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Studies of the Thiocarbonyl Compounds. III. The Mechanism of the Thermal Rearrangement of Aryl Thionocarboxylates[1]

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The thermal rearrangement of aryl thionocarboxylates was kinetically investigated in diphenyl ether. The rate constants of the rearrangement of aryl *N,N*-dimethylthionocarbamates were well correlated with the σ^- values, but the plots of the electron-releasing *para*-substituents deviated slightly on the lower side of the *meta* correlation line. A good linear free-energy relationship existed between the rearrangement of aryl *N,N*-dimethylthionocarbamates and the bimolecular nucleophilic reaction of 4- or 5-substituted 1-chloro-2-nitrobenzenes with piperidine. By the use of the substituent constants obtained from the latter reaction for the electron-releasing *para*-substituent constants, a fairly good ρ–σ^- relationship was obtained. Linear free-energy relationships also existed between the rearrangements of aryl *N,N*-dimethylthionocarbamates and aryl thionobenzoates, and between the rearrangements of aryl *N,N*-dimethylthionocarbamates and *O*-aryl *S*-phenyl dithiocarbonates. The order of the reaction constants was in accord with that of the inductive effects of the α-substituents of the thiocarbonyl group, so the electron-releasing conjugative effects of the α-substituents of the thiocarbonyl group did not play important roles in the rate-determining step. The present results indicate that the thermal rearrangement of aryl thionocarboxylates is an intramolecular S_N–Ar which involves a four-membered cyclic transition state formed by a nucleophilic attack of the lone-pair electrons of the thiocarbonyl sulfur atom on the migrating aromatic ring.

Since Schönberg and his co-workers reported the thermal rearrangement of diaryl thionocarbonates (I) to diaryl thiolcarbonates (II)[2,3] (the so-called Schönberg rearrangement), a number of thermal rearrangements have been reported regarding the intramolecular 1,3 aryl migration from oxygen to sulfur. Tarbell and his co-workers reported that the Schönberg rearrangement proceeds by a nucleophilic attack of the thiocarbonyl sulfur atom on the aromatic ring, with a four-membered cyclic transition state.[4,5]

Recently we reported the rearrangement of *O,S*-diaryl dithiocarbonates (III) to *S,S*-diaryl dithiocarbonates (IV)[6] and the rearrangement of aryl thionobenzoates (V) to aryl thiolbenzoates (VI).[7] These rearrange-

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[1] Presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.

[2] A. Schönberg and L. Vargha, *Ber.*, **63**, 178 (1930).

[3] A. Schönberg, L. Vargha, and W. Paul, *Ann. Chem.*, **483**, 107 (1930).

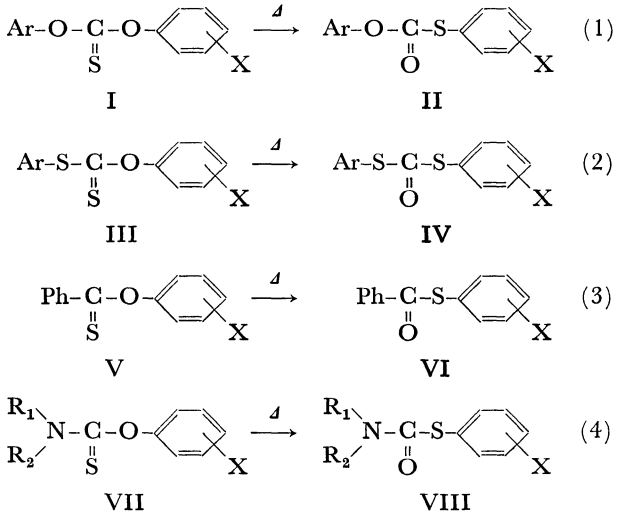
[4] H. R. Al-Kazimi, D. S. Tarbell, and D. Plant, *J. Amer. Chem. Soc.*, **77**, 2479 (1955).

[5] D. H. Powers and D. S. Tarbell, *ibid.*, **78**, 70 (1956).

[6] Y. Araki, This Bulletin, **43**, 252 (1970).

[7] Y. Araki and A. Kaji, *ibid.*, **43**, 3214 (1970).

ments are facilitated by an electron-withdrawing group on the migrating aromatic ring and proceed *via* a four-membered cyclic transition state through the intramolecular nucleophilic attack of the thiocarbonyl sulfur atom on the migrating aromatic ring. Since a good linear free-energy relationship exists between these rearrangements, the existence of hetero-atoms directly bound to the thiocarbonyl group is not essential for the rearrangements with intramolecular 1,3 aryl migration from oxygen to sulfur.



