of perylene and chloro-, difluoro-, and chlorofluoroperylene, while the last band was perylene containing small amounts of fluoro- and chlorofluoroperylene.

B. In Perfluorohexane. The same procedure was used with 158 mg (0.63 mmol) of perylene suspended in 50 mL of perfluorohexane and 257 mg (1.52 mmol) of XeF_2. However, neither of these compounds is very soluble in the perfluorohexane so that after removal from the drybox the mixture was agitated periodically during 48 h. Reaction occurred on the surface of the perylene which became blackened. The suspension was shaken with aqueous sodium carbonate and filtered to give 177 mg of solid. This was dissolved in 100 mL of benzene and 10 mL of the solution was used for TLC (91 plates). Separation gave the crude products (in band order) as a difluoroperylene (10%), 3-fluoroperylene (30%), and perylene (60%). Each of the fluoro compounds was found by HPLC to contain very small amounts of the other products. The disposition of HPLC peaks was such that purification of the 3-fluoro- and difluoroperylene by recycling and preparative HPLC would have been possible but tedious and this was not attempted.

Registry No. 1, 198-55-0; $1^{+}\cdot$, ClO_4^-, 12576-63-5; 2, 77629-23-3; 3, 77647-88-2; 4, 77647-95-1; F^-, 16984-48-8; XeF_2, 13709-36-9.

Trifluoroacetic Acid Catalyzed Rearrangement of Dialkyl Xanthates to Dithiocarbonates with Inversion of Configuration

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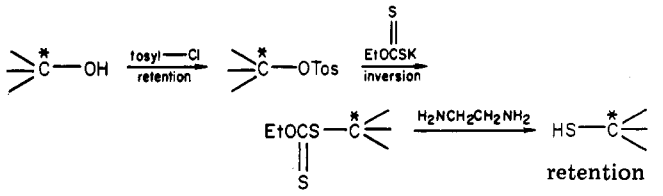
The thermal rearrangement of alkyl xanthates to *S,S*-dialkyl dithiocarbonates has long been known, usually occurring when the xanthates have no β hydrogen[1] or as a side reaction in the normal olefin formation during the Chugaev reaction. More recently, this rearrangement of xanthate to dithiocarbonate has been found to be catalyzed by Lewis acids, although side products are also observed.[2] The ready conversion of xanthates and *S,S*-dialkyl dithiocarbonates to thiols upon treatment with 2-aminoethanol or ethylenediamine can offer an attractive synthesis of mercaptans from alcohols,[4] particularly, if optically active thiols can be formed.[5] During our work on the synthesis of 1,3-dithiol-2-ones via xanthate intermediates, we discovered that trifluoroacetic acid catalyzed the rearrangement of dialkyl xanthates to *S,S*-dialkyl dithiocarbonates in high yields and under mild conditions. The rearrangement occurred without evidence of olefin formation even with xanthates with a β hydrogen on the oxygen alkyl group.

