of purines that the 260-nm envelope contains an n → π^* transition. Assignment of the 270-nm transition as n → π^* and the 260- and 250-nm transitions as $\pi \rightarrow \pi^*$ is consistent with these conclusions and is supported by the following observations made in this study.

The 270-nm transition is characterized by low ϵ_m and low $R(j)$. Upon changing the solvent from water to ethanol, the 270-nm transitions undergo a small but reproducible red shift, the half-band widths broaden, and $|R(j)|$ values increase 50–100%; for the same solvent change, the 260- and 250-nm transitions do not change position, their half-band widths do not broaden, and there is little enhancement of $|R(j)|$ values. Upon changing the solvent from water to DMSO, the 270-nm transition red-shifts ~10 nm while the 260-nm transition red-shifts only ~5–6 nm. Furthermore, for a pH change from 7 to 1.3, the 270-nm transition apparently blue-shifts 30 nm while the 260- and 250-nm transitions undergo no change in position (see Figure 2).

The 225-nm transition may also be an n → π^* transition since it occurs at the uv minimum. The half-band widths and $|R_{225}|$ values increase upon changing the solvent from water to ethanol, behavior similar to that of the 270-nm transition (presumably n → π^*) and in contrast to that of the 260- and 250-nm transitions ($\pi \rightarrow \pi^*$). An estimate of the ratio of the rotational strength to the dipole strength (the anisotropy factor)[36] for the 225-nm transition is an order of magnitude larger than for the 260- and 250-nm transitions (~10^{-4} compared to ~10^{-5}). This is consistent with the assignment of the 225-nm transition as an n → π^* transition.

These assignments suggest that $R(j)$ values of n → π^* transitions in adenine nucleosides can be as large as or larger than $R(j)$ values of $\pi \rightarrow \pi^*$ transitions (for example, for β-ribo). They also suggests that the intensity of n → π^* transitions can be large in MCD spectra.

Acknowledgments. The author is grateful to Drs. Leon Goodman and Peter Lim for arranging for support of this work.

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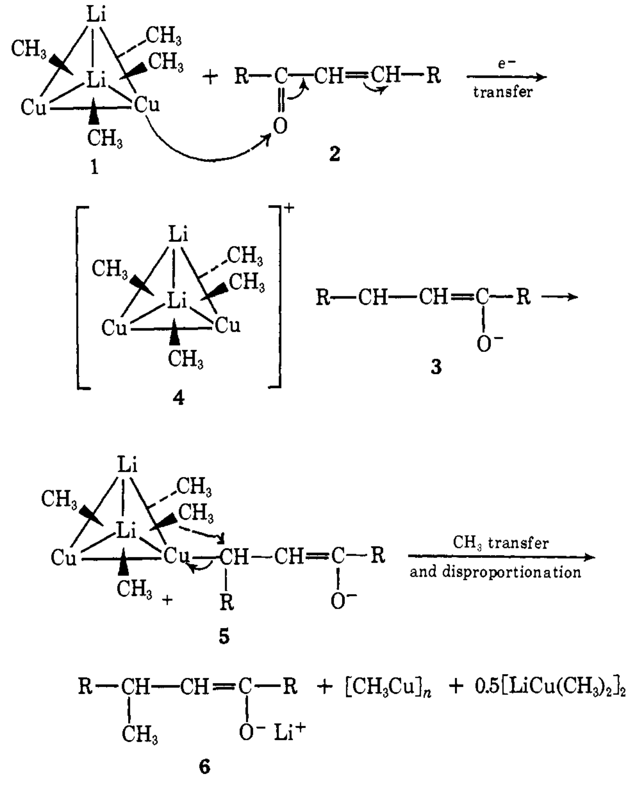
(36) The dipole strength for each transition i was calculated using the equation $D_i = 1.63 \times 10^{-38}\, \epsilon_i\Delta_i/\lambda_i$, where ϵ_i is the molar extinction coefficient and λ_i is the wavelength at the center of transition i while Δ_i is its half-width at ϵ_i/e.

Communications to the Editor

Reactions Involving Electron Transfer. III. The Conjugate Addition of Lithium Dimethylcuprate to α,β-Unsaturated Carbonyl Compounds[1]

Sir:

The introduction of lithium dialkyl- (or diaryl-) cuprates [$LiR_2Cu(I)$] as selective reagents for the conjugate addition of alkyl or aryl groups to unsaturated carbonyl compounds[2] has led to the widespread utilization of these reagents both for conjugate additions and for the related generation of specific enolate anions.[3] The reaction was suggested[2] to involve an initial electron transfer from the cuprate **1** (which we tentatively formulate as a dimeric tetrahedral structure analogous to other "ate" complexes[4]) to an unsaturated carbonyl compound **2** to form an intermediate anion radial **3** and an electron-deficient metal cluster such as **4**. Rebonding of **3** and **4** followed by the intramolecular rearrangement of a methyl group (*i.e.*, **5**) from the metal cluster to carbon accounts for the retention of stereochemistry observed with alkyl and vinyl groups[5] and



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(1) Supported by Public Health Service Grant No. RO1-CA-12634 from the National Cancer Institute.