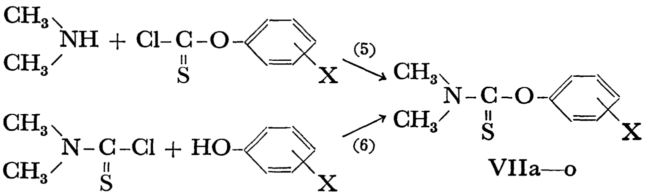
Aryl *N*,*N*-disubstituted thionocarbamates (VII) were also found to rearrange to aryl *N*,*N*-disubstituted thiolcarbamates (VIII).[8] A kinetical investigation in the absence of any solvent showed that this rearrangement proceeds by the intramolecular mechanims just as in the above rearrangements. It was also reported that ordinary Hammett plots of log k against σ^- do not give a satisfactory linear relationship (the correlation coefficient is 0.982), and that, by assuming that $r=1.60$ in the Yukawa-Tsuno equation,[9] the plots between log k and $\sigma^0+r\Delta\sigma_R$ give a better straight line (the correlation coefficient is 0.987). It is noteworthy that this value of r is extraordinary large. On the other hand, Relles and Pizzolato, in their study of the substituent effect of the same rearrangement in dipheny ether, reported that, when the log k values are plotted against Hammett σ values, the correlation coefficient is only 0.839, but when the log k values are plotted against the σ^- values, the correlation coefficient is 0.954,[10] which is inferior to the correlation coefficient reported by Miyazaki. However, they did not report the effects of the *meta*-substituents and of the strongly electron-withdrawing *para*-substituents.

It is obvious that all of the Schönberg-type rearrangements proceed *via* a four-membered cyclic transition state through an intramolecular nucleophilic attack of the thiocarbonyl sulfur atom on the migrating aromatic ring. However, as for the substituent effects, many obscure points remain. Therefore, we studied kinetically the thermal rearrangements of the various *meta*- or *para*-substituted aryl *N*,*N*-dimethylthionocarbamates and diaryl thionocarbonates in diphenyl ether and compared them with other Schönberg-type rearrangements.

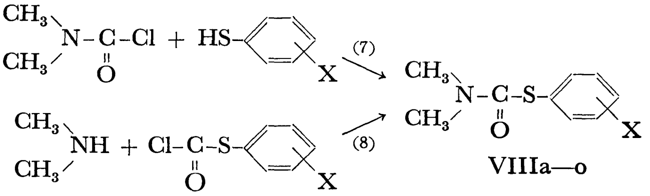
This paper will discuss a detailed mechanism of the Schönberg-type rearrangements.

Results and Discussion

The various aryl *N*,*N*-dimethylthionocarbamates (VIIa—o) were synthesized by the reaction of dimethylamine with an aryl chlorothionoformate (Eq. (5)) and/or by the reaction of *N*,*N*-dimethylthiocarbamoyl chloride with an appropriate phenol (Eq. (6)).



The various aryl *N*,*N*-dimethylthiolcarbamates (VIIIa—o) were obtained by heating the corresponding compounds VII. The compounds VIII were identified by a mixed-melting-point test and by a comparison of the infrared spectra with those of the corresponding authentic samples, which were prepared by the reaction of *N*,*N*-dimethylcarbamoyl chloride with an appropriate thiophenol (Eq. (7)) and/or by the reaction of dimethylamine with an aryl chlorothiolformate (Eq. (8)).



In order to clarify the substituent effects, the kinetics of the thermal rearrangement of aryl *N*,*N*-dimethylthionocarbamates were investigated at 200.5±0.1°C in diphenyl ether. The reactions were followed by the ampoule techniques, and the rates were determined by ultraviolet spectrophotometric measurements. As has been noted previously, [8,10] this rearrangement obeyed fairly good first-order kinetics. The first-order rate constants were derived from the slopes of the straight lines obtained by plotting ln[VII]/([VII]+[VIII]) against the time; the results are summarized in Table 1. The rates of the rearrangement are much faster for the electron-withdrawing substituents than for the electron-releasing substituents.

The logarithms of the rate constants can be plotted against the σ^- values[11] to give a straight line (Fig. 1). By means of the method of least-squares, the ρ value was calculated to be 1.97 (the correlation coefficient is

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8) K. Miyazaki, *Tetrahedron Lett.*, **1968**, 2793. A preliminary report of this work was presented in part at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

9) Y. Yukawa, Y. Tsuno, and M. Sawada, This Bulletin, **39**, 2274 (1966).

10) H. M. Relles and G. Pizzolato, *J. Org. Chem.*, **33**, 2249 (1968).

11) J. Clark and D. D. Perrin, *Quart. Rev.* (London), **18**, 295 (1964).