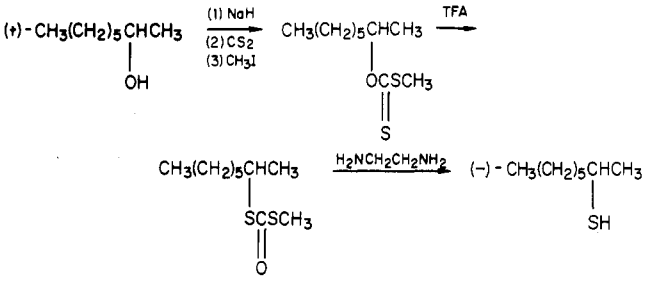
Results and Discussion

Recently, the mechanism of the Lewis acid catalyzed rearrangement of dialkyl xanthates to *S,S*-dialkyl dithiocarbonates has been investigated.[3] The rate constants for the rearrangement of several *O*-alkyl *S*-methyl xanthates increased in the order Me, Et, *n*-Pr < *i*-Pr. In addition, the catalysis racemized the rearranged products derived from optically active alcohols. Both of these results are consistent with a carbenium ion intermediate. In our method for the same transformation, the *O*-alkyl *S*-methyl xanthate is stirred in trifluoroacetic acid at room temperature. Table I summarizes the synthetic data for the dithiocarbonates that were prepared. The progress of the conversion is nicely followed by NMR spectroscopy by observing the upfield shift for the *O*-alkyl to *S*-alkyl multiplets. This method also allows a convenient comparison of reaction rates. The rates of the rearrangement of *O*-alkyl *S*-methyl xanthates varied in the order Me > Et > *i*-Pr. For comparison, when the *O*-alkyl group was methyl, the transformation was 88% complete after 5 min at room temperature. With an *O*-ethyl group, the rearrangement was only 35% complete after 30 min and only 75% complete after 2 h at room temperature.[6] These results suggest that the mechanism for the trifluoroacetic acid catalyzed rearrangement differs from that observed for the Lewis acid catalyzed reaction.[3] To examine this difference more thoroughly, we prepared the *S*-methyl xanthate derived from (+)-2-octanol and subjected it to the rearrangement conditions. The derived *S*-methyl *S*-octyl dithiocarbonate was optically active (see Table II). There was no direct way to assess the stereospecificity of the rearrangement, because optical rotation data for this compound had not been reported. We determined the stereospecificity as follows. It has been demonstrated that a given optically active alcohol can be converted to the corresponding thiol in a sequence of steps in which inversion can occur at one of the steps only. The sign of the optical rotation of the mercaptan so obtained is opposite to that of the starting alcohol[4] (Scheme I). This information provides a convenient method for assessing the significance of the magnitude and sign of the optical activity obtained in the formation of the *S*-methyl *S*-(2-octyl) dithiocarbonate. By converting this material to the corresponding thiol with ethylenediamine and comparing its optical rotation with that from the thiol obtained via Scheme I, we would have an indication of the degree of inversion, retention, or racemization about the secondary

Scheme I



Scheme II



(1) Taguchi, T.; Nakao, M. *Tetrahedron* **1962**, *18*, 245–55.
(2) Kawata, T.; Harano, K; Taguchi, T. *Chem. Pharm. Bull.* **1973**, *21*, 604–8.
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(4) Beretta, E.; Cinquini, M.; Colonna, S.; Fornasier, R. *Synthesis* **1974**, 425–6.
(5) Taguchi, T.; Kiyoshima, Y.; Komori, O.; Mori, M. *Tetrahedron Lett.* **1969**, *41*, 3631–34.

(6) Reaction times can be decreased without ill effects by warming the reaction at 55–60 °C.

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Table I. Synthetic and Physical Data for Dithiocarbonates

R	% yield[a]	bp, °C (mmHg)[b]	^{1}H NMR,[c] δ	IR (C=O), cm^{-1}	UV (C=O),[d] nm
CH_3	99	56 (14)	2.3 (6 H, s), 3.1 (2 H, q),	1670	249
CH_3CH_2	99		2.4 (3 H, s), 1.4 (3 H, t)	1670	249
$(CH_3)_2CH$	70	76 (14)	3.8 (1 H, m), 2.4 (3 H, s), 1.3 (6 H, d)	1660	
$CH_3CH_2CHCH_3$	65	86 (14)	3.75 (1 H, m), 2.4 (3 H, s), 1.2-1.8 (5 H, m), 1.0 (3 H, t)		251
$CH_3(CH_2)_5CHCH_3$	55	90-91 (0.015)	3.7 (1 H, m), 2.4 (3 H, s), 1.1-1.8 (13 H), 0.9 (3 H, m)		

[a] Yields were not maximized. [b] All boiling points are comparable to previously published values. [c] Measured in $CDCl_3$. [d] Measured in CH_2Cl_2.

octyl carbon during rearrangement. As Table II shows, the 2-octanethiol obtained via the *S,S*-dialkyl dithiocarbonate has an optical rotation in the same direction as the thiol obtained via Scheme I. This indicates that the rearrangement step, the only point at which bonds to the optically active center might be broken, must proceed with inversion of configuration (Scheme II). From a comparison of the magnitude of the rotations for the two mercaptans, it can be seen that the rearrangement does not proceed with complete stereospecificity but that the 2-octanethiol formed is 89% optically pure.

