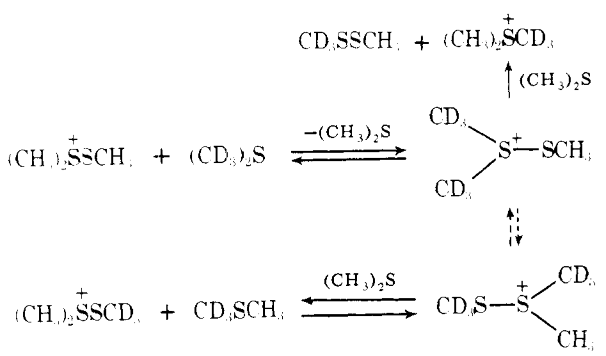
Because these reactions utilize relatively inexpensive materials, are simple to perform, and give good to excellent yields, they deserve attention as practical routes to the labeled products in question.

To solve the question of a degenerate rearrangement in dimethyl(methylthio)sulfonium fluoroborate (**1**, R = CH_3) the unlabeled salt was mixed with a slight excess of dimethyl-d_6 sulfide in nitromethane at 25 °C. It is known from NMR studies that a rapid exchange reaction occurs between **1** and dimethyl sulfide[12] while a slower irreversible displacement leads to trimethylsulfonium fluoroborate and methyl disulfide (eq 2). If methyl migration in **1** occurs within the time span of these reactions, then methyl exchange in dimethyl sulfide will be observed. Mass spectral analysis of recovered dimethyl sulfide from the reaction showed molecular ions corresponding to m/e 62 (CH_3SCH_3) and m/e 68 (CD_3SCD_3) only. The absence of m/e 65 means that CD_3SCH_3 is *not* formed, and therefore that **1** does *not* rearrange. On the other hand, MS analysis of recovered methyl disulfide showed molecular ions at 94:97:100 corresponding to CH_3SSCH_3, CD_3SSCH_3, and CD_3SSCD_3 in the ratio of 36:29:7. This result is attributable to methylthio exchange between disulfide and **1** as has been observed previously (eq 3).[12]



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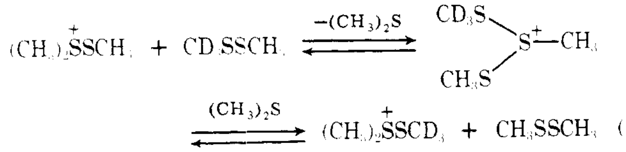

(3)

Preparation of the labeled salt 1-d_6 by methylation of dimethyl-d_6 disulfide confirmed the absence of methyl transfer. Thus solutions of 1-d_6 in nitromethane showed no NMR resonance at 2.90 ppm corresponding to the sulfenyl methyl over a period of 3–4 days at 25 °C or 2–3 h at 60 °C. Only a single resonance at 3.27 ppm was observed corresponding to the unlabeled sulfonium methyl. We conclude therefore that alkyl rearrangement in thiosulfonium salts of type **1** is confined to alkyl groups that can form stabilized cations, and that cleavage of CH_3–S^+ bonds in **1** is a straightforward S_N2 displacement at carbon.

Experimental Section

Dimethyl-d_6 Sulfide. A mixture of benzenethiol (76.2 g, 0.69 mol) and dimethyl-d_6 sulfoxide (28.8 g, 0.34 mol, 99.5 atom % D) was heated while stirring within the temperature range 78–95 °C as the product, dimethyl-d_6 sulfide, distilled from the mixture. When the temperature of the distillate reached 55 °C, heating was discontinued. Redistillation gave 21.1 g (91%) of pure sulfide-d_6 (99.5 atom % D, bp 36.5 °C).

