsequent purification procedures. The structure



of the reducing species in this case is presumably similar

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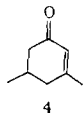
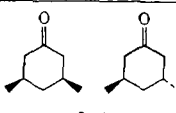


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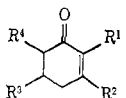
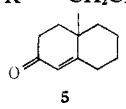
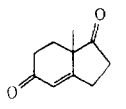
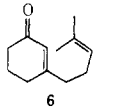
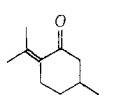
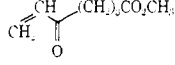

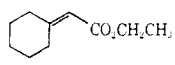


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Table I

Substrate	Reducing agent ^a	Time, hr	Temp, ^b °C	Products ^c	Yield, ^d %
	$\text{CH}_3(\text{CH}_2)_2\text{C}\equiv\text{CCuH}^-\text{Li}^+$ HMPA (10%)	24	-20		90
	$t\text{-BuOCuH}^-\text{Li}^+$	24	25	4:1	50 (80)
	$\text{PhSCuH}^-\text{Li}^+$	24	25	10:0	50
	HMPA (10%)				
	$\text{CH}_3(\text{CH}_2)_2\text{C}\equiv\text{CCuH}^-\text{Li}^+$ HMPA (10%)	24	-20		50
	$t\text{-BuOCuH}^-\text{Li}^+$	24	-20		20 (75)

^a Ratio of reducing agent to substrate of 6:1 on a 1-3 mmol scale. ^b Temperature of -20° was that of a thermostated cold box. ^c Products identified by comparison with authentic materials. ^d Yields determined by vpc utilizing internal standardization and checked by isolation for accuracy ($\pm 5\%$). Figures in parentheses indicate conversions if not complete.

Table II

Entry no.	Substrate ^a	Time, hr	Temp, °C ^b	Addition	% yield ^{c-e}
1	 $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$ $\text{R}^4 = i\text{-C}_3\text{H}_7$	24	-20		95 (95)
2	$\text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$ $\text{R}^1 = \text{CH}_3$	48	-20		64
3	$\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$	24	-20		60 (94)
4	$\text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$ $\text{R}^1 = \text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$	24	-20		76
5		24	-20	HMPA (10%)	67 (67) (70:30; cis:trans)
6		24	-20	HMPA (10%)	22 (89)
7		24	-20	HMPA (10%)	74 (80)
8		48	-20	HMPA (10%)	85 (81)
9		0.25	-120		42
10		0.50	-78		86 (82)
11		24	-20		47
12		1.0	-20		70
13		0.25	-20		85 (75)

^a Experiments performed on 1-3 mmol scale with a molar ratio of substrate to complex of 1:6. ^b Temperatures achieved by use of Dry Ice-solvent baths: carbon tetrachloride (-20°), acetone (-78°). A slush bath of liquid nitrogen and pentane was used for -120°. The freezing compartment of a refrigerator (-20°) was used for long periods of storage. ^c Yields determined by vpc utilizing internal standardization; checked by isolation in cases 1, 4, 6, 10, and 11 and found to agree within $\pm 5\%$ (10 mmol scale). ^d Products identified by comparison with authentic materials. All compounds had satisfactory ir and nmr data. ^e Figures in parentheses indicate conversion if not complete.

to the comparable alkyl complexes. House and Umen have suggested that a species of this type is responsible for the observed reduction of isophorone during conjugate addition.⁶

The experiments summarized in Table I indicate that the preferred reducing agent for unsaturated carbonyl derivatives is the 1-pentynyl complex (1). The ability to function as a reducing agent appears qualitatively to decrease in the order of nontransferable ligand: 1-pentyne > SPh > *O-t*-Bu, with the latter two being significantly less effective (apparently less reactive). We have also found that added hexamethylphosphoramide (HMPA) appears to facilitate somewhat the reduction in cases where the β -carbon is highly substituted. The HMPA probably functions in one of two ways: (1) by mediating electron transfer or (2) by increasing the nucleophilicity of the complex. The reductions are regiospecifically 1,4 and other normally reducible functionalities are unaffected.

