binuclear complex may have a magnetic susceptibility that is solvent dependent. This value is also taken into account in the pseudocontact shift equation.

In a study of the solvent effects on shift reagent experiments employing lanthanide tris chelates, the association constant between the shift reagent and substrate was found to be solvent dependent, while the geometry and magnetic susceptibility were independent of solvent.[9] The magnitude of the shifts in the NMR spectrum of a substrate in the presence of a lanthanide shift reagent are highly dependent on the equilibrium constant for association between the two.[10] The spectrum of a substrate in the presence of a lanthanide shift reagent is a time average of its spectrum in the complexed and uncomplexed form. Solvents that bond effectively to either the silver or lanthanide, acetone, acetonitrile, benzene, dimethyl sulfoxide, and carbon disulfide, significantly reduce the effectiveness of the binuclear reagents.[2]

A larger equilibrium constant for association in pentane compared to $CDCl_3$ may reflect a reduction in the competitive effects of the solvent for coordination sites on the shift reagent. This seems especially reasonable considering that the greater enhancements are observed for those substrates that bond only weakly to Ag(I). Chloroform is known to hydrogen bond to the π system of the β-diketone ligands in some metal chelate complexes.[11] It is also possible that the chloroform could bond to the silver by a Lewis acid–Lewis base interaction. Any such competition of the chloroform would be enhanced because of the large excess of solvent relative to substrate.

The induced shifts in the NMR spectrum of chloroform (0.1 M) in pentane were recorded with either $Dy(fod)_3$ or $Dy(fod)_3/Ag(fod)$ at a concentration of 0.2 M and were found to be 0.77 and 0.78 ppm, respectively. These values represent rather small induced shifts. They do indicate that the chloroform bonds to both shift reagents in some fashion; however, the ability of chloroform to compete with other substrates for coordination sites on the shift reagent would appear to be negligible. If the association constants are solvent dependent, it may result from changes in the solvent polarity alone. This conclusion was reached in a previous study of the solvent effects on lanthanide tris chelates.[9]

Without a more detailed study, a solvent dependence of the association constants, geometry, or magnetic susceptibility cannot be eliminated as a possible contributing factor to the observed solvent effects with binuclear Ln(III)–Ag(I) NMR shift reagents. For the study of aromatic and chlorinated compounds with the binuclear shift reagents, the use of pentane as the solvent is recommended.

Experimental Section

Proton NMR spectra were recorded on a Varian EM 360L spectrometer. Shift reagents were purchased from Aldrich Chemical Co. or prepared and purified according to literature procedures.[12] Binuclear shift reagent studies were carried out by using previously described procedures.[6] Pentane and cyclohexane were reagent grade, and all solvents, including $CDCl_3$, were stored over molecular sieves. The following nomenclature has been used to denote the various ligands: 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione, H(fod); 4,4,5,5,6,6,6-heptafluoro-1-(2-thienyl)-1,3-hexanedione, H(hfth); 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, H(tta); and 3-(trifluoroacetyl)-*d*-camphor, H(facam).

Acknowledgment. We thank Bates College and Roger C. Schmutz for their support through a College Research Grant.

Registry No. $Dy(fod)_3$, 18323-98-3; $Eu(fod)_3$, 17631-68-4; $Pr(fod)_3$, 17978-77-7; $Ag(fod)_3$, 18716-26-2; 1-chloropentane, 543-59-9; 1-bromopentane, 110-53-2; toluene, 108-88-3; cyclohexene, 110-83-8; chloroform, 67-66-3; pentane, 109-66-0; cyclohexane, 110-82-7; *dl*-camphene, 565-00-4.

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Communications

Concerning Hydride Reduction of Diels–Alder Products of Danishefsky's Diene[1]

Summary: A nonacidic method for unveiling the latent α-enone moiety from a Diels–Alder adduct of Danishefsky's diene involves the use of lithium aluminum hydride to obtain an allylic alcohol, followed by manganese dioxide oxidation. A mechanism for the hydride-induced reaction is proposed.

Sir: Since its introduction in 1974,[5] Danishefsky's diene **2**, and variations thereof, have proved themselves to be agreeable[6–9] and versatile[10] for Diels–Alder reactions both