Dimethyl-d_6 Disulfide. Ammonia (~200 mL) was condensed into a 500-mL three-neck flask fitted with a mechanical stirrer, dry-ice condenser, and gas-inlet tube. Methyl-d_6 sulfide (23 g, 0.34 mol) was added followed by addition of sodium metal (15.5 g, 0.675 g-atom) in small pieces until the blue color persisted for up to 2 h. The ammonia was allowed to evaporate overnight and the white residue, which was a mixture of $NaSCD_3$ and $NaNH_2$, was dissolved in 100 mL of ethanol and 100 mL of water. To this stirred solution was added 20 mL of 30% hydrogen peroxide (17.5 mmol) while the temperature of the mixture was maintained at 65–8 °C. The mixture was cooled and the organic and aqueous phases separated. The aqueous layer was extracted twice with 25-mL portions of pentane. The organic layer was diluted with 200 mL of water and extracted with two 75-mL portions of pentane. The combined pentane extracts were washed with water, dried ($MgSO_4$), and distilled. The fraction of bp 96–8 °C was dimethyl-d_6 disulfide (14.6 g, 88%, >99 atom % D).

Methane-d_3-thiol and Sodium Methiolate. Method A. The white residue obtained after evaporation of ammonia from the reaction of $(CD_3)_2S$ (6.8 g, 0.1 mol) and sodium (5.4 g, 0.23 mol) described earlier was dissolved in 50 mL of 1,2-ethanediol. The pressure was reduced to 10–20 mm (house vacuum) for 1 h and the volatiles were trapped in liquid nitrogen. The flask was then equipped with a distillation head and a dropping funnel. Concentrated H_2SO_4 (~12 g) was added to the mixture as methane-d_3-thiol was liberated and condensed into a receiver cooled in a dry-ice–isopropyl alcohol bath. The clear liquid condensate was then treated with anhydrous $MgSO_4$ and redistilled. The yield of methane-d_6-thiol was 3.8–4.3 g (75–84%). Mass spectral analysis showed no isotopic dilution. **Method B.** Dimethyl-d_6 disulfide (10 g, 0.1 mol) was converted to sodium methiolate-d_3 by adding freshly cut sodium metal (4.7 g, 0.2 mol) in 200 mL of liquid ammonia as described for the reductive cleavage of $(CD_3)_2S$. After evaporation of the ammonia, the white solid residue was treated with 1,2-ethanediol following the procedure described in method A. Methane-d_3-thiol was obtained in 80% yield.

Preparation of 1-d_6. To a cold solution of trimethyloxonium fluoroborate (4.5 g, 30 mmol) in 10 mL of acetonitrile (dried over $CaCl_2$ and freshly distilled before use) was slowly added dimethyl-d_6 disulfide (3.1 g, 31 mmol, 99 atom % D). The mixture was stirred in an ice–water bath for 1 h after which the salt 1-d_6 was precipitated by the addition of anhydrous ether (50 mL). The crystalline white precipitate was collected by filtration and recrystallized from acetonitrile and ether which gave 5.1 g (84%) of salt 1-d_6, mp 84–6 °C (lit.[13] mp 81.5–84 °C). NMR analysis of the salt indicates the purity of 1-d_6 as 98% (NMR (CD_3NO_2) δ 3.27 with a minor singlet at 2.96 corresponding to $(CH_3)_2S^+CD_3BF_6^-$ which is formed as a byproduct).

Acknowledgment. This investigation was supported by Grant No. CA 19944, awarded by the National Cancer Institute, DHEW.

Registry No.—1-d_6, 67612-76-4; dimethyl-d_6 sulfide, 926-09-0; dimethyl-d_6 disulfide, 7282-94-2; methane-d_3-thiol, 7175-74-8; sodium methiolate-d_3, 67612-77-5; dimethyl-d_6 sulfoxide, 2206-27-1; trimethyloxonium fluoroborate, 420-37-1.

