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# Rearrangement and *trans*-Elimination contrary to the Chugaev Reaction Rule. VIII.[1a] Thermal Rearrangement of 2-Alkenyl S-Alkyl Xanthate[2]

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In general, S-alkyl xanthates of 2-alkenol thermally rearranged to the dithiolcarbonates accompanying allylic shift. When a mixture of two xanthates having different S-alkyl and O-alkenyl groups is allowed to rearrange thermally, no crossover products are obtained. A pair of position isomers did not transform to a same product, but to isomeric products with allylic shift respectively. 3-Aryl-substituted allylic xanthates, on the other hand, rearrange to the corresponding dithiolcarbonates without allylic shift. On the basis of these findings, mechanisms of the transformations are discussed.

In the foregoing papers,[1b,2,4] it was reported that alkyl xanthates, thionobenzoates and thionocarbamates rearranged thermally to the corresponding dithiolcarbonates, thiolbenzoates and thiolcarbamates respectively when they hold an anchimeric group such as dialkylamino or alkylthio at the neighbourhood of the thionic ester group. This rearrangement reaction offered some interesting problems in the mechanistic and preparative views, especially in connection with the Chugaev reaction and accordingly, it led to the present study where pyrolyses of 2-alkenyl S-alkyl xanthates were attempted.

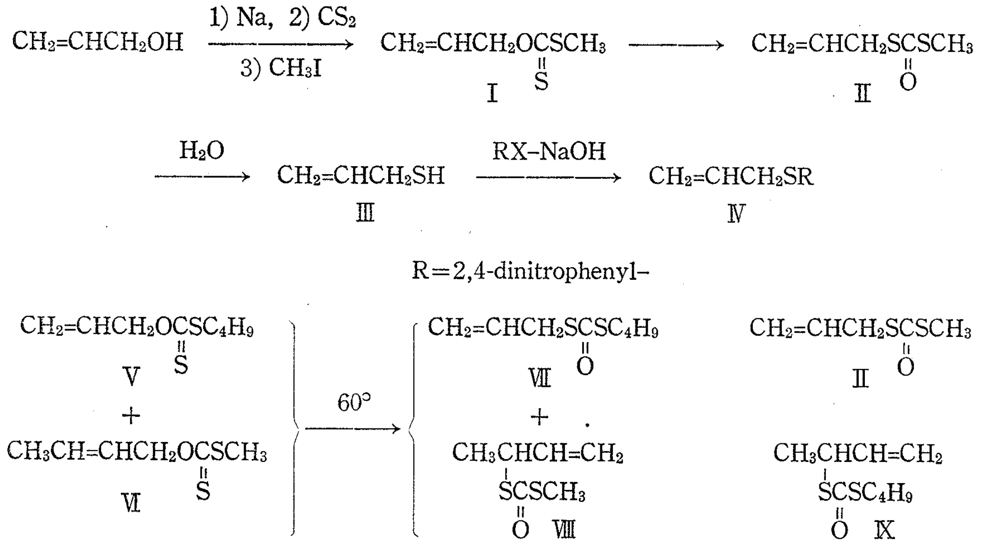

Chart 1

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[1] *a*) This forms "Studies in Stereochemistry. XLVII," by T. Taguchi; *b*) Part VI: M. Mori, H. Kanayama, K. Tabata and T. Taguchi, *Yakugaku Zasshi*, **89**, 1631 (1969); Part VII: Y. Kawazoe and T. Taguchi, *ibid.*, **92**, 677 (1972).

[2] Parts of this work have appeared in preliminary forms: *a*) T. Taguchi and M. Nakao, *Tetrahedron*, **18**, 245 (1962); *b*) T. Taguchi, Y. Kawazoe, K. Yoshihira, H. Kanayama, M. Mori, K. Tabata and K. Harano, *Tetrahedron Letters*, **1965**, 2717.

[3] Location: *Katakasu, Fukuoka.*

[4] K. Yoshihira and T. Taguchi, *Yakugaku Zasshi*, **89**, 1225 (1969).

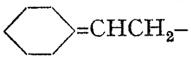
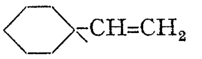
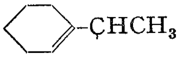
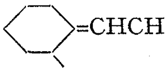
Allyl S-methyl xanthate (I) was first prepared by Oddo and Rosso in 1909.5) They reported that I was readily prepared by distillation (bp 200—203°) of the product which was obtained by the reaction of potassium allylxanthate with dimethyl sulfate.

However, tracing the work of Oddo, we found that even by the low temperature distillation, bp 57° (3 mmHg), I rearranged to the corresponding dithiolcarbonate (II). An evidence of the rearrangement was provided with the observation that absorption bands at 1217 and 1060 cm$^{-1}$ characteristic of the xanthate group existed in the infrared (IR) spectrum of the product before distillation, but after distillation, the bands disappeared and instead, bands at 1658 and 873 cm$^{-1}$ characteristic of the dithiolcarbonate group appeared. Furthermore, the following two findings support the rearrangement of I to II and accordingly the structure of II: 2,4-dinitrochlorobenzene reacted with the product (III) obtained by alkaline hydrolysis of II to give allyl 2,4-dinitrophenyl sulfide (IV) and II did not react with phenylhydrazine6) (Chart 1).

