Structure and Reactivity of α,β-Unsaturated Ethers. 16. Electrophilic Addition of Benzenesulfenyl Chloride to α,β-Unsaturated Ethers and Sulfides

Kenzo Toyoshima, Tadashi Okuyama,* and Takayuki Fueno

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Received December 20, 1977

The rates of addition of benzenesulfenyl chloride to α,β-unsaturated ethers and sulfides have been measured in CCl_4 at 30 °C. Reactivities of alkyl vinyl ethers and sulfides increase with the electron donating ability of alkyl group, ρ^* being −5.4 and −1.7, respectively. β-Alkyl and β-methoxy substitutions enhance the reactivity of vinyl ether while α-methyl substitution influences it little. Adducts are exclusively the Markownikoff type. With ethyl propenyl ethers, anti addition is slightly dominant over syn addition. It was concluded from these results that the rate-determining transition state resembles a symmetrically bridged sulfonium ion intermediate **23** and that an open carbonium ion mediates between the rate- and product-determining steps.

It is established that the addition of a sulfenyl halide to an olefin proceeds through an episulfonium ion intermediate to give stereospecifically an anti adduct.[1] One example of a nonstereospecific addition of an arenesulfenyl chloride to an olefin has recently been found with 1-(*p*-alkoxyphenyl)propenes.[2] It was suggested that the rate-determining transition state closely resembles the bridged sulfonium ion even in the latter reaction.

Enol ethers undergo electrophilic attack to give a carbonium ion intermediate stabilized by the direct conjugation with the alkoxy oxygen atom. This conjugative stabilization of an open carbonium ion might make the contribution of a bridged structure unnecessary in the transition state.[3]

In view of these considerations, we have investigated the addition of benzenesulfenyl chloride to various enol ethers as well as vinyl sulfides. Structures of the substrates studied here are shown in Tables II–IV.

Experimental Section

Materials. Benzenesulfenyl chloride (**1**) was prepared from diphenyl disulfide and sulfuryl chloride according to the literature,[4] boiling at 70 °C (10 mm) [lit.[4] 49 °C (4 mm)]. Carbon tetrachloride and carbon disulfide were distilled from P_2O_5. 2,4-Dinitrophenylhydrazine of reagent grade (Wako) was used without further purification.

Commercial ethyl (**3**), *n*-butyl (**6**), and isobutyl vinyl ethers (**7**) were distilled from $LiAlH_4$. Methyl (**2**) and *tert*-butyl vinyl ethers (**5**) were prepared by the alcohol exchange of **3** and **6**, respectively.[5] Isopropyl vinyl (**4**) and other alkenyl alkyl ethers (**9–15**) were obtained by the pyrolysis of an appropriate acetal as described previously.[6] Preparations of phenyl vinyl ether (**8**),[7] 1,2-dimethoxyethylene (**16**),[8] alkyl vinyl sulfides (**17–20**),[9] and phenyl vinyl sulfide (**21**)[10] were described before. Styrene (**22**) was distilled from *tert*-butylcatechol just before use. Geometric isomers were separated by the distillation through a spinning band column, isomeric purity >96% by VPC.

Kinetic Measurements. All the reactions were carried out at 30.0 ± 0.1 °C in a CCl_4 solution under pseudo-first-order conditions with a 50 times excess of olefin. Each stock solution of an olefin (~0.1 M) and **1** (~0.2 M) in CCl_4 was prepared by weighing. Concentration of **2** was determined spectrophotometrically after hydrolysis (λ 285 nm, acetaldehyde). Three milliliters of an olefin stock solution was thermally equilibrated at 30 °C in a stoppered quartz cuvette inserted in a water-jacketted cell holder. Into the olefin solution was injected 30 μL of a stock solution of **1** with use of a microsyringe. The reaction was monitored by the disappearance of **1** (λ_{max} 390 nm) using a Shimadzu spectrophotometer UV-200.

The fast reactions with **10–12** were followed with the use of a stopped flow spectrophotometer Union RA-1100. In this case, a stock solution of **1** was 2×10^{-3} M in concentration.

Pseudo-first-order plots were linear over 80% reactions for all the runs studied. Rate constants are given as averages of at least three measurements.