References and Notes

(1) J. K. Kim and M. C. Caserio, *J. Am. Chem. Soc.*, **96**, 1930 (1974).
(2) S. A. Anderson, J. K. Kim, and M. C. Caserio, *J. Org. Chem.*, in press.
(3) M. Oki and K. Kobayashi, *Bull. Chem. Soc. Jpn.*, **43**, 1223, 1229 (1970).
(4) J. K. Kim, M. L. Kline, and M. C. Caserio, *J. Am. Chem. Soc.*, in press.
(5) I. B. Douglass, *Int. J. Sulfur Chem.*, **8**, 441 (1973).
(6) E. Block and J. O'Conner, *J. Am. Chem. Soc.*, **96**, 3921 (1974).
(7) D. N. Harp and T. G. Back, *J. Labelled Compd.*, **11**, 95 (1975).
(8) Methyl-d_3 iodide (99.5 atom % D) retails for about $30 per 5 g, and dimethyl-d_6 sulfate (99 atom % D) for $121 per 10 g, whereas dimethyl-d_6 sulfoxide (99.5 atom % D) is supplied as an NMR solvent for $7–8 per 5 g.
(9) M. Tranquille, M. Fouassier, M. F. Lautie-Mouneyrc, P. Dizabo, and M. T. Forel, *C. R. Acad. Sci., Ser. C*, **270**, 1085 (1970).
(10) C. N. Yiannios and J. V. Karabinos, *J. Org. Chem.*, **28**, 3246 (1963).
(11) (a) F. E. Williams and E. Gebauer-Fuelnegg, *J. Am. Chem. Soc.*, **53**, 352 (1931); (b) C. C. Price and G. W. Stacy, "Organic Syntheses", Vol. III, Wiley, New York, 1955, p 86.
(12) S. H. Smallcombe and M. C. Caserio, *J. Am. Chem. Soc.*, **93**, 5826 (1971); J. L. Kice and N. A. Favtritsky, *ibid.*, **91**, 1751 (1969).
(13) D. J. Meerwein, K. F. Zesner, and R. Gipp, *Justus Liebigs Ann. Chem.*, **688**, 67 (1965).

Rates of Cycloaddition of Tetracyanoethylene to α,β-Unsaturated Sulfides and Ethers

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Thermal 2 + 2 cycloaddition of tetracyanoethylene (TCNE) to enol ethers has been extensively investigated by Huisgen

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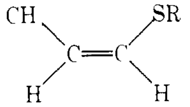
and his co-workers.[1] The reaction takes place through a zwitterionic intermediate.

In our continuous interest in the structure–reactivity relationship of α,β-unsaturated ethers and sulfides,[2] we have studied the rates of cycloaddition of TCNE to various unsaturated sulfides as well as some vinyl ethers in methylene chloride. The compounds investigated here include alkyl vinyl (**1**), alkyl *cis*- and *trans*-propenyl (**2** and **3**), ethyl isopropenyl (**4b**), and ring-substituted phenyl vinyl sulfides (**5**), together with vinyl ethers (**6** and **7b**) as the oxygen homologues of **5** and **1b**.

$CH_2=CHSR$

1



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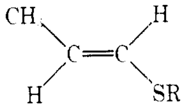

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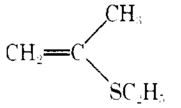


4b

a, R = CH_3, b, R = C_2H_5

c, R = $CH(CH_3)_2$ d, R = $C(CH_3)_3$

$CH_2=CHSC_6H_4X$ 5

$CH_2=CHOC_6H_4X$ 6

$CH_2=CHOC_2H_5$ 7b

Experimental Section

Materials. Methylene chloride was distilled from CaH_2. Commercial TCNE was recrystallized from CH_2Cl_2. Preparations of unsaturated sulfides (**1–5**)[2f,g] and ethers (**6**)[2b] were described elsewhere. Ethyl vinyl ether (**7b**) of reagent grade was distilled from $LiAlH_4$.

Kinetics. The reaction rates were measured by following the disappearance of the absorption of a charge-transfer (CT) complex.[1d] To 3 mL of a CH_2Cl_2 solution of an olefin equilibrated at the constant temperature of 25.0 °C in a quartz cuvette was added 5 μL of a stock solution of TCNE in CH_2Cl_2 with use of a microsyringe. Initial concentrations of an olefin and TCNE in reaction mixtures were 0.03–0.3 and 0.001–0.01 M, respectively. The absorption due to the formation of a CT complex developed immediately in the visible region. Its decrease with time was followed at the apparent λ_{max} on a Shimadzu spectrophotometer UV-200.