Table 1. First-order rate constants of the thermal rearrangement of aryl *N*,*N*-dimethylthionocarbamates (VII) in diphenyl ether at 200.5±0.1°C

Compd. No.	X	$k\times10^6$ (sec^{-1})
VIIa	*p*-OCH_3	0.813
VIIb	*p*-CH_3	2.22
VIIc	H	5.92
VIId	*p*-Cl	9.40
VIIe	*p*-Br	13.1
VIIf	*m*-$COCH_3$	16.8
VIIg	*m*-Cl	24.8
VIIh	*m*-Br	28.5
VIIi	*m*-CF_3	31.6
VIIj	*m*-NO_2	72.1
VIIk	*p*-CO_2CH_3	137
VIIl	*p*-$CO_2C_2H_5$	142
VIIm	*p*-$COCH_3$	148
VIIn	*p*-CN	372
VIIo	*p*-NO_2	1210

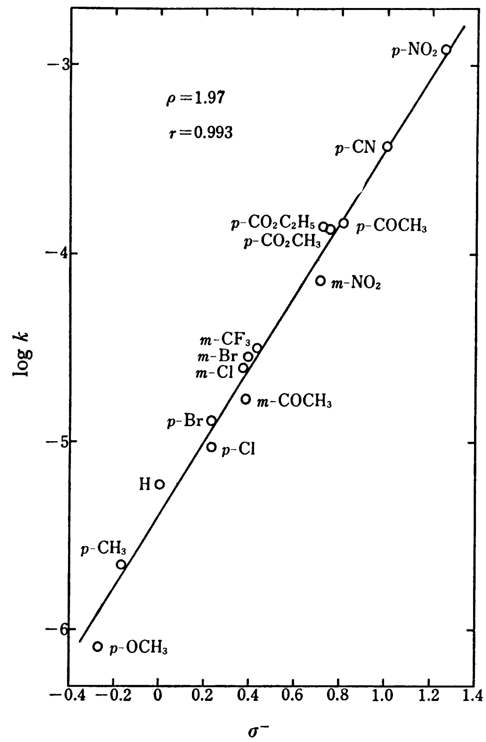

Fig. 1. Hammett plot for the rates of the thermal rearrangement of aryl *N*,*N*-dimethylthionocarbamates (VII) in diphenyl ether at 200.5±0.1°C.

0.993). These results establish that this rearrangement is an intramolecular nucleophilic aromatic substitution reaction and that the additional delocalization by the resonance of the negative charge produced at the reaction site occurs in the transition state in diphenyl ether. The good correlation coefficient shows that it is sufficient if the r value in the Yukawa-Tsuno equation is 1.00 for this rearrangement in diphenyl ether. On the other hand, the r value of 1.60 has been obtained in the absence of any solvent.[8] It is clear that the solvent affects the rates of this rearrangement. In the absence of any solvent, the substrates themselves behave as solvents; these solvent effects, "self-solvent effects," presumably vary in parallel with the variation in the substituents on the materials, so that r in Yukawa-Tsuno equation may become as large as 1.60.

The Hammett plots of the electron-releasing *para*-substituents deviate slightly on the lower side of the *meta* correlation line (Fig. 1). The electron-releasing *para*-substituents may be expected to cause an additional resonance between the substituent and the reaction center in a manner similar to that of the electron-withdrawing *para*-substituents. However, such a resonance is ordinarily found to be very minor and negligible. Consequently, with regard to the electron-releasing *para*-substituents, the Hammett σ values are usually used instead of σ^- values in such nucleophilic reactions. However, the electron-releasing *para*-substituents of aryl *N*,*N*-dimethylthionocarbamates obviously exert a higher retardation of the rearrangement than would be anticipated from the ρ—σ^- relationship. It is necessary to give suitable σ^- values for the electron-releasing *para*-substituents instead of the Hammett σ values in this case. With respect to the σ^- value of the *para*-methoxy group, values of −0.11 for the reactions of phenols and −0.25 for the reactions of anilines have been provided,[12] but these values are very unsatisfactory for correcting the above Hammett plots.

The bimolecular nucleophilic aromatic substitution reactions[13] are reactions very similar to the Schönberg-type rearrangements. These nucleophilic aromatic substitution reactions do not correlate with the Hammett σ values, σ^n values[14] and σ^0 values,[15] but correlate well with the σ^- values.

Brieux and his co-workers, in their study of the substituent effects on the nucleophilic aromatic substitution reactions, calculated the *para*-substituent constants by using ρ values obtained from the *meta*-substituent series.[16,17] These *para*-substituent constants are very similar to the σ^- values. Two series are available. They are the $\sigma_{C_6H_5S^-}$ values obtained from the reactions of 4- or 5-substituted 1-chloro-2-nitrobenzenes with sodium thiophenoxide, and the $\sigma_{C_5H_{10}NH}$ values obtained from the reactions of the same compounds with piperidine. When the logarithms of the rate constants in Table 1 were plotted against $\sigma_{C_6H_5S^-}$ instead of the σ^- values, a rather unsatisfactory correlation was obtained (the correlation coefficient was 0.980) (Fig. 2). However, a very good linear relationship was observed against $\sigma_{C_5H_{10}NH}$ instead of the σ^- values (the correlation coefficient was here 0.994)

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[12] P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

[13] For reviews on the subject, see a) J. F. Bunnett, *Quart. Rev.* (London), **12**, 1 (1958); b) S. D. Ross, "Progress in Physical Organic Chemistry," Vol. 1, ed. by S. G. Cohen, A. Streitweiser, Jr., and R. W. Taft, Interscience Publishers, New York, N. Y. (1963), p. 31; c) E. Buncel, A. R. Norris, and K. E. Rusell, *Quart. Rev.* (London), **22**, 123 (1968).

