

Thermal Rearrangement of Thiocarboxylates

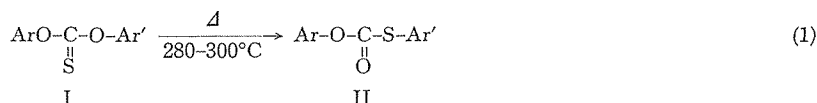
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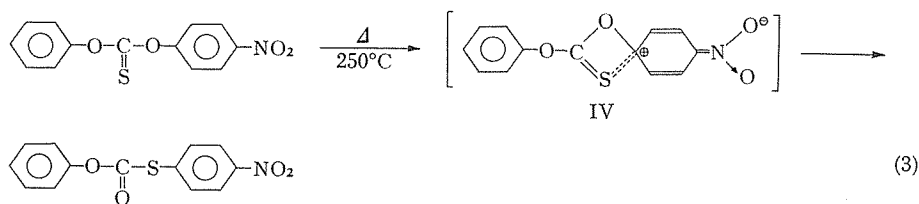
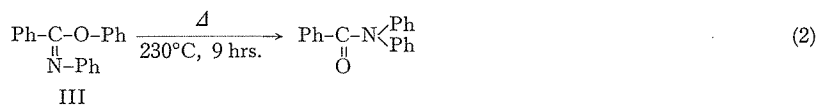
Many kinds of thiocarboxylic acid esters and their analogues such as thiolimidates and isothioureas, are occasionally possible to undergo thermal rearrangement reactions. In many cases of them, the reaction is unimolecular, of which the mechanism is considered to be ionic one and the yield is often satisfactory. So the reaction may be an interesting subject for the study of reaction mechanism and synthesis.

Rearrangement of Thionocarbonate

Diaryl thionocarbonate (I) can be smoothly converted by thermal rearrangement into the thiol-ester (II) (eq. 1).

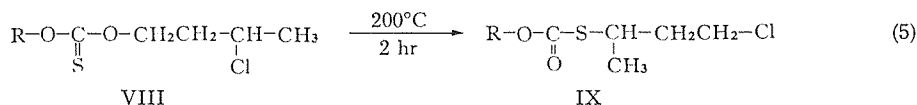
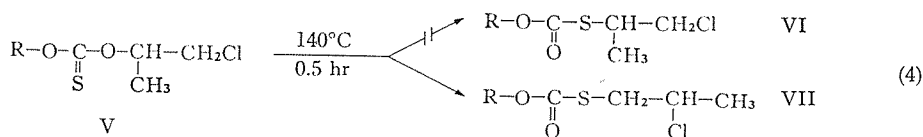


This reaction was early found by Schönberg *et al.*,¹⁾ and is generally called the Schönberg rearrangement. Tarbell *et al.*²⁾ studied this reaction kinetically and found that it was unimolecular, and the introduction of electron-withdrawing substituent at the *ortho* or *para* position of the aryl moiety facilitated the reaction. Since the activation energy (38.2 Kcal/mole) and the entropy of activation (−12.6 eu.) were similar to the case of the Chapman rearrangement of α -phenoxybenzanile (III)³⁾ (eq. 2), they proposed a mechanism involving a four-membered cyclic transition state (IV) (eq. 3).

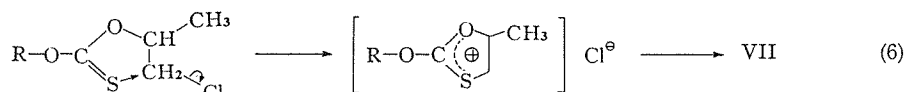


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But this type of rearrangement ($C=S \rightarrow C=O$) does not always proceed according to this mechanism. Garmise *et al.*⁴⁾ found that the thermal rearrangement of chloroalkyl thionocarbonate (V) did not give VI, but afforded VII predominantly (eq. 4), and also VIII gave IX (eq. 5).

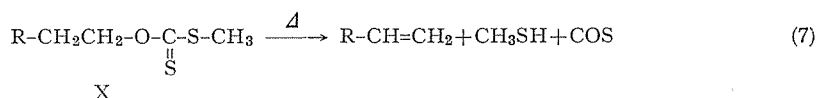


In these cases, the nucleophilic attack of sulfur atom would occur selectively on the carbon atom jointed with chlorine atom, *i.e.* the reaction would not proceed via the four-membered transition state, but through an ionic state according to eq. 6.