Preparation of Some Tetracyanocyclobutanes. The cyclobutanes were prepared by adding a 10% excess of an olefin to a solution of TCNE (0.05 g) in CH_2Cl_2 (20 mL) at room temperature. After continuous stirring till the disappearance of the characteristic color of the complex, the solvent was evaporated in vacuo. The residues were crystallized from cyclohexane-1,2-dichloroethane (3/1). The crude yields of the adducts were essentially quantitative.

1-Ethylthio-2,2,3,3-tetracyanocyclobutane obtained from **1b**: mp 126.5–127.5 °C; NMR ($CDCl_3$) δ 1.37 (3 H, t, J = 7.5 Hz), 2.76 (2 H, q, J = 7.5 Hz), 2.90 (1 H, dd, J = 11.6 and 12.8 Hz), 3.32 (1 H, dd, J = 8.6 and 12.8 Hz), 4.34 (1 H, dd, J = 8.6 and 11.6 Hz). Anal. Calcd for $C_{10}H_8N_4S$: C, 55.53; H, 3.74; N, 25.91. Found: C, 55.19; H, 3.46; N, 25.64.

1-Phenylthio-2,2,3,3-tetracyanocyclobutane obtained from **5** (X = H): mp 111–112.5 °C; NMR ($CDCl_3$) δ 2.97 (1 H, dd, J = 11.6 and 12.8 Hz), 3.44 (1 H, dd, J = 8.6 and 11.6 Hz), ~7.48 (5 H, broad singlet). Anal. Calcd for $C_{14}H_8N_4S$: C, 63.61; H, 3.06; N, 21.20. Found: C, 63.28; H, 2.86; N, 21.14.

1-Ethylthio-2-methyl-3,3,4,4-tetracyanocyclobutane obtained from **2b**: 127–128.5 °C; NMR ($CDCl_3$) δ 1.35 (3 H, t, J = 7.5 Hz), 1.55 (3 H, d, J = 7.5 Hz), 2.74 (2 H, q, J = 7.5 Hz), 3.63 (1 H, dq, J = 7.5 and 9.4 Hz), 4.39 (1 H, d, J = 9.4 Hz). Anal. Calcd for $C_{11}H_{10}N_4S$: C, 57.36; H, 4.39; N, 24.33. Found: C, 57.06; H, 4.55; N, 23.97.

Results

On mixing TCNE with a sulfide, a pink to violet color of the CT complex develops immediately and disappears gradually. When the color fades, an expected tetracyanocyclobutane is formed quantitatively. Benzyl vinyl sulfide was previously found to give a similar adduct on treatment with TCNE.[3] The adducts of enol ethers are well characterized.[1,3]

Table I. Rate Constants for the Cycloaddition of TCNE to Sulfides 1–4

no.	registry no.	λ,[a] nm	10^3k_2, M^{-1} s^{-1}
1a	1822-74-8	519	21.0
1b	627-50-9	528	34.2
1c	18888-46-5	534	85.4
1d	14094-13-4	543	252
2b	40069-87-2	574	7.69
3b	61865-98-3	570	25.6
2c	61865-97-2	575	14.3
3c	61865-99-4	574	52.7
2d	61865-96-1	570	51.3
3d	61866-00-0	575	93.1
4b	7594-45-8	580	2150
7b	109-92-2	433	19.9

[a] Wavelength used for the rate measurements.

Table II. Rate Constants for the Cycloaddition of TCNE to Ring-Substituted Phenyl Vinyl Sulfides, 5

subst	registry no.	λ_{max},[a] nm	10^4k_2, M^{-1} s^{-1}
p-OCH_3	16411-17-9	626	447
p-CH_3	16336-54-2	598	71.9
m-CH_3	16798-93-9	584	25.1
H	1822-73-7	570	10.2
p-F	64287-53-2	555	2.23
p-Cl	16411-16-8	561	0.35
m-Cl	42150-16-3	545	0.18

[a] Wavelength of maximum absorption of CT complex which is used for the rate measurements.

