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Studies on Organo Sulfur Compounds. III.[1] The Reaction of Sodium *prim*-α-Acetylenyl Xanthates and Alkyl Halide

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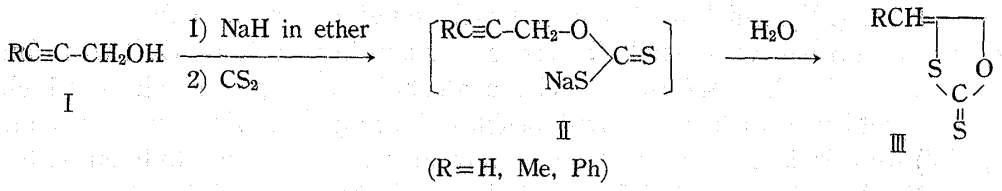
The reaction of sodium xanthates of *prim*-α-acetylenic alcohols and methyl iodide in an aprotic solvent gave corresponding xanthates. But in the case of propargyl alcohol, in addition to propargyl xanthate, dipropargyl thioncarbonate and dimethyltrithiocarbonate could be isolated.

Since sodium methyl xanthate had been synthesized by W.C. Zeise, many chemists have investigated on synthesis of various xanthic esters and their interesting chemical behavior. Nevertheless, there is no report on xanthates derived from α-acetylenic alcohols. Authors have previously reported on the synthesis of 4-alkylidene-1,3-oxathiolane-2-thiones (III) from *prim*-α-acetylenic alcohols (I) and carbon disulfide.[3] It is considered that



the corresponding sodium xanthates (II) are first formed from sodium α-acetylenic alcoholates and carbon disulfide, and then cyclized to III by treatment with water. Therefore, it is expected that when sodium *prim*-α-acetylenyl xanthates (II) are treated with methyl iodide instead of hydrolysis, the corresponding S-methyl xanthates should be obtained. In the present paper authors wish to report on the synthesis of *prim*-α-acetylenyl xanthates.

Sodium 3-phenyl-2-propynyl xanthate, which was prepared from 3-phenyl-2-propyn-1-ol (IV) and carbon disulfide in anhydrous ether under a similar condition as carried out for preparation of 4-benzylidene-1,3-oxathiolane-2-thione,[3] was treated with methyl iodide to afford S-methyl-O-3-phenyl-2-propyn-1-yl xanthate (V) as a pale yellow oil in good yield, being accompanied with small amounts of 4-benzylidene-1,3-oxathiolane-2-thione (VI). The structure of the former compound V was determined on the basis of analytical and spectral data. Characteristic infrared absorption bands were observed at 2225 cm^{-1} for a carbon-carbon triple bond, and at 1198 and 1068 cm^{-1} for a xanthate group (-O-CS-S-). Further confirmation of the structure was obtained from its nuclear magnetic resonance (NMR) spectrum, which showed a singlet at 7.45 τ for three protons (-S-$\underline{CH_3}$), a singlet at 4.62τ for two protons (-C-CH_2-O-) and a multiplet at 2.15—2.32τ for five protons (C_6H_5-). The latter compound VI was coincided with an authentic sample.[3]

In place of 3-phenyl-2-propyn-1-ol (IV), 2-butyn-1-ol (VII) was treated with carbon disulfide and methyl iodide under similar condition to give two main products after silica gel chromatography. One of them was identified as S-methyl-O-2-butyn-1-yl xanthate

1) Part II: K. Tomita and M. Nagano, *Chem. Pharm. Bull.* (Tokyo), **16**, 1324 (1968).
2) Location: *Hiromachi, Shinagawa-ku, Tokyo.*
3) K. Tomita, M. Nagano, and H. Oka, *Chem. Pharm. Bull.* (Tokyo), **16**, 914 (1968).