[14] H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim. Pays-Bas*, **78**, 815 (1959).

[15] R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

[16] W. Greizerstein, R. A. Bonelli, and J. A. Brieux, *J. Amer. Chem. Soc.*, **84**, 1026 (1962).

[17] A. M. Porto, L. Altieri, A. J. Castro, and J. A. Brieux, *J. Chem. Soc.*, *B*, **1966**, 963.

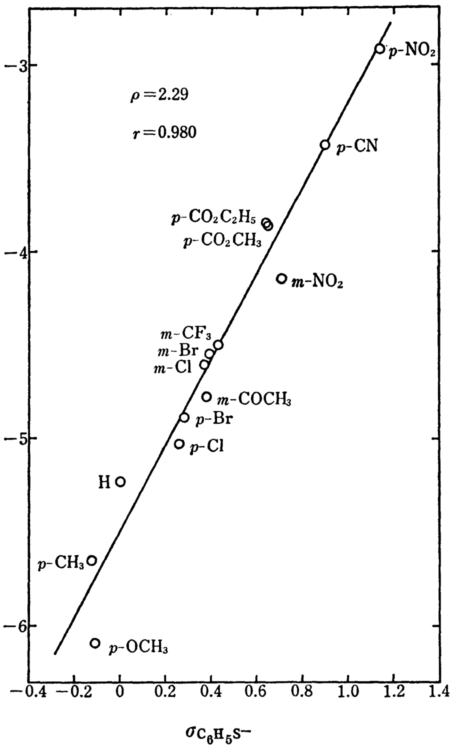


Fig. 2. Plot of the rates of the thermal rearrangement of aryl *N*,*N*-dimethylthionocarbamates (VII) in diphenyl ether at 200.5±0.1°C against $\sigma_{C_6H_5S^-}$.

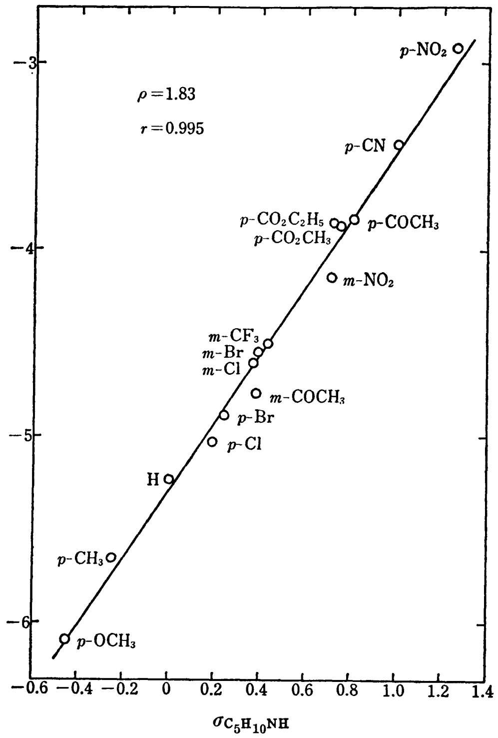


Fig. 3. Plot of the rates of the thermal rearrangement of aryl *N*,*N*-dimethylthionocarbamates (VII) in diphenyl ether at 200.5±0.1°C against $\sigma_{C_5H_{10}NH}$.

(Fig. 3).

Then, by the use of $\sigma_{O_5H_{10}NH}$ for the electron-releasing *para*-substituent constants, a linear free-energy correlation between log *k* from Table 1 and the σ^-

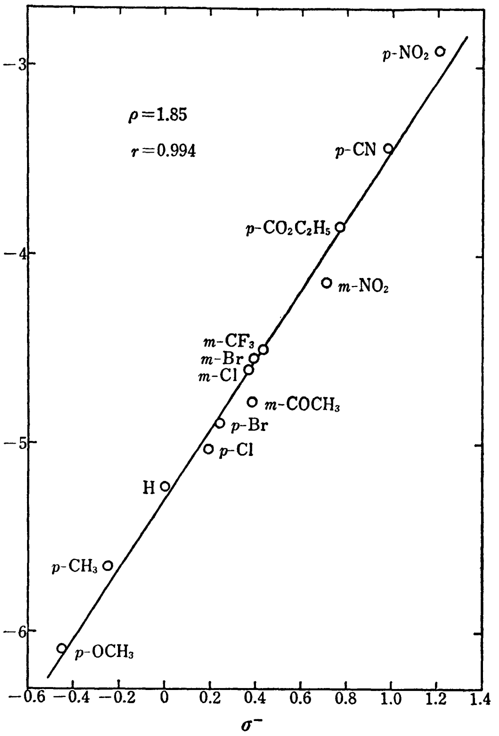


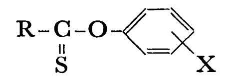
Fig. 4. Plot of the rates of the thermal rearrangement of aryl *N*,*N*-dimethylthionocarbamates (VII) in diphenyl ether at 200.5±0.1°C against σ^-, using $\sigma_{C_5H_{10}NH}$ for the electron-releasing *para*-substituent constants.

values was established. This was the best correlation (Fig. 4). The ρ value calculated using the method of least squares is 1.83, and the correlation coefficient is 0.995.

