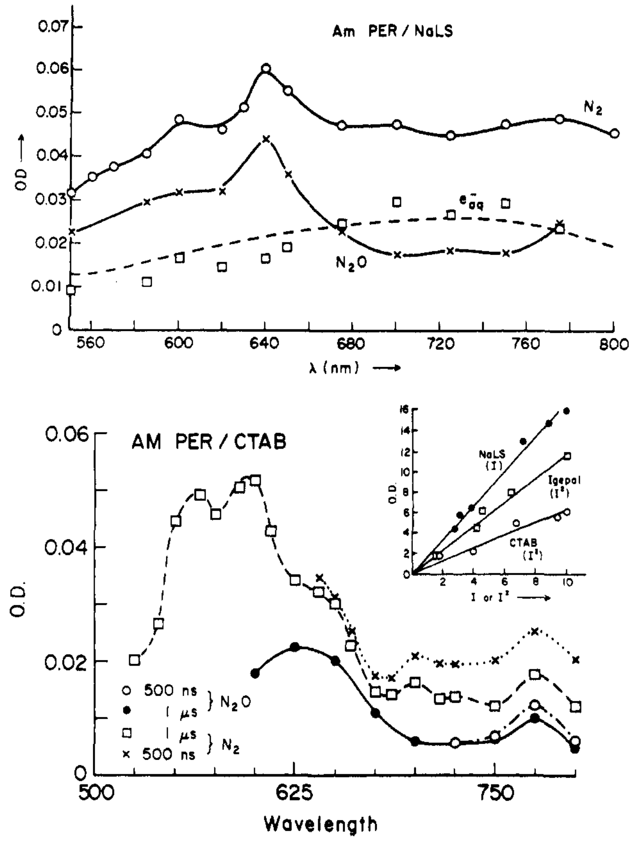

Figure 1. Photoionization of aminoperylene in micellar solution and spectra of short-lived transients with pulses of 530-nm light. Insert: effect of laser intensity or square of laser intensity on the yield of photoionization in NaLS, CTAB, and Igepal micelles.

biphotonic mechanism. The measurement of photocurrent produced in the Igepal sample also supports a biphotonic mechanism for photoionization.

The data clearly show the marked effect of micellar environment on the yield of photoionization of 3-aminoperylene. By comparison with other systems[10] this molecule is most probably situated in the surface region of the micelle between the polar head groups and the decrease in the ionization potential is due to the energy gained by the excited molecule at the micelle surface. The ionization potential in solution, I_s, is related to that in the gas phase I_g by the expression

$$I_s = I_g + P_+ + V_0$$

where V_0 is the energy state of the electron in water which is reported -1.5 eV,[11] and the cation polarization P_+ which is reported as -1.6 eV for 3-aminoperylene in alkanes.[12] The polarization energy may be approximated by the Born equation

$$P_+ = -\frac{e^2}{2r}\left(1 - \frac{1}{\epsilon}\right)$$

where r is the separation of the solvent and ion, e the electron charge, and ϵ the effective high frequency dielectric constant of the medium. In isooctane with $\epsilon \simeq 2$ and $r \simeq 2.1$ Å a P_+ of -1.5 eV is calculated in agreement with experimental data. Aminoperylene is situated between the negatively charged sulfate groups of the NaLS micelle. The polarization energy of the cation could be much larger under these conditions owing to the availability of the delocalized electron of the head group which can participate in and enhance the polarization effect. A cationic or neutral micelle cannot participate to the same enhanced degree in the polarization effect. The Born equation value for P_+ in NaLS may be as large as -3.2 eV or double that in an alkane if the effective ϵ on the micelle surface is large. The total lowering of the IP is then -4.7 eV.

The experimental data give the first example of the one photon photoionization of a simple molecule with long wavelength light, and illustrate possible designs for systems where light energy is converted to ion chemistry which may be later utilized to recover the stored energy. This latter aspect of the energy storage cycle is now under further study.

Acknowledgment. We acknowledge Branka Razem for the time and energy spend in the tedious preparation and purification of the title compound.

