BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3214—3219 (1970)

Studies of the Thiocarbonyl Compounds. II. Syntheses and Thermal Rearrangement of Aryl Thionobenzoates[*1]

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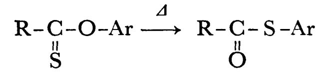
(Received March 6, 1970)

Various aryl thionobenzoates were prepared. When maintained at elevated temperatures, they rearranged smoothly to aryl thiolbenzoates. The mechanism of this rearrangement was kinetically investigated. The rearrangement rates were correlated with the first-order kinetic equation, and the rearrangement was found to be facilitated by substitution with an electron-withdrawing group in the migrating aromatic rings. The Hammett ρ value was found to be 2.11 in diphenyl ether at 200.5°C. The entropies of activation were negative. A linear free-energy relationship existed between this rearrangement and the rearrangement of *O,S*-diaryl dithiocarbonates. From these observations, a four-membered cyclic structure can be suggested as the transition state for this rearrangement. The present results indicate that the existence of hetero atoms directly bound to the thiocarbonyl group is not essential for the thermal rearrangement with intramolecular 1,3 aryl migration from oxygen to sulfur.

In a previous paper,[1] the intramolecular thermal rearrangement of *O,S*-diaryl dithiocarbonates (Ia) to *S,S*-diaryl dithiocarbonates (IIa) at elevated temperatures was reported. In addition to this rearrangement, of the thermal rearrangements with intramolecular 1,3 aryl migration from oxygen to sulfur, the thermal rearrangement of aryl *N,N*-disubstituted thionocarbamates (Ib) to aryl *N,N*-disubstituted thiolcarbamates (IIb) (Miyazaki-Newman-Kwart rearrangement)[2-6] and the thermal rearrangement of diaryl thionocarbonates (Ic) to diaryl thiolcarbonates (IIc) (Schönberg rearrangement)[3,7-10] are known. All of the compounds I



$$\mathrm{R{-}\underset{\underset{S}{\|}}{C}{-}O{-}Ar} \xrightarrow{\Delta} \mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}S{-}Ar} \qquad (1)$$

I II

a: R=Ar'S- b: R=R_1R_2N- c: R=Ar'O-

have hetero atoms with lone-pair electrons, such as sulfur, nitrogen, and oxygen, in the R group. In order to ascertain the nature of this kind of thermal rearrangement, it is necessary to examine whether hetero atoms, which are connected to the thiocarbonyl group, are required in the R group for rearrangement. Accordingly, the thermal rearrangement of aryl thionobenzoates (III), which

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[*1] Presented at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1969.

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1) Y. Araki, This Bulletin, **43**, 252 (1970).

2) J. D. Edwards and M. Pianka, *J. Chem. Soc.*, **1965**, 7338.

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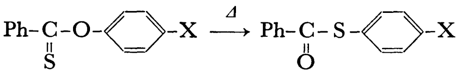
have no hetero atom in the R group, to aryl thiolbenzoates (IV) was investigated.


(2)

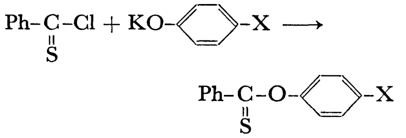
IIIa—g IVa—g

$X = \begin{cases} a: OCH_3 \quad b: CH_3 \quad c: H \quad d: Cl \\ e: COCH_3 \quad f: CN \quad g: NO_2 \end{cases}$

In regard to the thermal rearrangements of thionobenzoates to thiolbenzoates, the thermal rearrangements of dialkylaminoalkyl thionobenzoates[11–13] (an anchimerically-assisted rearrangement), allyl thionobenzoates[14,15] (an allylic rearrangement), and benzhydryl thionobenzoates[16] (a rearrangement through an intimate ion-pair) have been reported. Of the thermal rearrangement of aryl thionobenzoates, however, an example has been reported[4] in which the thermal rearrangement of *p*-*t*-butylphenyl thionobenzoate was qualitatively tested. The present authors have now studied the kinetics of the thermal rearrangement of aryl thionobenzoates in order to establish the reaction mechanism and in order to compare it with the thermal rearrangement of other compounds with the formula I which have hetero atoms in the R group.