Table III. Rate Constants for the Cycloaddition of TCNE to Ring-Substituted Phenyl Vinyl Ethers, 6

subst	registry no.	λ_{max},[a] nm	10^5k_2, M^{-1} s^{-1}
p-OCH_3	4024-19-5	360, 575	2.40
p-CH_3	1005-62-5	374, 528	0.98
m-CH_3	1005-40-9	335, 502	0.65
H	766-94-9	363, 485	0.35

[a] Wavelengths of maximum absorption of CT complex. Longer wavelength was used for the rate measurements.

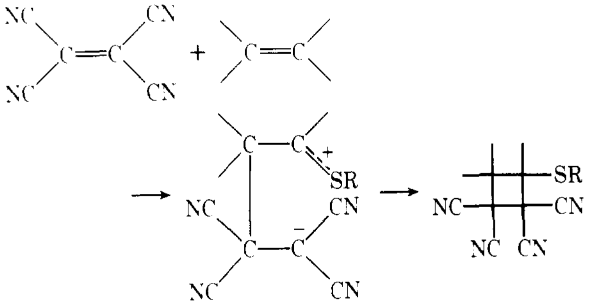
The rates of cycloaddition can be determined by following the disappearance of the absorption of the CT complex,[1d] since the formation of the complex is a fast equilibrium and its absorbance is proportional to the TCNE concentration in the presence of a large excess of an olefin (a 30 times excess used for kinetics). Pseudo-first-order plots were linear over 90% reaction. The pseudo-first-order rate constants k_1 obtained were proportional to the olefin concentration:

$$\text{rate} = k_1[\text{TCNE}] = k_2[\text{olefin}][\text{TCNE}] \qquad (1)$$

The second-order rate constants k_2 for various sulfides and ethers are given in Tables I–III. The wavelengths used for the rate measurements are also listed in the tables. They are approximate wavelengths of maximum absorption of the CT complex. In cases of its rapid decay (i.e., large k_2) the wavelength used would be somewhat too large as compared with that of the true maximum because the scanning was carried out always from the longer wavelength side at a finite scanning rate of 8 nm/s.

Discussion

The cycloaddition rates of alkenyl alkyl sulfides (**1**–**4**) change in a manner similar to those obtained with enol ethers.[1d] The reactivity increases with the increasing electron-donating ability of the alkylthio group. The α-methyl substitution enhances the reactivity by a factor of ca. 60 while the β-methyl group reduces it slightly. These trends are consistent with the mechanism involving a zwitterionic intermediate; factors stabilizing the carbonium ion end of the zwitterion should enhance the reactivity. The situations are also analogous to those observed in the rate-determining electrophile additions (e.g., acid-catalyzed hydrolysis).[2a,f]



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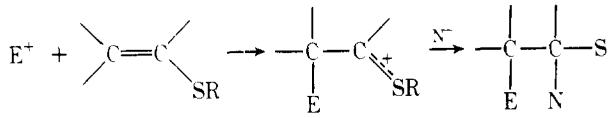

(3)

Logarithms of the rate constants k_2 obtained for substituted phenyl vinyl sulfides (**5**) and ethers (**6**) are plotted against the Hammett σ constants in Figure 1. The reaction constants ρ are −5.52 and −3.08 for **5** and **6**, respectively. These ρ values are considerably greater in magnitude than those found in the acid-catalyzed hydrolysis (−1.98[2g] and −2.14[2b] for **5** and **6**, respectively) and in the cationic polymerization (−1.76 for **6**[2c]). Similar results are reported for the reactions of styrene derivatives; $\rho^+ = -7.1$ for the cycloaddition of TCNE,[4] $\rho^+ = -3.43$ for the acid-catalyzed hydration,[5] and $\rho^+ = -2.03$ for the cationic polymerization.[6] The substituent effects greater than those in electrophilic additions are rather unexpected. At any rate, the carbon atom bearing a phenylthio or phenoxy group is no doubt highly electron deficient at the transition state.