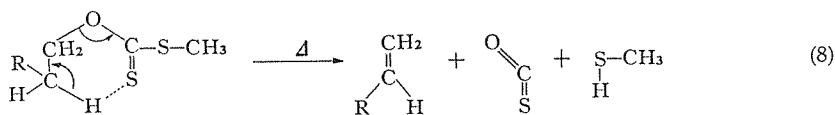


Rearrangement of Xanthate

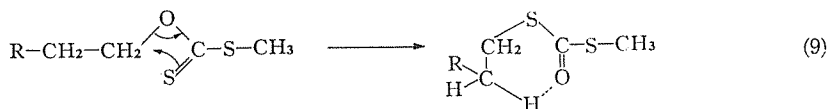
The olefin is eliminated from alkyl xanthate (X) by the thermal decomposition known as the Chugaev reaction⁵⁾ (eq. 7).



Stevens *et al.*⁶⁾ suggested a mechanism involving the attack of thiocarbonyl sulfur atom on the hydrogen atom which is jointed to the β -carbon of the etheral oxygen atom (eq. 8). This suggestion was supported by Hückel,⁷⁾ Barton,⁸⁾ and Cram.⁹⁾



Since sulfur atom has low tendency to form hydrogen bonding, Tabel *et al.*¹⁰⁾ contrarily supposed the mechanism in which the β -hydrogen is abstracted by the carbonyl oxygen precedently formed by the rearrangement via four-membered cyclic transition state (eq. 9).

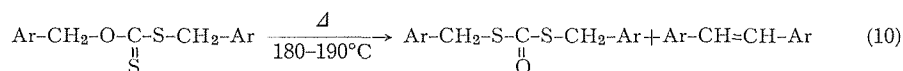


This supposition seems to be reasonable because oxygen has strong ability to form hydrogen bonding, and the β -hydrogen of the sulfur atom may be more easily abstracted than that of the oxygen atom. But there is no evidence that the Schönberg rearrangement of such xanthates having β -hydrogen in ester group may precede the Chugaev reaction. Furthermore, Bader *et al.*¹¹⁾ found the isotope effects of the sulfur atom and the carbonyl carbon atom in the thermal decomposition of methyl trans-2-methyl-1-indanylxanthate to be consistent with the values predicted from the results of the hydrogen abstraction by the thiocarbonyl sulfur atom as shown in Table 1.

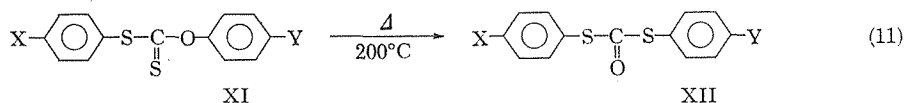
Table 1. Isotope Effects in the Pyrolysis (at 80°C) of S-Me Trans-2-Me-1-Indanylxanthate.

	percent isotope effect (k^D/k^H -1) $\times 10^2$		
	Thiol-S	Thione-S	Carbonyl-C
Predicted	S^{32}/S^{34}	S^{32}/S^{34}	C^{12}/C^{13}
Thiol-S	~ 1.2	~ 0.0	$3.4 \sim 4.0$
Thione-S	~ 0.0	$0.7 \sim 1.0$	~ 0.0
Found	0.21 ± 0.07	0.86 ± 0.16	0.04 ± 0.06

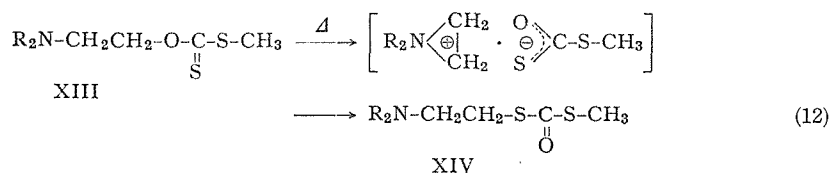
Though we know an example of the Schönberg rearrangement of xanthate,¹²⁾ the reaction mechanism is not obvious owing to the by-product (eq. 10).



The author *et al.*^{13,14)} have found the thermal rearrangement reaction of aryl arylxanthates (XI) (eq. 11) is unimolecular, and no crossover products are obtained. Concerning the influence of substituents X and Y on the reaction rate, $\rho_{X, \text{NO}_2} = -0.4$, $\rho_{H, Y} = 1.2$ were found according to Hammett's σ .