Results

The various aryl thionobenzoates (III) were synthesized by the reaction of a *p*-substituted phenol with a thiobenzoyl chloride (Eqs. (3) and (4)). The results are shown in Table 1.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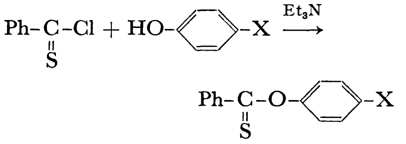
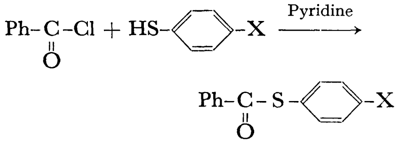
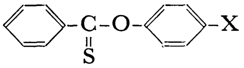

(4)

When maintained at 200°C without any solvent under a nitrogen atmosphere, the compounds III gradually rearranged to aryl thiolbenzoates (IV). The compounds thus obtained were identified by a mixed-melting-point test and by a comparison of the infrared spectra with those of the corresponding authentic samples prepared by the reaction of a *p*-substituted thiophenol with a benzoyl chloride (Eq. (5)).


(5)

In order to clarify the influence of the substituents upon the rates of the rearrangement, the kinetics of the rearrangement were studied in a diphenyl ether solution. The reaction rates were followed by the ampoule technique and were determined by ultraviolet spectrophotometric measurements. It was found that the rearrangement reaction

TABLE 1. ARYL THIONOBENZOATES



Compd. No.	X	Appearance	Mp[a] °C	Formula	Analysis					
					Found			Calcd		
					C(%)	H(%)	S(%)	C(%)	H(%)	S(%)
IIIa	OCH_3	yellow needles[b]	65.5—66.0	$C_{14}H_{12}O_2S$	69.10	4.93	12.88	68.84	4.95	13.10
IIIb	CH_3	yellow needles[b]	44.0—44.5	$C_{14}H_{12}OS$	73.43	5.48	13.96	73.67	5.30	14.02
IIIc	H	yellow needles[b]	40.0—40.5[c]	$C_{13}H_{10}OS$	73.16	4.58	14.87	72.89	4.71	14.94
IIId	Cl	yellow prisms[b]	53.0—55.0	$C_{13}H_9ClOS$	62.78	3.79	13.14	62.79	3.65	12.87
IIIe	$COCH_3$	yellow needles[b]	97.0—98.0	$C_{15}H_{12}O_2S$	70.10	4.72	12.44	70.30	4.72	12.49
IIIf	CN	yellow prisms[d]	112.0—113.0	$C_{14}H_9NOS$	70.56	3.90	13.67	70.29	3.79	13.38
IIIg	NO_2	yellow needles[b]	108.0—109.0[e]	$C_{13}H_9NO_3S$	60.40	3.43	12.19	60.23	3.50	12.35

a) All melting points are uncorrected. b) Recrystallized from *n*-hexane. c) Y. Sakurada, *Mem. Coll. Sci. Kyoto*, [A] **10**, 71 (1927); bp 155—160°C/40 mmHg. R. Mayer and St. Scheithauer, *J. Prakt. Chem.*, **21**, 214 (1963); bp 92°C/0.1 mmHg. d) Recrystallized from benzene-*n*-hexane. e) Ref. 4; mp 98—100°C.

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11) S. A. Karjala and S. M. McElvain, *ibid.*, **55**, 2966 (1933).

12) T. Taguchi, Y. Kawazoe, K. Yoshihira, H. Kanayama, M. Mori, K. Tabata and K. Harano, *Tetrahedron Lett.*, **1965**, 2717.

13) K. Yoshihira and T. Taguchi, *Yakugaku Zasshi*, **89**, 1225 (1969).

14) S. G. Smith, *J. Amer. Chem. Soc.*, **83**, 4285 (1961).

15) K. D. McMichael, *ibid.*, **89**, 2943 (1967).

16) S. G. Smith, *Tetrahedron Lett.*, **1962**, 979.

