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Rearrangement and *trans*-Elimination contrary to the Chugaev Reaction Rule. XIII.[1] Solvent Effect on Rearrangement Reaction of Allylic Xanthates and a Correction of the Former Report[2a,b]

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To provide an additional evidence which confirms the concerted mechanism postulated[2] for the thermal rearrangement reaction of allylic xanthates, the kinetic study on the rearrangement of them was conducted in a variety of solvent. The rearrangement showed a first order process with relatively low sensitivity to the ionizing power of the medium indicating that it proceeds by a mechanism which involves very little change in charge separation between the ground state and the transition state.

In addition, this paper includes the correction of the former report[2a,b] referring to the product formation in the thermolysis of cinnamyl S-methyl xanthate.

In the past, solvolysis reaction of esters of allylic alcohols accompanying allylic rearrangement have been extensively studied.[4] As an outcome, it was proposed that in polar solvents the allylic rearrangement proceeds through an ion pair intermediate like A shown in Fig. 1. On the other hand, in relatively more nonpolar solvents such as chlorobenzene it seemed difficult to distinguish between an ion pair and a more concerted mechanism from the existing data. However, it was suggested[5] considering the sensitivity of such rearrangement to the ionizing power of the medium that such reactions proceed probably through a highly polar transition state. On such a mechanistic background of the allylic rearrangement, Smith[6] studied the rearrangement of allylic thionbenzoates to thiolbenzoates in a variety of solvents. As a conclusion, it was pointed out that, as the reactions showed low sensitivity to the ionizing power of solvents, they might proceed through a cyclic mechanism where is just a small difference in charge separation between ground state and transition state (See B in Fig. 1 for the intermediate).

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[1] Part XII: K. Harano and T. Taguchi, *Yakugaku Zasshi*, **94**, 1495 (1974).

[2] *a*) T. Taguchi, Y. Kawazoe, K. Yoshihira, H. Kanayama, M. Mori, K. Tabata, and K. Harano, *Tetrahedron Letters*, **1965**, 2717; *b*) K. Harano, and T. Taguchi, *Chem. Pharm. Bull.* (Tokyo), **20**, 2348 (1972); *c*) *Idem*, *ibid.*, **20**, 2357 (1972).

[3] Location: *Maedashi, Higashiku, Fukuoka.*

[4] Summarizing discussions may be found in *a*) P. B. D. de la Mare, "Molecular Rearrangements," Part 1, ed. by P. de Mayo, Interscience Publishers, Inc., New York, 1963, pp. 27—110; *b*) R.H. DeWolfe and W.G. Young, "The Chemistry of Alkenes," ed. by S. Patai, Interscience Publishers, Inc., London, 1964, pp. 681—738.

[5] *a*) S. Winstein and G.C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958); *b*) S.G. Smith, A.H. Fainberg, and S. Winstein, *ibid.*, **83**, 618 (1961).

[6] S.G. Smith, *J. Am. Chem. Soc.*, **83**, 4285 (1961).

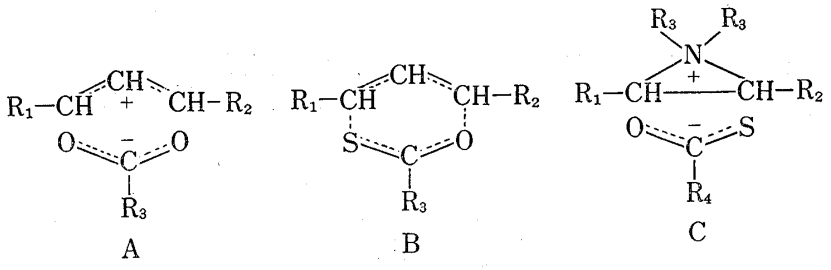

Fig. 1

In continuation with studies on rearrangement of xanthates to dithiolcarbonates anchimerically assisted,[2,7] the authors have reported[2] the rearrangement of allylic xanthates to dithiolcarbonates which, it was deduced by the following observations, proceeds through such a cyclic intermediate as B in Fig. 1: 1) A pair of xanthates which are in position isomerism each other converted not to same dithiolcarbonate, but to isomeric dithiolcarbonates with allylic shift by thermal treatment. 2) Heating of a mixture of xanthates of two kinds did not give any product of crossover reaction. Thus, on the basis of product formation it was suggested that this case is mechanistically closely similar to the case of the thionbenzoates.[6] To get an additional support for the mechanistic consideration, the solvent effect produced on the rearrangement of allylic xanthates was examined in the present study by treating them in various solvents. At the same time, the same examination was done about the rearrangement of 2-diethylaminoethyl S-methyl xanthate[7a] in contrast to the case of allylic system, because the former case has been presumably shown with some proofs[7a,b] as an example of rearrangement which progresses *via* an ion pair intermediate (C in Fig. 1).

