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

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S-Methyl xanthates of 2-cyclohexen-1-ol (IV), 3-methyl-2-cyclohexen-1-ol (V) and *cis*-3,5-dimethyl-2-cyclohexen-1-ol (VI) transformed to dithiolcarbonates (VIII, IX and X) accompanying allylic shift (S_{Ni}'). On the other hand, S-methyl xanthate of 3,5,5-trimethyl-2-cyclohexen-1-ol (VII) transformed to 3,5,5-trimethyl-2-cyclohexenyl methyl dithiolcarbonate (XI), without allylic shift (S_{Ni}). Of polycyclic system, S-methyl xanthates of $\Delta^{1,9}$-octalin-2-ol (XIII) and Δ^{4}-cholesten-3β-ol (XIX) were submitted to pyrolysis and consequently it was found that they decomposed into methylthio derivatives (XVI and XXI) *via* rearragement to the dithiolcarbonates (XV and XX). In homoallylic system, pyrolysis of S-alkyl xanthates of cholesterol in the presence of phenolic solvent caused the rearrangement to the corresponding dithiolcarbonates with retention of configuration. In each rearrangement reaction, reaction courses are discussed.

In the preceding paper,[1b] it was described that pyrolysis of open-chain allylic xanthates (I) caused usually the rearrangement to the corresponding dithiolcarbonates (III) with allylic shift through the intramolecular cyclic intermediate (II), and by application of the method that thiols are easily generated from thiolesters by heating with 2-aminoethanol,[4] this procedure came to be of synthetic value in obtaining some allylic thiol which might otherwise be difficult to prepare (Chart 1).

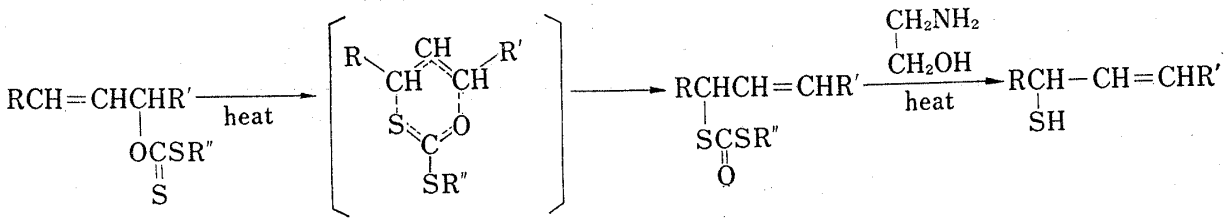


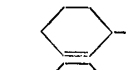
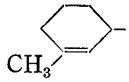
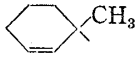
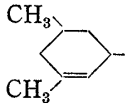
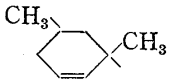
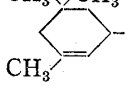
Chart 1

The present paper reports an analogous research in the field of cycloalkenyl compounds, because there has been no information about the pyrolysis of cycloalkenyl xanthate except a few example of homoallylic system such as S-methyl xanthate of *endo*-5-hydroxybicyclo-[2,2,1]-2-heptene[5] and cholesterol.[6] Of monocyclic system S-methyl xanthates of 2-cyclohexen-1-ol (IV), 3-methyl-2-cyclohexen-1-ol (V), *cis*-3,5-dimethyl-2-cylcohexen-1-ol (VI) and 3,5,5-trimethyl-2-cyclohexen-1-ol (VII) were obtained in moderate yields by treating sodium salt of alcohol with carbon disulfide and then methyl iodide in benzene. Though the infrared (IR) spectrum suggested that the mere evaporation of the solvent caused the rearrangement

1) *a*) This forms "Studies in Stereochemistry. XLVIII," by T. Taguchi; *b*) Part VIII: K. Harano and T. Taguchi, *Chem. Pharm. Bull.* (Tokyo), **20**, 2348 (1972).
2) Parts of this work have appeared in preliminary form: T. Taguchi, Y. Kawazoe, K. Yoshihira, H. Kanayama, M. Mori, K. Tabata and K. Harano, *Tetrahedron Letters*, **1965**, 2717.
3) Location: *Katakasu, Fukuoka.*
4) T. Taguchi, Y. Kiyoshima, O. Komori and M. Mori, *Tetrahedron Letters*, **1969**, 3631.
5) W.E. Parham, W.T. Hunter, R. Hanson and J. Lahr, *J. Am. Chem. Soc.*, **74**, 5646 (1952).
6) G.L. O'Connor and H.R. Nace, *J. Am. Chem. Soc.*, **74**, 5454 (1952); *idem, ibid.*, **75**, 2118 (1953).

of xanthates to dithiolcarbonates, the products were further submitted to distillation for purification and completion of the rearrangement. The products (VIII—XI) were identified by elemental analysis, IR and nuclear magnetic resonance (NMR) spectra, and by the isolation of corresponding thiols as 2,4-dinitrophenyl derivatives. As a general feature in each case, the allylic shift associated with the rearrangement was explored by the study of olefinic proton on NMR spectra. The results obtained were summarized in Table I, II and IV.

