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Studies of the Thiocarbonyl Compounds. I. Syntheses and Thermal Rearrangement of *O*,*S*-Diaryl Dithiocarbonates[*1]

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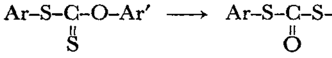
Various *O*,*S*-diaryl dithiocarbonates with the general formula of p-X–C_6H_4–S–C(=S)–O–C_6H_4–Y-p (I) were prepared. When these substances were kept at an elevated temperature, they rearranged smoothly to *S*,*S*-diaryl dithiocarbonates of this general formula: p-X–C_6H_4–S–C(=O)–S–C_6H_4–Y-p (II). Kinetic studies showed that the rearrangement followed fairly good first-order kinetics. The rate constants in diphenyl ether at 200°C increased in the order: $Y=OCH_3<CH_3<H<Cl<COCH_3<CN<NO_2$. The entropies of activation were negative, and no crossover products were obtained. A four-membered cyclic structure can be suggested as the transition state for this rearrangement.

It is well known that the reaction mechanism of the formation of olefins by the pyrolysis of xanthate esters which have a β-hydrogen atom in the alcohol moiety, commonly called the Chugaev reaction, is an intramolecular *cis* elimination through a cyclic transition state.[1] On the other hand, xanthate esters which have no β-hydrogen atom, such as methyl benzyl xanthate, rearrange on pyrolysis to give dithiolcarbonates.[2] However, it has been thought that this reaction is unusual, and no mechanistic work has yet been made. It seemed that it would be interesting to investigate whether *O*,*S*-diaryl dithiocarbonates (I) also rearrange to *S*,*S*-diaryl dithiocarbonates (II) at elevated temperatures.

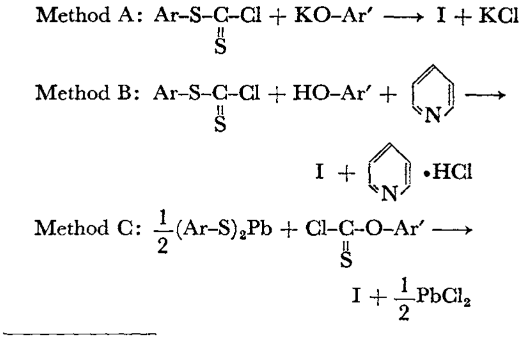


$$\underset{\text{(I)}}{\text{Ar-S-}\underset{\underset{\text{S}}{\|}}{\text{C}}\text{-O-Ar}'} \xrightarrow{\Delta} \underset{\text{(II)}}{\text{Ar-S-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-S-Ar}'}$$

The present author synthesized twelve compounds I (I-1—I-12), all of them were new compounds except the diphenyl ester (I-3);[3] he also studied the kinetics of their thermal rearrangements in order to establish the reaction mechanism.

Results and Discussion

Syntheses of *O*,*S*-Diaryl Dithiocarbonates (I). The compounds I were synthesized by the



$$\text{Method A: Ar-S-}\underset{\underset{\text{S}}{\|}}{\text{C}}\text{-Cl} + \text{KO-Ar}' \longrightarrow \text{I} + \text{KCl}$$

$$\text{Method C: } \frac{1}{2}(\text{Ar-S})_2\text{Pb} + \text{Cl-}\underset{\underset{\text{S}}{\|}}{\text{C}}\text{-O-Ar}' \longrightarrow \text{I} + \frac{1}{2}\text{PbCl}_2$$

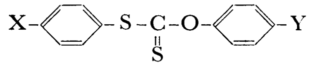
[*1] Presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

1) H. R. Nace, "Organic Reactions," Vol. 12, p. 57 (1962).