Reaction of 1 with 3. A solution of 0.1 g of **3** in 0.3 mL of CS_2 was placed in an NMR sample tube and cooled at −78 °C. To this solution was added slowly 0.2 g of **1** in 0.2 mL of CS_2. The temperature of the mixture was raised slowly under spinning on an NMR spectrophotometer JNM-4H-100. The spectra were recorded at −60, −30, and 22 °C. The ^{1}H NMR spectra showed a gradual formation of the single product with the disappearance of **3**. The spectrum of the product was not changed after 1 week at room temperature. The reaction at room temperature gave the same product spectrum (Table I).

The reaction was also conducted in a greater scale (**1**, 1 g; **3**, 0.5 g; CCl_4, 5 mL) and the reaction product was subjected to the acid-catalyzed hydrolysis. After 5 min of reaction at room temperature, the reaction mixture was shaken with 5 mL of 1 N HCl in 80% aqueous ethanol. Hydrolysis products were treated with 2,4-dinitrophenylhydrazine. There was obtained after recrystallization (95% ethanol) ca. 1 g (ca. 44% yield) of the hydrazone, melting at 94–96 °C. Anal. Calcd for $C_{14}H_{12}N_4O_4S$: C, 50.61; H, 3.61; N, 16.87. Found: C, 50.42; H, 3.56; N, 16.83. The results show that the hydrolysis product is phenylthioacetaldehyde.

Reactions of 1 with 8, 17, and 21. These reactions were carried out in an NMR sample tube at room temperature. The ^{1}H NMR spectra of the reaction mixture showed the formation of the single adduct. The spectral data are given in Table I. The hydrolysis products of the adduct were identified as above. All the adducts gave only phenylthioacetaldehyde as an aldehydic product.

Reactions of 1 with 9c and 9t. The reactions in an NMR sample tube were carried out in the same way as above. The reactions at room temperature resulted in an essentially identical ^{1}H NMR spectrum both from **9c** and from **9t**. The spectrum showed the formation of two isomeric adducts, the spectra (e) and (t) in Table I, in the ratio of about 4/6.

The sulfenyl chloride **1** was added to the CS_2 solution of **9** at lower temperature. ^{1}H NMR spectra were recorded with raising temperatures. The reaction mixture obtained from **1** and **9t** showed the ^{1}H NMR spectra of changing ratio of the adducts (e) and (t); 7.5/2.5 at −60 to −30 °C, 7/3 at 0 °C, and 4/6 at 22 °C. On the other hand, the reaction between **1** and **9c** gave the adducts (e) and (t) in the ratio of 3/7 at −60 to −30 °C which changed to 4/6 at 22 °C.

The mixture of the two adducts (of the ratio 4/6) was subjected to the hydrolysis in the same way as above. The aldehydic product was isolated as 2,4-dinitrophenylhydrazone in ca. 60% yield, mp 105–106.5 °C (95% ethanol). Anal. Calcd for $C_{15}H_{14}N_4O_4S$: C, 52.03; H, 4.04; N, 16.18. Found: C, 51.94; H, 3.97; N, 16.20. The hydrolysis product must be α-phenylthiopropionaldehyde.

Results

Kinetics. The rates of addition of benzenesulfenyl chloride (**1**) to various enol ethers as well as vinyl sulfides were measured in CCl_4 solution in the presence of a large excess of the latter substrate. Pseudo-first-order plots were linear over 80% reactions. The geometric isomer of alkenyl alkyl ethers, which may undergo possible isomerization, was carefully investigated in its kinetic behavior. Both cis and trans isomers showed excellent linearity in their first-order plots during about 4 halflives. This indicates that the geometrical isomerization does not take place during the reaction to affect the rate of addition.

