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# Studies on Organo Sulfur Compounds. VI.[1] The Reaction of S-Methyl-O-α-acetylenyl Xanthates and Metal Xanthates

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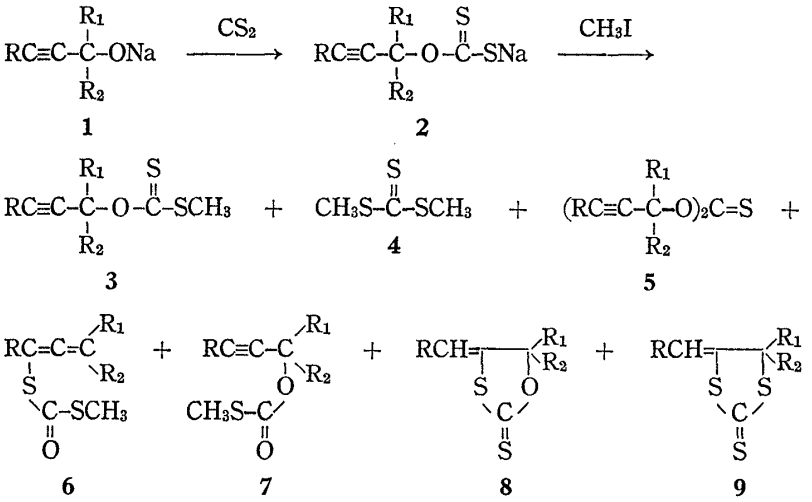
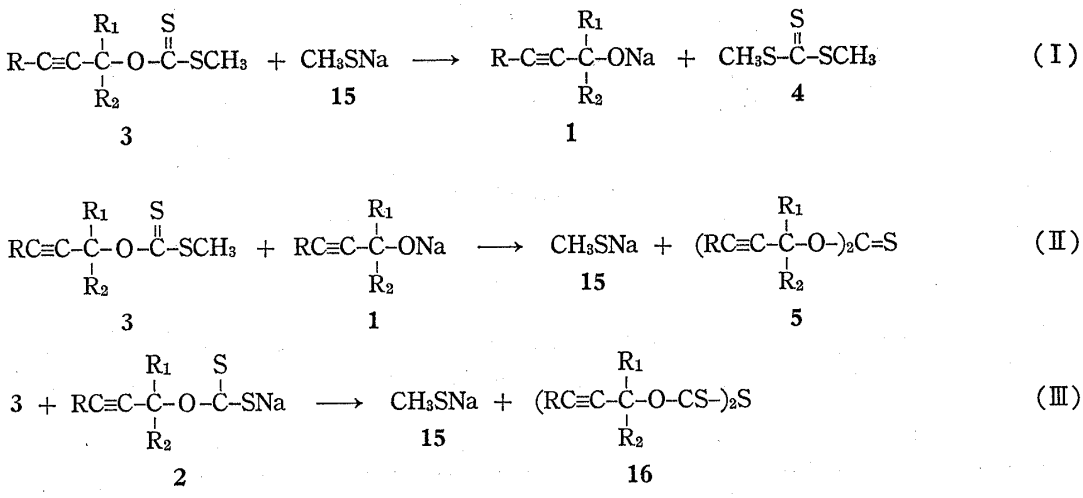
Dimethyl trithiocarbonate (**4**), which was formed as one of by-products in the preparation of α-acetylenyl xanthate (**3**), was obtained by treating 2-propynyl xanthate (**10**) or 3-phenyl-2-propynyl xanthate (**18**) with potassium xanthate (**17**). The reaction pathway for the formation of **4** from **18** was studied in detail, and the mechanism of the formation of dimethyl trithiocarbonate (**4**) and other by-products were consequently clarified.

In the previous papers,[3,4] the reaction of sodium α-acetylenyl xanthate (**2**) and methyl iodide was reported to afford S-methyl-O-α-acetylenyl xanthate (**3**) and to be frequently accompanied by several by-products (**4**, **5**, **6**, **7**, **8** and **9**). Furthermore, in this reaction, there seemed to be a strong correlation between the formation of the xanthate (**3**) and that of dimethyl trithiocarbonate (**4**). In this paper, we attempted to clarify the mechanism of the formation of **4** and the relationship between the yield of **3** and that of **4**.