Variation of S-alkyl group of I did not affect the essential feature of the rearrangement (Table I). The research was expanded to pyrolysis of other 2-alkenyl S-methyl xanthates. The xanthates were generally prepared by reactions of carbon disulfide and then methyl iodide with sodium salt of alkenol which was yielded by action of sodium hydride or sodium sand on 2-alkenol.

Table I shows examples in which even *in vacuo*, distillation caused rearrangement of xanthate to dithiolcarbonate accompanying allylic shift.

TABLE I. 2-Alkenyl Alkyl Dithiolcarbonate $\mathrm{RO}\underset{\overset{\|}{\mathrm{S}}}{\mathrm{C}}\mathrm{SR''}\rightarrow\mathrm{R'S}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{SR''}$

| R | R′ | R″ | Yield (%) | bp (°C/mmHg) or mp (°C) | Formula | Analysis | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Calcd. | | Found | |
| | | | | | | C | H | C | H |
| CH$_2$=CHCH$_2$– (I) | R (II) | –CH$_3$ | 84 | 57/3 | $C_8H_8OS_2$ | 40.51 | 5.44 | 40.41 | 5.41 |
| CH$_2$=CHCH$_2$– (V) | R (VII) | –C$_4$H$_9$ | 53 | 81—83/3 | $C_8H_{14}OS_2$ | 50.49 | 7.42 | 50.34 | 7.58 |
| CH$_2$=CHCH$_2$– | R | –CH$_2$C$_6$H$_5$ | 64 | 123—124/3.5 | $C_{11}H_{12}OS_2$ | 58.89 | 5.39 | 59.20 | 5.41 |
| CH$_2$=CHCH$_2$– | R | –CH$_2$COOH | 72 | 67.5—69 | $C_6H_8O_3S_2$ | 37.48 | 4.19 | 37.39 | 4.21 |
| CH$_2$=CHÇHCH$_3$ (XII) | CH$_3$CH=CHCH$_2$– (XIII) | –CH$_3$ | 63 | 86.5/7 | $C_6H_{10}OS_2$ | 44.41 | 6.21 | 44.59 | 6.40 |
| CH$_3$CH=CHCH$_2$– (VI) | CH$_2$=CHÇHCH$_3$ (VIII) | –CH$_3$ | 59 | 76—78/5.5 | $C_6H_{10}OS_2$ | 44.41 | 6.21 | 43.98 | 6.19 |
| CH$_3$CH=CHÇHCH$_3$ | R | –CH$_3$ | 58 | 79—81/2.5 | $C_7H_{12}OS_2$ | 47.69 | 6.86 | 47.78 | 6.74 |
| CH$_3$CH=CHÇHC$_2$H$_5$ | CH$_3$CH$_2$CH=CHÇHCH$_3$ | –CH$_3$ | 69 | 92—94/3 | $C_8H_{14}OS_2$ | 50.49 | 7.41 | 50.67 | 7.28 |
| (CH$_3$)$_2$C=CHCH$_2$– | CH$_2$=CHÇ(CH$_3$)$_2$ | –CH$_3$ | 73 | 69/3 | $C_7H_{12}OS_2$ | 47.69 | 6.86 | 47.45 | 7.20 |
| (CH$_3$)$_2$C=CHÇH–CH$_3$ | (CH$_3$)$_2$ÇCH=CHCH$_3$ | –CH$_3$ | 31 | 80—82/3 | $C_8H_{14}OS_2$ | 50.49 | 7.41 | 50.16 | 7.45 |
| C$_6$H$_{11}$C(CH$_3$)=CHCH$_2$– | C$_6$H$_{11}$Ç(CH$_3$)CH=CH$_2$ | –CH$_3$ | 37 | 118—118.5/3 | $C_{12}H_{20}OS_2$ | 58.96 | 8.25 | 58.86 | 8.44 |
|  |  | –CH$_3$ | 61 | 118/2.5 | $C_{10}H_{16}OS_2$ | 55.51 | 7.45 | 55.72 | 7.63 |
|  |  | –CH$_3$ | 60 | 108/1.5 | $C_{10}H_{16}OS_2$ | 55.51 | 7.45 | 55.37 | 7.39 |
| CH$_3$(CH=CH)$_2$–CH$_2$– (XXI) | CH$_3$CH=CHÇH CH=CH$_2$ (XXII) | –CH$_3$ | 53 | 96—97/2.5 | $C_8H_{12}OS_2$ | 51.03 | 6.42 | 51.18 | 6.55 |

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5) B. Oddo and G. del. Rosso, *Gaz. Chim. Ital.*, **39**, 21 (1909) [*C.A.*, **3**, 1004 (1909)].

6) G. Bulmer and F.G. Mann, *J. Chem. Soc.*, **1965**, 666.