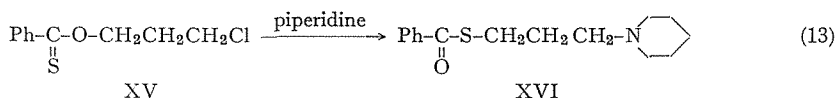


So this rearrangement may also proceed via four-membered transition state similar to that of the Schönberg rearrangement. Even some kinds of alkyl xanthate, in which the " β -hydrogen" is contained, rearrange to the dithiolocarbonate without occurrence of the Chugaev reaction. For example, Taguchi *et al.*¹⁵⁾ have shown that methyl 2-dialkyl-aminoethylxanthate (XIII) is converted to the dithiolocarbonate (XIV) by distillation. From the results of the stereochemical studies on the rearrangement of the analogues, they supposed that this reaction should proceed via immonium ion-pair as shown in eq. 12.

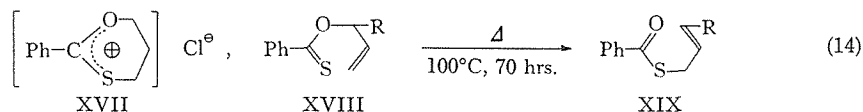


Rearrangement of Alkyl Thionobenzoate

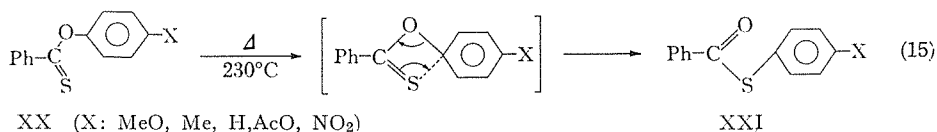
Concerning to the rearrangement of alkyl thionobenzoate, an early example shown in eq. 13 was reported by Karjale *et al.*¹⁶⁾



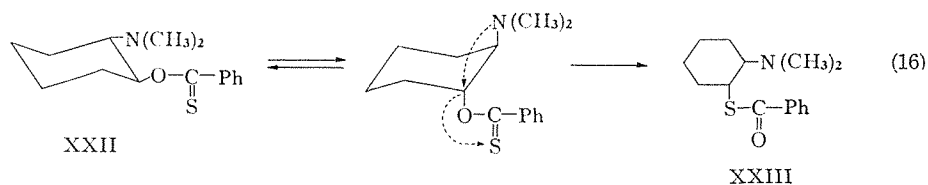
Although the possibility of intermolecular reaction has not been excluded, this reaction may proceed via an intermediate XVII similar to that in the case of the thionocarbonate VII. Rearrangement of allyl thionobenzoate (XVIII) to the thiobenzoate (XIX) was found by Smith¹⁷⁾ (eq. 14). From the studies of the solvent effects upon the reaction rate, it was suggested that the structural difference between the ground state and the transition state is rather small.



From the secondary isotope effect upon the rearrangement of α - and γ -deuterized allyl thionobenzoate, a similar conclusion was given by Mc. Michael¹⁸⁾. The author *et al.*¹⁹⁾ have found that the rate constants of the thermal rearrangement of *p*-substituted-phenyl thionobenzoate are well correlated with the σ^- -values and ρ is equal to +2.0. So this reaction may also proceed via a four-membered transition state (eq. 15) similarly to that of the Schönberg rearrangement.

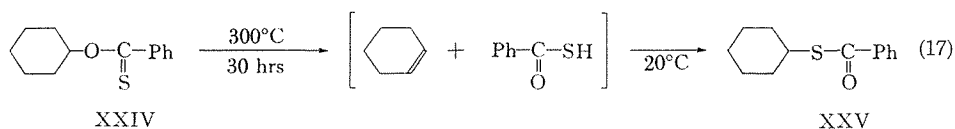


Taguchi *et al.*²⁰⁾ clarified that β -dialkylaminoethyl thionobenzoate thermally rearranges via immonium ion pair similarly to the xanthate XIII. In this case, trans-2-dimethylaminocyclohexyl ester (XXII) smoothly rearranges by distillation (175°C/4mm) to the thiol-ester (XXIII) (eq. 16), but the cis ester to which the contribution of the β -amino group is sterically difficult, does not rearrange even at 200°C.



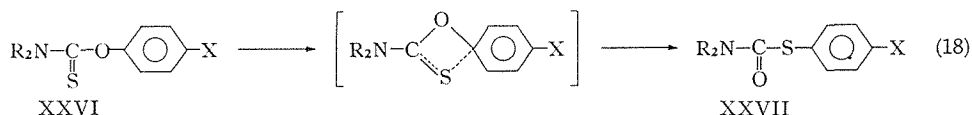
On the other hand, cyclohexyl thionobenzoate (XXIV) is converted to the thiol-ester

(XXV); Taguchi *et al.* supposed a reaction mechanism involving the recombination of cyclohexene and thiolobenzoic acid which were produced by the Chugaev type reaction (eq. 17), though the evidence appeared to be not sufficient.