Table I shows that the isolated yields of *S*-alkyl *S*-methyl dithiocarbonates derived from secondary alcohols were significantly less than those for those derived from primary alcohols. In those cases, the NMR spectra taken during the rearrangement showed evidence of the formation of a secondary product. This is seen as a methine multiplet slightly upfield of the *O*-alkyl *S*-methyl methine absorption, suggesting an *O*-*sec*-alkyl group. This side-product formation poses no purification problems with the rearrangements of xanthates derived from the lower molecular weight alcohols, because the impurities are volatile enough to be removed with the excess trifluoroacetic acid upon concentration on a rotary evaporator at room temperature and reduced pressure. With the rearrangement of *S*-methyl *O*-(2-octyl) xanthate, however, this byproduct could be isolated by distillation of the product mixture at aspirator vacuum. It had no optical activity. Its infrared spectrum showed two major absorptions, at 1780 and 1160 cm^{-1}, both suggestive of the trifluoroacetate group. The NMR spectrum showed only the downfield methine proton at δ 5.0 and higher field alkyl absorptions in a ratio of 1:16. These results indicate that the secondary prouct in the xanthate rearrangement is the trifluoroacetate ester of the starting alcohol. The lack of optical activity in this material can be rationalized by assuming a carbenium ion intermediate. This would be consistent with the observation that only those xanthates whose *O*-alkyl groups are derived from secondary alcohols and thereby can generate stable carbenium ions will give this secondary reaction product.

Experimental Section

The xanthates were spectrally pure as obtained after initial workup. Samples were distilled to gather boiling point data and for elemental analyses.

Elemental analyses were obtained from either Galbraith Laboratories or the Analytical Sciences Division of the Kodak Research Laboratories. The NMR data were obtained on a Varian EM-390 spectrometer and the infrared data on a Beckman IR 4250 spectrometer.

Table II. Optical Rotation Data

compd	$[\alpha]_D$, deg
$CH_3(CH_2)_5CH(OH)CH_3$	$[\alpha]^{17}_D$ +9 (neat)
$CH_3(CH_2)_5CH(CH_3)OC(=S)SCH_3$	$[\alpha]^{23}_D$ −12.3 (*c* 4.0, EtOH)
$CH_3(CH_2)_5CH(SH)CH_3$	$[\alpha]^{24}_D$ −24.6 (*c* 2.70, EtOH)[a]
$CH_3(CH_2)_5CH(SH)CH_3$ (via Scheme I)	$[\alpha]^{24}_D$ −31.8 (*c* 1.05, EtOH)[b]

[a] $[\alpha]^{24}_{546}$ −29.1 (*c* 2.70, EtOH). [b] $[\alpha]^{24}_{540}$ −37.5 (*c* 1.05, EtOH).

All organic starting materials were obtained from Kodak Laboratory Chemicals except (+)-2-octanol, which was obtained from Aldrich Chemicals. All were used as received without further purification.

Preparation of *O*-Alkyl *S*-Methyl Xanthates. *O*-methyl, *O*-ethyl, *O*-isopropyl, and *O*-2-butyl xanthates were prepared in the usual manner.[3b,7]

(−)-*O*-(2-Octyl) *S*-Methyl Xanthate. This compound was prepared from sodium hydride (1.68 g, 0.07 mol), (+)-2-octanol (9.11 g, 0.07 mol), carbon disulfide (6.08 g, 0.08 mol), and methyl iodide (9.94 g, 0.07 mol) by the usual procedure except that the alcohol was added to a refluxing suspension of sodium hydride in 175 mL of dry tetrahydrofuran and the reaction was refluxed an additional 2 h after all the alcohol was added. A pale yellow liquid (14.8 g, 96%) suitable for the next step was obtained. An analytical sample was purified by vacuum distillation, bp 70 °C (0.015 mmHg).[3a] Anal. Calcd for $C_{10}H_{20}OS_2$: C, 54.5; H, 9.1; O, 7.3; S, 29.1. Found: C, 54.4; H, 8.9; O, 7.4; S, 29.0.

