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Studies on Organo Sulfur Compounds. IV.[1] The Reaction of Sodium *sec-* and *tert-α*-Acetylenyl Xanthates with Alkyl Halide

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The reaction of sodium *sec-* and *tert-α*-acetylenyl xanthate with methyl iodide afforded corresponding *α*-acetylenyl xanthate in a few cases, and other products such as allenic dithiolcarbonate, thioncarbonate and cyclic compound were isolated in case by case. Nevertheless, in all cases, dimethyl trithiocarbonate (IV) was obtained.

A certain correlation between the formations of *α*-acetylenyl xanthate, allenic dithiolcarbonate, and dimethyl trithiocarbonate (IV) was observed.

In the preceding paper, the authors have reported that primary *α*-acetylenic alcohol (I) affords corresponding xanthate (II) by the reaction with carbon disulfide and methyl iodide under anhydrous condition, and in the case of propargyl alcohol (Ia), the yield of corresponding xanthante (IIa) is rather small and considerable amounts of dimethyl trithiocarbonate (IV) and dipropargyl thioncarbonate (III) are obtained.

$$\underset{\text{I}}{RC{\equiv}C\text{-}CH_2OH} \xrightarrow[2)\ CS_2\ 3)\ CH_3I]{1)\ NaH} \underset{\text{II}}{RC{\equiv}C\text{-}CH_2\text{-}O\text{-}\overset{\overset{S}{\|}}{C}\text{-}SCH_3}$$

$$\underset{\text{Ia}}{HC{\equiv}C\text{-}CH_2OH} \xrightarrow[2)\ CS_2\ 3)\ CH_3I]{1)\ NaH} \underset{\text{IIa}}{HC{\equiv}C\text{-}CH_2\text{-}O\text{-}\overset{\overset{S}{\|}}{C}\text{-}SCH_3} + \underset{\text{III}}{(HC{\equiv}C\text{-}CH_2O\text{-})_2C{=}S} + \underset{\text{IV}}{CH_3S\text{-}\overset{\overset{S}{\|}}{C}\text{-}SCH_3}$$

To clarify the influence of the structure of *α*-acetylenic alcohol to the formation of *α*-acetylenyl xanthate, this reaction was extended to secondary and tertiary *α*-acetylenic alcohols.

The alcoholate prepared from sodium sand and small excess of 2-heptyn-4-ol (V) was treated in dry benzene with carbon disulfide and methyl iodide to afford S-methyl-O-2-heptyn-4-yl xanthate (VI), S-methyl-S'-2,3-heptadien-2-yl dithiolcarbonate (VII), S-methyl-O-2-heptyn-4-yl thiolcarbonate (VIII) and dimethyl trithiocarbonate (IV). These compounds were identified on the basis of analytical and spectral data. The analytical data of compound VII was agreed with that of xanthate (VI). The infrared spectrum of compound VII was devoid of significant absorption at 2200—2000 cm^{-1} region, but showed characteristic absorption bands at 1954 cm^{-1} for an allenic group (-C=C=C-), and at 1725, 1645 and 855 cm^{-1} for the dithiolcarbonate group (-S-CO-S-)[3] (see Fig. 1). The nuclear magnetic resonance (NMR) spectrum showed a multiplet at 9.26—8.26 τ for seven protons of propyl group, a singlet at 7.61 τ for three protons of S-methyl, a doublet at 7.95 τ for three protons of C-methyl with coupling constant of 3.0 cps[4,5] and a multiplet centered at 4.76 τ for one proton $\left(=C=C\langle^{n\text{-}Pr}_{H}\right)$ with coupling constants of 6.0 and 3.0 cps.

1) Part III: K. Tomita and M. Nagano, *Chem. Pharm. Bull.* (Tokyo), **16**, 1907 (1968).
2) Location: *Hiromachi, Shinagawa-ku, Tokyo.*
3) T. Taguchi and M. Nakao, *Tetrahedron*, **18**, 245 (1961).
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5) E.I. Snyder and J.D. Roberts, *J. Am. Chem. Soc.*, **84**, 1582 (1962).