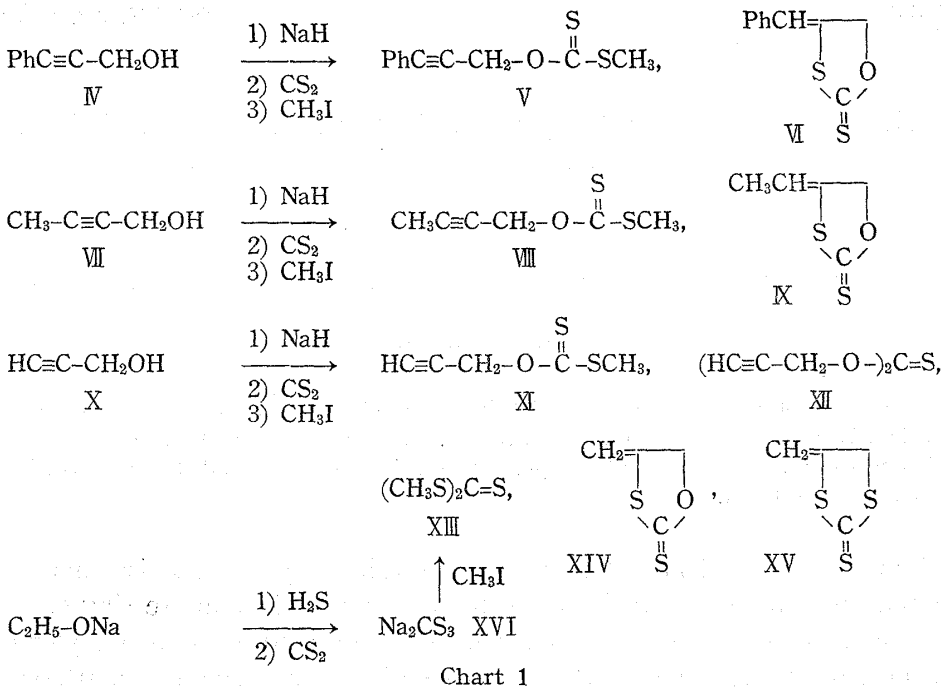


Chart 1

(VIII) on the basis of the spectral and analytical data, and the other as 4–ethylidene–1,3–oxathiolane–2–thione (IX), which was coincided with an authentic sample.[3]

In the case of propargyl alcohol (X), the corresponding xanthate (XI) was obtained as same as the cases of other *prim–α*–acetylenic alcohols by repeated silica gel chromatography, but the yield was rather low, and besides the xanthate (XI) four compounds (XII, XIII, XIV, XV) were isolated. Two of them were identified as 4–methylidene–1,3–oxathiolane–2–thione (XIV) and 4–methylidene–1,3–dithiolane–2–thione (XV) in comparison of their spectral data with those of authentic samples,[3] respectively. One of the remaining two compounds was agreed with dimethyl trithiocarbonate (XIII) prepared from sodium trithio-

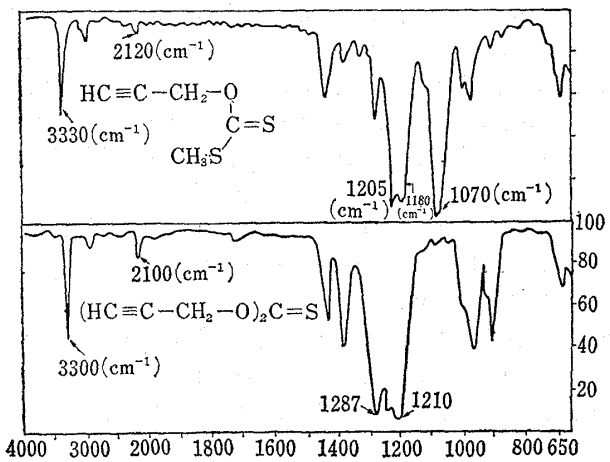


Fig. 1. IR Spectra of S–Methyl–O–propargyl Xanthate (XI) and Dipropargyl Thioncarbonate (XII)

