

Table I. Barriers and Related Parameters for Amides Containing One, Two, and Three Acyl Groups

Compound	Solvent	T_0 , °C	k_c , sec ⁻¹	ΔG^\ddagger , kcal/mol (kJ/mol)	Ref
HCONH ₂	Diglyme			17.8 (77)	5
(HCO) ₂ NH	Acetone	-23	45	12.6 (53)	1
(HCO) ₂ NCOCH ₃	CHClF ₂	-126 ^a	20	7.5 (31) ^a	This work

^a We regard ΔG^\ddagger as accurate to ± 0.2 kcal/mol (± 1 kJ/mol). The main source of error in the free energy of activation derives from the uncertainty in the sample temperature. Temperatures were measured with a copper-constantan thermocouple and are estimated to be accurate to $\pm 2^\circ$.

the case of dipivalamide),³ in which nonbonded (steric) interactions are expected to make the *E,E* and *E,Z* conformations unfavorable. In triformamide ($R_1 = R_2 = R_3 = H$), the existence of the *Z,Z* relationship in **3** is expected to cause this form to be of higher energy than **2**. Indeed, Allenstein⁴ has assigned the triskelion conformation to this compound in the solid state on the basis of its infrared and Raman spectra. For triamides with groups larger than hydrogen, the conformations in which the larger groups are components of imide segments having the *E,E* configuration are likely to be further destabilized because of steric interactions between the R groups of these segments.

If triformamide were to adopt conformation **2** in solution, it would exhibit an nmr spectrum invariant with respect to the rate of torsion about amide bonds. As a consequence, we chose the less symmetrical compound, *N*-acetylformimide (**1**), for our nmr study. Allenstein, *et al.*,⁴ have suggested that **1** adopts conformation **2** ($R_1 = CH_3$, $R_2 = R_3 = H$) on the basis of the similarity between its infrared and Raman spectra and those of triformamide. In addition to the single triskelion conformation, three conformations of type **3** are possible, corresponding to the replacement of R_1 , R_2 , or R_3 by CH_3 . Inspection of all four possible conformations of **1** shows that the formyl protons in each form are diastereotopic and would be expected to exhibit chemical shift nonequivalence at temperatures where torsion about amide bonds is slow on the nmr time scale.

The pmr spectrum of **1** in chlorodifluoromethane at -84° consists of two singlets at δ 9.45 and 2.61 for the formyl and methyl protons, respectively, indicating rapid conformational interchange at this temperature. On cooling, torsion about amide bonds becomes slow on the nmr time scale, and the resonance at lower field broadens and splits by -142° into two peaks of equal intensity centered at δ 9.47 and separated by 10.0 Hz at 60 MHz (Figure 1). The rate constant at the coalescence point was determined using complete line shape analysis (Table I).

The slow-exchange spectrum is consistent with the sole presence of the triskelion conformation suggested by the infrared and Raman studies⁴ but would not rule out the sole presence of a single nontriskelion conformation. If conformation **2** is, in fact, the correct conformation, then topomerization requires rotation about all three amide bonds. Based on the behavior of amides and imides, it seems likely that the transition state involves torsion about a formyl group, since acetamides and diacetamides generally exhibit lower barriers than the corresponding formyl compounds.^{1,2}

Comparison of the barrier in **1** with those in form-

(3) G. Toth, *Acta Chim. Sci. Hung.*, **64**, 101 (1970).

(4) E. Allenstein, V. Beyl, and W. Eitel, *Chem. Ber.*, **102**, 4089 (1969).

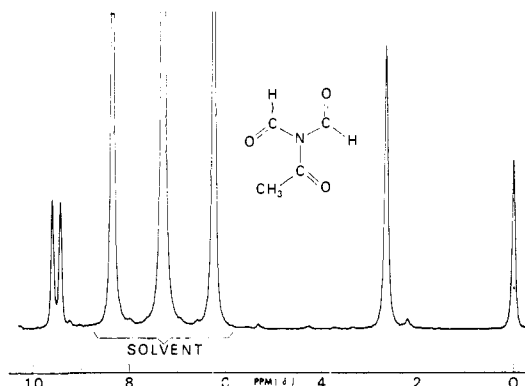


Figure 1. Pmr spectrum of *N*-acetylformimide (**1**) at -142° in chlorodifluoromethane solution (60 MHz). A small peak at δ 2.2 is due to acetic anhydride, which is present as an impurity.

amide⁵ and formimide¹ affords a measure of the effect of successive replacement of formamide hydrogens by acyl groups (Table I). Although increased conjugation attenuates the amide barrier, it is noteworthy that a substantial barrier, well within the range amenable to determination by nmr spectroscopy, remains even with three carbonyl groups in conjugation with the nitrogen lone pair.