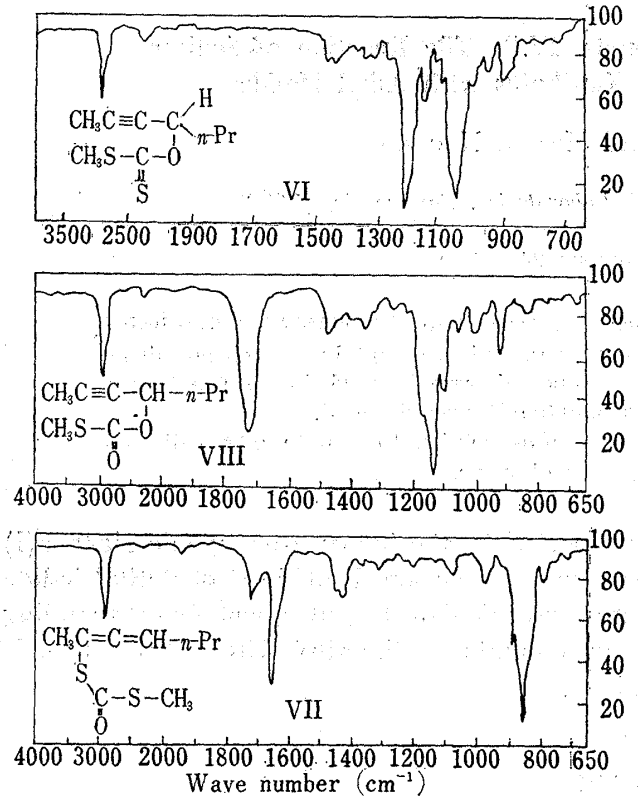


Fig. 1. The IR Spectra of S-Methyl-O-2-heptyn-4-yl Xanthate (VI), S-Methyl-S'-2,3-heptadien-2-yl Dithiolcarbonate (VII) and S-Methyl-O-2-heptyn-4-yl Thiolcarbonate (VIII)

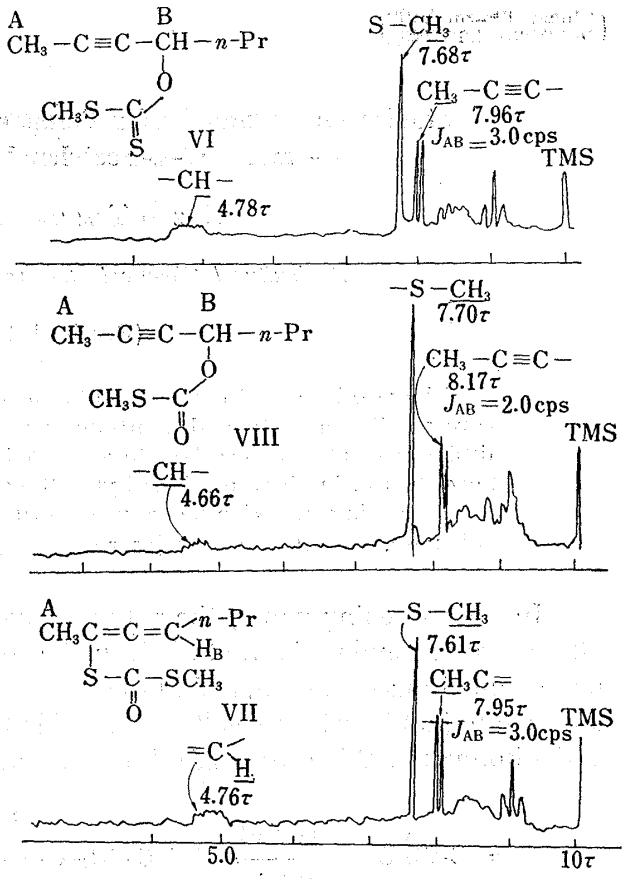
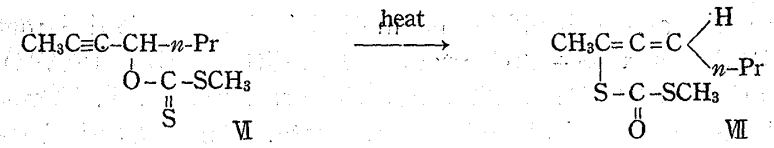


Fig. 2. The NMR Spectra of S-Methyl-O-2-heptyn-4-yl Xanthate (VI), S-Methyl-S'-2,3-heptadien-2-yl Dithiolcarbonate (VII) and S-Methyl-O-2-heptyn-4-yl Thiolcarbonate (VIII)

Distillation of S-methyl-O-2-heptynyl xanthante (VI) afforded the mixture of VI and allenic dithiolcarbonate, which was coincided with VII. It was considered that xanthate (VI) was thermally rearranged to the corresponding allenic dithiolcarbonate (VII).



It is well known that a propargyl group (-C≡C-CH-) rearranges to an allenic group (-CH=C=C-) in the presence of basic catalysts,[6,7] and certain xanthates are thermally rearranged to corresponding dithiolcarbonates.[3,8]

The characteristic infrared absorption bands of thiolcarbonate (VIII) were observed at 2220 cm^{-1} for carbon-carbon triple bond (-C≡C-), and at 1721 and 1144 cm^{-1} for thiolcarbonate group (-O-CO-S-). Furthermore, the structure of this compound VIII was confirmed by the analysis of the NMR spectrum, which was closely resemble to that of xanthate (VI) (see Fig. 2).