2) a) P. V. Laakso, *Suomen Kemistilehti*, **13B**, 8 (1940); *Chem. Abstr.*, **34**, 5059 (1940); b) P. V. Laakso, *Suomen Kemistilehti*, **16B**, 19 (1943); *Chem. Abstr.*, **40**, 4687 (1946); c) G. Bulmer and F. G. Mann, *J. Chem. Soc.*, **1945**, 666.

3) a) G. Daccomo, *Annali di Chimica e di Farmacologia*, **13**, 273; *Chem. Zentr.*, **1891II**, 532; b) G. Daccomo, *Annali di Chimica e di Farmacologia*, **16**, 129; *Chem. Zentr.*, **1892II**, 827; c) M. H. Rivier, *Bull. Soc. Chim. Fr.*, [3] **35**, 837 (1906); d) M.H. Rivier, *ibid.*, [4] **1**, 733 (1907).

TABLE 1. *O,S*-DIARYL DITHIOCARBONATES



Compd. No.	X	Y	Appearance	Mp[a] °C	Method	Yield %	$\lambda_{max}^{CHCl_3}$ (mμ) ($\varepsilon \times 10^{-4}$)	Formula	Analysis (%) Found (Calcd) C	H	S
I-1	H	OCH_3	pale yellow prisms[b]	48.5—49.5	A	89	286 (1.28)	$C_{14}H_{12}O_2S_2$	61.08 (60.84)	4.36 (4.38)	22.92 (23.20)
I-2	H	CH_3	pale yellow plates[b]	59.5—60.5	A	85	289 (1.08)	$C_{14}H_{12}OS_2$	64.40 (64.58)	4.48 (4.65)	24.56 (24.63)
I-3	H	H	pale yellow plates[b]	42.5—43.0[c]	A C	100 63	289.5 (1.05)	$C_{13}H_{10}OS_2$	63.14 (63.38)	4.02 (4.09)	25.66 (26.03)
I-4	H	Cl	pale yellow needles[b]	68.0—69.0	A	97	289 (1.06)	$C_{13}H_9ClOS_2$	55.71 (55.61)	3.16 (3.23)	22.61 (22.84)
I-5	H	$COCH_3$	pale yellow plates[b]	93.0—94.0	A	93	286 (1.24)	$C_{15}H_{12}O_2S_2$	62.65 (62.47)	4.24 (4.19)	22.06 (22.24)
I-6	H	CN	pale yellow plates[b]	108.0—109.0	A	96	290 (1.06)	$C_{14}H_9NOS_2$	61.68 (61.97)	3.17 (3.34)	23.43 (23.63)
I-7	H	NO_2	pale yellow plates[b]	111.0—111.5	A	91	287.5 (1.75)	$C_{13}H_9NO_3S_2$	53.39 (53.59)	3.01 (3.11)	21.80 (22.01)
I-8	OCH_3	NO_2	pale yellow plates[b]	102.5—103.5	A	95	282.5 (1.79)	$C_{14}H_{11}NO_4S_2$	52.25 (52.32)	3.33 (3.45)	19.75 (19.95)
I-9	CH_3	NO_2	pale yellow prisms[b]	103.0—103.5	A	96	288.5 (1.75)	$C_{14}H_{11}NO_3S_2$	54.81 (55.07)	3.44 (3.36)	20.85 (21.00)
I-10	Cl	NO_2	pale yellow needles[b]	105.5—106.5	A	91	287 (1.79)	$C_{13}H_8ClNO_3S_2$	48.03 (47.93)	2.72 (2.48)	19.80 (19.68)
I-11	NO_2	NO_2	orange prisms[d]	170.0—171.0	B	95	272 (2.36)	$C_{13}H_8N_2O_5S_2$	46.13 (46.42)	2.49 (2.40)	19.13 (19.07)
I-12	NO_2	Cl	pale yellow needles[b]	109.0—110.0	B	90	272 (1.60)	$C_{13}H_8ClNO_3S_2$	48.08 (47.93)	2.73 (2.48)	19.43 (19.68)