General Method for the Preparation of *S*-Alkyl *S*-Methyl Dithiocarbonates. An ~0.3 M solution of the xanthate in tirfluoroacetic acid was allowed to stand at room temperature for 1-24 h.[6] The course of the reaction was monitored by the disappearance of the starting-material absorption in the NMR spectrum. Removing the excess acid at reduced pressure at 30 °C gave spectrally pure dithiocarbonates. These materials were distilled through a Vigreux column to obtain samples for elemental analysis.

In the case of (+)-*S*-(2-octyl) *S*-methyl dithiocarbonate, the crude product was first distilled at 70–72 °C (~10 mmHg) to obtain the trifluoroacetate byproduct. Further distillation at 0.015 mmHg gave the desired product, analytically pure. Anal. Calcd for $C_{10}H_{20}OS_2$: C, 54.5; H, 9.1; O, 7.3; S, 29.1. Found: C, 54.6; H, 9.3; O, 7.3; S, 29.4.

(7) Reid, E. E. "Organic Chemistry of Bivalent Sulfur"; Chemical Publishing: New York, 1962; Vol. 4.

Registry No. *O*-Methyl *S*-methyl xanthate, 19708-81-7; *O*-ethyl *S*-methyl xanthate, 623-54-1; *O*-isopropyl *S*-methyl xanthate, 35200-02-3; *O*-*sec*-butyl *S*-methyl xanthate, 7694-21-5; (-)-*O*-(2-octyl) *S*-methyl xanthate, 77714-50-2; (+)-2-octanol, 6169-06-8; (-)-2-octanethiol, 10435-93-5; (+)-*S*-(2-octyl) *S*-methyl dithiocarbonate, 77629-22-2; *S*,*S*-dimethyl dithiocarbonate, 868-84-8; *S*-ethyl *S*-methyl dithiocarbonate, 10596-55-1; *S*-isopropyl *S*-methyl dithiocarbonate, 22426-84-2; *S*-*sec*-butyl *S*-methyl dithiocarbonate, 22426-85-3; trifluoroacetic acid, 76-05-1.

Kinetic Formation of Stereoisomeric Propionaldehyde Dimethylhydrazone Lithium Reagents

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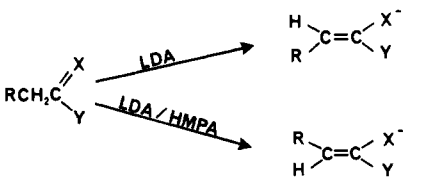
The sense and degree of stereoselectivity in deprotonations of ketones and esters and their synthetic equivalents can be critical in determining the overall stereoselectivity obtained in electrophilic substitution reactions employing enolate-like intermediates. Thus, several studies have been directed toward determining the stereochemistry of the lithio intermediates formed in deprotonations of substituted active methylene compounds and at how that stereoselectivity could be controlled experimentally.[2] Studies of deprotonations of various monosubstituted carbonyl compounds and derivatives by lithium diisopropylamide (LDA) have been found to occur as shown in Scheme I. With few exceptions,[3] deprotonation by LDA in the absence of hexamethylphosphoramide (HMPA) gives the lithium reagent wherein the substituent (R) is trans to the charge-bearing heteroatom. Deprotonation by LDA in the presence of HMPA, however, usually gives predominantly the cis lithium reagent. Products obtained in these studies were tacitly assumed to be the kinetic products of the deprotonation reactions, and rationalizations for the results involving different transition states in the deprotonations with or without HMPA have been presented.[5] Recently, Rathke and co-workers have shown that deprotonation of 3-pentanone by LDA/HMPA gives a mixture of stereoisomeric enolates, the ratio of which clearly changes during the course of the deprotonation, showing that an equilibration process occurs in this case.[6] One implication of these results is that HMPA may activate equilibration processes in other enolate-like species. In this note we show that the propionaldehyde dimethylhydrazone (DMH) lithium reagents formed by LDA deprotonation in the absence or presence of HMPA do not equilibrate under typical deprotonation conditions; thus distinctly different transition states for the deprotonation reactions must exist under these different deprotonation conditions.