6) R.A. Raphael, "Acetylenic Compounds in Organic Synthesis."
7) T.L. Jacobs, R.A. Kawie and R.G. Cooper, *J. Am. Chem. Soc.*, 73, 1273 (1951).
8) T. Taguchi, Y. Kawazoe, K. Yoshihira, H. Kanayama, M. Mori, K. Tabata and K. Harano, *Tetrahedron Letters*, 1965, 2717—2722.

Table I. The Correlation between the Yields of α-Acetylenyl Xanthate and Allenic Dithiolcarbonate, and Dimethyl Trithiocarbonate (IV)

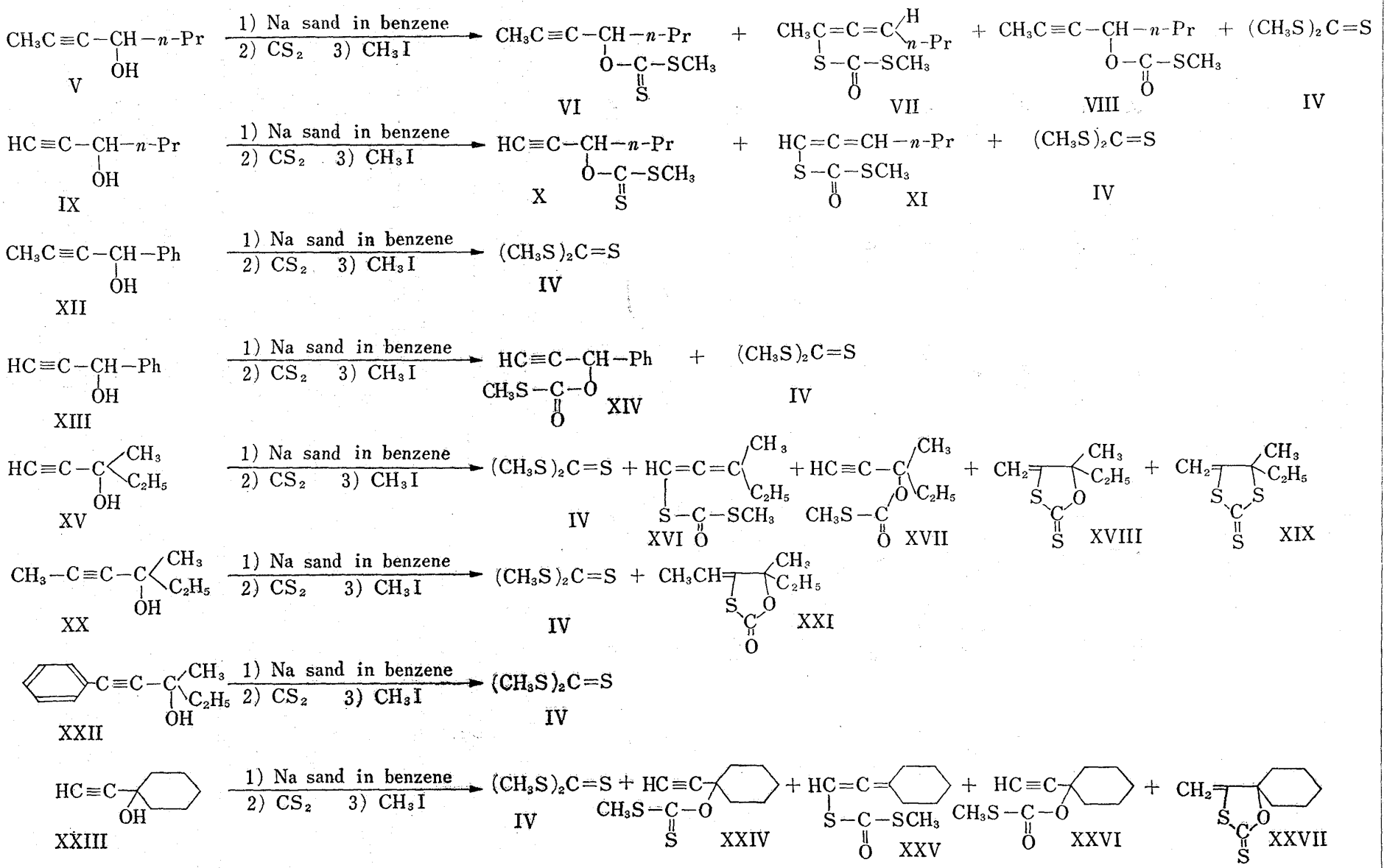
Comp. No.	*sec*- or *tert*- α-Acetylenic alcohol	$RC\equiv C-C(R_1)(R_2)-CH_3S-C(=S)-O$	$RC=C=C(R_1)(R_2)-S-C(=O)-SCH_3$	$CH_3S-C(=S)-SCH_3$ IV
V	$CH_3C\equiv C-CH(OH)-n\text{-Pr}$	48.2%	6.5%	4.7%
IX	$HC\equiv C-CH(OH)-n\text{-Pr}$	48.0%	6.5%	4.7%
XXIII	$HC\equiv C-C(OH)$(cyclohexyl)	12.0%	8.0%	32.0%
XXX	$C_6H_5-C\equiv C-C(OH)$(cyclohexyl)	6.5%	not isolated	22.4%
XXVIII	$CH_3C\equiv C-C(OH)$(cyclohexyl)	not isolated	8.0%	37.0%
XV	$HC\equiv C-C(CH_3)(C_2H_5)(OH)$	not isolated	8.0%	32.0%
XX	$CH_3C\equiv C-C(CH_3)(C_2H_5)(OH)$	not isolated	not isolated	22.8%
XII	$CH_3C\equiv C-CH(OH)-Ph$	not ioslated	not isolatde	43.0%
XXII	$C_6H_5-C\equiv C-C(CH_3)(C_2H_5)(OH)$	not isolated	not isolated	42.0%
XIII	$HC\equiv C-CH(OH)-Ph$	not isolated	not isolated	42.0%