Table I. 2-Cycloalkenyl Methyl Dithiolcarbonate $ROCSCH_3 \rightarrow R'SCSCH_3$ (S / O)

R		R′		Yield (%)	bp (°C/mmHg)	Formula	Analysis (%) Calcd. C	Calcd. H	Found C	Found H
	IV	R	VIII	40	95/3	$C_8H_{12}OS_2$	51.03	6.42	51.38	6.63
	V		IX	80	94/4	$C_9H_{14}OS_2$	53.42	6.97	53.51	7.07
	VI		X	59	104/1	$C_{10}H_{16}OS_2$	55.51	7.45	55.83	7.62
	VII	R	XI[a]	26	105/3.5					

a) identified by conversion to 2 4-dinitrophenylsulfide (XI′) (TableIV)

Table II. IR and NMR Spectra of 2-Cycloalkenyl Methyl Dithiolcarbonate

Compound		VIII	IX	X	XI
IR ($\nu_{max}^{Film}cm^{-1}$)	$\nu_{C=O}$	1642	1640	1637	1642
	ν_{C-S}	861	856	853	866
NMR (in CCl_4) δ (ppm)	=CH–	5.40—6.00 (m)	5.82 (m)	5.64 (m)	5.30 (s)
	C_1–CH_3		1.68 (m)	1.53 (s)	
	C_3–CH_3				1.68 (s)
	C_5–CH_3			0.98 (d)	0.98 (s)
	S–CH_3	2.37 (s)	2.32 (s)	2.28 (s)	2.38 (s)
	>CH–S	4.10—4.45 (m)			4.05—4.54 (m)

Multiplicity is indicated as follows: s, singlet; d, doublet;m; multiplet.

Only in the reaction of VII, the product could not be isolated in pure form by distillation owing to the difficulty of separation from a small amount of by-product[7] and to instability much more than the others. Therefore, after practicable purification through column chromatography on silica gel, it was characterized by hydrolysis followed by conversion to the 2,4-dinitrophenyl sulfide. In consequence, it was found that S-methyl xanthate of IV, V and VI transformed to dithiolcarbonates (VIII, XI and X) accompanying allylic shift (S_{Ni}'), on the other hand, S-methyl xanthate of VII did not accompany allylic shift transforming to 3,5,5-trimethyl-2-cyclohexenyl methyl dithiolcarbonate (XI), (S_{Ni}).

If the reaction would normally through the cyclic transition state (S_{Ni}') to form XII, it would suffer remarkably the steric compression which is resulted from 1,2-nonbonded

7) The subsequent paper will explore that it consists mainly of the trithiocarbonate.

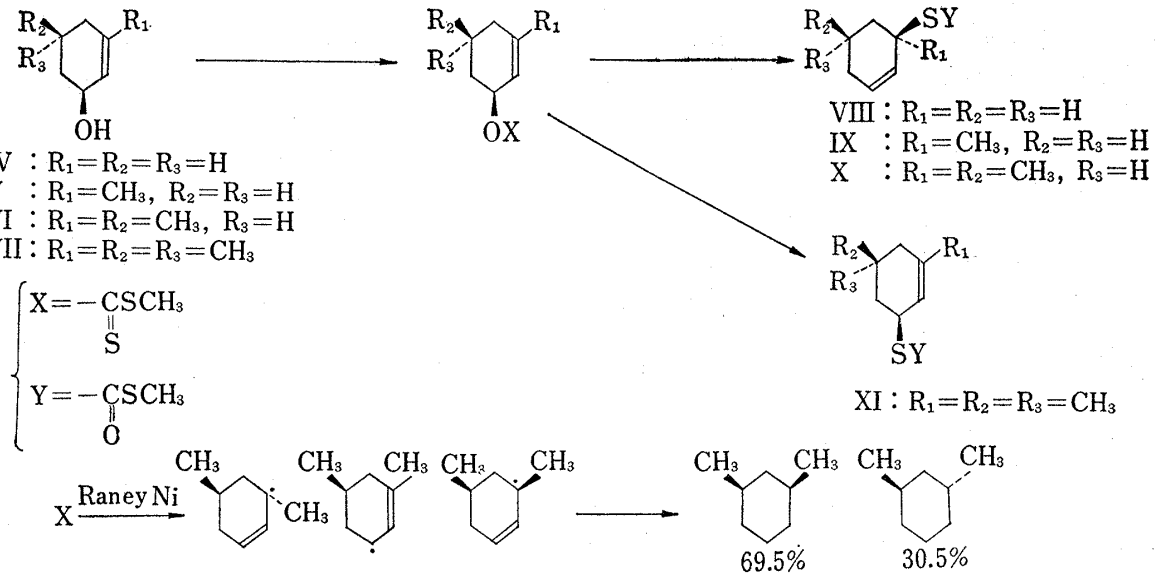


Chart 2

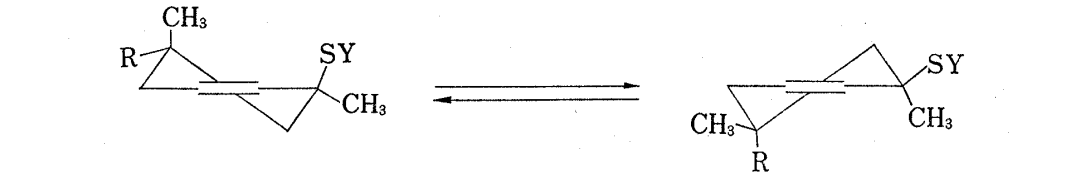


Chart 3

interaction[8] in addition to 1,3-*a*,*a*′ interaction in the half-chair conformation of XII which holds four substituents at C_1 and C_5 (Chart 3).