0022-3263/78/1943-2789$01.00/0

Table I. NMR Spectra of the Adducts $C_6H_5SCH_2CHCl(XR)$ or $CH_3CH(SC_6H_5)CHCl(XR)$[a]

Substrate			δ, ppm (*J*, Hz)			
No.	Registry no.	XR	CH_3	CH_2S or CHS	CHCl	R
3	66303-47-7	OC_2H_5		3.33 d (4.5), 3.36 d (8.3)	5.48 dd (4.5, 8.3)	3.75 q, 1.10 t
8	66303-48-8	OC_6H_5		3.35 d (4.1), 3.67 d (7.4)	5.43 dd (4.1, 7.4)	
17	66303-49-9	SCH_3		3.35 d (15.0)	4.93 t (15.0)	2.10 s
21	66303-50-2	SC_6H_5		3.33 d (15)	5.08 t (15)	7.05–7.70 m
9	66303-51-3	OC_2H_5 (e)	1.40 d (7.0)	3.2–3.6 m	5.42 d (4.8)	1.09 t, 3.6–4.0 m
	66303-52-4	(t)	1.46 d (7.0)	3.2–3.6 m	5.62 d (2.1)	1.20 t, 3.6–4.0 m

[a] Solvent: CCl_4.

Table II. Rate Constants for the Addition of 1[a] to Vinyl Ethers, $CH_2{=}CHOR$, at 30 °C in CCl_4

No.	Registry no.	R	10^2k_2, $M^{-1}\,s^{-1}$
2	107-25-5	CH_3	3.39
3	109-92-2	C_2H_5	10.6
4	18888-46-5	*i*-C_3H_7	33.6
5	926-02-3	*t*-C_4H_9	143
6	111-34-2	*n*-C_4H_9	9.80
7	109-53-5	*i*-C_4H_9	8.21
8	766-94-9	C_6H_5	0.294
22	52601-97-5	Styrene	0.778

[a] Registry no. 931-59-9.

The pseudo-first-order rate constants k_1 were proportional to the olefin concentration ranging 0.04–0.15 M. That is, the reaction is second order in reactants.

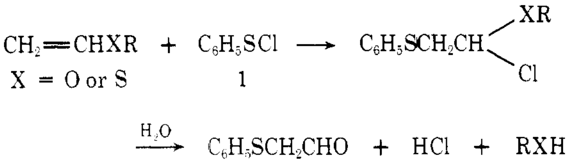
$$\text{rate} = k_1[1]$$

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

The rates were measured in the presence of a small amount of a radical inhibitor, benzoquinone, but the rate constants k_2 obtained were within experimental errors equal to those obtained in its absence. The addition must occur electrophilically but not through a free-radical mechanism.

The second-order rate constants k_2 are summarized in Tables II–IV for vinyl ethers, substituted vinyl ethers, and vinyl sulfides, respectively.

Structure of Adducts. The ^1H NMR spectra of the reaction mixtures with vinyl ethers, **3** and **8**, and vinyl sulfides, **17** and **21**, showed the formation of single product. Each of these reaction products was subjected to acid-catalyzed hydrolysis in 1 N HCl aqueous ethanol. The hydrolysis products were treated with 2,4-dinitrophenylhydrazine. The hydrazone isolated was identified as that of phenylthioacetaldehyde in all the cases examined above.



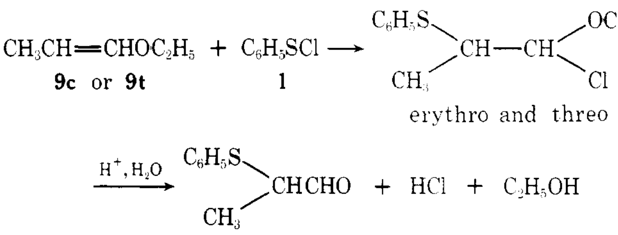
$$CH_2{=}CHXR + C_6H_5SCl \longrightarrow C_6H_5SCH_2CH(XR)Cl \xrightarrow{H_2O} C_6H_5SCH_2CHO + HCl + RXH \qquad (2)$$

$X = O$ or S 1

The product of the addition is no doubt exclusively the Markownikoff-type adduct. The ^1H NMR spectra are consistent with this structure.

In order to examine a possible rearrangement of the initially formed adducts during the addition, the reaction between **1** and **3** was followed carefully on an NMR spectrometer at lower temperatures of −60 °C to room temperature. No incipient signals other than those of the Markownikoff adduct were observed. Furthermore, the spectra were stable over 1 week at room temperature.

