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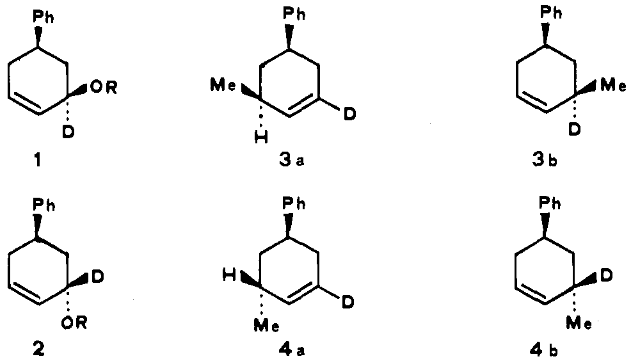
Conversion of Allylic Carbamates into Olefins with Lithium Dimethylcuprate. A New Formal S_N2' Reaction

Sir:

Coupling of $LiCuMe_2$ with acetates of cyclic allylic alcohols was shown by Goering[1] to proceed with anti attack and competitive α/γ substitution at the allylic system. An allylic cyclopentenyl lactone[2] and cyclohexenyl mesitoates,[3] where α/γ substitution appears to be controlled by steric factors, were found to react accordingly. Previous work on noncyclic allylic esters[4] showed that α/γ attack is little affected by the nature of the leaving group and primarily controlled by the degree of substitution of the two ends of the allylic system.[5] We report that coupling of *cis*- and *trans*-1-deuterio-5-phenyl-2-cyclohexenylcarbamates **1a** and **2a** (R = CONHPh) with $LiCuMe_2$ gives the syn S_N2' products, **3a** and **4a**, respectively. Exclusive syn γ attack on the allylic system has been thus achieved.



One enantiomer only shown

The esters **1a–f** and **2a–e**[6] (Table I) were obtained by standard procedures from alcohols **1** and **2** (R = H).[7] Experimental details of the coupling with $LiCuMe_2$ and results are reported in Table I. Control experiments on 3-*d* isomers and nondeuterated **1d** and **2d** are in accordance with the reported data. Products were >99% pure by GLC,[8] and gave mass, IR, and ^1H NMR spectra in accordance with the expected alkenes.[9] Cis and trans configurations were attributed according to the stereochemistry of conversion of allylic cyclohexenyl acetates[1] and mesitoates[3] with $LiCuMe_2$. Hydrogenation of the individual alkenes gave *cis*- and *trans*-1-methyl-3-phenylcyclohexane whose ^1H NMR spectra agree with the shielding properties of equatorial and axial methyl groups.[10] The ratios of **3a/3b** and **4a/4b** were obtained by evaluating the abundance of the vinylic protons relative to the aromatic protons through careful integration of their NMR signals; CH_3CD signals in the middle of the CH_3CH doublet could not be observed for the products obtained from **1a** and **2a.**

Table I. Reaction of 1-Deuterio-5-phenyl-2-cyclohexenyl Esters with $LiCuMe_2$[a]

R	cis esters	products 3a/3b	products 4a/4b	trans esters	products 3a/3b	products 4a/4b
CONHPh[b]	**1a**	>98/2		**2a**		>98/2
HCO[c]	**1b**		58/42	**2b**	45/55	
MeCO[c]	**1c**		51/49	**2c**	47/53	
PhCO[c]	**1d**		50/50	**2d**	50/50	
EtOCO[c]	**1e**		53/47	**2e**	46/54	
Me(Ph)NCO[c]	**1f**		54/46			

[a] 0.10 M solutions of $LiCuMe_2$ were prepared at 0 °C under nitrogen from CuI (Fluka) purified by extraction with THF (Posner, G. H.; Whitten, C. R.; Sterling, J. J., *J. Am. Chem. Soc.* **1973,** *95,* 7789–7800) and ~2 M ethereal LiMe (Fluka). Esters (2 mmol) were allowed to react for 24 h. Products (80–90% isolated yield) were obtained by quenching with 20% NH_4Cl, washing with 2 N HCl, 1 N $NaHCO_3$, and water, and distillation at 90 °C (bath) and 18 mm. [b] 3 equiv of $LiCuMe_2$ was used; reaction mixture was allowed to warm to 25 °C. [c] 2 equiv of $LiCuMe_2$ was used; reaction temperature was 0 °C.