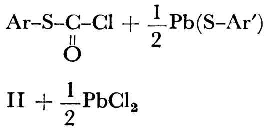
a) All melting points are uncorrected.
b) Recrystallized from ethanol.
c) Ref. 3c and Ref. 3d; mp 51°C.
d) Recrystallized from acetone-ethanol.

reaction of a substituted phenol with an aryl chlorodithioformate (Methods A and B). In order to establish the structure of the compounds I, another method (Method C) was also used; in this aryl chlorothionoformates were treated with lead thiophenolates, giving the compounds I. By these three methods, the various compounds I were obtained in good yields. The data are shown in Table 1.

Thermal Rearrangement. In order to examine the possibility of the thermal rearrangement, the compounds I were kept at 200°C without any solvent under a nitrogen atmosphere; the reaction mixture was then analyzed by thin-layer chromatography on silica gel. It was found that the compounds I were gradually converted to other compounds. The elemental analysis showed that the composition of the products was identical with that of original compounds I. The infrared spectra of the products showed peaks at *ca.* 1720 cm^{-1} ($\nu_{C=O}$). These data suggest that the products are *S,S*-diaryl dithiocarbonates (II).

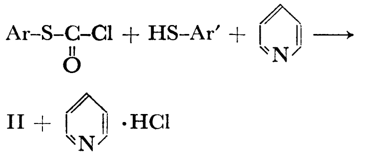
Identification of the Thermal Rearrangement Products. In order to identify the thermal rearrangement products, the compounds II were synthesized by Methods D and E. The results are shown in Table 2. The compounds which

Method D:



$$\text{Ar-S-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-Cl} + \frac{1}{2}\text{Pb(S-Ar}')_2 \longrightarrow \text{II} + \frac{1}{2}\text{PbCl}_2$$

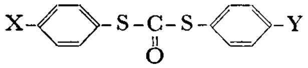
Method E:



were produced by heating the compounds I at 200°C were identified with the compounds II by mixed-melting-point tests and by a comparison of the IR spectra.

Kinetics of the Rearrangement. In order to clarify the influence of the substituents upon the rearrangement rates, the kinetics of the rearrangement were investigated in a diphenyl ether solution. The rates were followed by the ampoule technique and were determined by measuring the amounts of the remaining reactants, I, and of the products, II, by UV spectrophotometry. It was found that the rearrangement followed fairly good first-order kinetics. A typical run is shown in Table 3 and Fig. 1. The first-order rate constants

Table 2. *S,S*-Diaryl dithiocarbonates



								Analysis[b)] (%)		
Compd. No.	X	Y	Appearance	Mp[a)] °C	Method	Yield %	$\lambda_{max}^{CHCl_3}$ (mμ) ($\varepsilon \times 10^{-4}$)	C Found	H Found	S Found
II-1	H	OCH_3	colorless prisms[c)]	65.5—66.0	E	98	—[d)]	60.94	4.38	22.92
II-2	H	CH_3	colorless needles[c)]	69.5—73.5	E	98	—[d)]	64.83	4.71	24.42
II-3	H	H	colorless prisms[c)]	41.5—42.0[e)]	D	91	—[d)]	63.12	4.37	25.78
II-4	H	Cl	colorless prisms[c)]	61.5—62.0	E	100	—[d)]	55.67	3.24	22.72
II-5	H	$COCH_3$	colorless plates[c)]	34.0—35.0	E	100	277 (1.56)	62.54	4.34	22.07
II-6	H	CN	colorless needles[c)]	69.0—70.0	E	100	276 (1.50)	62.18	3.26	23.76
II-7	H	NO_2	colorless plates[c)]	68.7—69.2	D E	100 100	297.5(1.28)	53.85	3.37	21.84
II-8	OCH_3	NO_2	colorless needles[c)]	108.0—109.0	E	97	298 (1.50)	52.05	3.27	19.82
II-9	CH_3	NO_2	colorless needles[c)]	95.0—95.5	E	98	298 (1.35)	54.81	3.36	20.90
II-10	Cl	NO_2	colorless needles[f)]	128.0—129.0	E	99	294.5(1.40)	48.16	2.48	19.69
II-11	NO_2	NO_2	pale yellow needles[g)]	191.5—192.5[h)]	E	100	297 (2.25)	46.12	2.41	18.78