The steric compression will be severer than what are found in the other examples above mentioned and presumably the reason why the xanthate of VII was forced to transform to XI *via* S*N*i without rearrangement to XII. In the course of this study, the reductive desulfurization of X was undertaken for the expectation yielding DL-*trans*-1,3-dimethylcyclohexane less stable than the *cis*-isomer because X holds dimethyl groups at C_1 and C_3 in the *trans* relationship. However, the result was contrary to the expectation giving a mixture of *cis*- and *trans*-1,3-dimethylcyclohexane in a ratio of 69.5: 30.5 which was determined by gas chromatography. Thus, no advantage was found in this attempt because the ratio coincided nearly with the result in the catalytic reduction of *m*-xylene.[9] An analogous study is found in Weitkamps report[10] which examined the reductive desulfurization of *p*-menthen[6,8]-ylene sulfide. He showed that the reaction began with hydrogenolysis of C-S bond to form an allylic free radical intermediate and then hydrogenation of double bond followed to give *p*-menthane. It is presumed that the formation of 1,3-dimethylcyclohexane proceeded along the analogous course to the case of *p*-menthane as shown in Chart 2. To expand the study to polycyclic system, $\Delta^{1,9}$-octalin-2-ol (XIII) was prepared by lithium aluminum hydride (LAH) reduction of the corresponding ketone according to the reported

8) P.B.D. de la Mare, "Molecular Rearrangement," Part One, ed. P. de. Mayo, John Wiley, and Sons, Inc., New York London, 1963, p. 40.
9) R.H. Baker and R.D. Schuetz, *J. Am. Chem. Soc.*, **69**, 1250 (1947); K.S. Pitzer, and C.W. Beckett, *ibid.*, **69**, 977 (1947).
10) A.W. Weitkamp, *J. Am. Chem. Soc.*, **81**, 3434 (1959).

method.[11] On the basis of the stereochemistry of LAH reduction, β-configuration has been temporarily assigned to the alcohol formed in major. However, in order to assign the conformation exactly, it was needed to begin with separation of the isomeric mixture of alcohol produced. For this purpose, XIII was converted to 3,5-dinitrobenzoate (XIV) and recrystallized from *n*-hexane–benzene. Consequently, only 3,5-dinitrobenzoate (XIV) of the major alcohol could be isolated.

The NMR spectrum of XIV exhibited the C_1 vinyl proton absorption (5.53 ppm) as a broad singlet (W_H=3 Hz) overlapping with a broad absorption band of C_2 methine proton (5.35—5.80 ppm). Using the dihedral relationship for spin-spin coupling in close analogies,[12] the NMR spectrum of XIV was in agreement with the previous assignment of structure. However, in the absence of comparable spectral data with the other isomer, β-configuration assigned to the major alcohol (XIII) seems to lack certainty a little since the 3,5-dinitrobenzoyl group is bulky and the A ring of XIII is flexible enough to suffer conformational change as Dauben pointed out. XIII was converted in the usual way to the xanthate which transformed gradually to the dithiolcarbonate (XV) in the same manner as the case of monocyclic system. For purification, the crude product was distilled under a reduced pressure to give a colorless oil (XVI), bp 89—91° (3 mmHg), which contained sulfur and neverthless, showed no absorption band characteristic of -SCS- group in the IR spectrum. The structure

of XVI was assigned to 2-methylthio-$\Delta^{1,9}$-octalin by NMR spectrum, which exhibited a singlet at 1.98 ppm due to the $-SCH_3$ group, a broad peak at 3.00—3.40 ppm attributable to the C_2 methine proton, and a broad singlet at 5.34 ppm (W_H=5 Hz) due to the C_1 vinyl proton.

Besides, the crude XV was reduced with LAH to give $\Delta^{1,9}$-octalin-2-thiol (XVII) which, without isolation, was further converted to 2,4-dinitrophenyl sulfide (XVIII), mp 147—149°, and characterized by the following observation. The NMR spectrum of XVIII showed the presence of a methine (S-CH<, 4.00—4.35 ppm) and an olefinic protons (=CH-, 5.48 ppm, doublet, J=5.6 Hz) in the same intensity.