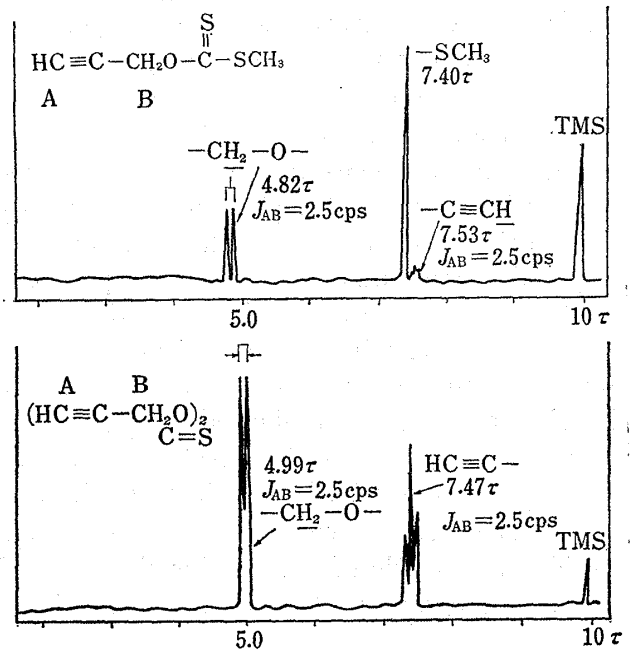


Fig. 2. NMR Spectra of S–Methyl–O–propargyl Xanthate (XI) and Dipropargyl Thioncarbonate (XII)

carbonate and methyl iodide.[4,5] The other compound was identified as dipropargyl thioncarbonate (XII) on the basis of the analytical and spectral data. Characteristic infrared (IR) absorption bands of compound XII were observed at 3300 cm^{-1} for ethynyl group (CH≡C–), at 2100 cm^{-1} for carbon–carbon triple bond (–C≡C–), and 1287 and 1210 cm^{-1} for thioncarbonate group (–O–CS–O–). Further confirmation of the structure was obtained from its NMR spectrum which exhibited the proton signals at 4.99 τ (doublet) and at 3.42τ (triplet) with an intensity ratio of 2 to 1, and with a coupling constant of 2.5 cps.

The formation of cyclization products was due to hydrolysis of remaining sodium xanthates. But the formation of dimethyl trithiocarbonate and dipropargyl thioncarbonate was due to complicated mechanism.

The studies on the mechanism of formation of dipropargyl thioncarbonate (XII) and dimethyl trithiocarbonate (XIII) are in progress.

Experimental[6]

Reaction of Sodium 3-Phenyl-2-propynyl Xanthate with Methyl Iodide——To a suspension of NaH (0.05 mole) in anhyd. ether (100 ml), 3–phenyl–2–propyn–1–ol (IV) (7.25 g) was added dropwise under ice–salt cooling and stirred continuously at room temperature until no bubbles were recognized when a drop of the reaction mixture was added into EtOH. To the reaction mixture, freshly distilled carbon disulfide (4.2 g) was added under ice cooling, and after stirring for 3 hr at room temperature, methyl iodide (8.5 g) was added and let alone over night at room temperature, and then the reaction mixture was poured into ice–water (200 ml). The aqueous layer was extracted with ether, and the combined extracts were washed successively with satd. NaCl solution and H_2O, and dried over anhyd. Na_2SO_4. Solvents were evaporated under reduced pressure and the residue was chromatographed over silica gel column (Cica:[7] over 100 mesh). Elution with hexane–benzene (4:1) afforded the following two substances: (1) 9.65 g of S–methyl–O–3–phenyl–2–propyn–1–yl xanthate (V)[8] as a pale yellow oil. Yield: 85.0%. *Anal.* Calcd. for $C_{11}H_{10}OS_2$ (V): C, 59.42; H, 4.53; S, 28.84. Found: C, 59.58; H, 4.60; S, 28.30. IR ν_{max}^{liquid} cm^{-1}: 3330 (HC≡C–), 2225 (–C≡C–), 1198 and 1060 (–S–CS–O–). UV λ_{max}^{liquid} mμ (log ε): 243 (3.23), 279 (4.02). NMR (in CCl_4) τ(J=cps): 7.45 (3H, s.), 4.62 (2H, s.), 2.85—2.33 (5H, m.). (2) 0.52 g of 4–benzylidene–1,3–oxathiolane–2–thione (VI) as pale yellow crystals. The melting point and infrared spectrum of this compound VI were agreed with those of the authentic sample.[3]