The ^1H NMR spectra of the reaction mixture from *cis*- and *trans*-propenyl ethyl ethers, **9c** and **9t**, showed the formation of two isomers of the adduct. Both the isomers give α-phenylthiopropionaldehyde on hydrolysis. That is, the two isomeric adducts obtained must be stereochemical isomers (erythro and threo) of the Markownikoff-type adduct.



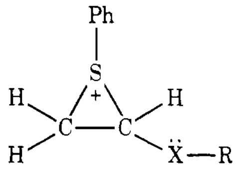
$$CH_3CH{=}CHOC_2H_5 + C_6H_5SCl \longrightarrow (C_6H_5S)(CH_3)CH{-}CH(OC_2H_5)Cl \xrightarrow{H^+,\,H_2O} (C_6H_5S)(CH_3)CHCHO + HCl + C_2H_5OH \qquad (3)$$

9c or **9t** 1 erythro and threo

The isomer of greater coupling constant of a CHCl signal (e) may be assigned to that of the erythro configuration and that of smaller coupling constant the threo configuration.[11] Thus, the cis isomer **9c** gave a slightly greater amount of the threo adduct (70%) at a lower temperature of −60 °C while the trans isomer **9t** resulted in the preponderant formation of the erythro isomer (75%) at lower temperature. That is, the anti addition is favored over the syn addition. At higher temperature, however, both **9c** and **9t** gave the same ratio of the erythro and the threo adducts of 4/6. The isomer ratio of the adducts obtained at lower temperature also changed to this ratio (4/6) on the rise of the temperature (to 22 °C), which indicates it to be a thermodynamic equilibrium ratio.

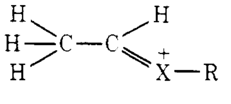
Discussion

The Effects of Alkoxy and Alkylthio Groups. The rate constants given in Tables II and IV show that alkyl vinyl ethers are 3–5 times more reactive than the corresponding sulfides. Such a reactivity difference found in the acid-catalyzed hydrolysis was as great as 10^2–10^4 times.[6,9,12] The rather small difference observed for the present reaction must be due to a smaller contribution for the pπ conjugation involving the O or S lone pair electrons in the transition state like **23**. The carbonium ionlike transition state (**24**) in the hydrolysis owes



(X = O or S)

23

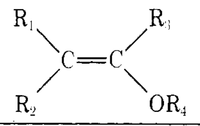


(X = O or S)

24

its stability greatly to the pπ conjugation. The pπ conjugative stability is attained more effectively with the 2p orbitals of oxygen than with the 3p orbitals of the sulfur atom.[9,10] Such effects must be moderate in the transition state **23**, in which a positive charge resides partly on the sulfenyl S atom.[1] Consequences of these factors are the greater reactivity of the

Table III. Rate Constants for the Addition of 1 to Ethers (at 30 °C in CCl_4)



No.	Registry no.	R_1	R_2	R_3	R_4	k_2, $M^{-1} s^{-1}$
9c	4696-25-7	H	CH_3	H	C_2H_5	2.03
9t	4696-26-8	CH_3	H	H	C_2H_5	1.12
10c	4188-64-1	H	CH_3	H	i-C_3H_7	4.23
10t	4188-65-2	CH_3	H	H	i-C_3H_7	2.75
11c	10034-12-5	H	C_2H_5	H	CH_3	3.33
11t	10034-13-6	C_2H_5	H	H	CH_3	0.574
12c	4884-01-9	H	C_2H_5	H	C_2H_5	8.57
12t	1528-20-7	C_2H_5	H	H	C_2H_5	1.68
13c	16969-28-1	H	C_2H_5	H	i-C_3H_7	10.6
13t	16969-13-4	C_2H_5	H	H	i-C_3H_7	3.22
14	927-61-7	CH_3	CH_3	H	C_2H_5	1.84
15	926-66-9	H	H	CH_3	C_2H_5	0.117
16c	7062-96-6	H	CH_3O	H	CH_3	2.04
16t	7062-97-7	CH_3O	H	H	CH_3	1.19

Table IV. Rate Constants for the Addition of 1 to Vinyl Sulfides, $CH_2{=}CHSR$, at 30 °C in CCl_4