References and Notes

(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-1834 from the Notre Dame Radiation Laboratory.
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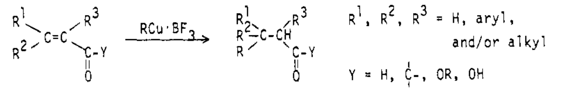
$\mathrm{RCu{\cdot}BF_3}$. 3.[1] Conjugate Addition to Previously Unreactive Substituted Enoate Esters and Enoic Acids[2]

Sir:

Conjugate addition reaction of an organometallic reagent to an α,β-unsaturated carbonyl compound is highly useful synthetic operation.[3] Today's method of choice is definitely the use of organocuprates (Gilman reagents). Unfortunately, however, β,β disubstitution prevents conjugate addition to enoate esters,[3,4] and α,β disubstitution also leads to poor results.[3] Furthermore, conjugate addition to α,β-ethylenic carboxylic acids has never been achieved by using any organometallic reagent. We wish to report that these difficulties, for the first time, can be overcome by using a new alkylating reagent, $\mathrm{RCu{\cdot}BF_3}$ (eq 1).



(1)

We recently reported that the substitution of allyl halides with complete allylic rearrangement is achieved by the use of $\mathrm{RCu{\cdot}BF_3}$.[5] As part of an attempt to broaden the scope of this new alkylating reagent it became of interest to explore the behavior toward α,β-unsaturated carbonyl compounds. The results are summarized in Table I.

As is apparent from Table I, conjugate addition of this new reagent to the ordinary α,β-unsaturated ketones and esters may be as effective as 1,4 addition of other organocopper reagents (entries 1-5). Although the new reagent also undergoes conjugate addition to α,β-unsaturated aldehydes, the reaction proceeds much better with $\mathrm{R_2CuLi}$ than with $\mathrm{RCu{\cdot}BF_3}$. The most remarkable feature is that this new reagent undergoes effective conjugate addition to the α,β- (entry 6) and β,β-disubstituted (entries 7-10) enoate esters, and even to the

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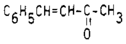
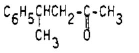
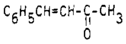
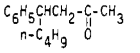
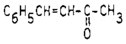
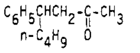
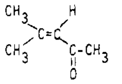
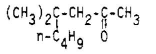
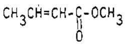
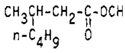
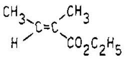
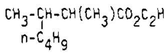
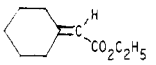
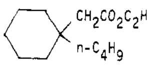
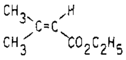
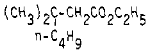
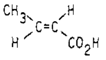
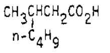
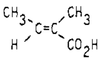
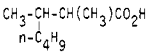
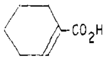
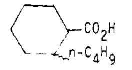
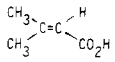
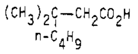
Table I. Reaction of $RCu{\cdot}BF_3$ with α,β-Unsaturated Carbonyl Compounds[a]