A very good linear free-energy relationship was observed in diphenyl ether between the rearrangements of aryl *N*,*N*-dimethylthionocarbamates and aryl thionobenzoates and also between the rearrangements of aryl *N*,*N*-dimethylthionocarbamates and *O*-aryl *S*-phenyl dithiocarbonates (the correlation coefficients were 0.999).

These results and the previously-reported results show that all of the Schönberg-type rearrangements probably proceed by the same mechanism in diphenyl ether. Therefore, on the rearrangements of aryl thionobenzoates[7] and *O*-aryl *S*-phenyl dithiocarbonates,[6] linear free-energy correlations between log *k* and the σ^- values were examined, using $\sigma_{C_5H_{10}NH}$ as the electron-releasing *para*-substituent constants. The ρ values calculated using the method of least squares and the correlation coefficients, *r*, are listed in Table 2.

TABLE 2. REACTION CONSTANTS AND CORRELATION COEFFICIENTS OF THE THERMAL REARRANGEMENT OF



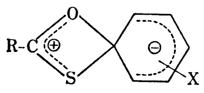
IN DIPHENYL ETHER AT 200.5±0.1°C

R	ρ	r
$(CH_3)_2N$	1.83	0.995
C_6H_5	1.33	0.997
C_6H_5S	1.19	0.995
C_6H_5O	1.06	—

From the foregoing discussion, it is evident that all of the Schönberg-type rearrangements are intramolecular nucleophilic aromatic substitution reactions. Therefore, it is very plausible that the Schönberg-type rearrangements proceed by an addition-elimination mechanism, in analogy with the intermolecular nucleophilic aromatic substitution reactions.

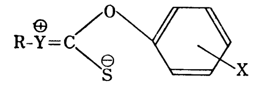
The rates of the thermal rearrangements of diphenyl thionocarbonate and *p*-nitrophenyl phenyl thionocarbonate[18] at 200.5±0.1°C in diphenyl ether were determined by the same method as was used for that of aryl *N*,*N*-dimethylthionocarbamates. Their first-order rate constants are 1.04×10^{-6} sec^{-1} (the half-value of the observed rate constant) and 2.34×10^{-5} sec^{-1} respectively. From these data, the ρ value was calculated (Table 2).

As is shown in Table 2, the order of the ρ values of the Schönberg-type rearrangements is as follows: aryl *N*,*N*-dimethylthionocarbamates>aryl thionobenzoates> *O*-aryl *S*-phenyl dithiocarbonates>aryl phenyl thionocarbonates. This order is in accord with that of the inductive effects of the α-substituents of the thiocarbonyl group.[19] This indicates that the proportions of the negative charge on aromatic rings in the transition state are governed by the inductive effects of the α-substituents of the thiocarbonyl group. According to Hammond's postulate,[20] it may be expected that, in endothermic steps, the transition states will resemble the products. Since the activation energies of the Schönberg-type rearrangements are highly positive values,[5–7,10] it may be expected that the transition state of the Schönberg-type rearrangements will closely resemble the intermediate. Therefore, the Schönberg-type rearrangements may proceed *via* an intermediate, as is shown in Scheme 1.



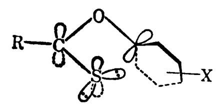
Scheme 1

Moreover, the rate constants of *p*-nitrophenyl *N*,*N*-dimethylthionocarbamate, *p*-nitrophenyl thionobenzoate,[7] *O*-*p*-nitrophenyl *S*-phenyl dithiocarbonate,[6] and *p*-nitrophenyl phenyl thionocarbonate in diphenyl ether at 200.5±0.1°C are $1.21 \times 10^{-3}\,\text{sec}^{-1}$, $1.18 \times 10^{-4}\,\text{sec}^{-1}$, $1.06 \times 10^{-4}\,\text{sec}^{-1}$, and $2.34 \times 10^{-5}\,\text{sec}^{-1}$, respectively. Since the Schönberg-type rearrangements may be governed by the enthalpy of activation at temperatures near 200°C[7], this order will not change under any possible conditions. It is suprising that this order is not in accord with that of the electron-releasing conjugative effects, but is in accord with that of the inductive effects of the α-substituents of the thiocarbonyl group. If the electron-releasing conjugative effects of the α-substituents of the thiocarbonyl group play important roles in the rate-determining step, as Newman and Karnes suggested with regard to the rearrangement of aryl *N*,*N*-disubstituted thionocarbamates[21] (Scheme 2), the rate constants should decrease in the order of: *p*-nitrophenyl *N*,*N*-dimethylthionocarbamate>*p*-nitrophenyl phenyl thionocarbonate>*p*-nitrophenyl thionobenzoate>*O*-*p*-nitrophenyl *S*-phenyl dithiocarbonate.[22]