TABLE 2. REARRANGEMENT OF *p*-CYANOPHENYL THIONOBENZOATE (IIIf) AT 200.5±0.1°C

Time (sec)	% of IIIf remaining	$k\times10^6$ (sec^{-1})
0	100	
3600	79.8	6.28
7200	65.3	5.92
10800	51.8	6.08
14400	41.7	6.07
18000	34.6	5.90

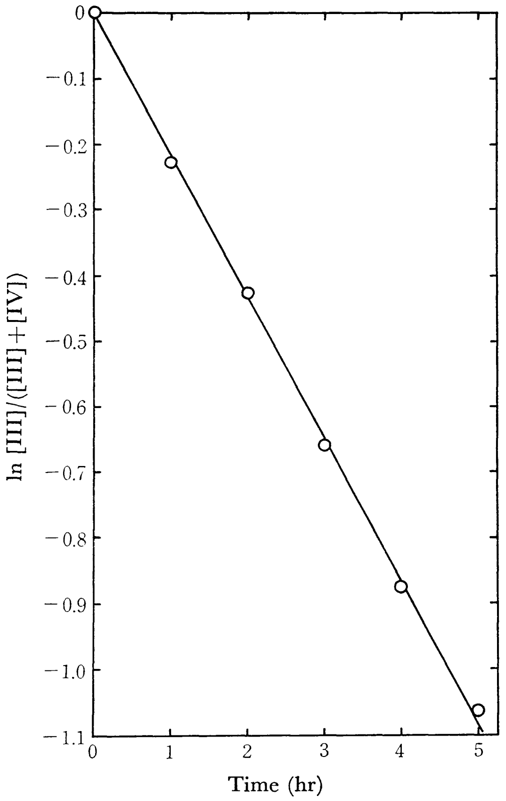


Fig. 1. Rate plot for the rearrangement of *p*-cyanophenyl thionobenzoate at 200.5±0.1°C.

TABLE 3. FIRST-ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS OF THE REARRANGEMENT

Compd. No.	$k\times10^6$ (sec^{-1}) 200.5°C	230.0°C	Ea (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
IIIa	0.542	7.07	41.2	−3.2
IIIb	1.46	17.2	39.5	−4.8
IIIc	2.87	30.0	37.6	−7.4
IIId	3.66	38.5	37.7	−6.7
IIIe	28.9	263	35.4	−7.5
IIIf	60.5	504	34.0	−9.0
IIIg	118	946	33.4	−8.9

obeyed first-order kinetics fairly well. A typical run is shown in Table 2 and Fig. 1; there do not seem to be any drifts in the rate constants. The first-order rate constants were derived from the slopes of the straight lines obtained by plotting ln [III]/([III]+[IV]) against the time. The rate constants found for the rearrangement are summarized in Table 3. From these data, the energies and entropies of activation were calculated. These results are also shown in Table 3.

Discussion

As is shown in Table 3, the rearrangement is accelerated by the electron-withdrawing substituents at the *p*-position on the migrating group. The plot of the logarithms of the first-order rate constants at 200.5°C against Hammett's σ values showed a good linear relationship (Fig. 2). The value of the reaction constant, ρ, determined by the least-squares method is 2.11 (the correlation coefficient is 0.987).

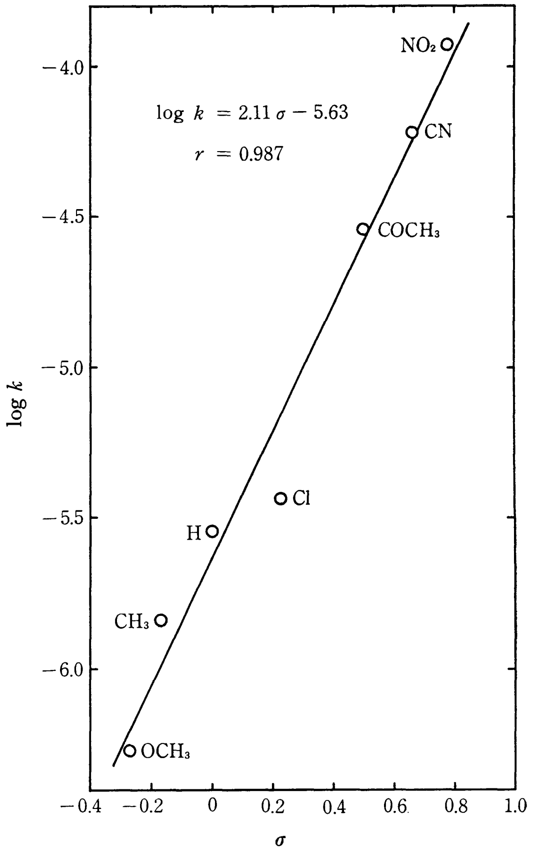
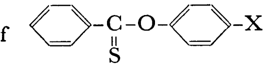