As shown in Table I, anti attack and little preference for α or γ substitution were observed for esters **1b–f** and **2b–e,** while carbamates **1a** and **2a,** bearing an active hydrogen atom, gave exclusive γ substitution with syn attack on the allylic system within experimental error.

Complete control of regio- and stereochemistry of this conversion promises to be of value in synthetic work since the method appears of general applicability. For example, *N*-phenylcarbamates of nerol and linalol could be converted into the product of γ substitution without any detectable (GLC) contamination of the complementary regioisomer. Moreover, the allylic carbamates required are in general configurationally stable and easily available starting materials.[11] A brief study of the method was therefore undertaken. Addition of **1a** to 1 equiv of $LiCuMe_2$ immediately afforded a yellow precipitate (probably CuMe). No conversion was observed even on warming at 25 °C and the carbamate could be recovered after quenching. Displacement took place only when a second equivalent of $LiCuMe_2$ was present. These findings strongly suggest that lithium carbamates and $LiCuMe_2$ are involved in the syn γ substitution. On the other hand, the carbamate **1e** lacking active hydrogen atoms behaves like the other esters.

To our knowledge, (i) conversion of lithium carbamates is the first example of $LiCuMe_2$ coupling with syn attack to the allylic substrate; (ii) only one precedent (without stereochemical evidence) of γ displacement in which the concurrent α displacement is forbidden by factors different from substitution and/or steric hindrance is known at present;[11] (iii) displacement of a very poor leaving group has been achieved with $LiCuMe_2$ under mild conditions. These findings appear to be of high mechanistic interest both in the field of the controversial S_N2' reaction and of the copper reagents.

Neither steric arguments considered by Goering nor the orbital distorsion technique[12] as applied to $LiCuMe_2$ coupling with allylic epoxides[13] seem to satisfactorily explain our results. In our opinion, the exclusive syn γ substitution of lithium carbamates should be regarded as a consequence of a preferred concerted process, possibly occurring by an electron-transfer[14] mechanism, which results in a formal syn S_N2' reaction. The behavior of the other esters may now be accommodated by assuming that an anti α/γ attack of the reagent follows a rate-limiting allylic carboxylate ion-pair formation. An analogous hypothesis was considered in the case of allylic ep-

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oxides.[13] This approach can also explain the conversion[14] of *Z* allylic derivatives into olefins with predominant *E* configuration by α displacement with LiCuMe$_2$. The nature of the leaving group should be decisive in determining which mechanism will be operative: ion pairs should be easily formed from common allylic esters compared with the corresponding lithium carbamates in the presence of copper reagents acting as Lewis acids.[15]

This hypothesis is now under investigation, while evaluation of the scope and limits of the carbamate method is continuing in the case of substituted, noncyclic allylic substrates.

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(8) A 4 m × 2 mm i.d. column filled with 10% Apiezon L on Chromosorb P at 185 °C was used; **3/4** relative retention, 1.02.
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Infrared Photochemistry of a Volatile Uranium Compound with 10-μ Absorption

Sir:

It has recently been demonstrated that efficient separation of isotopic species can be achieved by selective, laser-induced multiphoton vibrational excitation of polyatomic molecules.[1,2] Examples of separations reported to date include isotopes of hydrogen,[3] boron,[4] carbon,[4b] silicon,[4b] sulfur,[5] chlorine,[6] selenium,[7] molybdenum,[8] and osmium.[9] The key molecular requirements for such a process are volatility and the existence of an infrared-active normal vibrational mode (fundamental, overtone,[6b,8] or combination[6b,8]) which exhibits a nonzero isotopic shift. The molecular infrared absorption is brought into coincidence or near coincidence in the gas phase with an intense ($\sim 10^7$–10^9 W/cm^2) infrared laser source, resulting in isotopically selective decomposition or reaction. To date, most laser-induced isotope separation (LIS) experiments have been performed with pulsed, discretely tunable CO$_2$ infrared gas lasers. These devices have a usable output in the 10-μ region (9.2–10.8 μ) and are by far the most powerful, reliable, monochromatic, and economical sources of mid-infrared laser radiation presently available.