No.	Registry no.	R	10^2k_2, $M^{-1} s^{-1}$
17	1822-74-8	CH_3	1.03
18	627-50-9	C_2H_5	1.20
19	926-65-8	i-C_3H_7	2.29
20	14094-13-4	t-C_4H_9	3.04
21	1822-73-7	C_6H_5	0.274

Table V. Relative Reactivities of Substituted Vinyl Ethyl Ethers in the Sulfenyl Chloride Addition and the Acid-Catalyzed Hydrolysis

No.	Substituent	Addition	Hydrolysis[a]
3	H	1.0	1.0
15	α-CH_3	1.1	$\sim 10^3$
9c	cis-β-CH_3	19	0.39
9t	$trans$-β-CH_3	11	0.12
14	β,β-$(CH_3)_2$	17	0.03
12c	cis-β-C_2H_5	81	0.35
12t	$trans$-β-C_2H_5	16	0.09
16c[b]	cis-β-OCH_3	60	2.0×10^{-3} [c]
16t[b]	$trans$-β-OCH_3	35	0.5×10^{-3} [c]

[a] Reference 6. [b] Relative to **2**. [c] Reference 8.

vinyl ethers in electrophilic reactions and the greater reactivity difference between the ether and sulfide in the hydrolysis.

Phenyl vinyl ether (**8**) and sulfide (**21**) showed essentially the same reactivity. Similar results were found in the hydrolysis; **8** is only several times more reactive than **21**.[10] Involvement of the phenyl group in the conjugation may moderate the above stabilization effects of the O and S lone pairs.

The rate constants of alkyl vinyl ethers and sulfides are plotted against Taft's σ^* values[13] of alkyl groups in Figure 1. Both alkyl vinyl ethers and sulfides increase in their reactivities in the order $CH_3 < C_2H_5 < i\text{-}C_3H_7 < t\text{-}C_4H_9$, ρ^* being -5.4 and -1.7, respectively. The reactivity increases with the increasing electron release of the alkyl group. Similar trends are seen in the data of Table III with alkyl propenyl and butenyl ethers. These results are reasonably understood by the stability of a positively charged transition state **23**, although the ground-state electronic structure deduced from the NMR spectral investigations[9,14] is not straightforward. The absolute magnitude of ρ is greater for the ethers than for the sulfides.

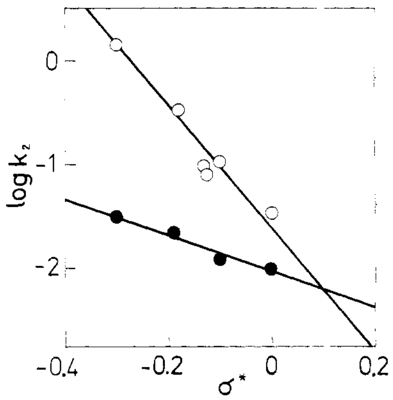


Figure 1. Correlations of the rate constants, k_2, with Taft's σ^* values: (○) vinyl ethers; (●) vinyl sulfides.

Similar results were found in the hydrations of alkyl ethynyl ethers[15] and sulfides[16] as well as in the hydrolysis of aryl vinyl ethers and sulfides.[10] The difference in the efficiency of electronic transmission between the O and S atoms may be attributed to their lone pair electrons in 2p and 3p orbitals. Anomalies found in the hydrolysis of alkyl vinyl sulfides ($\rho^* > 0$)[9] were not observed here in the sulfenyl chloride addition.