Despite these similarities between the present reaction (eq 2) and the electrophilic addition (eq 3), kinetic features of these reactions are distinct from each other in several respects. First of all, the magnitude of ρ for **5** is greater than that for **6**. That is, the efficiency of the sulfur atom in transmitting the electronic effect of substituents onto the reaction site is greater than that of the oxygen atom. The greater transmitting efficiency of the sulfur atom was observed earlier for some ground-state properties of unsaturated compounds.[7] However, the trend observed in the acid-catalyzed hydrolysis was opposite.[2g] The distinctive substituent effects observed in the present reaction must be a reflection of some special electronic structure of the transition state.

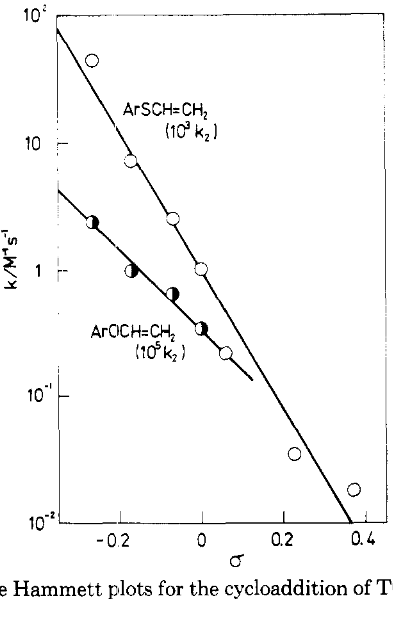

Figure 1. The Hammett plots for the cycloaddition of TCNE to **5** (○) and **6** (◐).

Second, the rates of the cycloaddition to sulfides are greater than those to the ether homologues. With alkyl derivatives (**1b** and **7b**) the difference is only a factor of about 2, while with aryl derivatives (**5** and **6**) the sulfides are 300–2000 times more reactive than the ethers. Opposite relative reactivities were observed in the acid-catalyzed hydrolysis; the ethers were two to three orders of magnitude more reactive than the sulfides.[2a,b,e-g] The latter reactivities were rationalized by the stability of an intermediate carbonium ion. Apparently, in the cycloaddition of TCNE, there must be some other factors governing the relative reactivities of the sulfide and ether.

Third, alkyl propenyl sulfides (**2** and **3**) show greater reactivity in their trans form than in the cis form. Similar results were previously obtained with alkenyl ethers.[1d] In the case of electrophilic additions, opposite reactivities (cis > trans) have been widely recognized[2e,8] and are attributed to the Coulombic interaction energy between electrophile and olefin at the transition state.[2e,9]

All these differences may be taken as an indication of some characteristic electronic structure of the transition state for the 2 + 2 cycloadditions in question. In this connection, it should be noted that the λ_{max} of the CT absorption is evidently much greater for the case of sulfides than for the corresponding ethers. Similar observations have been made with the gas-phase CT complexations of ethers and sulfides with carbonyl dicyanide.[10] The ionization potentials of sulfides are generally smaller than those of ethers. This should uniformly favor sulfides in the charge-transfer interaction with acceptor molecules.

In the system of our present concern, the charge-transfer interactions between two reactants are probably more important than the Coulombic ones at the transition state. Trans isomers of propenyl ethers and some other olefins are recognized to have slightly smaller ionization potentials as compared with the cis isomers.[11] The greater reactivity of sulfides and the greater reactivity of trans isomers can simultaneously be accounted for on these bases. However, the reason why the magnitude of ρ is greater for **5** than for **6** is still open to inquiry. The assumed importance of charge-transfer interaction at the transition state does not necessarily suggest the intermediacy of a CT complex in the course of cycloaddition.

In summary, the structure–reactivity relationship for the cycloaddition of TCNE to unsaturated sulfides and ethers superficially resembles that in the electrophilic additions, indicating the intermediacy of a zwitterion. Closer examination of the reactivities, however, does show some inherent distinctions and suggests the importance of the charge-transfer interaction between the unsaturated substrates and TCNE at the transition state of their cycloaddition.

Registry No.—TCNE, 670-54-2; 1-ethylthio-2,2,3,3-tetracyanocyclobutane, 67613-03-0; 1-phenylthio-2,2,3,3-tetracyanocyclobutane, 67613-04-1; 1-ethylthio-2-methyl-3,3,4,4-tetracyanocyclobutane, 67613-05-2.