a) All melting points are uncorrected.
b) In each compound, the molecular formula and the theoretical values for the elemental analysis are equal to those of the corresponding I in Table 1.
c) Recrystallized from ethanol.
d) No absorption maximum within the measurable range.
e) Ref. 3c; mp 41°C, Ref. 4; mp 43°C, Ref. 5; mp 41—43°C.
f) Recrystallized from acetic acid.
g) Recrystallized from benzene.
h) Ref. 5; mp 183.5—184.5°C.

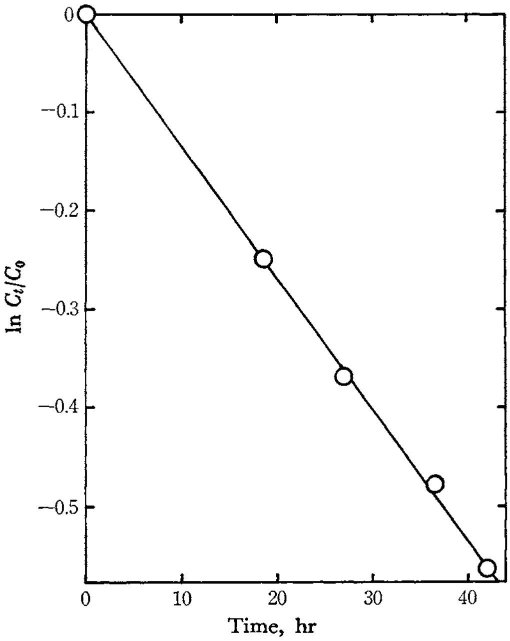


Fig. 1. Rate plot for the rearrangement of *O,S*-diphenyl dithiocarbonate at 200.5—0.1°C.

Table 3. Rearrangement of *O,S*-diphenyl dithiocarbonate (I-3) at 200.5±0.1°C

Time (sec)	% of I-3 remaining	$k \times 10^6$ (sec^{-1})
0	100	
666000	78.0	3.73
972000	69.3	3.78
1314000	62.1	3.63
1512000	57.1	3.71

Table 4. First-order rate constants of the rearrangement at 200.5±0.1°C

Compd. No.	$k \times 10^6$ (sec^{-1})	Relative rates
I-1	0.830	0.224
I-2	1.97	0.531
I-3	3.71	1.00
I-4	3.89	1.05
I-5	25.5	6.87
I-6	51.4	13.6
I-7	106	28.6

were derived from the slopes of the straight lines obtained by plotting ln C_t/C_0 against the time, where C_t and C_0 are the concentrations of I at time *t* and time 0 respectively. The data are summarized in Tables 4, 5, and 6. From these data,

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4) J. E. Purvis, H. O. Jones and H. S. Tasker, *J. Chem. Soc.*, **97**, 2287 (1910).

5) J. R. Cox, Jr., C. L. Gladys, L. Field and D. E. Pearson, *J. Org. Chem.*, **25**, 1083 (1960).

TABLE 5. FIRST-ORDER RATE CONSTANTS OF THE REARRANGEMENT AT 170.0±0.1°C

Compd. No.	$k\times10^6$ (sec^{-1})	Relative rates
I-8	8.87	1.07
I-9	8.89	1.07
I-7	8.27	1.00
I-10	6.05	0.732
I-11	3.54	0.428

TABLE 6. ACTIVATION PARAMETERS AND RATE CONSTANTS OF THE REARRANGEMENT

Compd. No.	$k\times10^6$ (sec^{-1}) at 230.0±0.1°C	E_a (kcal/mol)	$\varDelta S^{\ddagger}$ (e.u.)
I-1	9.57	39.2	−6.5
I-3	40.5	38.3	−5.4
I-7	—	34.7	−5.3

the energies and entropies of activation were calculated for some of the compounds I. The values are given in Table 6.