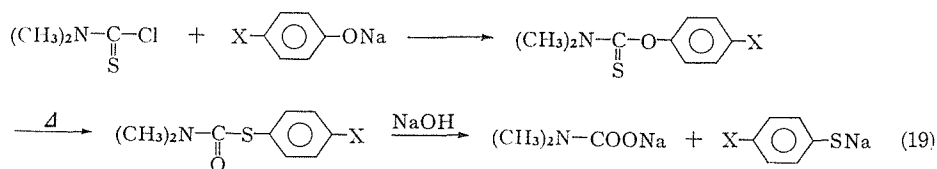


Rearrangement of Thionocarbamate

Aryl thionocarbamate thermally rearranges to the thiol ester. From the results of kinetic studies on thermal rearrangement of *p*-substituted-phenyl thionocarbamates (XXVI) *in neat*, Miyazaki²¹⁾ has supposed that the reaction is intramolecular and proceeds via a four-membered transition state similar to that of the Schönberg rearrangement too (eq. 18).



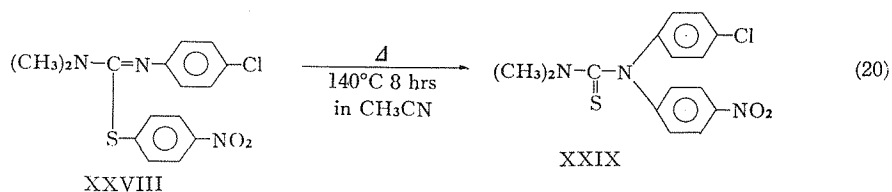
Relles *et al.*²²⁾ found that the acceleration of rate by the influence of the steric effect of *ortho*-substituent was observed in this series similarly to that of the Chapman rearrangement. When the aryl group contains an electron withdrawing substituent, this rearrangement occurs very smoothly. So it has been recommended by Newmann *et al.*^{23,24)} as a convenient new process for the synthesis of thiophenols from the corresponding phenols (eq. 19).



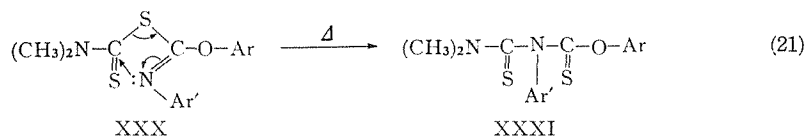
Although this reaction has been claimed to call "the Newmann reaction", it should be called "the Miyazaki-Newmann reaction" since Miyazaki had originally found this rearrangement.

Rearrangement of Thiolimidate

Previously mentioned eq. 2 shows the Chapman rearrangement of an imidate. However, for typical thiolimidate, no example of the Chapman type rearrangement has been reported. The authors *et al.*²⁵⁾ found that *S*-4-nitrophenyl-isothiourea (XXVIII) smoothly rearranges to the thiourea derivative (XXIX) (eq. 20).



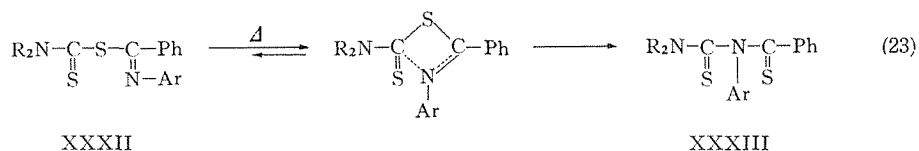
This reaction is unimolecular, and the activation energy (26.6 Kcal.) is in fair agreement with that of the corresponding pseudourea. These facts and negative value of the entropy of activation (-19.1 e.u.) support the reaction mechanism involving a four-centered transition state. The author *et al.*²⁶⁾ also found that aryl thiocarbamoylthiocarbimides (XXX) are smoothly converted to the thiourea derivatives (XXXI) by the thermal rearrangement (eq. 21).



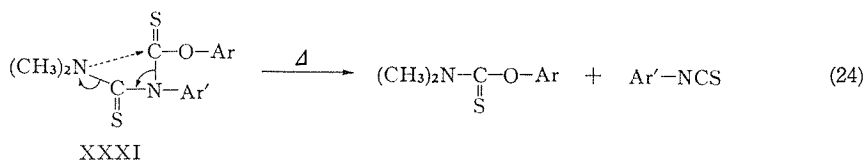
They supposed that this rearrangement might also proceed via a four-centered transition state, because the same product XXXI was obtained by the reaction of 1,1-dimethyl-3-aryl thiourea with an aryl chlorothionoformate (eq. 22).