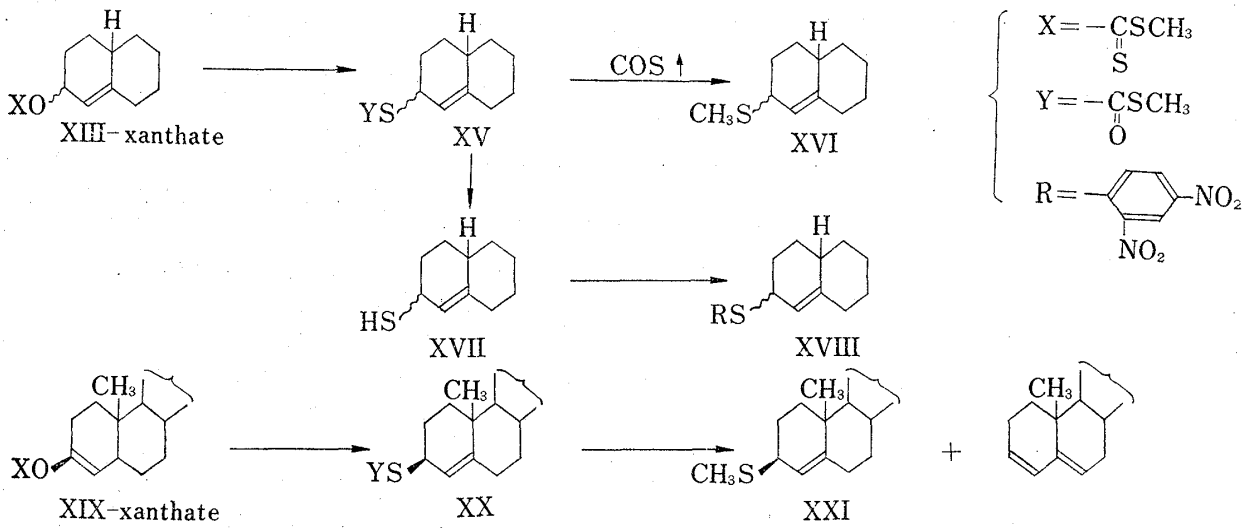


Chart 4

From all these facts, it became clear that the xanthate of XIII rearranged to the dithiolcarbonate (XV) without allylic shift and subsequently decomposed into sulfide (XVI) by

11) J.A. Marshall and W.I. Fanta, *J. Org. Chem.*, **29**, 2501 (1964); H.D. House and C.J. Blankley, *ibid.*, **33**, 53 (1968).

12) W.G. Dauben and A.C. Ashcraft, *J. Am. Chem. Soc.*, **85**, 3673 (1963); R.A. Finnegan and P.L. Bachman, *J. Org. Chem.*, **30**, 4145 (1965).

elimination of COS during distillation. Stereochemistry of transformation reaction of XIII-xanthate to XVI *via* XV was not made clear because the configuration of XIII has remained with some doubt.

Therefore, the same reaction was undertaken with Δ^4-cholesten-3β-ol (XIX), whose configuration has been well established. When XIX was subjected to the formation reaction of xanthate in the usual way, the contaminated product was obtained resulting originally from incomplete formation of sodium salt. The presence of the dithiolcarbonate (XX) instead of the xanthate in the crude product was recognized by thin-layer chromatography (TLC) and IR spectrum as indicated in the cases above-mentioned. But after chromatography on silica gel followed by recrystallization 3β-methylthio-Δ^4-cholestene (XXI) was isolated with 3,5-cholestadiene which would be formed as a product from the Chugaev reaction. The configuration of XXI was established by the NMR spectrum which showed a broad singlet (W_H=5 Hz) due to the C_4 vinyl proton, though it did not show splitting with the magnitude (J≒1) expected from the dihedral relationship. This establishment was supported by the observation that analogous vinyl proton in Δ^4-cholesten-3β-ol or its acetate shows similar spectral attitude.[13] Summerizing the results from the examples of polycyclic allylic system, it is clear that intramolecular rearrangement with allylic shift is not involved in the reaction path, because $\Delta^{1,9}$-octalin-2-thiol (XVII) was characterized as 2,4-dinitrophenyl derivative (XVIII) after hydrolysis of the dithiolcarbonate (XV). Accordingly, the reaction mechanism will be explained so that the xanthate (XXII) transformed to the dithiolcarbonate (XXIII) *via* S_{Ni}, excluding route B which give methylthio compound (XXIV) through XXV (Chart 5).