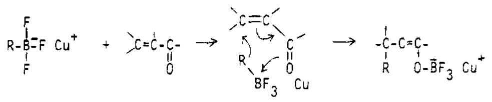
Entry	α,β-Unsaturated Carbonyl Compound	$RCu{\cdot}BF_3$ R (equiv)	Product[b]	Yield,%[c] (isold)
1	 $C_6H_5CH{=}CH\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_3$	CH_3 (2)	 $C_6H_5\underset{CH_3}{\underset{\mid}{C}}HCH_2\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_3$	72
2	 $C_6H_5CH{=}CH\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_3$	$n\text{-}C_4H_9$ (2)	 $C_6H_5\underset{n\text{-}C_4H_9}{\underset{\mid}{C}}HCH_2\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_3$	(90)
3	 $C_6H_5CH{=}CH\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_3$	$n\text{-}C_4H_9$ (1)	 $C_6H_5\underset{n\text{-}C_4H_9}{\underset{\mid}{C}}HCH_2\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_3$	81
4		$n\text{-}C_4H_9$ (1)	 $(CH_3)_2\underset{n\text{-}C_4H_9}{\underset{\mid}{C}}\text{-}CH_2\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_3$	(53)[d]
5	 $CH_3CH{=}CH\text{-}\underset{O}{\underset{\|}{C}}\text{-}OCH_3$	$n\text{-}C_4H_9$ (2)	 $CH_3\underset{n\text{-}C_4H_9}{\underset{\mid}{C}}H\text{-}CH_2\text{-}\underset{O}{\underset{\|}{C}}\text{-}OCH_3$	95
6		$n\text{-}C_4H_9$ (1)	 $CH_3\text{-}\underset{n\text{-}C_4H_9}{\underset{\mid}{C}}H\text{-}CH(CH_3)CO_2C_2H_5$	(53)[d]
7		$n\text{-}C_4H_9$ (2)		(51)[d]
8		$n\text{-}C_4H_9$ (2)	 $(CH_3)_2\underset{n\text{-}C_4H_9}{\underset{\mid}{C}}\text{-}CH_2CO_2C_2H_5$	52[d]
9	the same as above	$(n\text{-}C_4H_9)_2CuLi$ (2)	the same as above	<1
10	the same as above	$n\text{-}C_4H_9Cu$ (2)	the same as above	<1
11		$n\text{-}C_4H_9$ (3)	 $CH_3\underset{n\text{-}C_4H_9}{\underset{\mid}{C}}HCH_2CO_2H$	(81)
12		$n\text{-}C_4H_9$ (3)	 $CH_3\text{-}\underset{n\text{-}C_4H_9}{\underset{\mid}{C}}H\text{-}CH(CH_3)CO_2H$	(51)[d]
13		$n\text{-}C_4H_9$ (3)		(30)[e]
14		$n\text{-}C_4H_9$ (3)	 $(CH_3)_2\underset{n\text{-}C_4H_9}{\underset{\mid}{C}}\text{—}CH_2CO_2H$	< 6
15	$CH_2{=}CHCN$	$n\text{-}C_4H_9$ (1)	$n\text{-}C_4H_9CH_2CH_2CN$	40

[a] All reactions were performed on 1-mmol scales with the same procedure as described in the text. Isolation was carried out on a 10-mmol scale. [b] Identified by IR and NMR spectroscopy, elemental analysis, and/or comparison with authentic materials. [c] By GLC analysis, based on the carbonyl derivatives. [d] The starting materials were recovered in 30-40% yields. [e] The starting material was recovered in ~55% yield.

α,β-unsaturated carboxylic acids (entries 11-14). To our knowledge, such conjugate additions can not be realized with reagents previously available.[3,6] Unfortunately, however, conjugate addition to the β,β-disubstituted enoic acid leads to a poor result even under these conditions (entry 14). The new reagent also undergoes conjugate addition to the α,β-unsaturated nitrile (entry 15).

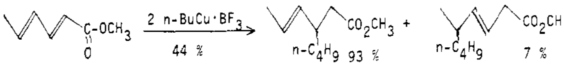
The following procedure for the synthesis of 3-methylheptanoic acid is representative. In a 200-mL flask, equipped with a magnetic stirrer and maintained under N_2, were placed 60 mL of dry ether and 5.7 g (30 mmol) of CuI which was purified by a reported procedure.[7] *n*-Butyllithium in hexane (1.3 M, 30 mmol) was slowly added at −30 ~ 40 °C, and the resulting dark brown suspension was stirred for 5 min. The mixture was then cooled to −70 °C, and $BF_3{\cdot}OEt_2$ (47%, 3.9 mL, 30 mmol) was slowly added. The color changed from dark brown to black and $BuCu{\cdot}BF_3$ seemed to be present as a precipitate. After the mixture was stirred for a few minutes, an ether solution of crotonic acid (0.86 g, 10 mmol) was added at −70 °C. The color immediately changed to deep black. The mixture was allowed to warm slowly to room temperature with stirring. Addition of water, separation, and distillation yielded the desired carboxylic acid: 1.16 g, 81%, bp 75-76 °C (1 mmHg).[8]