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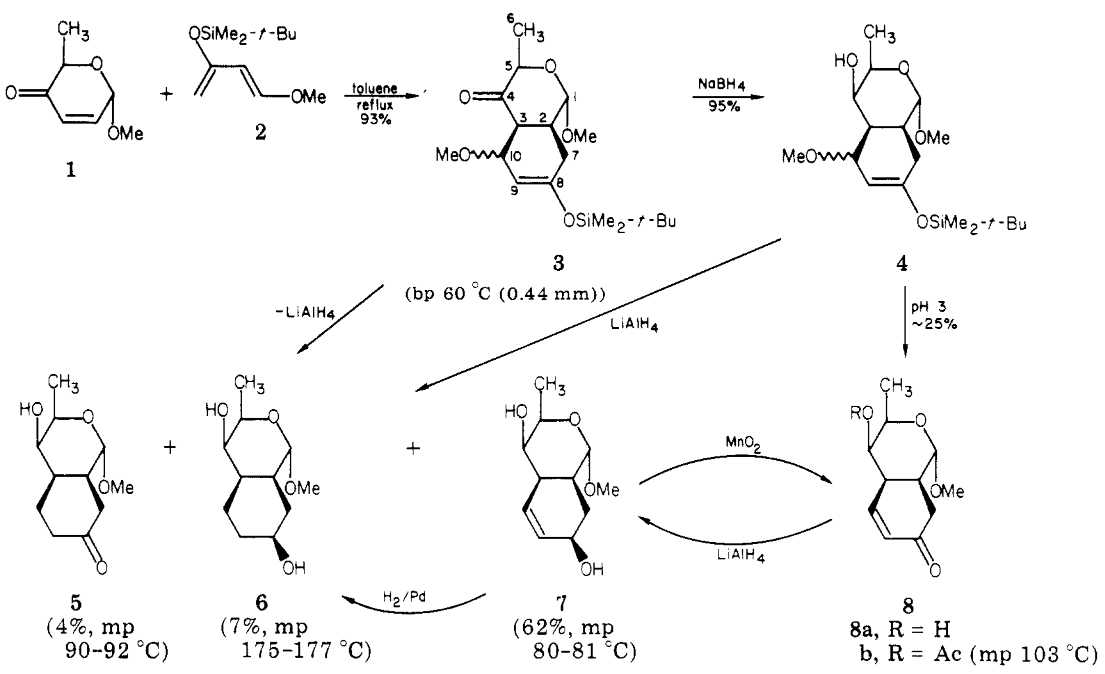
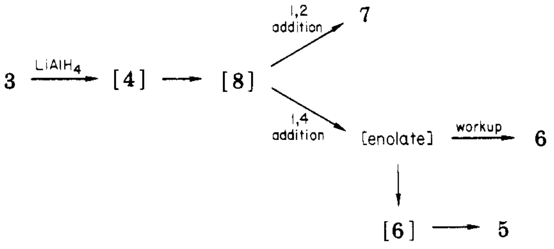
Scheme I[a]

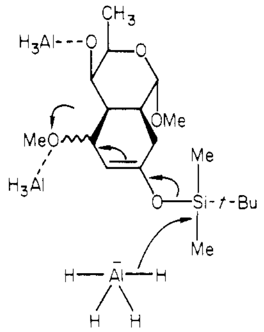


[a] Satisfactory elemental analyses and ^{1}H NMR spectroscopic data were obtained for compounds **3**-**8**.

Scheme II



Scheme III



of the traditional[6-10] and the "hetero"[5,11,12] varieties. For the traditional addition products, the functionality in the newly formed ring is normally processed so as to unveil the latent α-enone[6-8] or to give a β-oxygenated ketone.[9] However, on one occasion this unveiling was postponed until after a Grignard reagent had been added to the carbonyl group.[13] In connection with our work on the properties of annulated pyranosides,[14] we have added Danishefsky's diene to a variety of carbohydrate α-enones and attempted to reduce the adducts with lithium aluminum hydride (Scheme I). Such reductions have not been reported previously in the literature, and it is the purpose of this communication to alert readers to the pitfalls of this seemingly innocuous reaction, and, on the other hand, to point out that there are distinct advantages to be gained therefrom, *particularly with substrates where lability of the molecule precludes the usual[6-8] acid-catalyzed unmasking of the α-enone* (*vide infra*).

The reaction of enone **1**[15] with diene **2** in refluxing toluene required 24 h for completion, and the adduct **3** was obtained in 93% yield after isolation, as a mixture of C-10 epimers (endo/exo = 3). In the hope of obtaining the alcohol **4**, the product was treated with lithium aluminum hydride in tetrahydrofuran at 0 °C for 1 h and then overnight at room temperature. A complex mixture was produced which, upon chromatography, afforded three crystalline components, **5**, **6**, and **7** in yields of 4%, 7%, and 62%, respectively. Proof of structure of the major component **7** was obtained by oxidation with manganese dioxide to the hydroxy enone **8a**. The structure of the latter was completely assignable by analysis of the 200-MHz ^{1}H NMR spectrum of its acetate **8b**. Specifically we note that the patterns for H-1 (which is a singlet) and H-4 ($w_{1/2}$ = 6 Hz) established the configurations at C-2, -3, and -4.[14] The structure of diol **7** follows from its regeneration upon reduction of **8** with LAH. The structure of the minor components **5** and **6** were then verified by hydrogenation

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of 8 and 7, respectively, over palladium on carbon.

The formation of 5, 6, and 7 could be understood if 8 were an intermediate that reacted as outlined in Scheme II. Indeed, treatment of 8 with lithium aluminium hydride did afford 5, 6, and 7 in comparable ratios.