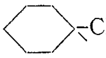
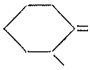
Thus, xanthates could not be purified by distillation, and therefore in cases where their purifications were needed contaminations with inorganic salts and unreacted alcohols were removed from products as far as possible by chromatography on silica gel. IR spectra (Table II) and nuclear magnetic resonance (NMR) spectra (Table III) support the structures assigned for the products remaining after distillation (dithiolcarbonates).

IR spectra of dithiolcarbonates exhibited the characteristic band due to carbonyl group in the vicinity of 1650 cm$^{-1}$.

Additionally ozonolysis of the products and conversion reaction of them to disulfide or 2-alkenyl-2,4-dinitrophenyl sulfide were carried out to confirm the structures further.

Moreover, it was made clear by NMR spectra and gas chromatograms that in each of the whole examples the rearrangement afforded only a 2-alkenyl methyl dithiolcarbonate in no company with any allylic isomer.

Table II. IR Spectra of 2-Alkenyl Alkyl Dithiolcarbonate $\mathrm{R'S}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{SR''}$

| R′ | R″ | $\nu_{CH_2}$ | $\nu_{CH}$ | $\nu_{C=O}$ | $\delta_{CH}$ | $\delta_{CH_2}$ | $\nu_{C-S}$ (cm$^{-1}$) |
|---|---|---|---|---|---|---|---|
| CH$_2$=CHCH$_2$– | –CH$_3$ (II) | 3066 | | 1638 | 990 | 918 | 864 |
| CH$_2$=CHCH$_2$– | –C$_4$H$_9$ (VII) | 3090 | | 1646 | 988 | 922 | 874 |
| CH$_2$=CHCH$_2$– | –CH$_2$C$_6$H$_5$ | | | 1641 | 992 | 925 | 878 |
| CH$_2$=CHCH$_2$– | –CH$_2$COOH | 3074 | | 1641 | 992 | 920 | 868 |
| CH$_2$=CHÇHCH$_3$ | –CH$_3$ (VIII) | 3114 | 3000 | 1649 | 984 | 923 | 873 |
| CH$_3$CH=CHCH$_2$– | –CH$_3$ (XIII) | | 3046 | 1645 | 962 | | 875 |
| CH$_3$CH=CHÇHCH$_3$ | –CH$_3$ | | 3036 | 1647 | 963 | | 864 |
| CH$_3$CH$_2$CH=CHÇHCH$_3$ | –CH$_3$ | | 3038 | 1645 | 972 | | 885 |
| CH$_2$=CHÇ(CH$_3$)$_2$ | –CH$_3$ | 3070 | | 1642 | 990 | 918 | 858 |
| (CH$_3$)$_2$ÇCH=CHCH$_3$ | –CH$_3$ | | 3036 | 1647 | 967 | | 849 |
| C$_6$H$_{11}$Ç(CH$_3$)CH=CH$_2$ | –CH$_3$ | 3066 | | 1643 | 988 | 918 | 856 |
|  –CH=CH$_2$ | –CH$_3$ | 3108 | | 1649 | 987 | 916 | 847 |
|  =CHCH$_3$ | –CH$_3$ | | | 1642 | | | 860 |
| C$_6$H$_5$CH=CHCH$_2$– | –CH$_3$ (XV) | | | 1637 | 962 | | 865 |
| C$_6$H$_5$CH=CHÇHCH$_3$ | –CH$_3$ (XVII) | | | 1645 | 970 | | 870 |
| CH$_3$CH=CHÇHCH=CH$_2$ | –CH$_3$ (XXII) | | | 1640 | 967 | 927 | 864 |

In regard to reaction mechanism, it was concluded on basis of the following findings that the rearrangement proceeds intramolecularly through cyclic intermediate shown as XI. A mixture of allyl S-butyl xanthate (V) and *trans*-2-butenyl S-methyl xanthate (VI) was heated at 60°. As a result, it afforded merely VII and VIII and any crossover product, II or IX, was never detected by gas chromatography (Chart 1). This tells us that the feature of rearrangement is never intermolecular, but intramolecular. Next, results in the rearrangement of a pair of position isomers, 1-methylallyl S-methyl xanthate (XII) and *trans*-2-butenyl S-methyl xanthate (VI), were analyzed in details.

As shown in Table I, VI rearranged to 1-methylallyl methyl dithiolcarbonate (VIII) and XII to *trans*-2-butenyl methyl dithiolcarbonate (XIII) (See also Chart 2).