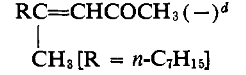
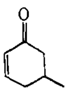
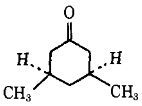
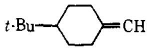
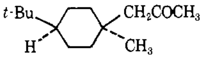
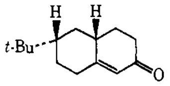
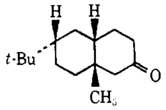
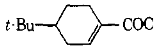
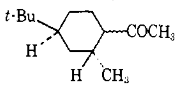
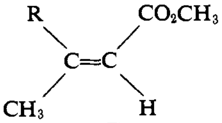
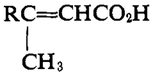
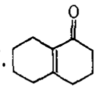
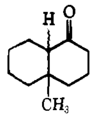
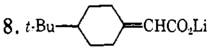
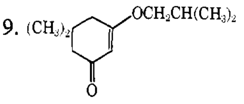
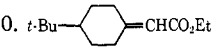
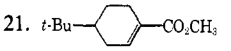
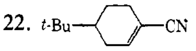
(2) (a) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966); (b) H. O. House and W. F. Fischer, Jr., *ibid.*, **33**, 949 (1968); **34**, 3615, 3626 (1969); (c) H. O. House, R. W. Giese, K. Kronberger, J. P. Kaplan, and J. F. Simeone, *J. Amer. Chem. Soc.*, **92**, 2800 (1970).

(3) (a) G. H. Posner, *Org. React.*, in press; (b) R. E. Ireland and G. Pfister, *Tetrahedron Lett.*, 2145 (1969); (c) E. Piers, R. W. Britton, and W. de Waal, *Chem. Commun.*, 1069 (1969). (d) If the unsaturated carbonyl system contains a vinyl halogen substituent, either coupling or metal halogen exchange occurs rather than conjugate addition. J. Klein and R. Levene, *J. Amer. Chem. Soc.*, **94**, 2520 (1972).

(4) (a) T. L. Brown, *Accounts Chem. Res.*, **1**, 23 (1968), and references therein; (b) L. D. McKeever, R. Waack, M. A. Doran, and E. B. Baker, *J. Amer. Chem. Soc.*, **90**, 3244 (1968); (c) also see K. Wada, M. Tamura, and J. Kochi, *ibid.*, **92**, 6656 (1970).

(5) (a) C. A. Casey and R. A. Boggs, *Tetrahedron Lett.*, 2455 (1971); (b) G. M. Whitesides and P. E. Kendall, to be submitted for publication; (c) F. Näf and P. Degen, *Helv. Chim. Acta*, **54**, 1939 (1971); F. Näf, P. Degen, and G. Ohloff, *ibid.*, **55**, 82 (1972).

Table I. Reactions of $(CH_3)_2CuLi$ with α,β-Unsaturated Carbonyl Compounds

Compound	$E_{1/2}$, V *vs.* sce[a]	Product (% yield)[b]
1. $(EtO_2C)_2C{=}C(CO_2Et)_2$	−0.97, −1.10	$(EtO_2C)_2CHCH(CO_2Et)_2$ (76)
2. Fluorenone	−1.29, −1.95	Pinacol (*ca.* 50) + 9-methylfluoren-9-ol (*ca.* 50)[c]
3. *trans*-$PhCH{=}CHCOPh$	−1.41, *ca.* −2.1	$PhCH(CH_3)CH_2COPh$ (96)
4. *trans*-$PhCH{=}CHCOCH_3$	−1.64, −2.61	$PhCH(CH_3)CH_2COCH_3$ (78)
5. *trans*-$PhCH{=}CHCO_2CH_3$	−1.81, −2.27	$PhCH(CH_3)CH_2CO_2CH_3$ (79)
6. $RC{\equiv}CCOCH_3$	−1.99 [R = *n*-Pr]	 $\underset{\displaystyle CH_3}{RC}{=}CHCOCH_3$ (−)[d] [R = *n*-C_7H_{15}]
7. 	−2.07	 (98)[e]
8. *trans*-$CH_3CH{=}CHCOCH_3$	−2.08	$(CH_3)_2CHCH_2COCH_3$ (96)[c]
9. 	−2.12	 (*ca.* 89)[c]
10. $(CH_3)_2C{=}C(CO_2Et)_2$	−2.13	$(CH_3)_3CCH(CO_2Et)_2$ (93)[f]
11. 	−2.15	 (69)
12. *trans*-*t*-$BuCH{=}CHCOBu$-*t*	−2.22	*t*-$BuCH(CH_3)CH_2COBu$-*t* (79)[e]
13. 	−2.25	 (75)[g]
14. $RC{\equiv}CCO_2CH_3$	−2.26 [R = *n*-Pr]	 (90–95)[h] [R = Et]
15. $RC{\equiv}CCO_2Li$	−2.31 [R = *n*-Pr]	 $\underset{\displaystyle CH_3}{RC}{=}CHCO_2H$ (−)[i] [R = Me]
16. *trans*-$CH_3CH{=}CHCO_2CH_3$	−2.33	$(CH_3)_2CHCH_2CO_2CH_3$ (79)
17. 	−2.34	 (−, both epimers)[j]
18. 	−2.37	(88% recovery)[c]
19. 	−2.43	(90% recovery)
20. 	−2.45	(95% recovery)[c]
21. 	−2.50	(90% recovery)
22. 	−2.55	(92% recovery)