Incidentally during this investigation, an error was found in description of the former report[2a,b] which treated the product formation in the thermolysis of cinnamyl S-methyl xanthate. The correction of this error is an additional purpose of the present report.

Material and a Correction of the Former Report[2a,b]

Allyl[2b] and 2-diethylaminoethyl[7a] S-methyl xanthates were synthesized by adaptation of the known method and purified by column chromatography on silica gel without submitting to distillation,[8] because distillation caused the rearrangement of them as have been reported. As the former report[2b] informed, cinnamyl S-methyl xanthate has not been able to be isolated in pure state. The reason arises originally from imcomplete sodium salt formation of cinnamyl alcohol which causes the contamination of products in the latter process introducing to the xanthate. Helplessly, impure cinnamyl S-methyl xanthate had been submitted to thermolysis followed by hydrolysis and then oxidation isolating a small quantity of cinnamyl disulfide. Thus, it was presumably concluded by the detection of the disulfide that the rearrangement of cinnamyl S-methyl xanthate to cinnamyl methyl dithiolcarbonate might be involved in the reaction course and occur on the same carbon *via* S_Ni. However, recently it was revealed that the dithiolcarbonate arised not from the rearrangement of the xanthate, but from another pathway.[1] Hence, to know exactly that cinnamyl S-methyl xanthate converts thermally to any compound, the preparation of pure material of the xanthate was wanted and succeeded as follows.

Cinnamyl alcohol was treated with carbon disulfide in dimethyl sulfoxide (DMSO) containing potassium hydroxide to afford sodium cinnamyl xanthogenate. After adding water,[9] the mixture was treated with methyl iodide to yield cinnamyl S-methyl xanthate in crystalline state, mp 46—48° in 70% yield. The pure material thus obtained was pyrolyzed to afford 1-phenylallyl methyl dithiolcarbonate through rearrangement with allylic shift, pointing out an error in the description of this matter in the former report.[2a,b]

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[7] *a*) T. Taguchi and M. Nakao, *Tetrahedron*, **18**, 245 (1962); *b*) T. Taguchi, Y. Kawazoe and M. Nakao, *Tetrahedron Letters*, **1963**, 131; *c*) K. Yoshirira and T. Taguchi, *Yakugaku Zasshi*, **89**, 1225 (1969); *d*) M. Mori and T. Taguchi, *ibid.*, **89**, 1496 (1969); *e*) M. Mori, H. Kanayama, K. Tabata, and T. Taguchi, *ibid.*, **89**, 1631 (1969); *f*) Y. Kawazoe and T. Taguchi, *ibid.*, **92**, 677 (1972).

[8] It was reported that allyl S-methyl xanthate could be isolated by low temperature distillation without isomerization; C. Christophersen and A. Holm, *Acta Chem. Scand.*, 24, 1512 (1970).

[9] If this operation is omitted, cinnamyl methyl dithiolcarbonate will be formed, see Exp. section and ref. 1.

Results in Kinetic Studies and Discussion

Xanthates display generally ultraviolet (UV) absorptions at 280 nm (log $\varepsilon_{\max}\simeq4$) and 360 nm (log $\varepsilon_{\max}\simeq2$) due to π-π^* and n-π^* transition respectively and on the other hand, dithiolcarbonates at 250 nm (log $\varepsilon_{\max}\simeq3.7$). Fig. 2 shows UV spectral change as a function of time upon heating allyl S-methyl xanthate in ethanol at 76°.