Scheme 2

From these results and the fact that the Schönberg-type rearrangements unsatisfactorily correlate the reactions of 4- or 5-substituted 1-chloro-2-nitrobenzenes with sodium thiophenoxide, but well correlate the reactions of the same compounds with piperidine, it is plausible that the Schönberg-type rearrangements are intramolecular S_N–Ar which involve a four-membered cyclic transition state formed by the nucleophilic attack of the lone-pair electrons of the thiocarbonyl sulfur atom on the migrating aromatic ring, as is shown in Scheme 3:



Scheme 3

If the π electron of the thiocarbonyl sulfur atom attacks the migrating aromatic ring, there will necessarily be considerable extra strain because of the necessity of the rotation of the thiocarbonyl sulfur atom to permit the overlap between a *p* orbital initially perpendicular to the plane of the four-membered ring and a *p* orbital of the migrating aromatic ring initially on the plane of the four-membered ring.

Experimental[23]

Materials. The *N*,*N*-dimethylcarbamoyl chloride was prepared according to the method reported by Sugasawa and Deguchi.[24] The *N*,*N*-dimethylthiocarbamoyl chloride was prepared by the procedure recorded for the synthesis of the diethyl-analogue;[25] mp 40—41°C (lit,[26] mp 41°C). The aryl chlorothionoformates were prepared by a known method:[27] *m*-acetylphenyl-, light yellow oil, bp 148—149°C/ 8.5 mmHg (Found: C, 50.28; H, 3.10; Cl, 16.41%. Calcd for $C_9H_7ClO_2S$: C, 50.35; H, 3.27; Cl, 16.55%). *p*-Cyanophenyl-, colorless needles (from ligroin), mp 65—67°C

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[18] This compound certainly rearranges only to *O*-phenyl *S*-*p*-nitrophenyl thiolcarbonate, but it is very probable that any other unsymmetrical thionocarbonate can rearrange to two products.

[19] The Hammett σ_m values of $(CH_3)_2N$, C_6H_5, C_6H_5S, and C_6H_5O are −0.21, 0.06, 0.18, and 0.25 respectively.

[20] G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

[21] M. S. Newman and H. A. Karnes, *J. Org. Chem.*, **31**, 3980 (1966).

[22] The $(\sigma_p^+ - \sigma_m^+)$ values of $(CH_3)_2N$, C_6H_5O, C_6H_5, and C_6H_5S are −1.49, −0.75, −0.29, and 0.11, respectively. The σ_m^+ values of $(CH_3)_2N$ and C_6H_5O are not available; accordingly, σ_m values were used in place of σ_m^+ values. The σ^+ values of C_6H_5S are not available, either; therefore, the $(\sigma_p - \sigma_m)$ value was used in place of the $(\sigma_p^+ - \sigma_m^+)$ value.

[23] All the boiling and melting points are uncorrected.

[24] S. Sugasawa and Y. Deguchi, *Yakugaku Zasshi*, **76**, 968 (1956).

[25] R. H. Goshorn, W. W. Levis, Jr., E. Jaul, and E. J. Ritter, "Organic Syntheses," Coll. Vol. IV, p. 307 (1963).

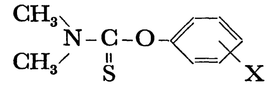
[26] E. Lieber and J. P. Trivedi, *J. Org. Chem.*, **25**, 650 (1960).

[27] M. H. Rivier, *Bull. Soc. Chim. Paris*, [3] **35**, 837 (1906).

(Found: C, 48.48; H, 1.79; N, 6.80%. Calcd for $C_8H_4ClNO_3S$: C, 48.60; H, 2.02; N, 7.08%). *m*-(Trifluoromethyl)phenyl-, light yellow oil, bp 98—99°C/19 mmHg (Found: C, 39.50; H, 1.89%. Calcd for $C_8H_4ClF_3OS$: C, 39.90; H, 1.66%). The physical properties for the other aryl chlorothionoformates were reported in an earlier paper.[28,29] The *p*-acetylphenyl chlorothiolformate was prepared from *p*-(acetyl)thiophenol and phosgene by a general method reported previously:[6] colorless needles (from *n*-hexane), mp 73—74.5°C (Found: C, 50.40; H, 3.02; Cl, 16.66%. Calcd for $C_9H_7ClO_2S$: C, 50.35; H, 3.27; Cl, 16.55%).

Aryl N,N-*Dimethylthionocarbamates (VIIa—o).* The following general methods were employed for the preparation of the compounds VII.