In Table 4 it can be observed that electron-withdrawing substituents attached to the migrating group accelerate the rearrangement. The logarithms of the rate constants in Table 4 were plotted against Hammett's σ values (Fig. 2). By means of the method of least-squares, the best straight line was obtained ($\rho=1.87$).

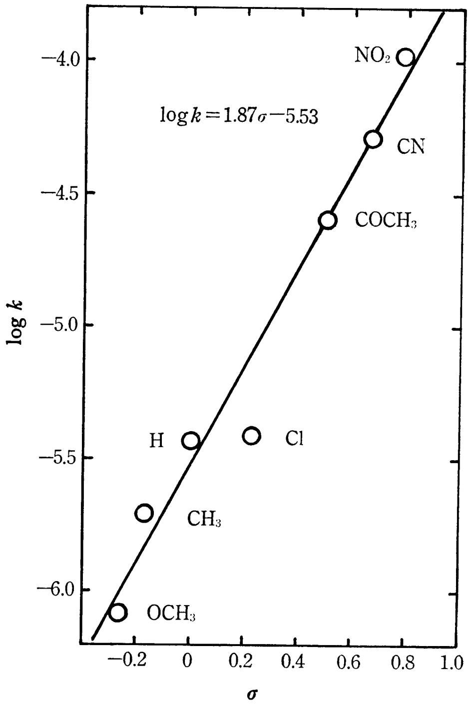
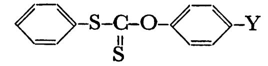


Fig. 2. Hammett plot for rate of rearrangement of

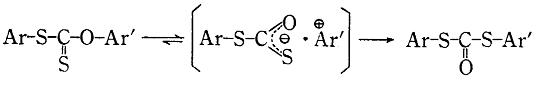


at 200.5±0.1°C.

On the other hand, the data in Table 5 show that electron-donating substituents attached to the phenylthio moiety accelerate the reaction. Figure 3 shows a Hammett plot of log *k* in Table 5 against the σ values ($\rho=-0.41$).

In order to establish the mechanism of the rearrangement of the compounds I, it was necessary to determine whether the mechanism of the rearrangement is intermolecular or intramolecular. A crossover reaction was performed with two compounds of I. That is, an equimolar mixture of I-3 and I-12*2 was heated without any solvent at 230°C under a nitrogen atmosphere. If the rearrangement is intermolecular, such crossover products as II-4 and/or II-7 should be detected in the crossover reaction mixture in addition to II-3 and II-10. In order to confirm this, the crossover reaction mixture obtained was analyzed by thin-layer chromatography on silica gel. The chromatograms of that reaction mixture, however, showed no detectable amounts of II-4 and/or II-7. This finding suggests that the rearrangement is intramolecular.

Furthermore, if the rearrangement proceeds through an intimate ion-pair,6) such as in Scheme 1, the order of the rate constants should be the inverse of the experimental results shown in Table 4, because the stability of the aryl cation, which contributes to the reaction rate, should decrease in



Scheme 1

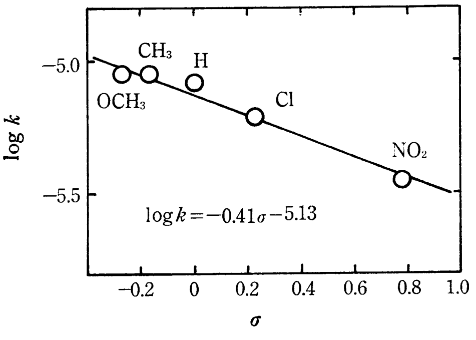
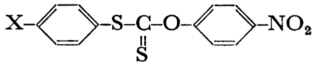


Fig. 3. Hammett plot for rate of rearrangement of



at 170.0±0.1°C.