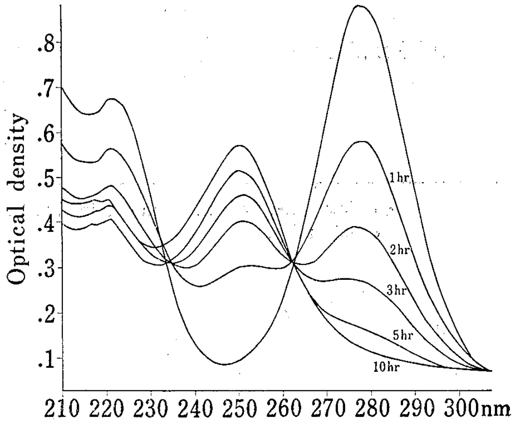

Fig. 2. UV Spectral Change with the Lapse of Time for the Rearrangement of Allyl S-Methyl Xanthate in Ethanol at 76°

The rate of reaction was determined by measuring the decrease of the absorbance at 360 nm. The first order rate constant (k) was calculated from multiplying slope of a plot of $\log(A_t-A_\infty)/(A_0-A_\infty)$ *versus* time by -2.303, where A_t is the absorbance at time t and A_∞ is the absorbance after about ten half-lives.

In this solvent the satisfactory first order behavior of the reaction was observed and it was same also in other solvents (See Table I). Experimental activation energies (Ea) and the frequency factors (s) were calculated for the rearrangement of allyl S-methyl xanthate from the Arrhenius theory, $k=s\exp(-Ea/\boldsymbol{R}T)$, by aid of the rate constants at varying temperatures which are shown in Table II. Then, the entropies of activation ($\Delta S^{\neq}$) were calculated from the equation[10] for the absolute reaction rates, $k=\kappa ek'T/h\exp(\Delta S^{\neq}/\boldsymbol{R})\exp(-Ea/\boldsymbol{R}T)$ (See Table II).

TABLE I. Rearrangement Rate Constant for Some Xanthate ($\mathrm{RO\underset{\underset{S}{\|}}{C}SCH_3}$) in Various Solvents at 76±0.05°

Solvent	E_T value	$k\times10^5$ sec^{-1} (log k)		
		CH_2=$CHCH_2$–	C_6H_5CH=$CHCH_2$–	$(C_2H_5)_2NCH_2CH_2$–[a]
$(CH_2OH)_2$	56.3	27.3(−3.56)		
80%C_2H_5OH	53.6	13.3(−3.88)		
C_2H_5OH	51.9	5.90(−4.23)		
(CH_3COOH)	(51.9)	(7.15(−4.15))		
iso-$C_5H_{11}OH$	47.0	4.55(−4.34)		
CH_3CN	46.0	10.9(−3.96)		
tert-C_4H_9OH	43.9	4.63(−4.33)		
Dimethylformamide	43.8	12.3(−3.91)	130(−2.88)[b]	
$CH_3COOC_2H_5$	38.1	3.92(−4.41)	21.0(−3.68)[b]	
C_6H_5Br	37.5			29.2(−3.54)
p-Dioxane	36.0		19.7(−3.71)[b]	29.8(−3.53)
$(C_6H_5)_2O$	35.3			18.7(−3.73)
C_6H_6	34.5	3.18(−4.50)	9.95(−4.00)[b]	9.93(−4.00)
$C_6H_5CH_3$	33.9			4.78(−4.32)
CCl_4	32.5			0.60(−5.22)
n-Hexadecane	30.9[c]	1.29(−4.89)	2.68(−4.57)[b]	*ca.* 0.11(−5.97)

[a] Treatment of 2-diethylaminoethyl S-methyl xanthate in protic solvents caused desulfurization to give 2-diethylaminoethyl S-methyl thiolcarbonate.
[b] value at 66°
[c] The value of *n*-hexane was applied.

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[10] S. Glasstone, K. Laidler, and H. Eyring, "The Theory of Rate processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 295.

TABLE II. Activation Parameters for the Rearrangement of Allyl S-Methyl Xanthate

Solvent	Temp. (°C)	$k\times10^6$ (sec^{-1})	Ea (kcal. mole^{-1})	$s\times10^{-11}$ (sec^{-1})[a]	$\Delta S^{\neq}$ (e.u.)[a]
C_2H_5OH	50	2.95	26.3	17.6	−4.8
	58	7.80			
	66	21.7			
	76	59.0			
n-Hexadecane	66	4.58	25.8	1.77	−9.4
	76	12.9			
	85	35.0			
	90	56.7			

a) Calculated from the data obtained at 76° by making the usual assumption that the transmission coefficient (k) equals unity.