TABLE 3. ARYL *N*,*N*-DIMETHYLTHIONOCARBAMATES



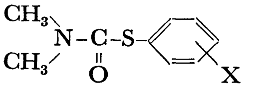
Compd. No.	X	Appearance	Mp[a] °C (lit)	Method	Yield[b] %
VIIa	*p*-OCH_3	colorless prisms[c]	85—85.5 (82—84)[d]	A B	72.5 67.6
VIIb	*p*-CH_3	colorless needles[c]	95—96[e] (86—88)[f]	A	66.7
VIIc	H	colorless needles[g]	29.5—30.5[h] (30—30.4)[i]	A B	63.5 54.7
VIId	*p*-Cl	colorless prisms[g]	58—59[e]	A B	75.0 71.4
VIIe	*p*-Br	colorless prisms[c]	87.5—88.5 (84—86)[f]	A	67.5
VIIf	*m*-$COCH_3$	colorless needles[c]	66—67	A	79.8
VIIg	*m*-Cl	colorless prisms[c]	92.5—93.5	A B	74.0 61.1
VIIh	*m*-Br	colorless prisms[c]	98—99	A	70.8
VIIi	*m*-CF_3	colorless plates[c]	64—65 (64—65)[d]	A B	65.0 63.7
VIIj	*m*-NO_2	colorless plates[j]	148—150 (153—155)[d]	A	65.8
VIIk	*p*-CO_2CH_3	colorless prisms[c]	102—103 (100—102)[d]	A	69.7
VIIl	*p*-$CO_2C_2H_5$	colorless needles[k]	81.5—82.5	A	53.5
VIIm	*p*-$COCH_3$	colorless needles[c]	102.5—103.5[e] (99—103)[d]	A B	73.1 60.8
VIIn	*p*-CN	colorless prisms[c]	116—117	A B	71.0 66.1
VIIo	*p*-NO_2	colorless plates[j]	146.5—147.5 (150—153)[d]	A	81.8

a) All melting points are uncorrected.
b) Yield of the pure product.
c) Recrystallized from methanol.
d) Ref. 21.
e) A. Kaji, This Bulletin, **34**, 254 (1961).
f) Ref. 10.
g) Recrystallized from ligroin.
h) bp, 120 °C/3 mmHg.
i) Ref. 27.
j) Recrystallized from acetone-ethanol.
k) Recrystallized from ethanol.

Method A (Eq. (5)): To a solution of 15 g (0.10 mol) of 30%-dimethylamine in 50 m*l* of acetone was added, drop by drop, 0.05 mol of aryl chlorothionoformate under agitation at 5—10°C over a period of 10 min. After the addition had been completed, the mixture was warmed to 40—50°C for 5 min. It was then cooled to room temperature and poured into *ca.* 150 m*l* of cold water; the desired product was thereby obtained as a pale yellow oil and crystallized spontaneously on standing. Recrystallization from a suitable solvent gave pure crystals. The data are shown in Table 3.

Method B (Eq. (6)): To a solution containing 0.05 mol of an appropriate phenol and 2 g (0.05 mol) of sodium hydroxide in 50 m*l* of aqueous acetone (90%) was added, all at once, 6.2 g (0.05 mol) of *N*,*N*-dimethylthiocarbamoyl chloride. The mixture was heated under reflux for 30 min and then cooled to room temperature. Thereafter, the reaction mixture was worked up in the same manner as has been described in Method A. The date are also shown in

TABLE 4. ARYL *N*,*N*-DIMETHYLTHIOLCARBAMATES



Compd. No.	X	Appearance	Mp[a] °C (lit)	Method	Yield[b] %
VIIIa	*p*-OCH_3	colorless needles[c]	94—95 (94—96)[d]	D	77.0
VIIIb	*p*-CH_3	colorless prisms[e]	36—37 (31—33)[f]	D	75.0
VIIIc	H	colorless prisms[e]	43—44	D	78.0
VIIId	*p*-Cl	colorless needles[g]	80.5—81	C(16)[h] D	30.0 66.5
VIIIe	*p*-Br	colorless prisms[i]	87—87.5 (81—83)[f]	C(15) D	33.0 62.5
VIIIf	*m*-$COCH_3$	colorless needles[e]	78—79	C(9) D	44.0 44.5
VIIIg	*m*-Cl	colorless needles[e]	47—48	C(16) D	50.5 65.0
VIIIh	*m*-Br	colorless needles[e]	53—54	C(9) D	50.5 56.0
VIIIi	*m*-CF_3	colorless needles[e]	31—32[j]	C(10) D	30.5 53.5
VIIIj	*m*-NO_2	colorless needles[i]	120—121 (117—120)[d]	C(6) D	68.5 68.0
VIIIk	*p*-CO_2CH_3	colorless needles[k]	93—94 (91—93)[d]	C(5) D	56.0 32.0
VIIIl	*p*-$CO_2C_2H_5$	colorless prisms[l]	55—56.5	C(3) D	55.0 38.7
VIIIm	*p*-$COCH_3$	colorless needles[i]	107—108 (106—109)[d]	C(3) E	63.0 61.0
VIIIn	*p*-CN	colorless needles[l]	103—104	C(3)	75.0
VIIIo	*p*-NO_2	colorless needles[i]	119—120 (122—124)[d]	C(0.5) D	85.0 57.5

a) All melting points are uncorrected.
b) Yield of the pure product.
c) Recrystallized from *n*-hexane.
d) Ref. 21.
e) Recrystallized from ligroin.
f) Ref. 10.
g) Recrystallized from aqueous methanol.
h) Heating time (hr).
i) Recrystallized from methanol.
j) Ref. 21.; bp, 100—103/0.2 mmHg.
k) Recrystallized from benzene-*n*-hexane.
l) Recrystallized from benzene-ligroin.