References and Notes

(1) (a) R. Huisgen and G. Steiner, *J. Am. Chem. Soc.*, **95,** 5054 (1973); (b) *ibid.*, **95,** 5055 (1973); (c) *ibid.*, **95,** 5056 (1973); (d) *Tetrahedron Lett.*, 3763 (1973); (e) *ibid.*, 3769 (1973); (f) R. Huisgen, R. Schug, and G. Steiner, *Angew. Chem., Int. Ed. Engl.*, **13,** 80 (1974); (g) *ibid.*, **13,** 81 (1974); (h) R.

Huisgen and R. Schug, *J. Chem. Soc., Chem. Commun.*, 59 (1975); (i) *ibid.*, 60 (1975); (j) I. Karle, J. Flippen, R. Huisgen, and R. Schug, *J. Am. Chem. Soc.*, **97**, 5285 (1975); (k) R. Huisgen, *Acc. Chem. Res.*, **10**, 117, 199 (1977).
(2) (a) T. Okuyama, T. Fueno, H. Nakatsuji, and J. Furukawa, *J. Am. Chem. Soc.*, **89**, 5826 (1967); (b) T. Fueno, I. Matsumura, T. Okuyama, and J. Furukawa, *Bull. Chem. Soc. Jpn.*, **41**, 818 (1968); (c) *J. Polym. Sci., Part A-1*, **7**, 1447 (1969); (d) T. Okuyama, T. Fueno, and J. Furukawa, *Tetrahedron*, **25**, 5409 (1969); (e) T. Okuyama and T. Fueno, *J. Org. Chem.*, **39**, 3156 (1974); (f) T. Okuyama, M. Nakada, and T. Fueno, *Tetrahedron*, **32**, 2249 (1976); (g) T. Okuyama, M. Masago, M. Nakada, and T. Fueno, *ibid.*, **33**, 2379 (1977).
(3) J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Am. Chem. Soc.*, **84**, 2210 (1962).
(4) P. D. Bartlett, *Q. Rev., Chem. Soc.*, **24**, 473 (1970).
(5) W. M. Schubert, B. Lamm, and J. R. Keeffe, *J. Am. Chem. Soc.*, **86**, 4727 (1964).
(6) J. P. Kennedy in "Copolymerization", G. E. Ham, Ed., Interscience, New York, 1964, p 308.
(7) T. Fueno, O. Kajimoto, K. Izawa, and M. Masago, *Bull. Chem. Soc. Jpn.*, **46**, 1418 (1973); O. Kajimoto, M. Kobayashi, and T. Fueno, *ibid.*, **46**, 1422, 1425, 2316 (1973).
(8) R. Bolton in "Comprehensive Chemical Kinetics", Vol. 9, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, Amsterdam, 1973, Chapter 1.
(9) T. Fueno, *Chem. Rev.* (*Jpn.*), **1**, 35 (1973).
(10) T. Fueno and Y. Yonezawa, *Bull. Chem. Soc. Jpn.*, **45**, 52 (1972).
(11) T. Fueno and Y. Yamaguchi, *Bull. Chem. Soc. Jpn.*, **45**, 3290 (1972).

Synthesis of Thermodynamically Less Stable Enol Thioethers. An Alternative Oxidative Decarboxylation of α-Thio Acids