S-Methyl-O-2-propynyl xanthate (**10**) was treated with sodium normal butane thiolate (**11**) in ethyl alcohol to afford **4**, S-normalbutyl-S'-methyl trithiocarbonate (**12**), dinormal butyl trithiocarbonate (**13**) and 2-propyn-1-ol (**14**) (Chart 1). This result suggested that the reaction of α-acetylenyl xanthate (**3**) with sodium methane thiolate (**15**) seemed to be responsible for the formation of **4** in an aprotic system (equation I), and **15** could be generated from the xanthate (**3**) by the attack of a nucleophilic reagent such as sodium α-acetylenyl alcoholate (**1**) or sodium α-acetylenyl xanthate (**2**), which was existing in the course of preparation of **3** (equation II or III).

1) Part V: K. Tomita and M. Nagano, *Chem. Pharm. Bull.* (Tokyo), **17**, 2442 (1969).
2) Location: *Hiromachi, Shinagawa-ku, Tokyo.*
3) K. Tomita and M. Nagano, *Chem. Pharm. Bull.* (Tokyo), **16**, 1907 (1968).
4) K. Tomita and M. Nagano, *Chem. Pharm. Bull.* (Tokyo), **16**, 1911 (1968).



When S-methyl-O-2-propynyl xanthate (**10**) was treated with sodium ethoxide in ethyl alcohol at room temperature, only **10** was recovered, and **4** could not be obtained; while in the reaction of **10** with potassium O-ethyl xanthate (**17**), **4** was obtained in a good yield. In the case of treating S-methyl-O-3-phenyl-2-propynyl xanthate (**18**) with **17**, **4** was also isolated in a good yield, along with 4-benzylidene-1,3-dithiolane-2-thione (**19**),[5] 3-phenyl-2-propyn-1-ol (**20**) and sodium O-3-phenyl-2-propynyl thiolcarbonate (**21**) whose structure was confirmed by conversion to S-methyl-O-3-phenyl-2-propynyl thiolcarbonate (**22**) (Chart 1).

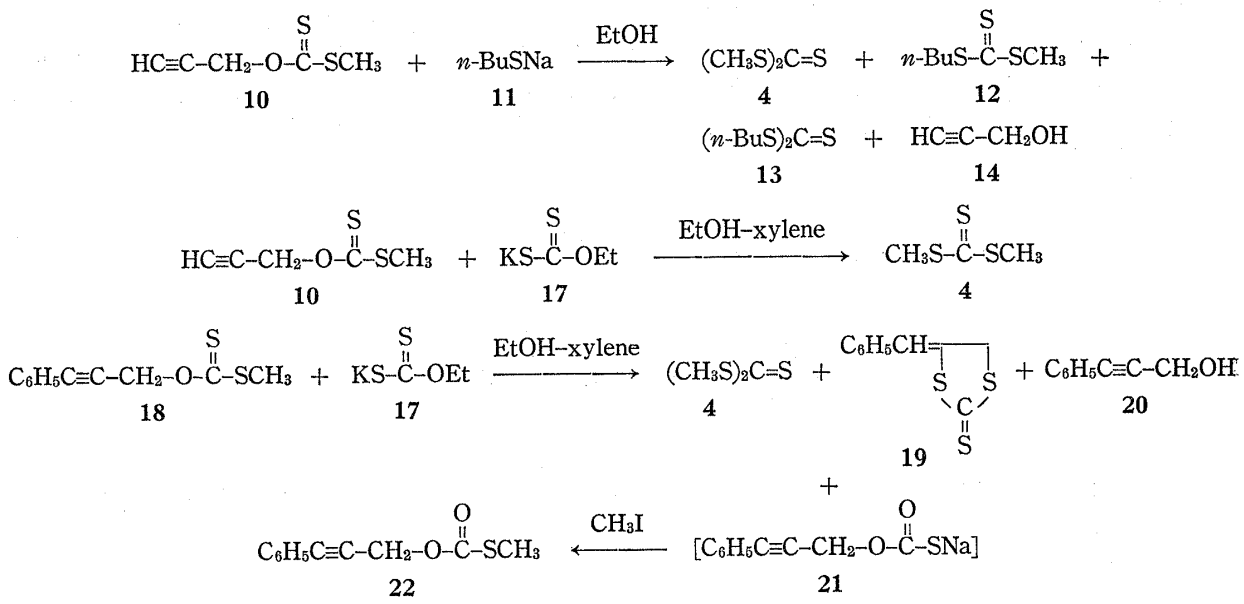
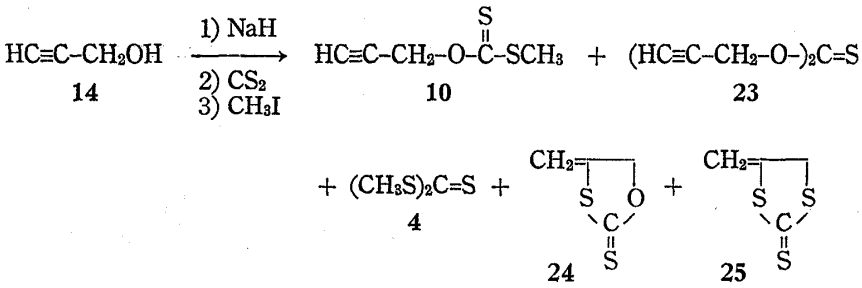