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28) A. Kaji and K. Miyazaki, *Nippon Kagaku Zasshi*, **87**, 272 (1966).

29) K. Miyazaki, This Bulletin, **42**, 1697 (1969).

Table 3. The compounds VIIf, VIIg, VIIh, VIIl, and VIIn are new compounds. VIIf, Found: C, 59.05, H, 5.35; N, 6.02%. Calcd for $C_{11}H_{13}NO_2S$: C, 59.20; H, 5.44; N, 5.86%. VIIg, Found: C, 49.87; H, 4.40; N, 6.33%. Calcd for $C_9H_{10}ClNOS$: C, 50.15; H, 4.64; N, 6.50%. VIIh, Found: C, 41.70; H, 3.67; N, 5.18%. Calcd for $C_9H_{10}BrNOS$: C, 41.55; H, 3.85; N, 5.38%. VIIl, Found: C, 56.70; H, 6.06; N, 5.76%. Calcd for $C_{12}H_{15}NO_3S$: C, 56.95; H, 5.93; N, 5.53%. VIIn, Found: C, 58.30; H, 4.91; N, 13.52%. Calcd for $C_{10}H_{10}N_2OS$: C, 58.30; H, 4.86; N, 13.60%.

Aryl N,N-*Dimethylthiolcarbamates (VIIIa—o).* The following general methods were employed for the preparation of the compounds VIII.

Thermal Rearrangement of VII, Method C (Eq. (4)): The apparutus used for this method consisted of a 5 m*l*, round-bottomed flask. About 500 mg of VII was placed in the flask and kept at 205—210°C in an oil bath for the desired period, nitrogen being passed into the flask at a slow rate throughout the heating. The flask was then cooled to room temperature, and the contents were scratched in an ice bath to induce crystallization. The product thus obtained was recrystallized from a suitable solvent. The results are summarized in Table 4.

Method D (Eq. (7)): The reaction conditions of *N,N*-dimethylcarbamoyl chloride with an appropriate thiophenol to give VIII correspond to those of the Method B used in the preparation of VII. The data are shown in Table 4.

Method E (Eq. (8)): The reaction conditions of dimethylamine with the aryl chlorothiolformate to give VIII are nearly identical with those described for the Method A used in the preparation of VII. The results are listed in Table 4. The compounds VIIIc, VIIId, VIIIf, VIIIg, VIIIh, VIIIl, and VIIIn are new compounds. VIIIc, Found: C, 59.33; H, 5.84; N, 7.70%. Calcd for $C_9H_{11}NOS$: C, 59.64; H, 6.12; N, 7.73%. VIIId, Found: C, 50.19; H, 4.29; N, 6.61%. Calcd for $C_9H_{10}ClNOS$: C, 50.12; H, 4.67; N, 6.49%. VIIIf, Found: C, 59.25; H, 5.87; N, 6.26%. Calcd for $C_{11}H_{13}NO_2S$: C, 59.20; H, 5.44; N, 5.86%. VIIIg, Found: C, 50.35; H, 4.37; N, 6.66%. Calcd for $C_9H_{10}ClNOS$: C, 50.15; H, 4.64; N, 6.50%. VIIIh, Found: C, 41.45; H, 3.96; N, 5.60%. Calcd for $C_9H_{10}BrNOS$: C, 41.55; H, 3.85; N, 5.38%. VIIIl, Found: C, 56.80; H, 5.81; N, 5.49%. Calcd for $C_{12}H_{15}NO_3S$: C, 56.95; H, 5.93; N, 5.53%. VIIIn, Found: C, 57.90; H, 5.05; N, 13.38%. Calcd for $C_{10}H_{10}N_2OS$: C, 58.30; H, 4.86; N, 13.60%.

Aryl Phenyl Thionocarbonates (I). The method of preparing diphenyl thionocarbonate was previously reported.[6] *p*-Nitrophenyl phenyl thionocarbonate was prepared by the reaction of phenol and *p*-nitrophenyl chlorothionoformate[6] with triethylamine in a manner similar to that described in an earlier paper.[6] Colorless plates (from acetone-ethanol), mp 184—185°C (lit,[4] 181—182°C).

O-*Phenyl* S-*Aryl Thiolcarbonates (II).* These compounds were prepared by the reactions of phenol and aryl chlorothiolformate with triethylamine in a manner similar to that described in an earlier paper.[6] Phenyl-: colorelss needles (from *n*-hexane), mp 53.5—54°C (lit,[2] 57°C). *p*-Nitrophenyl-: colorless needles (from *n*-hexane), mp 76.5—77.5°C (lit,[4] mp 65—67°C).

Kinetic Measurements. The rates were followed by the ampoule technique and were determined by ultraviolet spectrophotometric measurements in a manner similar to that described in an earlier paper.[6]

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