Fig. 2. Hammett plot for the rate of the rearrangement of

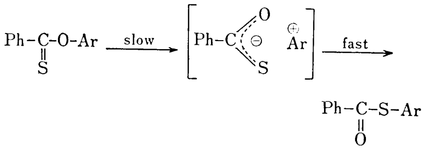


$C_6H_5\text{-}C(=S)\text{-}O\text{-}C_6H_4\text{-}X$

at 200.5±0.1°C.

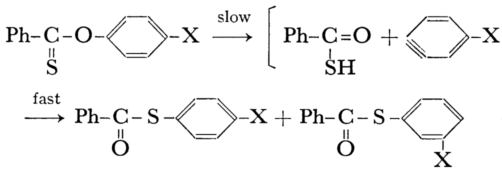
This result indicates that the rearrangement of aryl thionobenzoates is a nucleophilic reaction which may involve a nucleophilic attack of the thiocarbonyl sulfur atom in the rate-determining step.

The intermolecular reaction mechanism which involves a rate-determining initial ionization[16] (Eq. (6)) can be ruled out. In such a case, the rate should depend on the stability of the aryl cation which is stabilized by the electron-donating substituents.



(6)

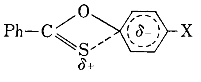
The fact that all of the *p*-substituted compounds III rearranged to only the *p*-substituted products, IV, with no accompanying *m*-substituted product, eliminates the benzyne mechanism (Eq. (7)).



(7)

The isokinetic temperature, β, was calculated to be 1300°K from the data in Table 3 (the correlation coefficient is 0.96). This shows that the rearrangement may be governed by the enthalpy of activation at temperatures near 200°C.

In addition to these results, the first-order kinetics and the negative entropies of activation (Table 3) lead to the conclusion that the rearrangement of aryl thionobenzoates may proceed *via* a four-membered cyclic transition state (Scheme 1) formed by a nucleophilic attack of the thiocarbonyl sulfur atom on the migrating aromatic ring.



Scheme 1

A very good linear free-energy relationship was found between the rearrangement of aryl thionobenzoates and the rearrangement of *O*-aryl *S*-phenyl dithiocarbonates, as is shown in Fig. 3 (the correlation coefficient is 0.999). The slope of the straight line is 1.12. This was rather astonishing considering the absence, in aryl thionobenzoates, of any hetero atoms, which may promote the rearrangement of this sort.

The present results indicate that the existence of hetero atoms in the R group of the formula I at the α position of the thiocarbonyl group is not essential for the thermal rearrangement with intramolecular 1,3 aryl migration from oxygen to sulfur. The rearrangements described above may all proceed analogously by means of an "intramolecular S_N-Ar" mechanism.