Further justification of the ideas in Scheme II rested on the assumption that reduction at C-4 of 3 would be the first event and that the resulting product 4 would collapse under the pressures depicted in Scheme III. The departure of the methoxy group is facilitated by complexation with a trivalent aluminum species[16] and is triggered by synchronous hydride-induced cleavage of the siloxy bond.[18] In order to test this notion, 4 was obtained from 3 in 95% yield by reduction with sodium borohydride. When 4 was not subjected to lithium aluminum hydride, 5, 6, and 7 were indeed obtained in the required ratios, therefore giving substance to the sequence in Scheme II.

The foregoing observations are particularly significant for compounds that bear sensitive functional groups, and which therefore cannot withstand the acidic conditions required for unveiling the latent enone.[6,8,10] Thus, hydrolysis of 4 at pH 3 afforded only a 25% yield of **8a**. Even under these mild conditions there was great loss of the glycosidic methoxyl. On the other hand, the route 3 → 7 → **8a** proceeded in 60% overall yield. This latter sequence *is, therefore, much better for such acid-sensitive molecules in spite of the fact that an extra step is required.*

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Registry No. 1, 71049-77-9; 2, 71735-01-8; 3 (isomer 1), 89828-00-2; 3 (isomer 2), 89828-01-3; 4, 89828-07-9; 5, 89828-02-4; 6, 89828-03-5; 7, 89828-04-6; **8a**, 89828-05-7; **8b**, 89828-06-8.

Supplementary Material Available: Experimental procedures and spectral data for compounds 3, 6, 7, and **8a** (3 pages). Ordering information is given on any current masthead page.

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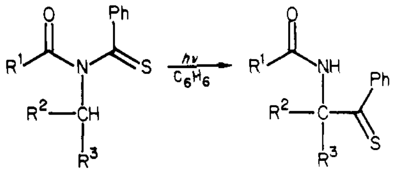
Photochemical Reactions of Acyclic Monothioimides. A Novel Photorearrangement Involving 1,2-Thiobenzoyl Shift

Summary: Photolysis of *N*-acylthiobenzamides in benzene gave thioketones via a novel photorearrangement involving 1,2-thiobenzoyl shift; the formation of the products was explainable in terms of β-hydrogen abstraction by the thiocarbonyl group.

Sir: Although the photoreactions of thioketones[1] and thioesters[2] are well studied, those of thioimides have not been reported except for [2 + 2] cycloaddition of cyclic thioimides with olefines.[3] In relation to our previous studies on photochemical reactions of nitrogen-containing thiocarbonyl compounds[4] and acyclic imides,[5] we now report the photorearrangement of *N*-acylthiobenzamide **1**, which involves an unprecedented 1,2-thiobenzoyl shift.

Table I. Photolysis of 1



1 **2**

	R¹	R²	R³	yield, %
a	Ph	Me	Me	62
b	Ph	Me	Et	80
c	Ph	Me	Ph	98
d	Me	Me	Me	64
e	Me	Me	Ph	95
f	Ph	H	Ph	43
g	Ph	H	*i*-Pr	0

The monothioimides **1a–g** were obtained almost quantitatively by acylation of the corresponding *N*-alkylthiobenzamides. The structure of these compounds was determined by the elemental analyses and spectral data. The visible spectrum of the monothioimide **1a** in *n*-hexane showed a maximum at 456 nm (ε 160) assignable to nπ* band of the thiocarbonyl group. Irradiation of *N*-isopropyl-*N*-benzoylthiobenzamide (**1a**) in benzene with a high-pressure mercury lamp under argon gave α-(benzoylamino)isobutyrothiophenone (**2a**) in 62% yield. The structure of **2a** was determined by the elemental analysis and spectra data. The IR spectrum (KBr) exhibited absorptions at 3260 (NH), 1630 (C=O), 1525 [C(=O)NH], and 1055 cm^{-1} (C=S). The mass spectrum showed the molecular peak at *m/e* 283 (M$^+$), and fragment peaks at *m/e* 187 (M - PhC=O), 163 [PhC(=S)C(CH$_3$)$_2$], 162 (M - PhC=S), 121 (PhC=S), and 105 (PhC=O). The ^{1}H NMR spectrum (CDCl$_3$) showed signals at δ 1.90 (s, 6 H, 2 × CH$_3$), 7.2–7.5 (m, 8 H, Ph), 7.6–7.8 (m, 2 H, Ph), and 7.9 (br, 1 H, NH). The ^{13}C NMR exhibited signals at δ 27.8 (q), 68.5 (s), 125.9 (d), 126.9 (d), 127.5 (d), 128.4 (d), 129.2 (d), 131.4 (d), 135.2 (s), 141.8 (s), 166.2 (s), and 255.6 (s). Furthermore, the visible spectrum of **2a** showed a maximum at 524 nm (ε 90) assignable to the nπ* band of thioketone moiety. Photolysis of other thioimides under the same conditions also gave the corresponding thio-

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