Chart 1

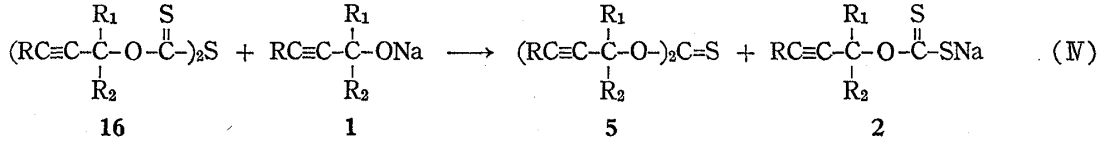
If sodium methane thiolate (**15**) could be generated in the course of the reaction of α-acetylenyl xanthate (**3**) with sodium α-acetylenyl xanthate (**2**), bis-O-α-acetylenyl dithiocarbonic thioanhydride (**16**) should be formed (equation III). However, in all cases, the corresponding thioanhydride (**16**) could not be obtained. Therefore, supposedly the thioanhydride (**16**) was cleaved by a nucleophilic reagent such as alcoholate (**1**), sodium methane thiolate (**15**) or sodium xanthate (**2**).

In the synthesis of S-methyl-O-2-propynyl xanthate (**10**) from 2-propyn-1-ol (**14**), bis-2-propynyl thioncarbonate (**23**)[3] was isolated as one of by-products. This result suggested

5) K. Tomita, M. Nagano and H. Oka, *Chem. Pharm. Bull.* (Tokyo), **16**, 914 (1968).



that sodium α-acetylenyl alcoholate (**1**) would be most suitable as a nucleophilic reagent to cleavage the thioanhydride (**16**) to form bis-α-acetylenyl thioncarbonate (**5**) (equation IV).