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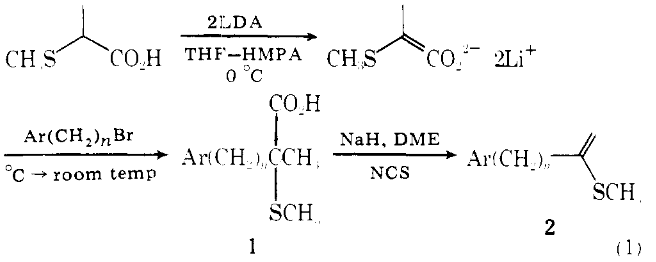
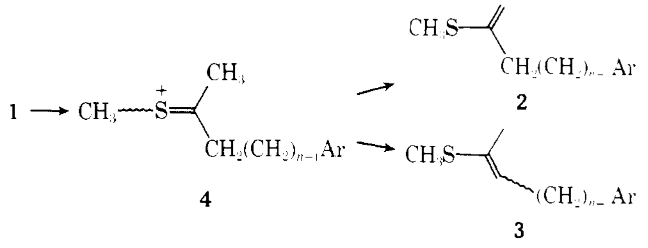
Enol thioethers, valuable synthetic intermediates, normally arise by elimination reactions from the corresponding thioketals (or thioacetals).[1] Such reactions generally proceed under thermodynamic control. Regiocontrolled synthesis via a Wittig-type[2] or Peterson-type[3] olefination is limited. During our investigations of the oxidative decarboxylation of α-methylthiocarboxylic acids,[4,5] we discovered a new approach to achieve this type of transformation and which provides direct access to the thermodynamically less stable enol thioethers.

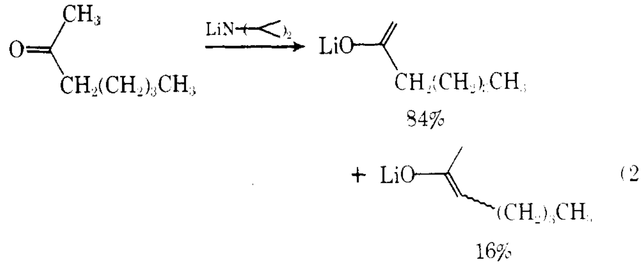
The requisite substrates were readily available by the alkylation of the dianion of 2-methylthiopropionic acid[6] with an alkyl bromide as summarized in eq 1 and Table I. Treatment of the sodium salts of the acids **1** with 1 equiv of *N*-chlorosuccinimide (NCS) in anhydrous DME led cleanly to the desired enol thioethers **2**. No detectable amounts of the alternative regioisomers are seen. That **2** represents the thermodynamically less stable enol thioethers is reflected by the rapid equilibration to the more substituted enol thioethers **3** upon treatment of **2** with anhydrous acid.



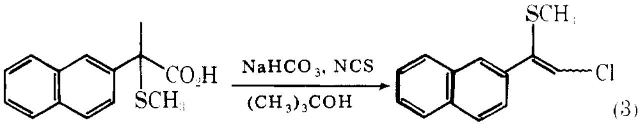
(1)

The regiochemistry presumably reflects kinetic deprotonation of the thionium intermediate **4**. This strikingly high regioselectivity may be contrasted to the kinetic enolate generation from 2-heptanone in which only an approximately 5:1 selectivity for deprotonation of the methyl group is observed (eq 2).[7] While the differences can be attributed to a variety of factors, including the differences in base and the effect of the stereochemistry of the thionium species, no convincing arguments can be seen. Synthetically, since the enol thioether can be an enolate or enol equivalent in some types of reactions, this selectivity can be very useful. These results also contrast with our earlier observations[4] in which the chlorinated vinyl sulfide (eq 3) was obtained when *tert*-butyl alcohol was employed as solvent. Presumably, the lower oxidation potential of NCS in an aprotic nonpolar solvent like DME accounts for the greater selectivity in the present cases.





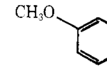
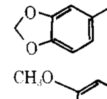
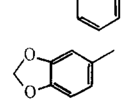
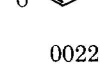
(2)



(3)

Thus, this new reaction makes 2-methylthiopropionic acid equivalent to the vinyl anion **5** and thus an alternative for the

Table I. Oxidative Decarboxylation Route to Vinyl Sulfides (see eq 1)

entry	Ar	*n*	yield 1, %	registry no.	2, %	registry no.
1	Ph	2	57	67556-31-4	82	67556-36-9
2	Ph	3	60	67556-32-5	85	67556-37-0
3		3	66–85	67583-96-4	84–100	67556-38-1
4		3	71–90	67556-33-6	85–86	67556-39-2
5		4	74–95	67556-34-7	85	67556-40-5
6		5	74	67556-35-8	85	67556-41-6