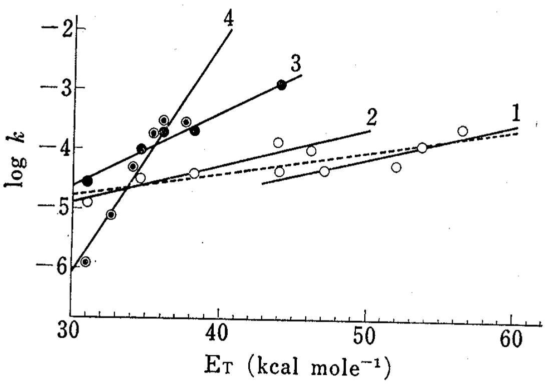

Fig. 3. Plot of log$k$ for Rearrangement against E_T Value

1: allyl S-methyl xanthate (in protic solvent)
2: allyl S-methyl xanthate (in aprotic solvent)
3: cinnamyl S-methyl xanthate (in aprotic solvent)
4: 2-diethylaminoethyl S-methyl xanthate (in aprotic solvent)
See Table I for solvents used.

To know the effect of solvent on the rate of this rearrangement, the E_T values of Dimroth,[11] based on the bands of solvatochromism of pyridinium N-phenolbetaines, was used as a scale of solvent ionizing power because it is obtained with a wider variety of solvents than the other known scales[5b,12,13] and moreover has a linear relationship with the rates of ionization of *p*-methoxyneophyl toluenesulfonate.[5b]

As illustrated in Fig. 3, plots of log k versus E_T values for allyl, cinnamyl and 2-diethylaminoethyl S-methyl xanthates showed the linear relationship in each case (log $k = aE_T + b$). The least squares slopes a are summarized in Table III.

However, examining precisely the slope a (3.90×10^{-2}, recorded by dotted line) which was obtained in ten solvents of each sort for allyl S-methyl xanthate, it is found that there are differences of rates by two or threefold between iso-pentanol and acetonitrile and between *tert*-butanol and dimethylformamide in spite that they have little different E_T values each other. This may be attributed to presence or absence of solvation[14] due to properties of solvents, either aprotic or protic. Hence, plotting log k *versus* E_T value separately with such the two sorts of solvents, there were obtained two straight lines which showed the least squares slopes a of the almost same magnitude (See (1) and (2) in Fig. 3). This a value is higher than the value which was obtained in solvents irrespective of aprotic and protic (dotted line in Fig. 3). Therefore, the a value obtained in a series of aprotic solvents was chosen as the solvent sensitivity parameter in the present study (Table III) (See also footnote b in Table I for the reason why this a value was chosen). As be seen in Table III, a value is

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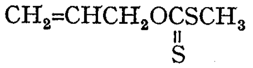
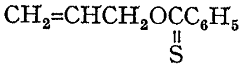
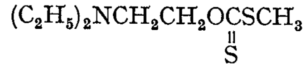
11) K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Ann. Chem.*, **661**, 1 (1963); K. Dimroth, C. Reichardt and A. Schweig, *ibid.*, **669**, 95 (1963); C. Reichardt, *Angew. Chem.*, **77**, 30 (1965).
12) E.M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253, 3261, 3267 (1958).
13) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948); S. Winstein, E. Grunwald, and H.W. Jones, *ibid.*, **73**, 2700 (1951); A.H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).
14) S.R. Rao, "Xanthates and Related Compounds," Marcel Dekker ,Inc., New York, 1971, pp. 183—188; For example, allyl S-methyl xanthate absorbs at 354.5 nm in *n*-hexane and 351 nm in ethylene glycol.

TABLE III. Sensitivity of Thion to Thiol Isomerization to Solvent Ionizing Power in Several Cases

Substrate	Solvent system	log $k=a\mathrm{E_T}+b$		Correlation, γ coefficient
		$a\times10^2$	b	
 $CH_2{=}CHCH_2O\underset{\overset{\|}{S}}{C}SCH_3$	—	3.90	−5.94	0.845
	protic[a]	5.92	−7.06	0.876
	aprotic[a]	6.31	−6.77	0.975
 $C_6H_5CH{=}CHCH_2O\underset{\overset{\|}{S}}{C}SCH_3$	aprotic[a]	12.6	−8.40	0.988
 $CH_2{=}CHCH_2O\underset{\overset{\|}{S}}{C}C_6H_5$	aprotic[b]	4.24	−6.25	0.971
 $CH_3CH{=}CHCH_2O\underset{\overset{\|}{S}}{C}C_6H_5$	aprotic[b]	5.96	−6.21	0.982
 $(C_2H_5)_2NCH_2CH_2O\underset{\overset{\|}{S}}{C}SCH_3$	aprotic[a]	40.3	−18.2	0.952

a) See Table I for solvents used.

b) Based on rearrangement rates[6] in CH_3CN, $(CH_3)_2CO$, C_6H_5Cl, $(CH_2)_4O$ and cyclo-C_6H_{12}.