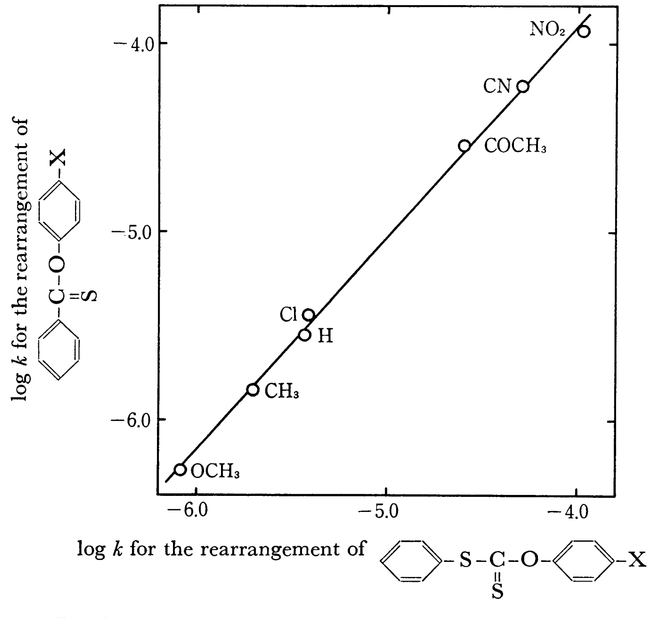


Fig. 3. Free-energy relationship between the rearrangement of aryl thionobenzoates and the rearrangement of *O*-aryl *S*-phenyl dithiocarbonates.

Experimental[*3]

Thiobenzoyl Chloride. This material was prepared by the method of Staudinger.[17]

Aryl Thionobenzoates (III). These compounds were prepared by two methods (Eqs. (3) and (4)). Method A (Eq. (3)) was generally employed, but Method B (Eq. (4)) was also used to prepare the compounds bearing electron-withdrawing substituents because of its convenience. The results are listed in Table 1.

Method A. To 20 m*l* of cold absolute methanol was added, in small portions, 0.78 g (0.02 mol) of potassium. After hydrogen evolution had ceased, 0.02 mol of *p*-substituted phenol was added. The resulting solution was then evaporated to dryness on a rotary evaporator. To the potassium *p*-substituted phenolate thus obtained was added 25 m*l* of dry acetone. This solution was cooled to 0°C in an ice-water bath, and then a solution of 3.13 g (0.02 mol) of freshly-distilled thiobenzoyl chloride in 20 m*l* of dry acetone was added all at once. The resulting mixture was then stirred for 3 hr at 5—10°C, after which the cooling bath was removed. After additional, overnight stirring at room temperature, the reaction mixture was poured into *ca.* 500 m*l* of cold water and then extracted with ether. The ethereal extract was washed with water, dried over anhydrous magnesium sulfate, and freed of solvent on a rotary evaporator. The crude product thus obtained was chromatographed on a silica-gel column, using benzene and/or *n*-hexane as the elution solvent, and then recrystallized from *n*-hexane, giving yellow crystals.

Method B. To a cold solution of 0.02 mol of *p*-substituted phenol and 3.13 g (0.02 mol) of freshly-distilled thiobenzoyl chloride in 40 m*l* of dry acetone in an ice-water bath, there was added, all at once, 2.03 g (0.02 mol) of triethylamine with vigorous agitation. The cooling bath was then removed, and stirring was continued overnight at room temperature. The reaction mixture was then poured into *ca.* 500 m*l* of cold water and extracted with ether. The ethereal extract was washed with water, dried over anhydrous magnesium sulfate, and freed of solvent on a rotary evaporator. The crude product thus obtained was chromatographed on a silica-gel column, using benzene and/or *n*-hexane as the elution solvent, and then recrystallized from *n*-hexane, giving yellow crystals.

Aryl Thiolbenzoates (IV). The following general procedure was employed for the synthesis of these compounds.