Acknowledgment. We thank the National Science Foundation for support of this work.

- (5) T. Drakenberg and S. Forsen, *J. Phys. Chem.*, **74**, 1 (1970).
 (6) A. P. Sloan Fellow, 1972-1974.

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On the Use of Tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium(III) as a Shift Reagent for Carboxylic Acids and Phenols

Sir:

Since the initial application of the lanthanide shift reagent europium(III) dipivaloylmethanoate ($Eu(dpm)_3$) to organic compounds by Hinckley,¹ numerous applications to structural problems of this class of compounds in organic chemistry have been found.

In an early study on the range of applicability of the reagent, it was stated that $Eu(dpm)_3$ was unsuited for use with carboxylic acids and phenols because it was slowly decomposed by these classes of compounds.² This statement seems to have been taken as a general

(1) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

(2) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).

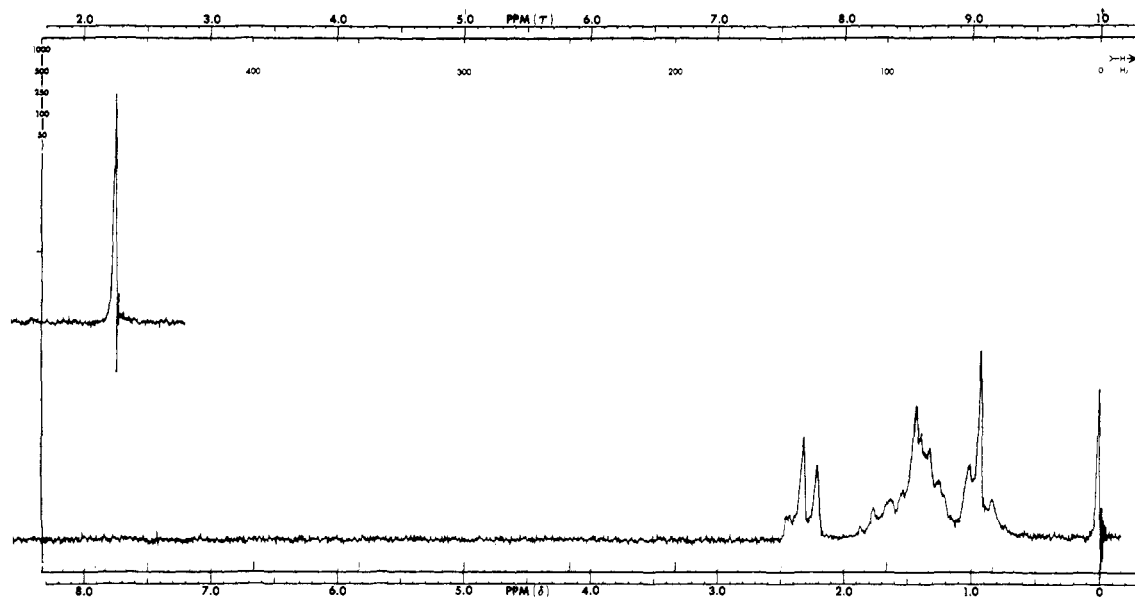


Figure 1. A 60-MHz spectrum of *n*-hexanoic acid (0.056 g) in CCl_4 (0.5 ml).