Bis-3-phenyl-2-propynyl dithiocarbonic thioanhydride (**28**), which was prepared by treating sodium 3-phenyl-2-propynyl xanthate (**26**) with phosgene according to the procedure by S.V. Zhuravelev, *et al.*,[6] was allowed to react with sodium 3-phenyl-2-propynyl alcoholate (**29**) to afford 4-benzylidene-1,3-oxathiolane-2-thione (**30**)[5] and bis-3-phenyl-2-propynyl thioncarbonate (**31**) whose structure was confirmed on the basis of the spectral and analytical date (Chart 2). The characteristic infrared absorption bands of **31** were observed at 2202 $cm^{-1}$ for a carbon-carbon triple bond (-C≡C-), and at 1287 and 1208 $cm^{-1}$ for a thioncarbonate group (-O-CS-O-). Further confirmation of the structure was obtained from it nuclear magnetic resonance (NMR) spectrum, which showed a singlet at 4.67 $\tau$ for two methylene protons ($-CH_2-$) and a multiplet at 2.90—2.41 $\tau$ for two phenyl groups with an intensity ratio of 2 to 5 (Fig. 1 and Fig. 2).

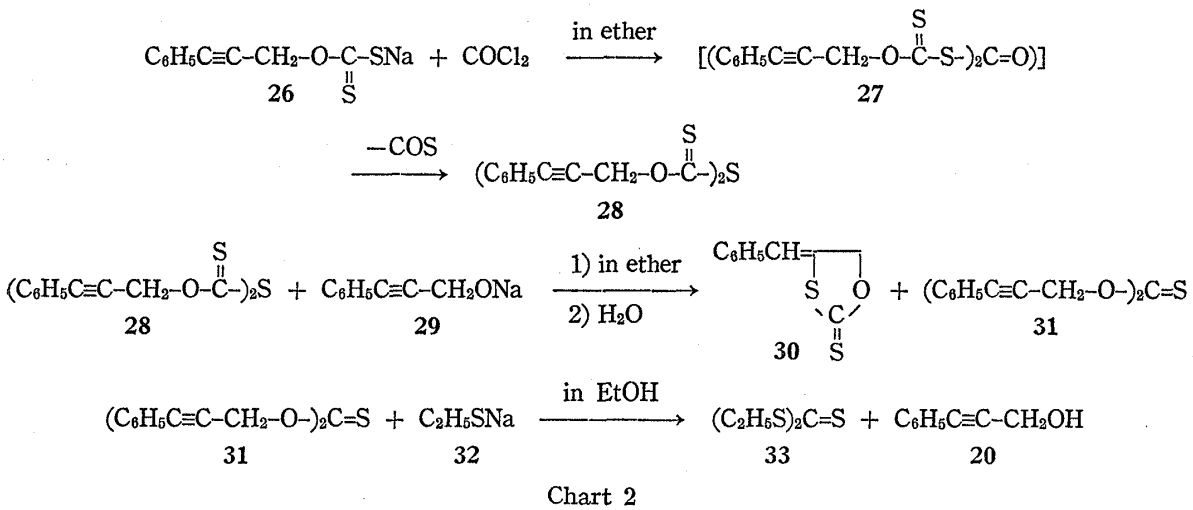


Chart 2

However, in the preparation of α-acetylenyl xanthate (**3**) from almost α-acetylenyl alcohols, except for the case of 2-propyn-1-ol (**14**), the corresponding thioncarbonate (**5**) could not be isolated. Therefore, **5** is presumably further decomposed by a nucleophilic reagent such as alcoholate (**1**), sodium methane thiolate (**15**) or sodium xanthate (**2**). Among these nucleophilic reagents, **15** seemed to be the most suitable for decomposing **5** to xanthate (**3**) and alcoholate (**1**) (equation V).

6) S.V. Zhuravelev and M.I. Galchenko, *J. Appld. Chem.* (U.S.S.R), **20**, 1038 (1947) [*C.A.*, **43**, 143 (1947)].