Three secondary α-acetylenic alcohols (IX, XII and XIII) and six tertiary α-acetylenic alcohols (XV, XX, XXII, XXIII, XXVIII and XXX) were treated with carbon disulfide and methyl iodide under the similar reaction condition as the case of 2-heptyn-4-ol (V), and isolated products were illustrated in Chart 1.

The corresponding xanthates could not be isolated except the cases of one *sec*- alcohol (IX) and two *tert*-alcohols (XXIII and XXX). Allenic dithiolcarbonates were obtained in four cases (IX, XV, XXIII and XXVIII). These dithiolcarbonates should be formed from rearrangement of the corresponding xanthates, but it was not clear whether the xanthates were rearranged to the allenic dithiolcarbonates in the processes of purification or during the reactions. Thiolcarbonates were isolated in three cases (XIII, XV and XXIII). But in every case no corresponding thioncarbonate $[(R-C\equiv C-\dot{C}-O-)_2CS]$ could be isolated, which was obtained in the case of propargyl alcohol.[1] Nevertheless, in every case, dimethyl trithiocarbonate (IV) was obtained.

The yields of α-acetylenyl xanthate, allenic dithiolcarbonate and dimethyl trithiocarbonate (IV) are summarized in Table I. The presence of a certain correlation between the yield of these xanthates and that of dimethyl trithiocarbonate (IV) is supposed.

When the yield of α-acetylenyl xanthate was fairly well, that of dimethyl trithiocarbonate (IV) was relatively small. When xanthates or allenic dithiolcarbonates were isolated in low yield, rather large amounts of compound IV were obtained, and when no formers were isolated, considerable amounts of the latter were obtained.



Dimethyl trithiocarbonate (IV) would be a key compound for clarifing the mechanism of the formation of other products, so study on the formation mechanism of dimethyl trithiocarbonate (IV) is in progress.

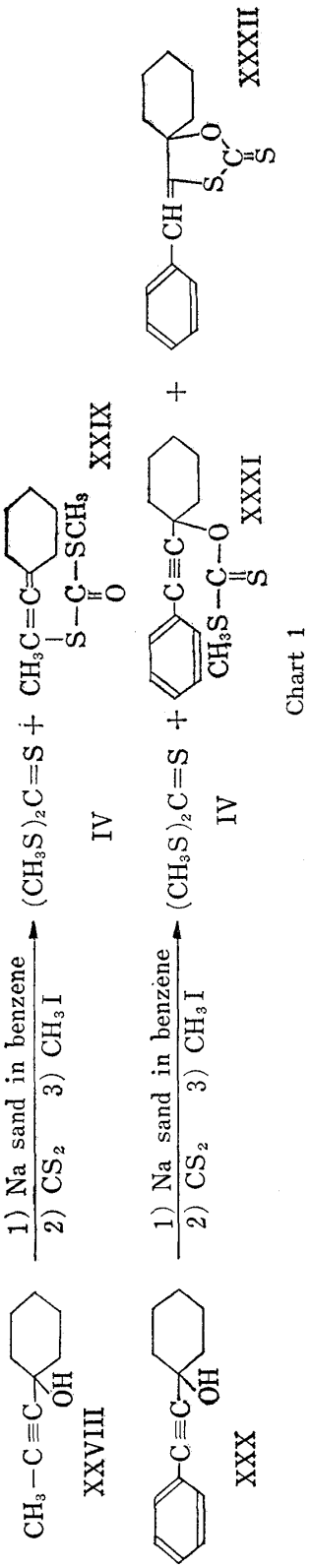


Chart 1

Experimental[9]