Scheme I



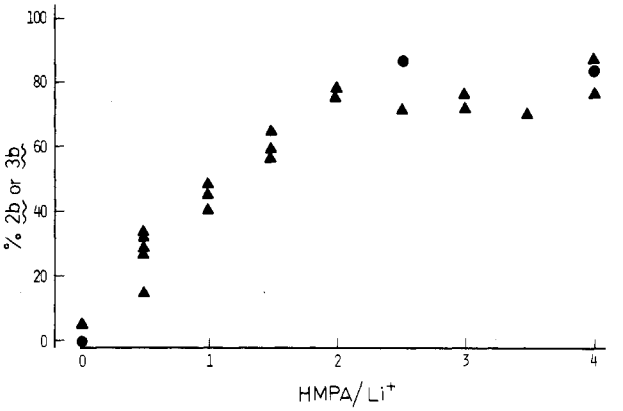
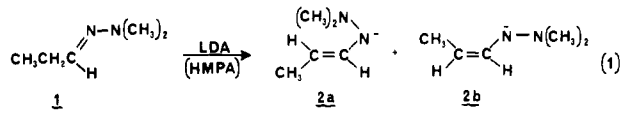


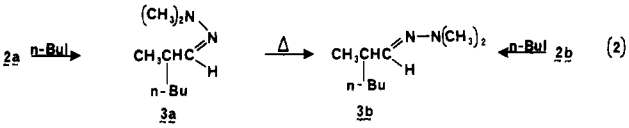
Figure 1. Percentage of **2b** (●) or **3b** (▲) formed from LDA deprotonation of **1** in the presence of increasing equivalents of HMPA per lithium ion.

As reported, propionaldehyde DMH (**1**) is deprotonated by LDA or LDA/HMPA to give the E_{C-C},Z_{C-N} (**2a**) and Z_{C-C},E_{C-N} (**2b**) azaallyllithium reagents as the only products detectable by ^{1}H NMR spectroscopy.[2d] The C–C



(1)

bond stereochemistry of **2a** and **2b** was determined by ^{1}H NMR spectroscopy of the azaallyllithium reagents; **2a** shows a trans coupling (J = 12.5 Hz) and **2b** a cis coupling (J = 7.7 Hz) to the formyl protons. The C–N stereochemistry was determined by alkylation of **2a** and **2b**, which gave the butylated products **3a** and **3b**, respectively



(2)

(this froze out the C–N stereochemistry), and subsequent ^{1}H NMR analysis. The formyl proton of **3a** gave a signal at δ 6.7 and that of **3b** gave a signal at δ 6.4; on standing at 25 °C **3a** slowly isomerized to **3b**. When **1** was treated with LDA containing 0.0 to 4.0 equiv of HMPA per lithium ion, the ratio of **2a**:**2b** changed smoothly from >95:<5 (0.0 equiv of HMPA) to ca. 20:80 (>2.0 equiv of HMPA) as shown in Figure 1. The **2a**:**2b** ratio either was obtained by integration of the proton signals at δ 6.2 and 6.6, re-

(1) Camille and Henry Dreyfus Teacher-Scholar, 1980–1985.

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(3) Exceptions include ketones[2e] and thioamides.[4a] The stereochemistry originally assigned to thioamide lithium anions[4b] appears to have been in error.

(4) (a) Tamaru, Y.; Harada, T.; Nishi, S.; Mizutani, M.; Hioki, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1980**, *102*, 7806–7808. (b) Tamaru, Y.; Harada, T.; Yoshida, Z. *Ibid.* **1978**, *100*, 1923–1925.

(5) Typically, these different transition states proposed involved coordination of lithium of the base to the heteroatom in the absence of HMPA and less or no coordination in the presence of HMPA.[2a,d,e]

(6) Fataftah, Z. A.; Kopka, I. E.; Rathke, M. W. *J. Am. Chem. Soc.* **1980**, *102*, 3959–3960.

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