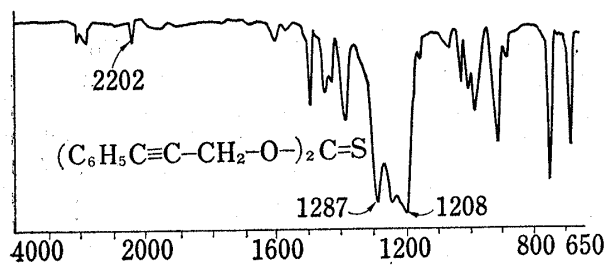



Fig. 1. IR Spectrum of Bis-3-phenyl-2-propynyl Thioncarbonate (31) Wave Number ($cm^{-1}$)

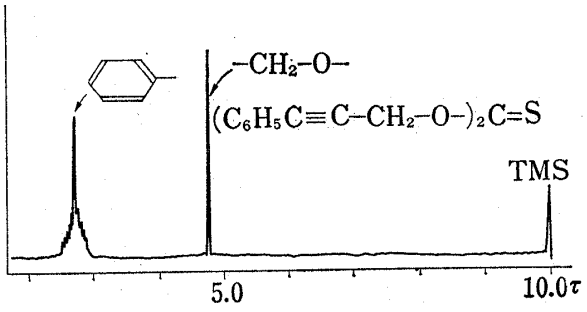



Fig. 2. NMR Spectrum of Bis-3-phenyl-2-propynyl Thioncarbonate (31) (in $CDCl_3$)

$$\underset{\mathbf{5}}{(R\text{–}C{\equiv}C\text{–}\overset{R_1}{\underset{R_2}{C}}\text{–}O\text{–})_2C{=}S} + \underset{\mathbf{15}}{CH_3SNa} \longrightarrow \underset{\mathbf{3}}{RC{\equiv}C\text{–}\overset{R_1}{\underset{R_2}{C}}\text{–}O\text{–}CS\text{–}SCH_3} + \underset{\mathbf{1}}{R\text{–}C{\equiv}C\text{–}\overset{R_1}{\underset{R_2}{C}}\text{–}ONa} \qquad (V)$$

Bis-3-phenyl-2-propynyl thioncarbonate (**31**) was treated with sodium ethane thiolate (**32**) to give diethyl trithiocarbonate (**33**) and 3-phenyl-2-propyn-1-ol (**20**).

On the basis of the above-mentioned experimental results, a pathway for the formation of dimethyl trithiocarbonate (**4**) and other by-products is shown shematically in Chart 3. This mechanism for the formation of the products is rather useful in explaning the correlation between the yield of α-acetylenyl xanthate (**3**) and that of dimethyl trithiocarbonate (**4**). It has been reported that 4-alkylidene-1,3-dithiolane-2-thione (**9**) and sodium O-α-acetylenyl thiolcabonate (**34**) are formed by the reaction of 4-alkylidene-1,3-oxathiolane-2-thione (**8**) with sodium α-acetylenyl xanthate (**2**).[1)]