General Method for Reaction of Sodium *sec*- and *tert*-Acetylenyl Xanthates with Alkyl Halide——To a suspension of powdered sodium (0.05 mole) in anhydrous benzene, *sec*- or *tert*-α-acetylenic alcohols (0.055 mole) were added at room temperature under stirring, and the mixture was refluxed until a grain of sodium disappeared. To the alcoholate solution, carbon disulfide (0.06 mole) was added under cooling. After stirring for 6 hr at room temperature, methyl iodide (9.0 g) was added and left alone over night. The reaction mixture was poured into ice-water (250 ml), benzene layer was separated and aqueous layer was extracted with ether. Combined extracts were washed with H_2O and dried over anhyd. Na_2SO_4. After removal of the solvent *in vacuo*, the residue was chromatographed over silica gel column, and the isolated compounds were refined by distillation or recrystallization.

Reaction of Sodium 2-Heptyn-4-yl Xanthate with Methyl Iodide——2-Heptyn-4-ol (V) (6.15 g) was reacted in anhydrous benzene with Na sand (1.15 g), carbon disulfide (4.2 g) and methyl iodide (9.0 g). The reaction mixture was poured into ice-water, organic layer was separated and aqueous layer was extracted with ether. Combined extracts were washed with H_2O and satd. NaCl solution, and dried over anhyd. Na_2SO_4. After removal of solvent, the residue was chromatographed (silica gel). Elution with *n*-hexane—benzene (4:1) afforded the following three compounds besides of dimethyl trithiocarbonate (IV) (0.16 g).

1) 4.88 g of S-methyl-O-2-heptyn-4-yl xanthate (VI) as a pale yellow oil (Yield 48.2%). *Anal.* Calcd. for $C_9H_{14}OS_2$ (VI): C, 53.50; H, 6.85; S, 31.60. Found: C, 53.73; H, 7.12; S, 31.55. IR ν_{max}^{liquid} cm^{-1}: 2220 (-C≡C-), 1210, 1050 (-S-CS-O-). UV λ_{max}^{EtOH} mμ (log ε): 224 (4.03), 278.5 (4.19). NMR (in CCl_4) τ (*J*=cps): 9.26—7.06 (7H, m.), 7.96 (3H, d., *J*=3.0), 7.65 (3H, s.), 4.78 [1H, t., q., J_1=6.0 (t.), J_2=3.0 (q.)].

2) 0.61 g of S-methyl-S'-2,3-heptadien-2-yl dithiolcarbonate (VII) as a pale yellow oil, bp 65° (0.2 mmHg) (Yield 6.5%). *Anal.* Calcd. for $C_9H_{14}OS_2$ (VII): C, 53.50; H, 6.85; S, 31.60. Found. C, 53.09; H, 6.98; S, 31.20. IR ν_{max}^{liquid} cm^{-1}: 1954 (-C=C=C-), 1725, 1649, 855 (-S-CO-S-). UV λ_{max}^{EtOH} mμ (log ε): 251 (3.70). NMR (in CCl_4) τ(*J*=cps): 9.26—8.26 (7H, m.), 7.61 (3H, s.), 7.95 (3H, d., *J*=3.0), 4.76 (1H, t., q., J_1=6.0, J_2=3.0). Distillation of compound VI at 68° under 4 mmHg afforded a yellow oil, which showed two spots on TLC. They were chromatographed over silica gel column (eluting agents: *n*-hexane-benzene (4:1)). One of them was compound VI, and the other was coincided with compound VII.

3) 0.17 g of S-methyl-O-2-heptyn-4-yl thiolcarbonate (VIII) as a colorless oil, bp 66° (0.25 mmHg) (Yield 3.6%). *Anal.* Calcd. for $C_9H_{14}O_2S$ (VIII): C, 58.03; H, 7.57; S, 17.21. Found: C, 58.45; H, 7.67; S, 17.01. IR ν_{max}^{liquid} cm^{-1}: 2220 (-C≡C-), 1721, 1144 (-O-CO-S-). NMR (in CCl_4) τ (*J*=cps): 9.28—8.0 (7H, m.), 7.70 (3H, s.) 8.17 (3H, d., *J*=2.0), 4.66 (1H, t., q., J_1=6.0, J_2=2.0).