This finding suggests that rearrangement does not proceed *via* an ion-pair intermediate (X), because, if *via* X, the position isomers, VI and XII, should afford the same result, the formation of VIII and/or XIII. This nature of rearrangement has been found in conversion of allyl thiocyanate to isothiocyanate⁷⁾ and allyl thionobenzoate to thiolbenzoate.⁸⁾ The

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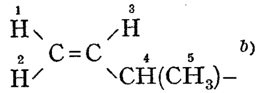
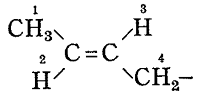
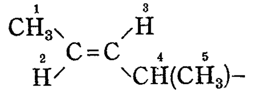
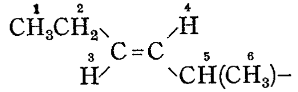
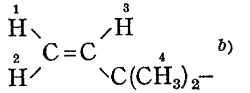
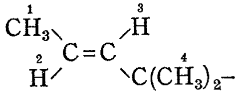
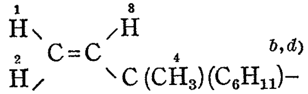
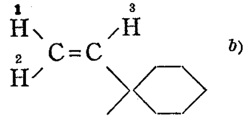
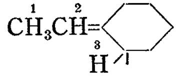
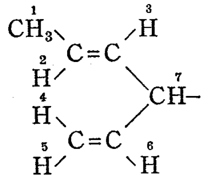
7) P.A.S. Smith and D.W. Emerson, *J. Am. Chem. Soc.*, **82**, 3076 (1960).

8) S.G. Smith, *J. Am. Chem. Soc.*, **83**, 4285 (1961).

Table III. NMR Data of 2-Alkenyl Methyl Dithiolcarbonate $R'S\underset{\underset{O}{\|}}{C}SCH_3$

| R | | Chemical shift(ppm), multiplicity[a] | | | | | | | | Coupling constant, $J$, Hz |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | $SCH_3$ | |
|  [b] | VIII | 5.08 dd | 5.21 dd | 5.91 ddd | 4.30 dq | 1.45 d | | | 2.38 s | $J_{1,2}\doteqdot 1$; $J_{1,3}=11$; $J_{2,3}=17$; $J_{3,4}=6$; $J_{4,5}=7$ |
|  | XIII | 1.71 d | ··· 5.15—6.10m ··· | | 3.60 d | | | | 2.40 s | $J_{1,2}=5.3$; $J_{3,4}=6$ |
|  | | 1.70 d | ··· 5.0—6.0m ··· | | 4.30 dq | 1.40 d | | | 2.38 s | $J_{1,2}=4.5$; $J_{2,3}=16$[c]; $J_{3,4}=6$; $J_{4,5}=7.5$ |
|  | | 0.99 t | 2.02m | ··· 5.18—5.95m ··· | | 4.25 dq | 1.41 d | | 2.37 s | $J_{1,2}=7.5$; $J_{3,4}=15$[c]; $J_{4,5}=5.5$; $J_{5,6}=7$ |
|  [b] | | 5.03 dd | 5.13 dd | 6.08 dd | 1.57 s | | | | 2.32 s | $J_{1,2}=1.3$; $J_{1,3}=10$; $J_{2,3}=17$ |
|  | | 1.71 d | ··· 5.4—5.7m ··· | | 1.56 s | | | | 2.32 s | $J_{1,2}=4.5$; $J_{1,3}\doteqdot 1$; $J_{2,3}=0$[c] |
|  [b,d] | | 5.16 dd | 5.17 dd | 6.09 dd | 1.59 s | | | | 2.33 s | $J_{1,2}\doteqdot 1$; $J_{1,3}=10.5$; $J_{2,3}=18$ |
|  [b] | | 5.13 dd | 5.16 dd | 6.07 dd | | | | | 2.30 s | $J_{1,2}=1.3$; $J_{1,3}=9.5$; $J_{2,3}=18$ |
|  | | 1.59 d | 5.44 q | 4.44 m | | | | | 2.33 s | $J_{1,2}=6$ |
|  | XXII | 1.72 d | ·······················5.06—6.23 m······················· | | | | | 4.8 m | 2.40 s | $J_{3,7}=J_{6,7}=6$ |

[a] S=singlet; d=doublet; t=triplet; q=quartet; dd=double doublet; dq=double quartet; ddd=doublet of double doublet; m=multiplet
[b] Vinyl protons form an ABX spin system; the chemical shifts of the AB protons are approximated by first-order analysis from the pair of overlapping quartets.
[c] The values were obtained by spin-spin decoupling experiments. [d] linalyl