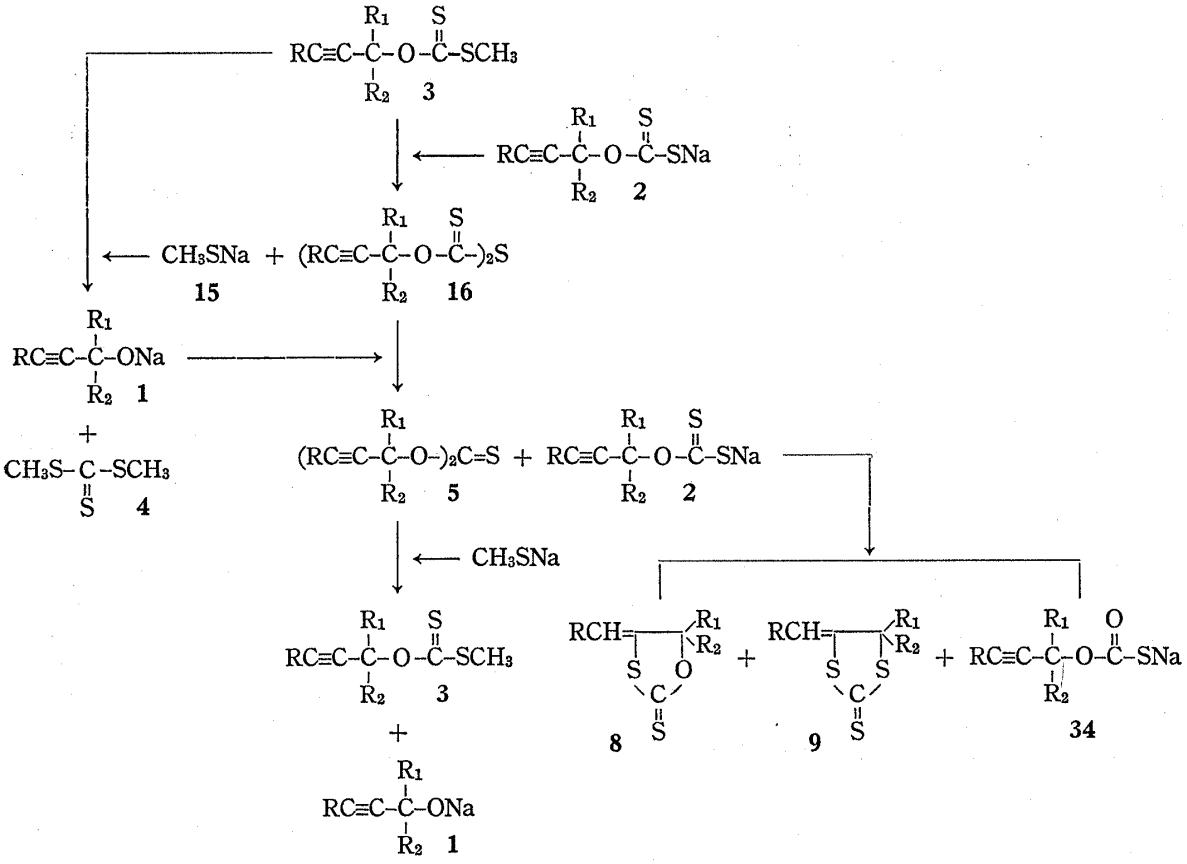



Chart 3

## Experimental[7]

**Reaction of S-Methyl-O-2-propynyl Xanthate (10) and Sodium *n*-Butane Thiolate (II)**——To EtOH–EtONa mixture, which was prepared from EtOH (30 ml) and Na (0.23 g), *n*-butyl mercaptan (1.0 g) and S-methyl-O-2-propynyl xanthate (**10**) (1.46 g) were added and stirred for 1 hr at room temperature. EtOH was evaporated under reduced pressure, a yellow oily residue was poured into ice–water (100 ml) and was extracted with ether. The ethereal layer was washed with $H_2O$ and dried over anhyd. $Na_2SO_4$. After removal of ether, a yellow oily residue was chromatographed over silica gel. Elution with *n*-hexane–benzene afforded a little of 2-propyn-1-ol (**14**), dimethyl trithiocarbonate (**4**) (0.1 g) and the following two trithiocarbonates. (a) 0.4 g of S-methyl-S′-*n*-butyl trithiocarbonate (**12**) as a yellow oil, bp 135° (16 mmHg, bath temp.). *Anal.* Calcd. for $C_6H_{12}S_3$: C, 39.95; H, 6.70; S, 53.53. Found: C, 40.12; H, 6.90; S, 52.60. IR $\nu_{max}^{liquid}$ $cm^{-1}$: 1050 (-S-CS-S-). UV $\lambda_{max}^{EtOH}$ $m\mu(\log\varepsilon)$: 305 (4.02). NMR (in $CCl_4$) $\tau$ ($J$=cps): 9.25—8.09 (7H, m), 7.28 (3H, s), 6.28 (2H, t, $J$=7.0).

(b) 0.3 g of di-*n*-butyl trithiocarbonate (**13**) as a yellow oil, bp 126° (4 mmHg, bath temp.). *Anal.* Calcd. for $C_9H_{18}S_3$: C, 48.95; H, 8.15; S, 43.24. Found: C, 48.72; H, 8.33; S, 42.84. IR $\nu_{max}^{liquid}$ $cm^{-1}$: 1045 (-S-CS-S-). UV $\lambda_{max}^{EtOH}$ $m\mu(\log\varepsilon)$: 3.08 (4.05). NMR (in $CCl_4$) $\tau$: 9.26—7.95 (14H, m), 6.67 (4H, m).