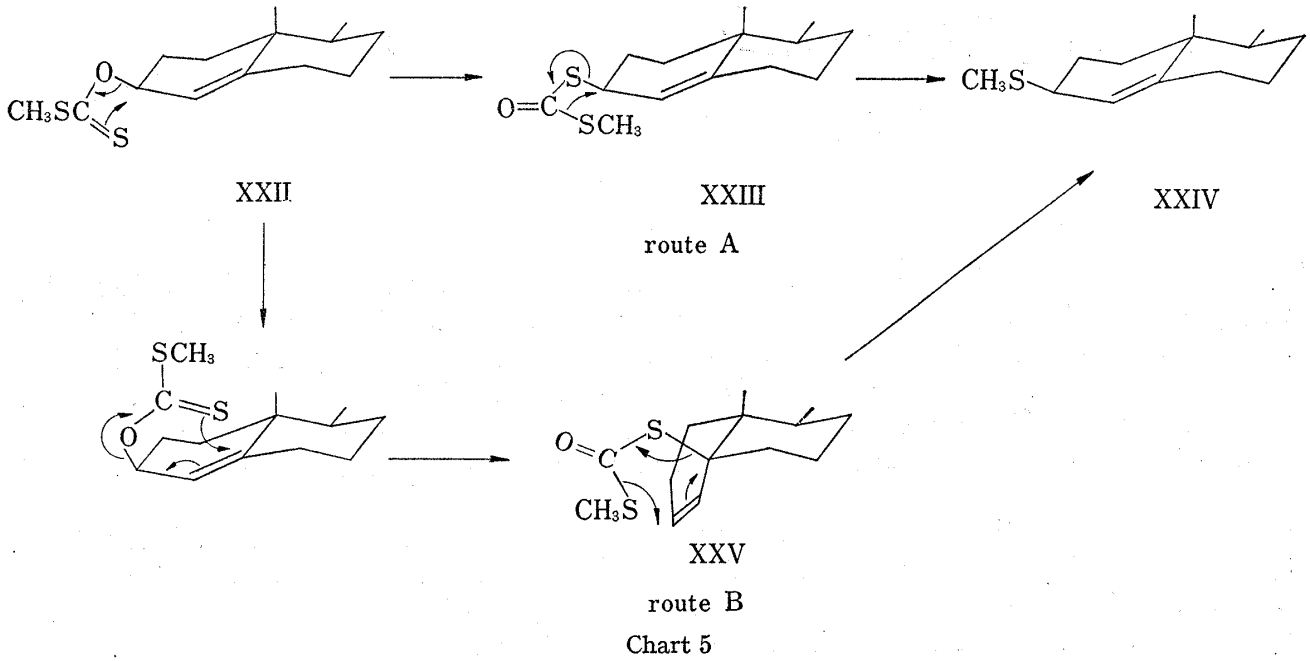


Chart 5

The reason why the rearrangement with allylic shift was inhibited in these cases is presumably due to the increase of instability which was caused by the migration of dithiolcarbonate group to bridge head with *cis*-fusion.

In regard to homoallylic system, pyrolysis of cholesteryl S-methyl xanthate (XXVIa) which produced 3,5-cholestadiene have been kinetically investigated by Nace.[5] At the same time, the influence by addition of radical inhibitors on pyrolysis of β-cholestanyl S-methyl xanthate have been examined to elucidate the mechanism of the Chugaev reaction, but the

13) D.J. Collins and J.J. Hobbs, *Tetrahedron Letters*, **1963**, 197.

same examination has not been done for the pyrolysis of XXVIa. Previously, the present authors found that the decomposition rate of allylic dithiolcarbonate was increased a little by addition of radical inhibitors.[14] On this background, pyrolysis of cholesteryl S-methyl xanthate (XXVIa) was reinvestigated in the existence of hydroquinone as a radical inhibitor. XXVIa alone is known to decompose at 150°, however, in the presence of hydroquinone it transformed to a new compound (XXVIIa) without serious decomposition at the same temperature though it accompanied a small amount of 3,5-cholestadiene as a decompotion product, which was detected by TLC on silica gel.