To a cold solution of 0.01 mol of *p*-substituted thiophenol and 1.41 g (0.01 mol) of benzoyl chloride in 20 m*l* of dry acetone in an ice-water bath, there was added, all at once, 0.79 g (0.01 mol) of dry pyridine with vigorous agitation. The cooling bath was then removed, and stirring was continued for two more hours at room temperature. The reaction mixture was poured into *ca.* 300 m*l* of cold water; colorless crystals were thus obtained quantitatively. These were recrystallized from a suitable solvent: IVa, colorless needles (from *n*-hexane), mp 100.0—100.5°C (lit,[18] mp 99—100°C). IVb, colorless prisms (from *n*-hexane), mp 76.0—76.5°C (lit,[19] mp 75—76°C). IVc, colorless prisms (from *n*-hexane), mp 56.0—57.0°C (lit,[19] mp 55—56°C). IVd, colorless prisms (from *n*-hexane), mp 75.5—76.0°C (lit,[20] mp 75—76°C). IVe, colorless needles (from benzene–*n*-hexane), mp 134.0—134.5°C (Found: C, 70.05; H, 4.65; S, 12.45%. Calcd for $C_{15}H_{12}O_2S$: C, 70.30; H, 4.72; S, 12.49%). IVf, colorless plates (from benzene–*n*-hexane), mp 101.0—102.0°C (Found: C, 70.00; H, 3.90; S, 13.35%. Calcd for $C_{14}H_9NOS$: C, 70.29; H, 3.79; S, 13.38%). IVg, pale yellow needles (from benzene–*n*-hexane), mp 125.0 — 126.0°C (lit,[21] mp 126—127°C).

Thermal Rearrangement of III. About 500 mg of III was placed in a test tube without any solvent and was heated at 200°C under a slow stream of nitrogen. The progress of the reaction could be followed by thin-layer chromatography on silica gel, with development by benzene and/or *n*-hexane. As a result, it was shown that the compound III was gradually converted to another compound. After the compound III had changed completely, the reaction mixture was chromatographed on a silica-gel column, using benzene and/ or *n*-hexane as the elution solvent. After the solvent had been removed under reduced pressure, the product was recrystallized and identified by means of its IR spectrum and by a mixed-melting-point test with an authentic sample.

Kinetic Measurements. The rates were followed by the ampoule technique. That is, approximately 10 mg of III was dissolved in diphenyl ether, giving a final volume of 5 m*l*. This corresponds to *ca.* a 0.01M solution. About a 0.8-m*l* portion of this solution was transferred to each of six ampoules. These ampoules were flushed with nitrogen and sealed. Five of these ampoules were then immersed in a constant-temperature bath controlled within ±0.1°C. These ampoules, taken out from the bath at appropriate intervals, were cooled immediately by immersion in cold water. From each run thus obtained, a 0.5-m*l* portion was accurately removed into a 5-m*l* measuring flask. The solution was made up to volume with chloroform, and then, further, the solution was diluted twenty times with chloroform to make it suitable for use as the sample for the ultraviolet spectrophotometric measurements.[*4] The optical densities for each run were measured at 300—320 mμ.[*5] The composition of III could be determined directly by substitution in the following equation:

$$\frac{[\mathrm{III}]}{[\mathrm{III}]+[\mathrm{IV}]}=\frac{\varepsilon_{\mathrm{III}}A_t-\varepsilon_{\mathrm{IV}}A_0}{\varepsilon_{\mathrm{III}}A_0-\varepsilon_{\mathrm{IV}}A_0}$$

where $\varepsilon_{\mathrm{III}}$ and $\varepsilon_{\mathrm{IV}}$ are the molar extinction coefficients of III and IV respectively at a stated wavelength, and

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[*3] All melting points are uncorrected.

17) H. Staudinger and J. Siegmant, *Helv. Chim. Acta*, **3**, 824 (1920).

18) M. F. Taboury, *Bull. Soc. Chim. Paris*, [3] **33**, 836 (1905).

19) K. Miyaki and S. Yamagishi, *Yakugaku Zasshi*, **76**, 436 (1956).

20) M. F. Taboury, *Bull. Soc. Chim. Paris*, [3] **31**, 646 (1904).

21) G. Cilento, *J. Amer. Chem. Soc.*, **75**, 3748 (1953).

[*4] A Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer was used for the ultraviolet spectrophotometric measurements.

[*5] In this range, the absorption of diphenyl ether could be negligible.

where A_t and A_0 are absorption intensities at the same wavelength, observed at time t and time 0 respectively. In all cases, a plot of the logarithms of [III]/([III]+[IV]) against the time gave a straight line, indicating the reaction to be of first-order (Fig. 1). The results of a typical kinetic run are illustrated in Table 2. From these data, the rate constants were calculated (Table 3).

The authors wish to express their sincere thanks to Dr. Jun-ichi Hayami for his invaluable discussions.