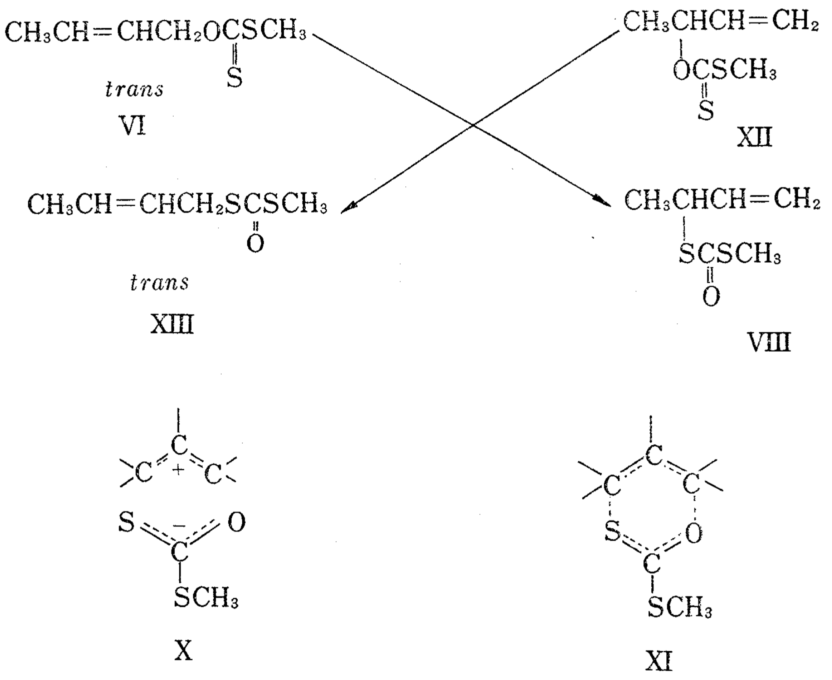


Chart 2

structual assignment of the products were established as follows. Compound XIII exhibited a strong band at 962 $cm^{-1}$ (*trans* olefin) in IR spectrum (Table II) and a doublet at 1.71 ppm (methyl), a doublet at 3.6 ppm (methylene) and a multiplet at 5.15—6.10 ppm (two olefinic hydrogens) in NMR spectrum (Table III). Additionally, the structure of XIII was confirmed by conversion to *trans*-2-butene-1-thiol.⁹⁾

Compound VIII showed a strong band at 923 $cm^{-1}$ and a medium band at 984 $cm^{-1}$ (terminal vinyl group) in IR spectrum and a doublet at 1.45 ppm (methyl), a quintet at 4.3 ppm (methine) due to nearly equivalent coupling of methine proton with both the vinyl

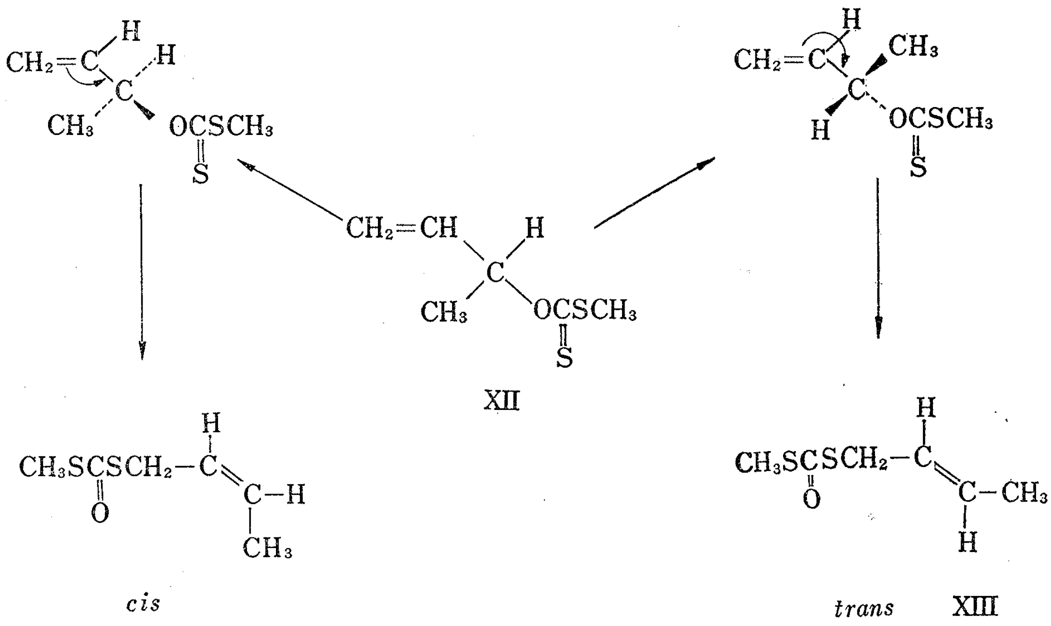


Chart 3

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9) S.F. Birch and D.T. McAllan, *J. Chem. Soc.*, **1951**, 2556.

proton and the methyl group and a distorted ABX pattern at 4.95—6.25 ppm (three olefinic hydrogens) (Table II and III).

As the rearrangement involves allylic shift, the geometrical change in the formation of rearrangement product is of interest. For example, it is questionable whether pyrolysis of 1-methylallyl S-methyl xanthate (XII) affords *trans*-2-butenyl methyl dithiolcarbonate or *cis* isomer. After trial, it was explored that the *trans* isomer was one-sidedly formed, indicating that steric requirement is more favorable for the cyclic transition state (XI) constituted in *trans* fashion (Chart 3).

In the pyrolysis reaction, 3-aryl-substituted allylic xanthate showed a quite different result from the 3-alkyl homologue. When cinnamyl S-methyl xanthate (XIV) was pyrolysed at 150° without isolation from the reaction mixture of synthesis, it afforded only cinnamyl methyl dithiolcarbonate (XV) without allylic shift as an isolatable product. The yield was very poor accompanying a large quantity of by-product[10] probably because the formation of sodium salt of cinnamyl alcohol was imcomplete and accordingly the xanthate would be formed inferior.