Miyazaki²⁷⁾ reported the analogous example in which XXXII rearranged to XXXIII via a four-membered transition state (eq. 23).



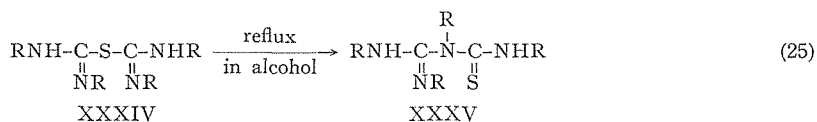
He also found²⁸⁾ that XXXI gave aryl dimethylthionocarbamate and aryl isothiocyanate by the thermal decomposition, and he presumed that the decomposition took place through an intramolecular mechanism involving a four-membered cyclic intermediate (eq. 24).



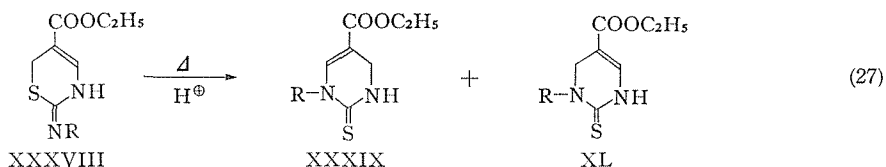
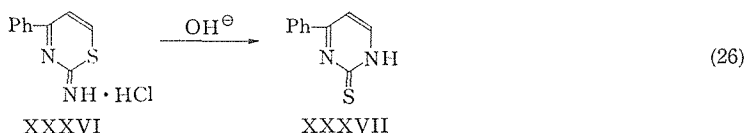
A sulfide (XXXIV) which is obtained by the oxidation of *N,N'*-dialkylthiourea rearranges to XXXV in refluxing alcohol²⁹⁾ (eq. 25). Though the reaction mechanism may be

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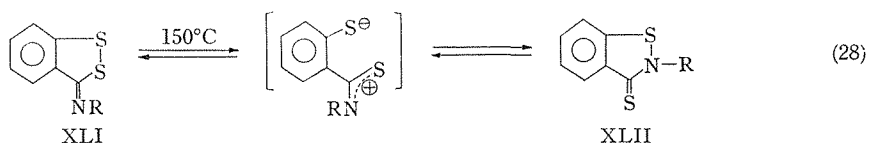
similar to the case of XXXII, it has not been studied.



The analogous rearrangements have also been known in some kinds of conjugated heterocyclic systems: Cavallito *et al.*³⁰⁾ obtained XXXVII by treating XXXVI with alkali (eq. 26). Takamigawa *et al.*³¹⁾ observed the rearrangement of XXXVIII to XXXIX and XL in acidic medium (eq. 27). Though a reshuffle of C-S bond by prototropy has been supposed, it remains the possibility of thermal rearrangement.

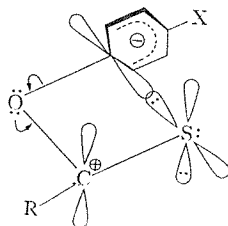


Boshagen *et al.*³²⁾ reported that there is a reversible rearrangement between XLI and XLII (eq. 28).



The results of the kinetic studies on the mechanism of the Schönberg type thermal rearrangement³³⁾ show that there is a good linear free-energy relationship between the rearrangement of aryl *N,N*-dimethylthionocarbamates (XXVI) and the bimolecular nucleophilic reaction of 4- or 5-substituted-1-chloro-2-nitrobenzenes with piperidine. In the former rearrangement a fairly good ρ - σ^- relationship was obtained by using the substituent constants obtained from the latter reaction for the electron-releasing *para*-substituent. Linear free-energy relationships also existed between the rearrangements of XXVI and aryl thionobenzoates (XX), and between the rearrangements of XXVI and aryl phenylxanthate (XI; X = H). The ρ values of these Schönberg-type reactions decreased according to the order of inductive effect of α -substituents of the thiocarbonyl group: $(\text{CH}_3)_2\text{N} > \text{Ph} > \text{Ph-S} > \text{Ph-O}$. So the electron-releasing conjugative effect of the α -substituents of the thiocarbonyl group seemed not to be important in the rate-determining step. The results indicate that the Schönberg type thermal rearrangement of aryl thionocarboxylates is an intramolecular S_N -Ar reaction which involves a four-membered cyclic transition state (XLIII) formed by a nucleophilic attack of the lone-pair

electrons of the thiocarbonyl sulfur atom on the migrating aromatic ring.



XLIII

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