Reaction of Sodium 2-Butynyl Xanthate with Methyl Iodide——By the same method as the case of sodium 3–phenyl–2–propynyl xanthate, 2–butyn–1–ol (VII) (3.85 g) was treated with NaH (0.05 mole), carbon disulfide (4.5 g) and methyl iodide (8.5 g) in ether (100 ml), 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 and ether was evaporated under reduced pressure. The resulting oil was chromatographed over silica gel. Elution with *n*–hexane–benzene (4:1) afforded the following two substances: (1) 3.04 g of S–methyl–O–2–butyn–1–yl xanthate (VIII), bp 60° (0.25 mmHg) (Yield: 38.0%). *Anal.* Calcd. for $C_6H_8OS_2$ (VIII): C, 44.96; H, 5.03; S, 40.01. Found: C, 44.73; H, 5.02; S, 39.02. IR ν_{max}^{liquid} cm^{-1}: 2220 (–C≡C–), 1205 and 1056 (–O–CS–S–). UV λ_{max}^{EtOH} mμ (log ε): 275 (3.99). NMR (in CCl_4) τ(J=cps): 8.11 (3H, t., J=2.4), 7.44 (3H, s.), 4.88 (2H, q., J=2.4). (2) 0.85 g of 4–ethylidene–1,3–oxathiolane–2–thione (IX) was isolated. The boiling point and infrared spectrum of this cyclic compound (IX) were agreed with those of the authentic sample.[3]

Reaction of Sodium Propargyl Xanthate with Methyl Iodide——Propargyl alcohol (X) (6.15 g) was treated with NaH (0.1 mole), carbon disulfide (9.1 g) and methyl iodide (17.0 g) in ether (200 ml), and 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 and ether was evaporated. The residue was chromatographed over silica gel. Elution with *n*–hexane–benzene (4:1) afforded the following five substances. (1) 6.95 g of S–methyl–O–propargyl xanthate (XI) as a pale yellow oil, bp 60° (3 mmHg) (Yield: 47.5%). *Anal.* Calcd. for $C_5H_6OS_2$ (XI): C, 41.06; H, 4.13; S, 43.85. Found: C, 41.32; H, 4.31; S, 43.54. IR ν_{max}^{liquid} cm^{-1}: 3330 (HC≡C–), 2120 (–C≡C–), 1250 and 1070 (–S–CS–O–). UV λ_{max}^{EtOH} mμ (log ε): 278.5 (4.00). NMR (in CCl_4) τ (J=cps): 7.53 (1H, t., J=2.5), 7.4 (3H, s), 4.28 (2H,

4) H. Hagiwara, M. Numata, K. Konishi, and Y. Oka, *Chem. Pharm. Bull.* (Tokyo), **13**, 253, 260 (1965).
5) E.W. Yeoman, *J. Chem. Soc.*, **1921**, 38.
6) All boiling points were uncorrected. The NMR spectra were recorded on Varian A–60 in carbon tetrachloride containing tetramethylsilane as internal standard.
7) Kanto Chemical Co., Inc.
8) This compound V decomposed at 180° and could not be distilled at 160° under 0.05 mmHg.

d., J=2.5). (2) 0.54 g of dipropargyl thioncarbonate (XII) as a pale yellow oil, bp 80° (2 mmHg) (Yield: 7.0%). *Anal.* Calcd. for $C_7H_6O_2S$ (XII): C, 54.52; H, 3.92; S, 20.79. Found: C, 54.81; H, 3.71; S, 20.75. IR ν_{max}^{liquid} cm^{-1}: 3300 (HC≡C–), 2100 (–C≡C–), 1287, 1210 (–O–CS–O–). UV λ_{max}^{EtOH} mμ (log ε): 227.5 (3.89). NMR (in CCl_4) τ(J=cps): 4.99 (4H, d., J=2.5), 7.49 (2H, t., J=2.5). (3) 1.45 g of dimethyl trithiocarbonate (XIII) as a yellow oil, bp 90° (10 mmHg) (Yield: 22.0%). *Anal.* Calcd. for $C_3H_6S_3$ (XIII): C, 26.05; H, 4.37; S, 69.56. Found: C, 26.48; H, 4.64; S, 69.04. IR ν_{max}^{liquid} cm^{-1}: 1078 (–S–CS–S–). UV λ_{max}^{EtOH} mμ (log ε): 303 (4.10). NMR (in CCl_4) τ(J=cps): 7.24 (s.). The physical properties of this compound (XIII) came to an agreement with those of dimethyl trithiocarbonate which was prepared by another method.[4] (4) Two cyclic compounds, 4–methylene–1,3–oxathiolane–2–thione (XIV) (1.32 g) and 4–methylene–1,3–dithiolane–2–thione (XV) (0.37 g) were isolated. The infrared spectra of those compounds were agreed with those of the authentic samples.[3]

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