The structure of XV was identified by conversion to cinnamyl disulfide on hydrolysis followed by oxidation. On the other hand, conversion reaction of *trans*-4-phenyl-3-buten-2-ol to the xanthate (XVI) proceeded more favorably by the usual method and it was indicated by IR and NMR spectrum that the reaction mixture changed mainly to the dithiolcarbonate (XVII) during evaporation of the solvent. But the dithiolcarbonate (XVII) was so unstable that it decomposed gradually to *trans*-1-methyl-3-phenyl-2-propenyl methyl sulfide (XVIII) evolving carbon oxysulfide on allowing to stand at room temperature or by chromatography on silica gel. When the reaction mixture was submitted to distillation, it decomposed completely to XVIII (40%) and a trace of 1-phenyl-1,3-butadiene (XIX). The position isomer of XVI, *trans*-1-phenyl-2-butenyl S-methyl xanthate (XX) derived from *trans*-1-phenyl-2-buten-1-ol, behaved quite analogously to XVI on distillation to give the same products in the case of XVI (Chart 4).

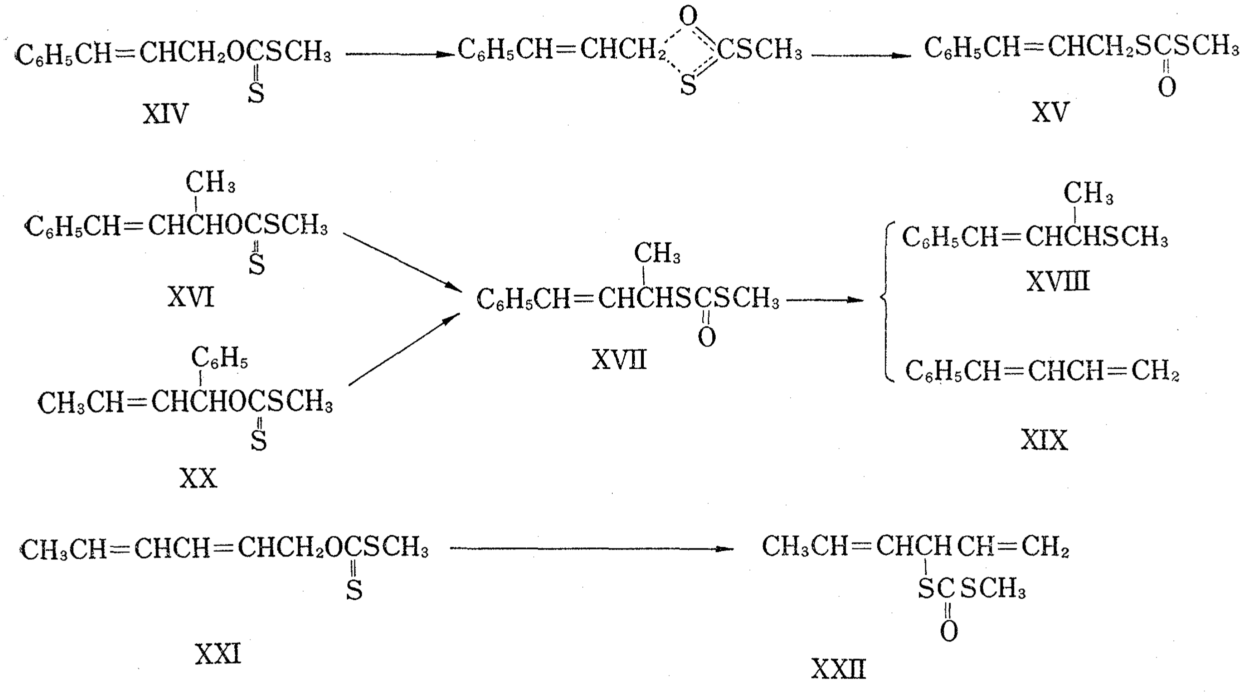

Chart 4

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[10] It will be reported in a coming paper that it consists almost of cinnamyl trithiocarbonate.

This might mean that the case of XX involves allylic shift, but that of XVI does not in the rearrangement reaction to the same dithiolcarbonate (XVII) which then decomposed immediately to the products, XVIII and XIX. Thus the stabilization by conjugation of double bond with phenyl group seems to prevent allylic shift in the case of XIV and XVI and the reaction might proceed *via* $S_{N_i}$ to give the dithiolcarbonate[11] (Chart 4).