**Reaction of S-Methyl-O-2-propynyl Xanthate (10) and Potassium Ethyl Xanthate (17)**——To the suspension of a commercial potassium ethyl xanthate (1.38 g) in EtOH (20 ml), S-methyl-O-2-propynyl xanthate (**10**) (1.46 g) in xylene (20 ml) was added at room temperature, and was refluxed for 2 hr. After removal of the solvent *in vacuo*, to the yellow oily residue ether (100 ml) was added, and then an insoluble substance was filtered off and the ethereal solution was washed with $H_2O$, and dried over anhyd. $Na_2SO_4$. Ether was removed and the residue was chromatographed over silica gel. Elution with *n*-hexane–benzene (4:1) afforded dimethyl trithiocarbonate (**4**) (0.25 g).

**Reaction of S-Methyl-O-3-phenyl-2-propynyl Xanthate (18) and Potassium Ethyl Xanthate (17)**——To the suspension of potassium ethyl xanthate (**17**) (2.3 g) in THF (40 ml) and EtOH (20 ml), S-methyl-O-3-phenyl-2-propynyl xanthate (**18**) was added at room temperature and stirred for 4 hr at 40—50°. The solvent was removed under reduced pressure, ether (200 ml) was added to the residue and an insoluble substance was filtered off. The filtrate was washed with $H_2O$ and dried over anhyd. $Na_2SO_4$. After removal of ether, a yellow oily residue was chromatographed over silica gel. Elution with *n*-hexane–benzene (4:1) afforded dimethyl trithiocarbonate (**4**) (0.2 g), 4-benzylidene-1,3-dithiolane-2-thione (**19**) and a little of 3-phenyl-2-propyn-1-ol (**20**). Moreover, the mixture of the ether insoluble salt and methyl iodide in ether (100 ml) was refluxed for 6 hr. The reaction mixture was cooled, the insoluble substance was filtered off, the filtrate was washed with $H_2O$ and dried over $Na_2SO_4$. After removal of ether, an oily residue was chromatographed over silica gel. Elution with *n*-hexane–benzene (3: 2) afforded 0.1 g of S-methyl-O-3-phenyl-2-propynyl thiolcarbonate (**22**) as a colorless oil, bp 140—150° (0.2 mmHg, bath temp.). *Anal.* Calcd. for $C_{11}H_{10}O_2S$: C, 64.05; H, 5.33; S, 15.54. Found: C, 63.70; H, 5.05; S, 15.40. IR $\nu_{max}^{liquid}$ $cm^{-1}$: 2220 (-C≡C-), 1720 and 1135 (-S-CO-O-). NMR (in $CCl_4$) $\tau$: 7.67 (3H, s), 5.02 (2H, s), *ca.* 2.7 (5H, m).

**Preparation of Bis-O-3-phenyl-2-propynyl Dithiocarbonic Thioanhydride (28)**——To the suspension of sodium 3-phenyl-2-propynyl xanthate (**26**) in ether (300 ml), which was prepared from 3-phenyl-2-propyn-1-ol (**20**) (5.3 g), Na sand (0.75 g) and carbon disulfide (3.1 g), phosgene ($COCl_2$) was introduced at 20—22° until the precipitation of sodium chloride was finished. An excess of $COCl_2$ was removed by $N_2$ stream, ice–water (200 ml) was added to the reaction mixture, the ethereal layer was separated and the aqueous layer was extracted with benzene. Combined extracts were washed with satd. NaCl solution and dried over anhyd. $Na_2SO_4$. After removal of solvent under reduced pressure, a yellow solid residue was chromatographed over silica gel. Elution with *n*-hexane–benzene (4:1) afforded 3.2 g of bis-O-3-phenyl-2-propynyl dithiocarbonic thioanhydride (**28**) as yellow crystals, mp 70° (Yield: 25%). *Anal.* Calcd. for $C_{20}H_{14}OS_3$: C, 62.79; H, 3.68; S, 25.14. Found: C, 62.78; H, 3.92; S, 24.82. IR $\nu_{max}^{Nujol}$ $cm^{-1}$: 2100 (-C≡C-), 1272 and 1014 (-O-CS-). UV $\lambda_{max}^{EtOH}$ $m\mu(\log\varepsilon)$: 244 (3.83), 303 (3.47). NMR (in $CDCl_3$) $\tau$: 4.16 (4H, s), *ca.* 2.62 (10H, m).