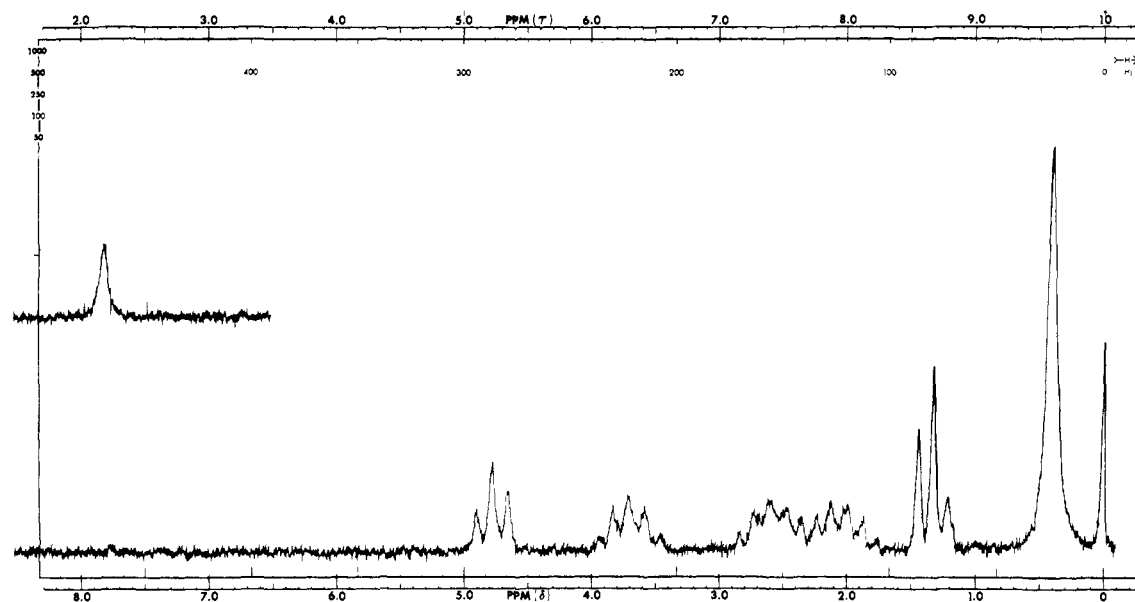


Figure 2. A 60-MHz spectrum of *n*-hexanoic acid (0.023 g) and $\text{Eu}(\text{fod})_3$ (0.087 g) in CCl_4 (0.5 ml).

proposition encompassing all reagents of this type. Indeed, we find that alternative shift reagents of a different type are being proposed for phenols and carboxylic acids because the lanthanides are supposed to be ineffective with these compounds.³

We have found experimentally that the shift reagent introduced by Rondeau and Sievers,⁴ tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium(III), is a useful reagent for both phenols and carboxylic acids. Examples to illustrate this are described herein. A recent monograph⁵ has also pointed out the stability of $\text{Eu}(\text{fod})_3$ in the presence of carboxylic acids. We

were not aware of this work when our investigation commenced.

The spectra of *n*-hexanoic acid in the absence and in the presence of $\text{Eu}(\text{fod})_3$ are shown in Figures 1 and 2. Table I gives the differences in chemical shift values for the free and complexed acid. The resonances of the shifted protons show little if any paramagnetic broadening and the splittings are readily discernible. The order of magnitude of the shifts is comparable to that obtained with other *n*-electron species. Furthermore, the reagent showed no sign of instability, and the shifts were constant over a period of several days. Certainly, this reagent has considerable utility for the characterization of carboxylic acids.

In Table II we have listed the shifts obtained when 2,4-xyleneol was treated with the reagent. There is more broadening observed for phenolic protons than

(3) J. E. Maskasky and M. E. Kenney, *J. Amer. Chem. Soc.*, **95**, 1443 (1973).

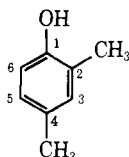
(4) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, **93**, 1522 (1971).

(5) R. E. Sievers, Ed., "Nuclear Magnetic Resonance Shift Reagents," Academic Press, New York, N. Y., 1973, p 26.

Table I. Differences in Chemical Shift for Protons of *n*-Hexanoic Acid on Treatment with Eu(fod)₃^a

	CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -COOH					
	6	5	4	3	2	1
	Proton no.					
	1	2	3	4	5	6
Untreated hexanoic acid	11.89	2.32	~1.6	~1.4	~1.4	0.89
Hexanoic acid + Eu(fod) ₃	16.31	4.79	3.70	2.60	2.03	1.30
Δδ	4.42	2.47	2.1	1.2	0.6	0.41

^a The treated samples were run at a lanthanide/substrate mole ratio of 0.43 in carbon tetrachloride.

Table II. Differences in Chemical Shift for Protons of 2,4-Xylenol on Treatment with Eu(fod)₃^a

	Proton no.					
	1	2	3	4	5	6
Untreated 2,4-xyleneol	5.42	2.12	6.80	2.17	6.72	6.48
2,4-Xyleneol + Eu(fod) ₃		3.47	7.40	2.42	7.12	8.10
Δδ		1.35	0.60	0.25	0.40	1.62

^a The samples were run at a lanthanide/substrate mole ratio of 0.18 in carbon tetrachloride. All spectra were obtained on a Varian Associates A60 spectrometer.

for those of the acid, and the chemical shift differences are not as great. The phenolic hydroxyl proton resonance could not be located in the spectrum, but this is not surprising in view of the broadness of this resonance in the untreated phenol. In any event, use of the reagent leads to considerable spectral clarification. As expected, the magnitude of the shifts and the amount of paramagnetic broadening is in the order ortho > meta > para. A more detailed account of the results obtained for both acids and phenols will be published at a later date.