The results of the reduction of a series α,β -unsaturated carbonyl compounds utilizing the most effective complex (1) may be found in Table II. Acyclic and more acidic cyclic carbonyl compounds generally give somewhat lowered yields and require low temperature conditions. This apparently is due to the relatively basic nature of these reducing agents which promotes proton transfer and polymerization. However, to the extent that reduction occurs, it occurs specifically in the 1,4 sense.

The stereochemistry of reduction is generally the expected antiparallel entry of hydride.⁷ In the case of 4 the results are comparable to hydrogenation.⁸ As the substitution surrounding the β -carbon increases, the reduction becomes more sluggish and is somewhat less selective. The reduction of octalone 5 produces a *cis*:*trans* ratio of 70:30 which is somewhat less specific than hydrogenation (80:20).⁹

Particularly noteworthy among the examples cited in Table II is the reduction of doubly unsaturated 6. The regiospecific reduction realized would not be trivially attainable by catalytic reduction. Initial attempts to utilize the complexes 1-3 for partial reduction of α,β -acetylenic derivatives have not been successful.

A typical experimental procedure follows. $\text{Cu}^{\text{I}}\text{H}$ is prepared from Cu^{I} (purified)-pyridine complex and diisobutylaluminum hydride in toluene ($\sim 2 M$) at *ca.* -50° under nitrogen.¹ The $\text{Cu}^{\text{I}}\text{H}$ is precipitated as a brown solid by dilution with dry ether, and washed four-six times with ether to remove residual aluminum salts and pyridine. A solution of lithio-1-pentyne (6 mmol) 0.5-1.0 *M* in dry tetrahydrofuran (THF)¹⁰ is added to the $\text{Cu}^{\text{I}}\text{H}$ (6 mmol) and the mixture shaken at -50° , affording an almost clear dark brown solution. This solution is diluted with THF ($\sim 0.25 M$) and HMPA (10% by volume) is added if desired. The unsaturated carbonyl compound (1 mmol) in a small amount of THF is added and the mixture is stored at the

desired temperature for the designated time period. After quenching with 10% NH_4Cl solution, the precipitated solids are removed by filtration and the products isolated by extraction (ether). Purification by distillation or chromatography then affords the reduction products.

We are presently exploring conditions for the successful reduction of other classes of substrates including those of the acetylenic type, and the chemistry of the derived enolate species. The present report demonstrates that (1) hydride is successfully transferred by copper "ate" complexes in the presence of a second nontransferable ligand, (2) the regiospecificity and functional selectivity of these reagents is high, and (3) the stereoselectivity is comparable to that obtained by hydrogenation in most cases. The selective nature of these complexes complements existing methods for this transformation and should make them useful reducing agents for multifunctional molecules.

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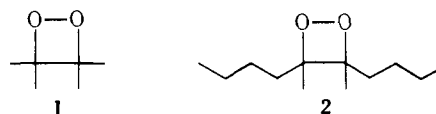
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Thermal and Photochemical Decomposition of 3,4-Dimethyl-3,4-di-*n*-butyl-1,2-dioxetane. Competitive Generation of Singlet and Triplet 2-Hexanone¹

Sir:

Numerous reports have appeared recently describing the thermal decomposition of various 1,2-dioxetanes to give electronically excited carbonyl products, as evidenced by chemiluminescence, sensitization, photochemical products, etc.² In the majority of cases the apparent total yield of excited species from simple alkyl-1,2-dioxetanes has been on the order of 10% or lower.^{2a-d} However, in a recent communication, Turro and coworkers reported that tetramethyl-1,2-dioxetane (1) yields triplet acetone (50%) with only a minor population of singlet (<1%) as primary thermolysis products.^{2f}

In light of the provocative theoretical implications of such a high triplet yield, we have investigated the closely related 3,4-dimethyl-3,4-di-*n*-butyl-1,2-dioxetane (2).



We report here results which differ surprisingly from those of Turro, *et al.*

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