6.31×10^{-2} for allyl S-methyl xanthate, 12.6×10^{-2} for cinnamyl S-methyl xanthate and 40.3×10^{-2} for 2-diethylaminoethyl S-methyl xanthate.

Incidentally, checking relative rate of each of these xanthates in the reactions conducted in *n*-hexadecane and ethyl acetate, it is 1: 3 for the allyl ester, 1: 8 for the cinnamyl ester and 1: 650 for the 2-diethylaminoethyl ester suggesting difference of sensitivity to the nature of solvents. In fact, *a* in the case of allyl S-methyl xanthate is small and very similar to the value in the case of allyl thionbenzoate.[6] This tells us that allyl S-methyl xanthate may rearrange by a mechanism which involves very little change in charge separation between the ground state and the transition state.[8] Moreover, it supports this conclusion that the activation parameters in *n*-hexadecane, *Ea* 25.8 kcal/mole $\Delta S^{\neq}-9.4$ e.u., are close to values of the same parameter in the rearrangement of allyl thionbenzoate[15] and allyl thiocyanate.[16]

In the case of cinnamyl S-methyl xanthate, it afforded the rearrangement product by S_Ni' and the reaction is about eight times faster in ethyl acetate than in *n*-hexadecane indicating that it proceeds through a mechanism with more ionic character than that in the reaction of allyl S-methyl xanthate.

Now, the S_Ni' mechanism is supposed to involve either a onestage, concerted process or ionization to a rigidly oriented intimate ion pair followed by internal return to give rearrangement product.[4] Allylic rearrangement of 1-phenylallyl-3,4,5-tribromobenzoate[17] has been proposed[5b,18] as an example of S_Ni' *via* a rigidly oriented intimate ion pair. As *a* value of this reaction ($a=13.5\times10^{-2}$) is very similar to the value of the case of cinnamyl S-methyl xanthate, both reactions seem to be closely related type of reaction.

On the other hand, *a* value in the rearrangement of 2-diethylaminoethyl S-methyl xanthate is much greater than the value in solvolysis of *p*-methoxyneophyltoluenesulfonate ($a=17.9\times10^{-2}$).[5b,11] This suggests that the rearrangement occurs through highly polarized transition state such as an ion pair which has been proposed previously with some evidences.[7a,b]

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15) K.D. McMichael, *J. Am. Chem. Soc.*, **89**, 2943 (1967).

16) P.A.S. Smith and D.W. Emerson, *J. Am. Chem. Soc.*, **82**, 3076 (1960).

17) J. Meisenheimer, W. Schmide, and G. Schäfer, *Ann.*, **501**, 131 (1933).

18) H.L. Goering and M.M. Pombo, *J. Am. Chem. Soc.*, **82**, 2515 (1960).

Experimental

All melting and boiling points were uncorrected. Infrared (IR) spectra were recorded with a JASCO DS-70G spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained with a Nihon Denshi C-60H spectrophotometer at 60 MHz using tetramethylsilane as an internal standard. Ultraviolet spectra were obtained with a Hitachi EPS-3T automatic recording spectrophotometer.

Solvent——Carbon tetrachloride, dimethylformamide and ethyl acetate, Kishida Kagaku Co. spectrograde, were used directly; acetonitrile, Tokyo Kasei Co. spectrograde, was used directly; *n*-hexadecane, diphenyl ether and ethylene glycol, Tokyo Kasei Co. guaranteed reagents, were redistilled; ethanol, Japan Alcohol Monopoly Co. absolute, was used directly; *tert*-butanol, iso-pentanol, and acetic acid were redistilled; benzene, toluene and 1,4-dioxane were dried with sodium wire and redistilled; bromobenzene was dried with phosphorus pentoxide and redistilled.

Materials——Allyl[2b] and 2-diethylaminoethyl[7a] S-methyl xanthates were prepared according to the previously described method respectively and purified by column chromatography on silica gel.