Two mechanistic rationales are possible for the present conjugate addition. One involves the activation of reactivity by the coordination of BF_3 with a carbonyl group. Indeed, addition compounds between BF_3 and carbonyl compounds are well known.[9] Another explanation assumes a transition state schematically depicted as eq 2. When a premixed ether solution of crotonic acid and $BF_3{\cdot}OEt_2$ was added to an ether solution of 2 equiv amounts of *n*-BuCu at −30 ~ 40 °C, only trace amounts of 3-methylheptanoic acid were detected.[10] This seems to indicate the first explanation is not favorable. If the second assumption is reasonable, a polyethylenic carbonyl derivative undergoes 1,4 addition.[11]

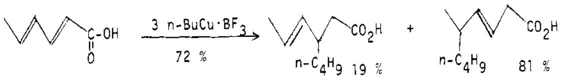


(2)

Actually, sorbic acid methyl ester reacted with *n*-$BuCu{\cdot}BF_3$ to give predominantly the 1,4 adduct (eq 3). The similar reaction with *n*-Bu_2CuLi produced only the 1,6 adduct (trans:cis, 1:1) in 82% yield. On the other hand, the reaction of sorbic acid with *n*-$BuCu{\cdot}BF_3$ gave preferentially the 1,6 adduct (eq 4).[12] Although the fact that the 1,4 adducts were obtained in both reactions seems to weigh on the side of the second explanation, it is not possible at present to completely eliminate the first possibility. Irrespective of the precise mechanism, conjugate addition to previously unreactive enoate esters and enoic acids as well as the controllable regioselectivity toward polyethylenic carbonyl derivatives provides an attractive synthetic methodology. The reaction mechanism and other extentions of our work are being pursued.



(3)



(4)

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References and Notes

(1) Part II: Y. Yamamoto and K. Maruyama, *J. Organomet. Chem.*, in press.
(2) The authors dedicate this contribution to Professor Herbert C. Brown, on the occasion of his 66th birthday and in honor of his distinguished contribution to chemistry.
(3) G. H. Posner, *Org. React.*, **19**, 1 (1972).
(4) H. O. House, *Acc. Chem. Res.*, **9**, 59 (1976).
(5) $RCu{\cdot}BF_3$. I: K. Maruyama and Y. Yamamoto, *J. Am. Chem. Soc.*, **99**, 8068 (1977).
(6) The corresponding reactions of the α,β- and β,β-disubstituted enoate esters, and of the enoic acids with *n*-Bu_2CuLi did not give the desired products.
(7) G. H. Posner, C. E. Whitten, and J. J. Sterling, *J. Am. Chem. Soc.*, **95**, 7788 (1973).
(8) The reaction of crotonic acid with an equivalent amount of *n*-$BuCu{\cdot}BF_3$ also gave 3-methylheptanoic acid in fair yield.
(9) H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives", Wiley, New York, N.Y., 1949, p 61; H. Steinberg, "Organoboron Chemistry", Vol. 1, Wiley, New York, N.Y., 1964, p 793.
(10) An ether solution of crotonic acid and $BF_3{\cdot}OEt_2$ was also treated with 2 equiv amounts of *n*-Bu_2CuLi. Here also, only trace amounts of 3-methylheptanoic acid were produced. It is anticipated that the copper borates in eq 2 does not easily undergo protonolysis under the reaction conditions; see also Y. Yamamoto, H. Yatagai, K. Maruyama, A. Sonoda, and S.-I. Murahashi, *J. Am. Chem. Soc.*, **99**, 5652 (1977).
(11) α,β,γ,δ-Dienones and dienoates undergo only 1,6 addition by using the previously known copper reagents.[3]
(12) It is noteworthy that the 1,6 adduct obtained from the reaction with *n*-$BuCu{\cdot}BF_3$ possesses trans configuration, though the geometrical integrity disappears in the reaction with *n*-Bu_2CuLi.

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