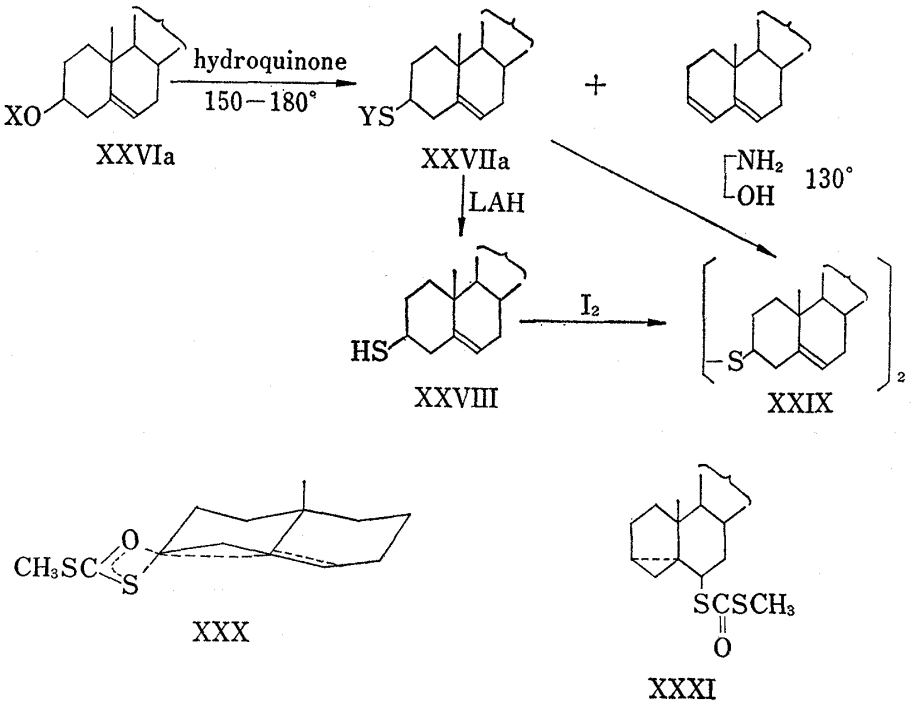


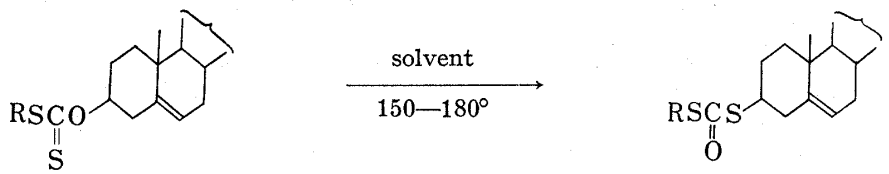
Chart 6

XXVIIa was stable even at 230° and its structure was characterized to be cholesteryl methyl dithiolcarbonate as shown by the following observations. The IR spectrum exhibited absorption bands characteristic of the dithiolcarbonate at 1645 and 858 cm^{-1}. In the NMR spectrum, the C_3 methine signal is observed at 3.0—3.7 ppm shifting to up field by 1.8 ppm from the signal of the corresponding xanthate (XXVIa). A broad peak with a half-band width of 23 Hz due to the C_3 methine proton indicated the -SCSCH$_3$ group equatorial. To confirm the configuration further, XXVIIa was reduced with LAH to the known Δ^5-cholestene-3β-thiol (XXVIII) which was then oxidized with I_2 to the known cholesteryl disulfide (XXIX).[15] The conversion of XXVIIa to XXIX was persued in such a good yield as 76% by application of our method[4] which consists of heating with ethanolamine at 130°. In order to find out the optimum condition of the rearrangement of XXVIa, the reaction was carried out in various solvents.

As Table III shows, of solvent used, the best result was obtained with phenol showing that XXVIIa was yielded in 93% by heating at 150—180° for 1 hr. Therefore, subsequent experiments were carried out by using phenol as solvent, though the remarkable role of phenol has been still obsecure. The change of S-alkyl in a xanthate gave no serious alternation on the reaction feature, though yields were varied as shown in Table III.

14) unpublished report.
15) L.C. King, R.M. Dodson and L.A. Subluskey, *J. Am. Chem. Soc.*, **70**, 1177 (1948).

Table III.



R=CH_3 (XXVIa) solvent=phenol

Solvent	Yield (%)
Phenol	93
Cresol	82
Hydroquinone	60
DMF	15
Diphenylamine	—
Diethylaniline	—

R	Yield (%)
$-CH_3$ (XXVIIa)	93
$-CH_2C_6H_5$ (XXVIIb)	52
$-CH_2C_6H_4$-*p*-NO_2 (XXVIIc)	38

However, alternation of reaction course occured in other thionic ester so that, for example, cholesteryl N-phenylthionocarbamate was decomposed to cholesterol and phenylisothiocyanate. In conclusion, it might be probable that the rearrangement of this type proceeds with retention of configuration through a mesomeric carbonium ion commonly represented by the non-classical structure (XXX) (Homoallylic participation). However, 6β-substituted 3,5-cyclo-steroid (XXXI) which is commonly reffered to as iso steroid[16] was not detected in the cases studied here.

Experimental

Melting and boiling points were 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 5% SE-30 on Chamelite CK (60—80 mesh, 4 m×3 mm) column.

Preparation of the Unsaturated Alcohols——2-Cyclohexen-1-ol[17] (IV) was prepared by hydrolysis of 3-bromocyclohexene. 3-Methyl-2-cyclohexen-1-ol[17] (V), *cis*-3,5-dimethyl-2-cyclohexen-1-ol[18] (VI), 3,5,5-trimethyl-2-cyclohexen-1-ol[19] (VII) and Δ^4-cholesten-3β-ol[17] (XIX) were conveniently prepared by LAH reduction of the corresponding ketones according to the established method.

$\Delta^{1,9}$-Octalin-2-ol[11] (XIII): Prepared by LAH reduction of $\Delta^{1,9}$-octalin-2-one by the procedure of House and Blankly, bp 97—98° (2 mmHg), yield 50%. The 3,5-dinitrobenzoate (XIV): mp 108° (reported mp 101.5—103.5°,[11] mp 110°[20]).

General Method for Preparation of Cycloalkenyl S-Alkyl Dithiolcarbonate *via* Cycloalkenyl S-Alkyl Xanthate——a) To a suspension of 1 mole of sodium sand or sodium hydride in anhydrous benzene was added 1 mole of cycloalkenol and refluxed with stirring. After the metal had reacted, 1.2 moles of carbon disulfide was added with ice-cooling, stirred for 2 hr at room temperature and then 1 mole of alkyl halide added with stirring.

After stirring overnight, the mixture was filtered, washed with water and dried over fused Na_2SO_4. The filtrate was freed of benzene by distillation at a reduced pressure. The residue was distilled in a Claisen flask to give the dithiolcarbonate.

Dithiolcarbonate VIII, IX, X and XI derived from IV, V, VI and VII were prepared in this manner (Table I).

b) $\Delta^{1,9}$-2-Octalyl methyl dithiolcarbonate (XV) was unable to be obtained from the corresponding xanthate by distillation according to heading a) because it decomposed at the temperature.

Therefore, the crude xanthate was chromatographed rapidly on silica gel for purification and eluted with *n*-hexane.