On the contrary, in the case of XX the stabilization by conjugation might promote the allylic shift to give the dithiolcarbonate (intermediate) same as the case of XVI. For the purpose of comparing with these examples, *trans*-2, *trans*-4-hexadienyl S-methyl xanthate (XXI) having conjugated double bonds was exposed to heat by distillation. As a result, it rearranged to 1-vinyl-*trans*-2-butenyl methyl dithiolcarbonate (XXII) with allylic shift, indicating that conjugated double bonds does not prevent allylic shift unlike the conjugation of double bond with aromatic nucleus (XIV and XVI). Seeing from the synthetic standpoint, the present study is useful for the preparation of allylic thiols. Allylic thiols are easily derived just by distillation with ethanolamine[12] from dithiolcarbonates which are prepared by the present method. As have been known, the preparative methods of allylic thiols by replacement reactions of 2-alkenyl derivatives are usually ready to produce isomeric thiols regarding to double bond and moreover to result in poor yields by oxidation and polymerization due to prolonged operation.[13]

This method is usually superior to the known methods in yield and in simplicity of operations. A work on pyrolysis of cycloalkenyl xanthates will follow this report.

## Experimental

Melting and boiling points are uncorrected. IR spectra were recorded with a Nihon Bunko DS-301 spectrometer. NMR spectra were obtained with a Nihon Denshi C-60H spectrometer at 60 MHz using TMS as an internal standard. Gas chromatographic analyses were performed with a Yanagimoto G-800T gas chromatograph with a thermal conductivity detector using a 20% EGAP on Chamelite CK(40—60 mesh, 4 m × 3 mm) column.

**Preparation of Unsaturated Alcohols**——Commercial available allyl alcohol, cinnamyl alcohol and geraniol were distilled before use. *trans*-2-Buten-1-ol,[14] 3-buten-2-ol,[15] *trans*-3-penten-2-ol,[16] *trans*-4-hexen-3-ol,[17] 3-methyl-2-buten-1-ol,[18] 4-methyl-3-penten-2-ol,[19] 1-(1-cyclohexenyl)ethanol,[20] 2-cyclohexylideneethanol,[21] *trans*-4-phenyl-3-buten-2-ol,[22] *trans*-1-phenyl-2-buten-1-ol,[23] and *trans*-2, *trans*-4-hexadien-1-ol[24] were prepared according to the literature cited.

**General Method for Preparation of Alkenyl Alkyl Dithiolcarbonate *via* Alkenyl S-Alkyl Xanthate**——To a suspension of 1 mole of sodium sand in anhydrous ether or benzene, 1 mole of alkenol was added and the mixture was refluxed with stirring. After sodium was consumed, 1.2 moles of carbon disulfide was added under ice cooling and the mixture was stirred for 2 hr at room temperature and then 1 mole of alkyl halide added. After stirring overnight, the mixture was filtered and the filtrate was washed with water and dried over fused $Na_2SO_4$. The filtrate was freed of solvent by evaporation under reduced pressure and the residue (xanthate) was distilled in a Claisen flask to give the dithiolcarbonate. The yields and pysical properties of the alkenyl dithiolcarbonates were summarized in Table I—III.

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**Formation of Alkenyl 2,4-Dinitrophenyl Sulfide**——a) A solution of 1.5 g of allyl methyl dithiolcarbonate (II) in 50 ml of 1N ethanolic NaOH was refluxed for 1 hr, precipitating sodium carbonate filtered off and ethanolic HCl added to liberate methanethiol and carbon dioxide. The resulting mixture was distilled. To the distillate was added a solution of 2,4-dinitrochlorobenzene in 10 ml of ethanol and then 10% aqueous NaOH until the mixture became slightly reddish. After setting aside overnight, the precipitate was filtered, washed with water and recrystallized from ethanol to afford yellow plates, weight 250 mg, mp 72° identical with an authentic sample.[25]

b) To a suspension of $LiAlH_4$ in abs. ether was added in portions under ice-cooling a solution of dithiolcarbonate in abs. ether and stirred for 20 min. After stirring for additional 40 min, the reaction mixture was decomposed by adding a saturated $NH_4Cl$ solution dropwise and allowed to stand for 30 min. A dense white precipitate was formed and adhered closely to the surface of the flask. The ether layer was separated by decantation and the precipitate was washed with ether. The combined ether solution was evaporated to dryness under a reduced pressure. The residual oil was dissolved in ethanol containing equimolar amount of 2,4-dinitrochlorobenzene. To this solution was added cautiously 10% aqueous NaOH until the mixture became slightly reddish. The yellow precipitate was filtered off and recrystallized from ethanol to afford alkenyl 2,4-dinitrophenyl sulfide; 1-methylallyl-, mp 69—71°. *Anal.* Calcd. for $C_{10}H_{10}O_4N_2S$: C, 47.24; H, 3.96; N, 11.02. Found: C, 47.24; H, 3.76; N, 11.03. *trans*-2-Butenyl, mp 99—100°. *Anal.* Calcd. for $C_{10}H_{10}O_4N_2S$: C, 47.24; H, 3.96; N, 11.02. Found: C, 47.48; H, 4.18; N, 11.15. 1-Methyl-2-butenyl-, mp 66—67°. *Anal.* Calcd. for $C_{11}H_{12}O_4N_2S$: C, 49.24; H, 4.51; N, 10.45. Found: C, 49.33; H, 4.45; N, 10.25. *trans*-1-Methyl-2-pentenyl-, mp 65.5—67.5°. *Anal.* Calcd. for $C_{12}H_{14}O_4N_2S$: C, 51.05; H, 5.00; N, 9.92. Found: C, 50.73; H, 4.97; N, 9.87. Linalyl-, mp 64—65°. *Anal.* Calcd. for $C_{16}H_{20}O_4N_2S$: C, 57.13; H, 5.99; N, 8.33. Found: C, 57.25; H, 5.93; N, 8.45.