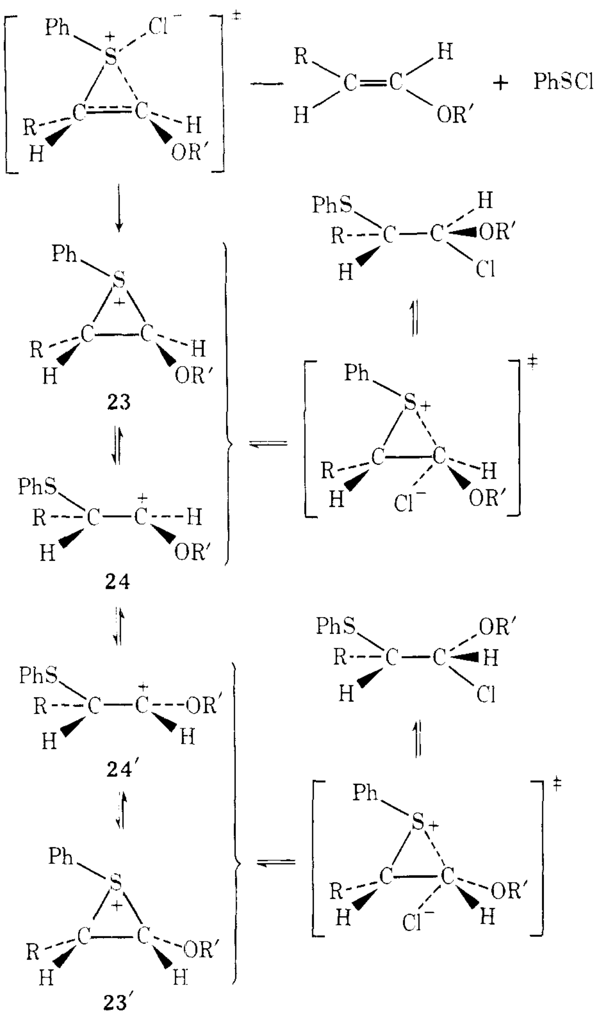
The Effects of Vinyl Substitution on the Reactivity of Vinyl Ether. The effects of alkyl and alkoxy substitutions of the vinyl hydrogen are found in the data summarized in Table III. The results are compared with those observed for the acid-catalyzed hydrolysis (Table V). A contrasting tendency between the two electrophilic reactions is apparent in Table V. Thus, the β substituents enhance the reactivity in the sulfenyl chloride addition while they reduce the hydrolysis reactivity of vinyl ether.[6] The α-methyl group has little effect on the former while it enhances greatly the latter.[17]

The reactivities in the hydrolysis were rationalized by the relative stabilities of an intermediate carbonium ion like **24**.[6] A β-methyl substitution diminishes the hyperconjugative stabilization of **24**, while an α-methyl substitution enhances it.[6] A β-methoxy group contributes greatly to the stabilization of the ground state but destabilizes the transition state by the inductive electron attraction.[8]

On the contrary, both the alkyl and alkoxy substitutions would increase the stability of the transition state like **23** of the sulfenyl chloride addition by the net electron donation to the double bond of vinyl ether. In the transition state, the charge transfer interaction between the double bond and the electrophilic sulfenyl sulfur atom must be important to its stability.[18] Small effects of α-methyl substitution may be due to the polarity of the double bond. The charge transfer interaction may be greater with the less polar electron-rich double bond of the β-substituted vinyl ether. In the β,β-disubstituted ether (**14**), a second methyl group seems to have little effect on the reactivity. This would be attributed to the concurrent inverse steric effect. Rate-enhancing effects of alkyl substitutions were previously noted with some alkenes.[19]

With β-monosubstituted vinyl ethers, cis isomers are 1.5–6 times more reactive than the corresponding trans isomers. The greater reactivity of cis isomer in electrophilic additions to olefins has been generally observed with a large variety of olefins and reactions[12,20] and is attributed to the favorable Coulombic interaction between the olefin and the electrophile in the transition state.[12] The present results are new additions to the data of a previously observed trend.

In conclusion, the reactivities of vinyl ethers and sulfides in the sulfenyl chloride addition can be rationalized by assuming a symmetrically bridged transition state like **23**.



Orientation and Stereochemistry of the Addition. The structure of adducts was determined by the hydrolysis experiments and by the ^{1}H NMR spectroscopy. All the adducts were exclusively of the Markownikoff type. Analysis of the adducts from a propenyl ether showed that the anti addition is favored at lower temperatures while the adducts rearrange to the thermodynamic mixture of the erythro and threo isomers at room temperature.