Cinnamyl S-Methyl Xanthate——To a suspension of powdered sodium hydroxide or pellets of potassium hydroxide (0.05 mole) in DMSO (30 ml) was added, all at once, a mixture of cinnamyl alcohol (0.05 mole) and carbon disulfide (0.05 mole) and the contents were stirred vigorously for 3 hr to get a clear solution. To the resulting red solution were added cold water (50 ml) and then methyl iodide (0.06 mole) under ice-cooling. After stirring overnight at room temperature, an appearing solid was collected and washed with water. Recrystallization from *n*-hexane gave pale yellow needles, mp 46—48°, yield 70%. *Anal.* Calcd. for $C_{11}H_{12}OS_2$: C, 58.92; H, 5.40. Found: C, 58.58; H, 5.39. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1221 and 1054 $(-\underset{\underset{\text{S}}{\|}}{\text{OCS}}-)$, 966 (*trans*-CH=CH–). NMR (in CCl_4) δ: 2.55 (3H, singlet, $-SCH_3$), 5.20 (2H, doublet, $J=6$ Hz, $-CH_2S-$), 6.30 (1H, triplet of doublet, $J=16$ Hz, =CH–C–S–), 6.68 (1H, doublet, $C_6H_5CH=$), 7.28 (5H, multiplet, C_6H_5-).

In this operation, when an addition of water to the reaction solution before methylation of the xanthogenate was omitted, it afforded cinnamyl methyl dithiolcarbonate which was distilled under 0.27 mmHg at bath temperature of 100—105°, yield 46%. *Anal.* Calcd. for $C_{11}H_{12}OS_2$: C, 58.92; H, 5.40. Found: C, 58.74; H, 5.48. IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 1644 and 867 $(-\underset{\underset{\text{O}}{\|}}{\text{SCS}}-)$, 964 (*trans*-CH=CH–). NMR (in CCl_4) δ:2.41 (3H, singlet, $-SCH_3$), 3.77 (2H, doublet, $J=7$ Hz, $-CH_2S-$). 6.08 (1H, triplet of doublet, $J=16$ Hz, =CH–C–S–), 6.55 (1H, doublet, $C_6H_5CH=$), 7.24 (5H, multiplet, C_6H_5-).

Thermal Rearrangement of Cinnamyl S-Methyl Xanthate to 1-Phenylallyl Methyl Dithiolcarbonate——100 mg of cinnamyl S-methyl xanthate was placed in a micromolecular distillation apparatus and heated at 100° in oil bath until the completion of reaction had been recognized by UV spectrometry. After heating at 85° additionally for 0.5 hr, the pressure was reduced (0.27 mmHg) to vaporize 1-phenylallyl methyl dithiolcarbonate, pale yellow liquid, yield quantitative.

Also, the use of solvents such as acetic acid and benzene for this reaction brought the same result. *Anal.* Calcd. for $C_{11}H_{12}OS_2$: C, 58.92; H, 5.40. Found: C, 59.15; H, 5.14. IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 1642 and 868 $(-\underset{\underset{\text{O}}{\|}}{\text{SCS}}-)$, 926 and 982 $(-CH=CH_2)$. NMR (in CCl_4) δ: 2.39 (3H, singlet, $-SCH_3$), 4.90—5.50 (3H, complex, $H_2C=$ and $\rangle$CHS–), 6.11 (1H, doublet of double doublet, $J_{\text{H-C-C-H}}=7$ Hz, $J_{\text{cis}}=10$ Hz, $J_{\text{trans}}=17$ Hz, –CH=), 7.27 (5H, multiplet, C_6H_5-). In the NMR spectrum of this sample, any signal ascribable to the isomeric dithiolcarbonate $(C_6H_5CH=CHCH_2S\underset{\underset{\text{O}}{\|}}{C}SCH_3)$, inclusive of the methylene proton signal at 3.77 ppm ($J=7$ Hz, doublet), was not observed entirely indicating that the product was freed from the isomeric dithiolcarbonate.

Kinetic Run——A solution (approx. 0.01 mole) of a xanthate in the given solvent was prepared in a volumetric flask. The solution was then pipetted into glass stoppered test tubes in quantity of approximately 3.0 ml per tube. The tubes were sealed with a ground glass stopper and then immersed in a constant temperature bath controlled to ±0.05°. After chosen times, tubes were removed from the bath and cooled. Reaction rates were determined by measuring the visible absorption of the xanthate at 360 nm using a Hitachi Model EPS-3T automatic recording spectrophotometer (See Table I and II).

Acknowledgement The authors are indebted to the staff of the analysis room of this faculty for elemental analyses and measurements of IR and NMR spectra.