**Ozone Oxidation of Alkenyl Methyl Dithiolcarbonate**——A stream of ozonized oxygen was passed into a solution of 400 mg of 1-methylallyl methyl dithiolcarbonate (VIII) in $CCl_4$ under ice cooling until TLC-spot of the starting material could not be observed. To the residual ozonide, after removal of $CCl_4$ *in vacuo*, was added Zn (excess) and AcOH and the mixture was heated on a water bath for 1 hr. The resulting solution was submitted to steam distillation. The earier distillate (50 ml) was treated with an aqueous dimedone solution. After standing overnight in a refrigerater, the resulting precipitate was collected, washed with water, and recrystallized from ethanol–water to afford 410 mg of formaldehyde dimethone, mp 189° identical with an authentic specimen. By oxidation with ozone in a similar fashion, formaldehyde was produced from 1,1-dimethylallyl and 1-vinylcyclohexyl methyl dithiolcarbonate, acetaldehyde from *trans*-2-butenyl methyl dithiolcarbonate (XIII), propionaldehyde from *trans*-1-methyl-2-pentenyl methyl dithiolcarbonate and benzaldehyde from cinnamyl disulfide.

**Pyrolysis of a Mixture of Xanthates**——A mixture of 1.6 g of crude *trans*-2-butenyl S-methyl xanthate (VI) and 1.9 g of crude allyl S-butyl xanthate (V) was heated in a test tube without any solvent for 2 hr in a bath at 100°. The reaction mixture was analyzed by gaschromatography. The gas chromatographic analysis indicated the presence of 1-methylallyl methyl dithiolcarbonate (VIII) and allyl butyl dithiolcarbonate (VII).

**Formation of Cinnamyl Disulfide**——A solution of 3 g of XV in 50 ml of 1N ethanolic NaOH was refluxed for 1 hr, precipitating sodium carbonate filtered off and ethanolic HCl added to liverate methanethiol and carbon dioxide. After evaporation to dryness, the residue was oxidized with an aqueous $I_2$–KI solution until the nitroprusside test for thiol group was negative. The precipitate was filtered, washed with water and recrystallized from ethanol to afford colorless plates, weight 150 mg, mp 89.5° identical with an authentic sample.[26]

**The Formation of XVII and XVIII from 1-Methyl-3-phenyl-2-propenyl S-Methyl Xanthate (XVI)**——*trans*-4-Phenyl-3-buten-2-ol (5.5 g) was xanthated in the usual way. The crude xanthate formed was chromatographed rapidly on silica gel to remove unreacted alcohol and colored substance. The fraction eluted with *n*-hexane gave 5.2 g (59%) of the crude dithiolcarbonate (XVII) instead of the xanthate, which was submitted to fractional distillation and the distillate, bp 140—144° (2 mmHg), was gathered.

The NMR spectrum analysis showed that it consisted of XVII and XVIII in a ratio of 2.5:1. The distillate was heated at 120—150° and distilled under a reduced pressure to give 2.6 g of *trans*-1-methyl-3-propenyl methyl sulfide (XVIII) as a colorless oil, bp 84—86° (3 mmHg). *Anal.* Calcd. for $C_{11}H_{14}S$: C, 74.10; H, 7.91. Found: C, 73.90; H, 7.80. IR $\nu_{\max}^{\text{liq.}}$ cm$^{-1}$: 964 (*trans*-CH=CH-). NMR (in $CCl_4$) $\delta$: 1.38 (3H, doublet, $J=6.8$ Hz, C-$CH_3$), 1.96 (3H, singlet, $SCH_3$), 3.28 (1H, double quartet, $J=7.5$ Hz, $\rangle$CH-S), 5.67 (1H, double doublet, $J=16.8$ Hz, =CH-C-S), 6.30 (1H, doublet, $C_6H_5CH$=).

The gas chromatographic analysis of the forerun indicated the presence of a small amount of 4-phenyl-1,3-butadiene (XIX). The position isomer of XVI, XX gave the same product as the case of XVI.

**Preparation of 2-Alkenethiol from 2-Alkenyl Alkyl Dithiolcarbonate by Reaction with 2-Aminoethanol**[12]——A mixture of dithiolcarbonate (1 mole) and 2-aminoethanol (1 mole) was heated at 80—120° until the

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evolution of methanethiol ceased. After heating for another few minutes, the reaction mixture was distilled under the atmosphere of nitrogen to afford corresponding thiol.

Compound VIII gave 3-butene-2-thiol in 48% yield, bp 70—75°. Compound XIII similarly gave *trans*-2-butene-1-thiol in 62% yield. These products were converted to 2,4-dinitrophenyl derivatives and characterized.

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