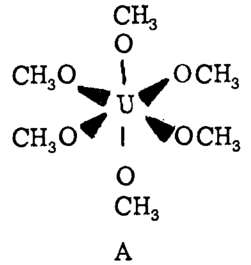
Table I. Irradiation Experiments with U(OCH$_3$)$_6$

expt	laser line	laser frequency, cm^{-1}	passes	enrichment factor (in ^{235}U)[a]
1	P(24)	940.56	1	0.9975 (22)
2	P(32)	933.01	1	1.0000 (20)
3	P(36)	929.02	1	1.0053 (17)
4	P(38)	927.04	1	1.0315 (46)
5	P(38)	927.04	1	1.0171 (26)
6	P(38)	927.04	1	1.0237 (27)
7	P(38)	927.04	1	1.0183 (26)[b]
8	P(38)	927.04	1	1.0258 (30)[b]
9	P(40)	924.98	1	1.0108 (27)

[a] Enrichment factor = (^{235}U/^{238}U)$_{\text{final}}$/(^{235}U/^{238}U)$_{\text{initial}}$; quantities in parenthesis are standard deviations. [b] Experiments with sample enriched (1.5%) in ^{235}U.

In principle, multiphoton infrared photochemistry would appear to be an ideal technique for the technologically important separation of uranium isotopes ^{235}U (0.72% natural abundance) and ^{238}U (99.27% natural abundance);[10] however, exhaustive spectral studies on the seemingly most attractive molecular candidate, UF$_6$, show it to lack significant absorption in the CO$_2$ laser region.[11] While the eventual development of powerful 16-μ lasers[10b,12] or other techniques using UF$_6$ may be possible, an attractive alternative approach would be the "tailoring" of uranium compounds for the CO$_2$ laser.[13] In this communication we report initial spectral and photochemical observations on a prototype molecule, U(OCH$_3$)$_6$. Among our results we note that it has proven possible, for the first time, to achieve uranium isotope separation by 10-μ infrared irradiation of a uranium-containing metal-organic molecule.

Uranium hexamethoxide, U(OCH$_3$)$_6$, was prepared by a modification of the original Gilman procedure[14] in which U(OCH$_3$)$_6^{-2}$ is oxidized in a single step,[13c,15a] or directly from UF$_6$ utilizing a procedure which will be discussed elsewhere.[15b] The compound readily sublimes (with minor decomposition) at 30 °C (10^{-5} mm) to form dark red, extremely moisture-sensitive crystals. Although U(OCH$_3$)$_6$ is less volatile than UF$_6$ (room temperature vapor pressure $\approx 10^{-3}$ [16] vs. 120 Torr[17]), LIS, unlike gaseous diffusion, does not require high volatility, and operation at high pressures can actually decrease isotopic selectivity through intermolecular energy transfer.[1] Unlike UF$_6$, U(OCH$_3$)$_6$ does not attack glass.[18] The hexamethoxide is monomeric in benzene by cryoscopy and displays a singlet in the ^{1}H NMR (C$_6$D$_6$) at δ 7.66. Preliminary single-crystal X-ray diffraction results indicate discrete monomers with an octahedral UO$_6$ framework, A.[19] The vibrational spectra of U(OCH$_3$)$_6$ are in accord with this configuration; they can be assigned by analogy to UF$_6$[11] and by ^{18}OCH$_3$ substitution.



A

Thus, the infrared spectrum (Nujol solution) of U(OCH$_3$)$_6$ exhibits a strong band at 464.8 cm^{-1} which, upon substitution of ~30% ^{18}OCH$_3$,[20,21] appears as a multiplet centered at ~15–18 cm^{-1} to lower frequency. The 464.8-cm^{-1} transition is assigned to a $\nu_{\text{U-O}}$, T$_{1u}$ (ν_3) stretching mode.[22,23] The Raman spectrum of U(OCH$_3$)$_6$ (ν_0 = 6471 Å Kr$^+$, spinning polycrystalline sample at −33 °C) exhibits low frequency transitions at 495.5 (s) and 400.6 (m) cm^{-1}, which are assigned to the Raman-active A$_{1g}$ (ν_1) and E$_g$ (ν_2) U-O stretching modes,

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