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Decomposition of Diazo Compounds in Alkylthio- and Alkoxytrimethylsilanes. A Possible 1,2-Trimethylsilyl Shift in Unstable Silylsulfonium and Silyloxonium Ylides

Sir:

There has been considerable interest in the rearrangement of organometallic compounds in the past few years. Several 1,2-shifts of the trialkylsilyl group have been established by the studies of West and coworkers.^{1,2}

(1) R. West and P. Boudjouk, *J. Amer. Chem. Soc.*, **95**, 3983, 3987 (1973), and references cited therein.

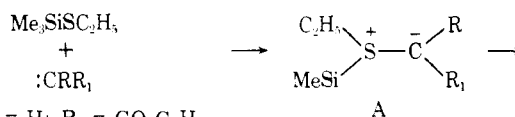
(2) For review of silane rearrangements, see R. West, *Pure Appl. Chem.*, **19**, 291 (1969).

Recently, 1,2-anionic rearrangements from oxygen and sulfur to carbon in alkoxy- and alkylthiosilanes were reported.^{3,4} These were shown to be examples of a Wittig-type rearrangement involving migration of a silyl group from oxygen and sulfur to a negatively charged carbon. However, no analogous rearrangement has been described for trialkylsilylsulfonium and -oxonium ylides.

We find that the photolysis of diazo compounds in alkylthio- and alkoxytrimethylsilanes produces the insertion products of the carbene into the Si-S and Si-O bonds. These reactions are probably initiated by carbene attack on lone pair electrons of sulfur and oxygen atoms to form the corresponding onium ylides⁵ followed by a 1,2-trialkylsilyl shift from onium sites to the carbanionic center. If this mechanism is correct, this is the first example of a 1,2-migration of an organometallic group in either anion or radical.

Carboethoxycarbene (Ia) was produced by photolysis of ethyl diazoacetate in ethylthiotrimethylsilane as solvent. In this reaction, the expected sulfonium ylide could not be observed upon analysis of the nmr spectrum of the reaction mixture. Product analysis by glpc showed the formation of ethyl trimethylsilyl(ethylthio)acetate (IIa) and ethyl ethylthioacetate (IIIa) in 38 and 29% yields, respectively;⁶ structure IIa was established by comparison of its spectra with those of an authentic sample⁷ prepared by the reaction of ethyl trimethylsilyldiazoacetate with ethyl mercaptan.

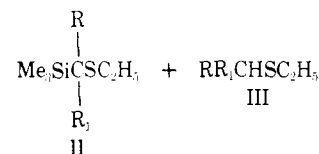
With phenylcarbene (Ib) produced by photolysis of phenyldiazomethane, trimethylsilyl(ethylthio)phenylmethane (IIb) and benzyl ethyl sulfide (IIIb) were formed in 28 and 8% yields, respectively. Product IIb was identified by nmr (CCl₄): τ 9.94 (CH₃Si-, singlet), 8.93 (-CH₂-, triplet), 7.75 (-SCH₂-, quartet), 6.81 (SiCH₂-, singlet), and 2.86 (Ph, broad singlet), intensity ratio 9:3:2:1:5. The ir absorption spectrum of IIb showed no Si-S band at 638 cm⁻¹. Similarly, photolysis of diphenyldiazomethane in ethylthiotrimethylsilane gave 29% trimethylsilyl(ethylthio)diphenylmethane (IIc) and 50% ethyl benzhydryl sulfide (IIIc).



1a, R = H; R₁ = CO₂C₂H₅

b, R = H; R₁ = Ph

c, R = R₁ = Ph



Since ylide formation in the reaction of a carbene with

(3) R. West, R. Lowe, H. F. Stewart, and A. Wright, *J. Amer. Chem. Soc.*, **93**, 282 (1971).

(4) A. Wright, D. Ling, P. Boudjouk, and R. West, *J. Amer. Chem. Soc.*, **94**, 4784 (1972).

(5) (a) W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 2786 (1969); (b) W. Ando, S. Kondo, K. Nakayama, K. Ichibori, H. Kohoda, H. Yamato, I. Imai, S. Nakaïdo, and T. Migita, *ibid.*, **94**, 3870 (1972); (c) W. Ando, M. Yamada, E. Matsuzaki, and T. Migita, *J. Org. Chem.*, **37**, 3791 (1972), and references cited therein.

(6) Direct insertions of the carbene into C-H bonds were also observed in 14% yields.

(7) W. Ando, T. Hagiwara, and T. Migita, *J. Amer. Chem. Soc.*, **95**, 7518 (1973).