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[a] These polarographic reduction potentials were measured in dimethylformamide containing 0.5 *M* *n*-Bu_4NBF_4 or *n*-Pr_4NClO_4 as a supporting electrolyte. [b] Unless otherwise noted, these reactions were performed in this study by adding an Et_2O solution of the unsaturated carbonyl compound to a slight excess of $LiCuMe_2$ in cold (−5 to 0°) Et_2O followed by a reaction period of 10–30 min at 0–10°. The yields reported are of isolated products which were either fully characterized or identified with authentic samples. [c] Data from ref 2a. [d] E. J. Corey and J. A. Katzenellenbogen, *J. Amer. Chem. Soc.*, **91**, 1851 (1969); J. A. Katzenellenbogen, Ph.D. Dissertation, Harvard University, 1969. [e] Data from ref 2b. [f] See footnote 7 in E. L. Eliel, R. O. Hutchins, and Sr. M. Knoeber, *Org. Syn.*, **50**, 38 (1970). [g] All four epimers were produced in this reaction; the two major products had the stereochemistry shown. [h] J. B. Siddall, M. Biskup, and J. H. Fried, *J. Amer. Chem. Soc.*, **91**, 1853 (1969). [i] J. Klein and R. M. Turkel, *ibid.*, **91**, 6186 (1969). [j] R. J. Balf, B. Rao, and L. Weiler, *Can. J. Chem.*, **49**, 3135 (1971).

leads to the initial reaction products, a lithium enolate **6** and, after redistribution of the metal cluster, an organocopper(I) compound which frequently precipitates from the reaction mixture as an insoluble polymer.

We present here a correlation (see Table I) of unsaturated carbonyl compound–lithium dimethylcuprate reactions and polarographic reduction potentials **2** → **3** of the carbonyl compounds in an aprotic medium

(DMF). This correlation is not only compatible with the first step in the mechanistic scheme suggested, but offers the ability *to predict* both when the conjugate additions will be successful and when reduction of the C═C double bond will be a serious competing reaction. Specifically, all of the unsaturated carbonyl compounds studied that will accept an electron at potentials less negative than -2.4 V *vs.* sce react with lithium dimethylcuprate whereas carbonyl compounds with reduction potentials more negative than -2.4 V *vs.* sce are recovered unchanged. If the unsaturated carbonyl compound (*e.g.*, **7**) is able to accept a second electron at a potential less negative than *ca.* -1.2 V *vs.* sce, then the system is reduced beyond the anion radical stage to form a dianion (*e.g.*, **8**) which is protonated either by reaction with the solvent or during isolation to form a dihydro derivative (*e.g.*, **9**).

$$\underset{\mathbf{7}}{(\mathrm{EtO_2C})_2\mathrm{C{=}C(CO_2Et)_2}} + [(\mathrm{CH_3})_2\mathrm{CuLi}]_2 \xrightarrow{2e^-}$$

$$\underset{\mathbf{8}}{2\mathrm{Li}^+(\mathrm{EtO_2C})_2\bar{\mathrm{C}}{-}\bar{\mathrm{C}}(\mathrm{CO_2Et})_2} + [\mathrm{CH_3Cu(I)}]_n \xrightarrow{\mathrm{H_3O^+}}$$

$$\underset{\mathbf{9}}{(\mathrm{EtO_2C})_2\mathrm{CHCH(CO_2Et)_2}}$$

It is apparent that a number of previous observations[2,5] concerning organocopper(I) derivatives are qualitatively explained by the reaction scheme presented. Notable among these are the failure of methylcopper(I) derivatives to react with simple enones unless a negatively-charged ligand (*e.g.*, I^- or CH_3^-) is bound to the metal cluster and the loss of reactivity of cuprates LiR_2Cu with enones when R is a group such as allyl, or especially cyano or α-keto alkyl, that can allow electron density to be delocalized from the metal cluster into the R groups. One would expect that the net oxidation potential (and the electron density) of the cuprates would be diminished either by the absence of negatively-charged donor ligands or by the presence of R groups capable of delocalizing the electron density of the metal cluster. We hope to obtain a quantitative measure of these effects with cuprate oxidation potential measurements which are in progress. Such data should permit predictions concerning the success of conjugate addition reactions with a variety of dialkyl-, diaryl-, and other cuprates.