**Reaction of Bis-O-3-phenyl-2-propynyl Dithiocarbonic Thioanhydride (28) and Sodium 3-Phenyl-2-propynyl Alcoholate (29)**——To the suspension of alcoholate (**29**) in ether (50 ml), which was prepared from 3-phenyl-2-propyn-1-ol (**20**) and sodium hydride (0.48 g, *ca.* 50% in oil) in ether, O-3-phenyl-2-propynyl dithiocarbonic thioanhydride (**28**) (0.82 g) was added, succeedingly stirred for 2 hr at room temperature and the reaction mixture was poured into ice–water (100 ml). Organic layer was separated, the aqueous layer was extracted with ether, the combined extracts were washed with satd. NaCl solution and was dried over anhyd. $Na_2SO_4$. After removal of ether, an oily residue was chromatographed over silica gel. Elution with *n*-hexane–benzene (4:1) afforded 0.15 g of 4-benzylidene-1,3-oxathiolane-2-thione (**30**)[8] and

7) The NMR spectra were recorded on Varian A-60 in deuteriochloroform or tetrachloromethane containing tetramethyl silan as internal standard.

8) The infrared spectrum of compound (**30**) became to an agreement with that of the authentic sample.[5]

0.35 g of bis-3-phenyl-2-propynyl thioncarbonate (**31**) as a yellow oil (Yield: 52%). *Anal.* Calcd. for $C_{19}H_{14}O_2S$: C, 74.48; H, 4.10; S, 10.46. Found: C, 74.74; H, 4.96; S, 10.46. IR $\nu_{max}^{liquid}$ $cm^{-1}$: 2202 (-C≡C-), 1287 and 1208 (-O-CS-O-). UV $\lambda_{max}^{EtOH}$ $m\mu(\log \varepsilon)$: 240 (3.53). NMR (in $CCl_4$) $\tau$: 4.77 (4H, s), 2.9—2.41 (10H, m).

**Reaction of Bis-3-phenyl-2-propynyl Thioncarbonate (31) and Sodium Ethane Thiolate**——To the suspension of sodium ethane thiolate (**32**) in EtOH, which was prepared from Na (0.23 g) and ethyl mercaptan (1.4 g) in EtOH (10 ml), bis-3-phenyl-2-propynyl thioncarbonate (**31**) was added and succeedingly stirred for 3 hr at room temperature. After EtOH was evaporated under reduced pressure, ice–water (100 ml) was added to the residue and the suspension was extracted with benzene. The benzene layer was washed with satd. NaCl solution and dried over anhyd. $Na_2SO_4$. After removal of benzene under reduced pressure, a yellow oily residue was chromatographed over silica gel. Elution with *n*-hexane–benzene afforded a little of 3-phenyl-2-propyn-l-ol (**20**), and 0.15 g of diethyl trithiocarbonate (**33**) as a yellow oil. bp 130° (7 mmHg, bath temp.). *Anal.* Calcd. for $C_5H_{10}S_3$: C, 36.10; H, 6.60; S, 57.83. Found: C, 36.45; H, 6.14; S, 57.24. IR $\nu_{max}^{liquid}$ $cm^{-1}$: 1075 and 1023 (-S-CS-S-). UV $\lambda_{max}^{EtOH}$ $m\mu$ $(\log \varepsilon)$: 370 (4.13). NMR (in $CCl_4$) $\tau$ ($J$=cps): 8.65 (6H, t, $J$=7.5), 6.66 (4H, q, $J$=7.5).

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