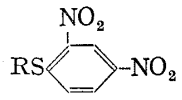
16) N.F. Blau and C.G. Stuckwisch, *J. Org. Chem.*, **25**, 1611 (1960).
17) A.W. Burgstahler and I.C. Nordin, *J. Am. Chem. Soc.*, **83**, 198 (1961).
18) G. Asato, *Dissertation Abstr.*, **22**, 2186 (1962).
19) M.S. Kharash and P.O. Jaewey, *J. Am. Chem. Soc.*, **63**, 2314 (1941).
20) S. Julia, M. Julia and L. Brasseur, *Bull. Soc. Chim. France*, **1962**, 374.

During this operation, conversion of the xanthate to the dithiolcarbonate occured. Yield 63%. IR $\nu_{max}^{liq.}$ cm^{-1}: 1640 (C=O), 855 (C-S). The structure of XV was proven by conversion to 2,4-dinitrophenyl sulfide, XVIII (Table IV).

c) See below for the dithiolcarbonate derived from Δ^4-cholesten-3β-ol.

Preparation of Thiol from Dithiolcarbonate——a) by LAH Reduction: Compounds VIII, IX, X, XI and XV were reduced with LAH in usual manner to the corresponding thiols which were identified as the 2,4-dinitrophenyl derivatives (Table IV).

b) by Improved Method[4]: Compound VIII (1 g) and 2-aminoethanol (3 ml) was heated in a water bath until the evolution of methanethiol had ceased. After a further 10 min, to the resulting mixture was added 2,4-dinitrochlorbenzene (1.1 g) and stirred for 30 min. The precipitate was collected and recrystallized from acetone–ethanol to afford yellow crystals of 2-cyclohexenyl 2,4-dinitrophenyl sulfide (VIII), mp 116°, weight 1.23 g (86%).

Table IV. 2-Cycloalkenyl 2,4-Dinitrophenyl Sulfide 

R	mp (°C)	Formula	Analysis (%) Calcd. C	H	N	Found C	H	N
2-Cyclohexenyl- VIII′	114.5—115.5	$C_{12}H_{12}O_4N_2S$	51.42	4.32	9.99	51.60	4.47	10.02
1-Methyl-2-cyclohexenyl- IX′	110	$C_{13}H_{14}O_4N_2S$	53.05	4.79	9.52	52.89	4.60	9.81
1,5-Dimethyl-2-cyclohexenyl- X′	129—130	$C_{14}H_{16}O_4N_2S$	54.53	5.23	9.08	54.59	5.52	8.93
3,5,5-Trimethyl-2-cyclohexenyl- XI′	130—132	$C_{15}H_{18}O_4N_2S$	55.89	5.63	8.69	55.78	5.72	8.44
Δ^2- Octalyl- XVIII	147—149	$C_{16}H_{18}O_4N_2S$	57.47	5.43	8.38	57.49	5.63	8.21

Reductive Desulfurization of 1,5-Dimethyl-2-cyclohexenyl Methyl Dithiolcarbonate (X)——A solution of X (0.5 g) in ethanol (10 ml) was refluxed with Raney Ni catalyst (W-4, 5 g) for 1 hr.

The catalyst was removed by filteration and throughly washed with ethanol. The gas chromatogram of the combined ethanol solution indicated the composition of the product to be 30.5% *trans*-1,3-dimethylcyclohexane and 69.5% *cis*-1,3-dimethylcyclohexane.

Pyrolysis of $\Delta^{1,9}$-2-Octalyl Methyl Dithiolcarbonate (XV)——Compound XV (2 g) was distilled under reduced pressure to give a colorless oil of $\Delta^{1,9}$-2-methylthiooctalin (XVI), weight 1.5 g, bp 89—91° (3 mmHg). *Anal.* Calcd. for $C_{11}H_{18}S$: C, 72.49; H, 9.96. Found: C, 72.31; H, 9.70. IR $\nu_{max}^{liq.}$ cm^{-1}: 1656 (C=C). NMR (in CCl_4): 1.98 (3H, singlet, CH_3S-), 3.00—3.40 (1H, broad, >CH-S), 5.34 (1H, broad singlet, W_H=5 Hz, >CH-).

3β-Methylthio-Δ^4-cholestene (XXI)——A mixture of Δ^4-cholesten-3β-ol (2 g) and 0.4 g of potassium was heated at 80° until the evolution of hydrogen had ceased. After cooling to room temperature, to the reaction mixture was added 0.5 ml of dry carbon disulfide, and the resulting red mixture was stirred for 6 hr at room temperature, 0.6 ml of CH_3I added and stirred for 12 hr. The mixture was filtered to remove the precipitate, washed with water, dried over fused Na_2SO_4, and evaporated *in vacuo* (80°) to give a red oil. The IR spectrum of the crude product showed the characteristic absorption bands of the dithiolcarbonate at 1638 (C=O) and 860 (C-S) cm^{-1}. This oil was chromatographed on silica gel. 1) From elution with pet. ether; 244 mg of 3,5-cholestadiene. 2) From elution with *n*-hexane; colorless needles of XXI, mp 74.5—76° (acetone–ether), $[\alpha]_D^{16}$ −41.5° (c=1.2, $CHCl_3$), yield 491 mg. *Anal.* Calcd. for $C_{28}H_{48}S$: C, 80.71; H, 11.61. Found: C, 80.51; H, 11.53. IR ν_{max}^{Nujol} cm^{-1}: 1647 (C=C). NMR (in CCl_4): 1.04 (3H, singlet, C_{19}-CH_3), 2.11 (3H, singlet, -SCH_3), 3.05—3.50 (1H, broad, >CH-S), 5.36 (1H, broad singlet, =CH-).