Reaction of Sodium 1-Hexyn-3-yl Xanthate with Methyl Iodide——1-Hexyn-3-ol (IX) (5.4 g) was reacted in benzene with Na sand (1.15 g), carbon disulfide (4.2 g) and methyl iodide (9.0 g), and then the ether residue was chromatographed (silica gel). Elution with *n*-hexane—benzene (4:1) afforded the following two substances besides dimethyl trithiocarbonate (IV) (0.18 g). (1) 4.5 g of S-methyl-O-1-hexyn-3-yl xanthate (X) as a pale yellow oil, bp

9) All boiling points were uncorrected. The NMR spectra were recorded on Varian A-60 in carbon tetra chloride containing tetramethyl silane as internal standard.

68°(4 mmHg) (Yield 48.0%). *Anal.* Calcd. for $C_8H_{12}OS_2$ (X): C, 51.02; H, 6.42; S, 34.02. Found: C, 49.57; H, 6.35; S, 34.48. IR ν_{max}^{liquid} cm^{-1}: 3330 (HC≡C–), 2100 (–C≡C–), 1205, 1052 (–O–CS–S–). UV λ_{max}^{EtOH} mμ (log ε): 273 (3.99). NMR (in CCl_4) τ (*J*=cps): 9.25—7.67 (7H, m), 7.55 (1H, d., *J*=2.0), 7.43 (3H, s.), 3.78 (1H, t., d., J_1=6.0, J_2=2.0).

2) 0.61 g of S–methyl–S′–1,2–hexadien–1–yl dithiolcarbonate (XI) as a pale yellow oil, bp 60—65° (0.25 mmHg) (Yield 6.5%). *Anal.* Calcd. for $C_8H_{12}OS_2$ (XI): C, 51.02; H, 6.42; S, 34.02. Found: C, 49.67; H, 6.35; S, 34.38. IR ν_{max}^{liquid} cm^{-1}: 1943 (–C=C=C–), 1735, 1649, 865 (–S–CO–S–). NMR (in CCl_4) τ(*J*=cps): 9.26—7.69 (7H., m.), 7.59 (3H, s.), 4.83—4.4 (2H, m).

Reaction of Sodium 1-Phenyl-2-butyn-1-yl Xanthate with Methyl Iodide——1–Phenyl–2–butyn–1–ol (XII) (8.1 g) was reacted in benzene with Na sand (1.15 g), carbon disulfide (4.2 g) and methyl iodide (9.1 g), and then the ether residue was chromatographed (silica gel). Elution with *n*–hexane—benzene (4:1) afforded dimethyl trithiocarbonate (IV) (1.4 g).

Reaction of Sodium 1-Phenyl-2-propyn-1-yl Xanthate with Methyl Iodide——1–Phenyl–2–propyn–1–ol (XIII) (7.3 g) was reacted in benzene with Na sand (1.15 g), carbon disulfide (4.2 g) and methyl iodide (9.0 g), and then the ether residue was chromatographed (silica gel). Elution with *n*–hexane—benzene (4:1) afforded 1.45 g of dimethyl trithiocarbonate (IV) and 0.35 g of S–methyl–O–1–phenyl–2–propyn–1–yl thiolcarbonate (XIV) as a pale yellow oil, bp 110° (0.07 mmHg) (Yield 6.8%). *Anal.* Calcd. for $C_{11}H_{10}O_2S$ (XIV): C, 64.05; H, 4.88; S, 15.54. Found: C, 64.23; H, 5.00; S, 15.25. IR ν_{max}^{liquid} cm^{-1}: 3300 (HC≡C–), 2100 (–C≡C–), 1720, 1130 (–S–CO–O–). NMR (in CCl_4) τ(*J*=cps): 7.68 (3H, s.), 7.40 (1H, d., *J*=2.5), 3.51 (1H, d., *J*=2.5), 2.82—2.32 (5H, m.).

Reaction of Sodium 3-Methyl-1-pentyn-3-yl Xanthate with Methyl Iodide——3–Methyl–1–pentyn–3–ol (XV) (5.4 g) was reacted in benzene with Na sand (1.15 g), carbon disulfide (5.7 g) and methyl iodide (10.8 g), and then the ether residue was chromatographed (silica gel). Elution with *n*–hexane—benzene (4:1) afforded dimethyl trithiocarbonate (IV) (1.1 g), 4–methylene–5–methyl–5–ethyl–1,3–oxathiolane–2–thione (XVIII) (1.3 g) and 4–methylene–5–methyl–5–ethyl–1,3–dithiolane–2–thione (XIX) (0.38 g) besides the following two compounds.