These results indicate that the rotation barrier of an intermediate is not high enough to attain the stereospecificity of addition. As the kinetic results suggested, the transition state of the rate-determining step resembles the bridged sulfonium ion **23**. After this step, an open ion **24** is formed, and the product-determining transition state may be of unsymmetrically bridged structure. This results in the formation of regiospecific (Markownikoff) but nonstereospecific adducts. Whether trapping of the intermediate by chloride ion occurs with a bridged or open ion, **23** or **24**, is not obvious at the present stage although the equilibrium concentration of **23** must be greater than **24**.

Similar observations have recently been made by Schmid and Nowlan[2] with 1-(p-alkoxyphenyl)propenes. The present results show more clearly the situation with olefins directly conjugated with an alkoxy group.

Registry No.—Phenylthioacetaldehyde, 66303-55-7; phenylthioacetaldehyde-DNP, 66303-53-5; α-phenylthiopropionaldehyde, 55064-96-5; α-phenylthiopropionaldehyde-DNP, 66303-54-6.

References and Notes

(1) For reviews, see (a) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems", Elsevier, New York, N.Y., 1966, pp 166–173; (b) N. Kharasch, "Organic Sulfur Compounds", Vol. 1, Pergamon Press, New York, N.Y., 1971, pp 375–396; (c) R. C. Fahey, *Top. Stereochem.*, **3**, 63 (1968); (d) W. H. Mueller, *Angew. Chem., Int. Ed. Engl.*, **8**, 482 (1969); (e) G. H. Schmid and D. G Garratt in "The Chemistry of Double-Bonded Functional Groups", S. Patai, Ed., Wiley, New York, N.Y., 1977, pp 828–854.

(2) (a) G. H. Schmid and V. J. Nowlan, *J. Org. Chem.*, **37**, 3086 (1972); (b) *Can. J. Chem.*, **54**, 695 (1976).

(3) T. Okuyama, K. Ohashi, K. Izawa, and T. Fueno, *J. Org. Chem.*, **39**, 2255 (1974).

(4) W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, **90**, 2075 (1968).

(5) H. Yuki, K. Hatada, K. Nagata, and K. Kajiyama, *Bull. Chem. Soc. Jpn.*, **42**, 3546 (1969).

(6) T. Okuyama, T. Fueno, H. Nakatsuji, and J. Furukawa, *J. Am. Chem. Soc.*, **89**, 5826 (1967).

(7) T. Fueno, I. Matsumura, T. Okuyama, and J. Furukawa, *Bull. Chem. Soc. Jpn.*, **41**, 818 (1968).

(8) T. Okuyama and T. Fueno, *J. Polym. Sci., Part A-1*, **9**, 629 (1971).

(9) T. Okuyama, M. Nakada, and T. Fueno, *Tetrahedron*, **32**, 2249 (1976).

(10) T. Okuyama, M. Masago, M. Nakada, and T. Fueno, *Tetrahedron*, **33**, 2379 (1977).

(11) G. Dana, O. Convert, and C. Perrin, *J. Org. Chem.*, **40**, 2133 (1975).

(12) T. Okuyama and T. Fueno, *J. Org. Chem.*, **39**, 3156 (1974); part XV of this series.

(13) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, Chapter 13; *J. Am. Chem. Soc.*, **79**, 1045 (1957).

(14) K. Hatada, K. Nagata, and H. Yuki, *Bull. Chem. Soc. Jpn.*, **43**, 3195 (1970); B. A. Trofimov, G. A. Kalabin, V. M. Bzhesovsky, N. K. Gusarova, D. F. Kushnarev, and S. V. Amossova, *Org. React. (USSR)*, **11**, 367 (1974).

(15) E. J. Stamhuis and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, **82**, 394 (1963).

(16) H. Hogeveen and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, **82**, 375 (1963).

(17) P. Salomaa, A. Kankaanpera, and M. Lajunen, *Acta Chem. Scand.*, **20**, 1790 (1966).

(18) K. Izawa, T. Okuyama, and T. Fueno, *Bull. Chem. Soc. Jpn.*, **47**, 1480 (1974).

(19) Reference 1e, p 830.

(20) R. Bolton in "Comprehensive Chemical Kinetics", Vol. 9, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, Amsterdam, 1973, Chapter 1.