[6] This work is part of the Ph.D. thesis of M. J. Umen done *in absentia* from the Department of Chemistry, Massachusetts Institute of Technology.

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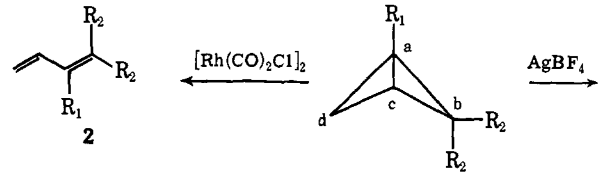
Received April 20, 1972

Solvent Determined Mechanisms in the Transition Metal Complex Promoted Rearrangement of Bicyclo[1.1.0]butanes[1]

Sir:

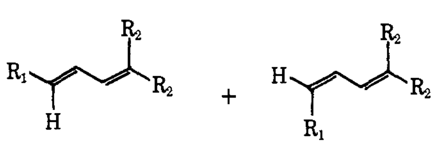
Recently, it has been demonstrated that a change of solvent can result in significant changes in the ratio of products formed in transition metal complex promoted rearrangements of highly strained polycyclic molecules.[2,3] We now wish to report that the solvent can play a much more overwhelming role in these rearrangements than was previously anticipated.[4] In fact, a complete change of mechanism and (consequently) of products can result from a change of solvent.

When either **1a** or **1b** was treated with rhodium dicarbonyl chloride dimer in nonprotic solvent, the only diene formed in the reaction was **2**.[5] It was demonstrated that **2** was derived *via* cleavage of the a–c and b–c bonds of **1**. In contrast, the presence of silver fluoroborate in nonprotic solvent promoted the formation of **3** and **4** from **1** *via* cleavage of the a–b and a–c bonds of **1**.[5,6] Changing from the nonprotic solvent, chloroform, to the protic solvent, methanol, resulted in a complete change in the mechanism and the products associated with the silver ion promoted reactions of **1**. When **1a** was treated with rhodium dicarbonyl chloride dimer[4] or silver fluoroborate[7] in methanol at 30°, **5a** was ob-

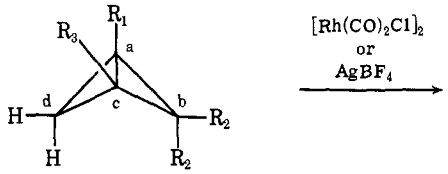


2

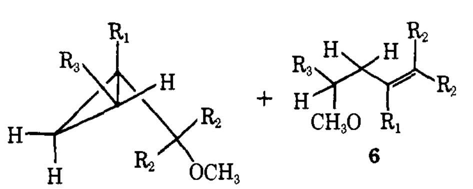
1a, $R_1 = R_2 = CH_3$
b, $R_1 = CH_3$; $R_2 = C_6H_5$



3 **4**



1a, $R_1 = R_2 = CH_3$; $R_3 = H$
1b, $R_1 = CH_3$; $R_2 = C_6H_5$; $R_3 = H$
1c, $R_1 = R_3 = CH_3$; $R_2 = C_6H_5$



5 **6**

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[1] Paper XXIX in a series on The Chemistry of Bent Bonds. For the previous paper in this series, see P. G. Gassman and T. Nakai, *J. Amer. Chem. Soc.*, **94**, 2877 (1972).

[2] P. G. Gassman and T. J. Atkins, *ibid.*, **93**, 4597 (1971).

[3] W. G. Dauben and A. J. Kielbania, Jr., *ibid.*, **93**, 7345 (1971).

[4] We have previously cautioned that some of the results reported for the transition metal complex promoted rearrangement of highly strained ring systems could be due to the influence of solvent. This report indicates that the effect of solvent can be even more dramatic than was previously suggested: P. G. Gassman and F. J. Williams, *J. Chem. Soc., Chem. Commun.*, 80 (1972).

[5] P. G. Gassman and T. Nakai, *J. Amer. Chem. Soc.*, **93**, 5897 (1971); P. G. Gassman and F. J. Williams, *ibid.*, **92**, 7631 (1970).

[6] L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **93**, 2335 (1971).

[7] F. J. Williams, unpublished work. The reaction of **1a** with silver fluoroborate to give only **5** has also been observed in the laboratories of Professor S. Masamune. We wish to thank Professor Masamune for informing us of his results prior to publication.