1) 0.78 g of S–methyl–S′–3–methyl–1,2–pentadien–1–yl dithiolcarbonate (XVI) as a pale yellow oil, bp 80° (0.3 mmHg) (Yield 8%). *Anal.* Calcd. for $C_8H_{12}OS_2$ (XVI): C, 51.02; H, 6.42; S, 34.05. Found: C, 50.89; H, 6.08; S, 34.42. IR ν_{max}^{liquid} cm^{-1}: 1940 (–C=C=C–), 1738, 1650, 868 (–S–CO–S–). UV λ_{max}^{EtOH} mμ (log ε): 252.5 (3.51). NMR (in CCl_4) τ(*J*=cps): 8.8 (3H, t., *J*=7.0), 9.25 (3H, d., *J*=3.0), 7.95 (2H, q., d., J_1=7.0, J_2=3.0), 3.88 (1H, m.).

2) 0.22 g of S–methyl–O–(3–methyl–1–pentyn–3–yl) thiolcarbonate (XVII) as a colorless oil, bp 89° (2 mmHg) (Yield 5.2 %). *Anal.* Calcd. for $C_8H_{12}O_2S$ (XVII): C, 55.87; H, 7.02; S, 18.61. Found: C, 55.67; H, 7.05; S, 18.90. IR ν_{max}^{liquid} cm^{-1}: 3320 (HC≡C–), 2100 (–C≡C–), 1725, 1155 (–O–CO–S–). NMR (in CCl_4) τ(*J*=cps): 8.96 (3H, t., *J*=7.0), 8.30 (3H, s.), 8.15 (2H, q., *J*=7.0), 7.70(3H, s.), 7.25 (1H, s.). The infrared spectra of cyclic compounds (XVIII, XIX) were agreed with those of authentic samples.[10]

Reaction of Sodium 1-Methyl-4-hexynyl Xanthate with Methyl Iodide——1–Methyl–4–hexyn–3–ol (XX) (6.2 g) was reacted in dry benzene with Na sand (1.15 g), carbon disulfide (5.7 g) and methyl iodide (10.8 g). After removal of the solvent, the oily residue was chromatographed (silica gel). Elution with *n*–hexane—benzene (4:1) afforded 0.79 g of dimethyl trithiocarbonate (IV) and 0.38 g of 4–ethylidene–5–methyl–5–ethyl–1,3–oxathiolan–2–one (XXI) as a colorless oil, bp 55° (0.2 mmHg) (Yield 8.2 g). This compound XXI could not be isolated in the cyclization of the sodium xanthate, which was prepared from 1–methyl–4–hexyn–3–ol (XX), sodium sand and carbon disulfide.[10] *Anal.* Calcd. for $C_8H_{12}O_2S$ (XXI): C, 55.78; H, 7.02; S, 18.61. Found: C, 55.81; H, 7.16; S, 18.56. IR ν_{max}^{liquid} cm^{-1}: 1656 (–C=C–), 1746, 1186 (–S–CO–O–). NMR (in CCl_4) τ(*J*=cps): 9.08 (3H, t., *J*=7.0), 8.46 (3H, s.), 8.27 (3H, d., *J*=7.0), 8.12 (2H, q., *J*=7.0), 4.47 (1H, q., *J*=7.0).

Reaction of Sodium 1-Phenyl-3-methyl-1-pentynyl Xanthate with Methyl Iodide——1–Phenyl–3–methyl–1–pentyn–3–ol (XXII) (9.6 g) was reacted in benzene with Na sand (1.15 g), carbon disulfide (5.7 g) and methyl iodide (10.8 g), and then the ether residue was chromatographed (silica gel). Elution with hexane—benzene (4:1) afforded dimethyl trithiocarbonate (IV) (1.45 g).

Reaction of Sodium 1-Ethynyl-cyclohexyl Xanthate with Methyl Iodide——1–Ethynylcyclohexanol (XXIII) (5.8 g) was reacted in benzene with Na sand (1.15 g), carbon disulfide (4.2 g) and methyl iodide (9.0 g), and then the ether residue was chromatographed (silica gel). Elution with *n*–hexane—benzene (4:1) afforded following three compounds besides dimethyl trithiocarbonate (IV) (1.1 g) and 4–methylene–1–oxa–3–thiospiro[4,5]decan–2–thione (XXVII) (0.12 g).

1) 0.7 g of S–methyl–O–1–ethynylcyclohexyl xanthate (XXIV)as a pale yellow oil, bp 60° (0.1 mmHg) (Yield 6.5%). *Anal.* Calcd. for $C_{10}H_{14}OS_2$ (XXIV): C, 56.03; H, 6.58; S, 29.91. Found: C, 56.38; H, 6.27; S, 29.43. IR ν_{max}^{liquid} cm^{-1}: 3310 (HC≡C–), 2100 (–C≡C–), 1204, 1050 (–O–CS–S–). UV λ_{max}^{EtOH} mμ (log ε): 278 (4.10). NMR (in CCl_4) τ(*J*=cps): 9.26—7.72 (10H, m.), 7.42 (3H, s.), 7.26 (1H, s.).