Cholesteryl S-Methyl, S-Benzyl and S-(*p*-Nitrobenzyl) Xanthate (XXVIa), (XXVIb) and (XXVIc)——Prepared from cholesterol and the corresponding halide along the procedure of O'Connor.[6]

Pyrolysis of Cholesteryl S-Methyl Xanthate (XXVIa) in the Presence of Hydroquinone——A mixture of XXVIa (1 g) and hydroquinone (0.2 g) was heated at 180° until the reaction had completed by indication of thin layer chromatography. The reaction mixture was poured into water, basified with aqueous Na_2CO_3 and extracted with ether. The ether extract was washed with water, dried over anhydrous $MgSO_4$ and evaporated to leave a colorless syrup, which was chromatographed on silica gel. 1) From elution with *n*-hexane; 280 mg of 3,5-cholestadiene. 2) From elution with *n*-hexane–benzene (8: 2): colorless needles of cholesteryl methyl dithiolcarbonate (XXVIIa), mp 158° (ethyl acetate), $[\alpha]_D^{23}$ −38° (c=2.15, $CHCl_3$). Yield 540 mg. *Anal.* Calcd. for $C_{29}H_{48}OS_2$: C, 73.05; H, 10.15. Found: C, 73.52; H, 10.14. IR ν_{max}^{KBr} cm^{-1}: 1645 (C=O), 858 (C-S). NMR (in CCl_4): 0.98 (3H, singlet, C_{19}-CH_3), 2.38 (3H, singlet, S-CH_3), 3.0—3.8 (1H, broad, >CH-S), 5.35 (1H, multiplet, =CH-).

Cholesteryl Disulfide (XXIX)——a) XXVIIa (500 mg) in abs. ether (20 ml) was added to LAH (100 mg) in abs. ether (10 ml) and working up in the usual way gave 5-cholestene-3β-thiol (420 mg, mp 85—86.5°) which was oxidized with I_2 to the disulfide, mp 145—146°, $[\alpha]_D^{22}$ −42° (c=2.0, $CHCl_3$), weight 408 mg, identical with an authentic sample.[15]

b) A mixture of XXVIIa (700 mg) and 2-aminoethanol (500 mg) was heated at 130° until the methanethiol had ceased to evolve.[4]

The reaction mixture was poured into water depositing a colorless solid. The solid was collected by filteration and washed with water. Recrystallization from benzene–ethanol gave colorless plates of XXIX, mp 145—146.5°, weight 468 mg (76%), identical with an authentic sample.[15]

Rearrangement of XXVIa—c to the corresponding Dithiolcarbonates in Phenol. Cholesteryl Methyl Dithiolcarbonate (XXVIIa)——A mixture of XXVIa (1 g) and phenol (3 ml) was heated at 180° in an oil bath for 1 hr until the reaction had been completed (thin layer chromatography). The reaction mixture was poured into water depositing a colorless solid. The solid was collected on a filter and washed with water. Recrystallization from ethyl acetate gave colorless needles of XXVIIa, 930 mg (93%).

Cholesteryl Benzyl Dithiolcarbonate (XXVIIb)——Prepared from XXVIb in 52% yield working up just as the case of XXVIa, mp 131° (acetone), $[\alpha]_D^{16}$ −36.2° (c=2.57, $CHCl_3$). *Anal.* Calcd. for $C_{35}H_{52}OS_2$: C, 76.03; H, 9.48. Found: C, 76.10; H, 9.48. IR ν_{max}^{KBr} cm^{-1}: 1643 (C=O), 860 (C-S). NMR (in CCl_4): 0.98 (3H, singlet, $C_{19}CH_3$), 3.1—3.6 (1H, broad, >CH-S), 4.09 (2H, singlet, -SCH_2-), 5.32 (1H, multiplet, =CH-).

Cholesteryl *p*-Nitrobenzyl Dithiolcarbonate (XXVIIc)——Prepared from XXVIc in 38% yield working up just as the case of XXVIIa, mp 116.5—117.5°, $[\alpha]_D^{16}$ −39.6° (c=2.27, $CHCl_3$). *Anal.* Calcd. for $C_{35}H_{51}O_3NS_2$: C, 70.31; H, 8.60; N, 2.34. Found: C, 69.99; H, 8.60; N, 2.40. IR ν_{max}^{KBr} cm^{-1}: 1643 (C=O), 850 (C-S). NMR (in $CDCl_3$): 0.98 (3H, singlet, C_{19}-CH_3), 3.2—3.8 (1H, broad, >CH-S), 4.3 (2H, singlet, S-CH_2-), 5.38 (1H, multiplet, =CH-).

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