10) K. Tomita and M. Nagano, *Chem. Pharm. Bull.* (Tokyo), **16**, 1324 (1968).

2) 0.28 g of S-methyl-S′-1-(2-cyclohexylidene)ethylenyl dithiolcarbonate (XXV) as a pale yellow oil, bp 130° (0.2 mmHg) (Yield 8%). *Anal.* Calcd. for $C_{10}H_{14}OS_2$ (XXV): C, 56.03; H, 6.58; S, 29.91. Found: C, 56.30; H, 6.84; S, 29.47. IR ν_{max}^{liquid} cm^{-1}: 1945 (-C=C=C-), 1730, 1650, 868 (-S-CO-S-). UV λ_{max}^{EtOH} $m\mu$ (log ε): 253 (3.17). NMR (in CCl_4) τ(J=cps): 8.7—7.64 (10H, m.), 7.51 (3H, s.), 4.0 (1H, t., t., $J_1=J_2=1.9$).

3) 0.28 g of S-methyl-O-1-ethynylcyclohexyl thiolcarbonate (XXVI) as a colorless oil, bp 80° (0.3 mmHg) (Yield 6%). *Anal.* Calcd. for $C_{10}H_{14}O_2S$ (XXVI): C, 60.57; H, 7.11; S, 16.17. Found: C, 60.87; H, 7.41; S, 15.72. IR ν_{max}^{liquid} cm^{-1}: 3300 (HC≡C-), 2090 (-C≡C-), 1722, 1130 (-S-CO-O-). NMR (in CCl_4) τ(J=cps): 9.27—7.74 (10H, m.), 7.74 (3H, s.), 7.46 (1H, s.). The infrared spectrum of cyclic compound XXVII was agreed with that of the authentic sample [10]

Reaction of Sodium 1-Propynylcyclohexyl Xanthate with Methyl Iodide——7.6 g of 1-propynylcyclohexanol (XXVIII) was reacted in benzene with Na sand (1.15 g), carbon disulfide (4.2 g) and methyl iodide (9.0 g), and the ether residue was chromatographed (silica gel). Elution with *n*-hexane—benzene (4:1) afforded dimethyl trithiocarbonate (IV) (1.28 g) and 0.91 g of S-methyl-S′-1-cyclohexylidene-propen-2-yl dithiolcarbonate (XXIX) as a pale yellow oil, bp 110° (0.1 mmHg) (Yield 8%). *Anal.* Calcd. for $C_{11}H_{16}OS_2$ (XXIX): C, 57.85; H, 7.00; S, 28.08. Found: C, 58 35; H, 7.10; S, 27.59. IR ν_{max}^{Liquid} cm^{-1}: 1960 (-C=C=C-), 1728, 1648, 855 (-S-CO-S-). UV λ_{max}^{EtOH} $m\mu$ (log ε): 250 (3.79). NMR (in CCl_4) τ (J=cps): 8.62—7.60 (10H, m.), 7.99 (3H, s.), 7.64 (3H, s.).

Reaction of Sodium 1-(2-Phenyl)ethynylcyclohexyl Xanthate with Methyl Iodide——11.0 g of 1-(2-phenyl) ethynyl cyclohexanol (XXX) was reacted in benzene with Na sand (1.15 g), carbon disulfide (4.2 g) and methyl iodide (9.0 g), and then the ether residue was chromatographed (silica gel). Elution with *n*-hexane—benzene (4:1) afforded dimethyl trithiocarbonate (IV) (0.79 g), 4-benzylidene-1-oxa-2-thiospro[4,5]decan-2-thione (XXXII) (4.3 g) and 0.94 g of S-methyl-1-(2-phenyl)ethynylcyclohexyl xanthate (XXXI) as a pale yellow oil, bp 100° (Yield 6.5%). *Anal.* Calcd. for $C_{18}H_{18}OS_2$ (XXXI): C, 66 25; H, 6.42; S, 22.05. Found: C, 66.69; H, 6.77; S, 21.80. IR ν_{max}^{liquid} cm^{-1}: 2250 (-C≡C-), 1220, 1050 (-S-CS-O-). UV λ_{max}^{EtOH} $m\mu$ (log ε): 289.5 (3.71). NMR (in CCl_4) τ (J=cps): 8.68—7.59 (10H, m.), 7.32 (3H, s.), 2.98—2.52 (5H, m.). The infrared spectrum of cyclic compound (XXXII) was agreed with that of the authentic sample.[10]

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