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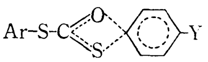
*2 I-3 and I-12 were chosen because of their similar rate constants (rate constant of I-12 is 3.39×10^{-5} sec^{-1} at 230.0°C).

6) a) T. Taguchi and M. Nakao, *Tetrahedron*, **18**, 245 (1962); b) T. Taguchi, Y. Kawazoe and M. Nakao, *Tetrahedron Lett.*, **1963**, 131; c) T. Taguchi, Y. Kawazoe, K. Yoshihira, H. Kanayama, M. Mori, K. Tabata and K. Harano, *ibid.*, **1965**, 2717.

the order: $Y = OCH_3 > CH_3 > H > Cl > COCH_3 > CN > NO_2$.

When these results are taken into consideration, it seems reasonable to conclude that the rearrangement of the compounds I take place through an intramolecular four-membered cyclic transition state, as in Scheme 2:



Scheme 2

Moreover, since the formation of the four-membered cyclic transition state requires a restriction of the rotation, the entropy should decrease in going from the reactants to the transition state. In fact, as is shown in Table 6, the entropies of activation are negative. These data are in agreement with this conclusion. Furthermore, the entropies of activation obtained for the rearrangements of arylimino ethers,[7] diaryl thionocarbonates,[8] and aryl *N*,*N*-dialkylthionocarbamates,[8e,9] all of which are regarded as having four-membered cyclic transition states, are in the same range as these data. This fact also supports this conclusion.

Consequently, a four-membered cyclic structure (Scheme 2) formed by a nucleophilic attack of the thiocarbonyl sulfur atom on the migrating aromatic ring can be considered to be the transition state in the rearrangement of the compounds I.

This conclusion is also supported by the kinetic data. That is, the positive slope of the straight line in Fig. 2 shows that this rearrangement is a nucleophilic reaction. The increased reactivity in Table 4 can be explained as follows: Since electron-withdrawing substituents decrease the electron density on the reaction center, these substituents facilitate a nucleophilic attack of the thiocarbonyl sulfur atom. On the other hand, electron-donating groups attached to the phenylthio moiety make the electrons on the thiocarbonyl sulfur atom more available for a nucleophilic attack, so these groups accelerate the rearrangement (Table 5).

Investigations of similar rearrangement reactions involving cyclic transition states are now in progress. These results will be reported elsewhere later.

Experimental[*3]

Materials. The aryl chlorodithioformates were synthesized by the reaction of a corresponding thiophenol, thiophosgene, and sodium hydroxide according to a known method:[3d] *p*-methoxyphenyl-, orange red oil, bp 126—129°C/0.95 mmHg; *p*-methylphenyl-, orange red oil, bp 112—113°C/0.8 mmHg (lit,[10] bp 102—104°C/1.0 mmHg); phenyl-, orange red oil, bp 143—144°C/22 mmHg (lit,[3d] bp 135°C/15 mmHg); *p*-chlorophenyl-, orange red oil, bp 102—103°C/0.8 mmHg; *p*-nitrophenyl-, orange crystals, bp 144—145°C/0.8 mmHg, mp 45.0—46.0°C.

The aryl chlorothionoformates were also prepared by a known method:[3c] phenyl-, colorless oil, bp 74.0°C/5 mmHg (lit,[3c] bp 91°C/10 mmHg); *p*-nitrophenyl-, colorless plates (from *n*-hexane), mp 59.0—60.0°C (lit,[11] mp 59.0—60.0°C).

The aryl chlorothiolformates were prepared as follows: To a solution of 1 mol of phosgene and 1 mol of thiophenol in 600 m*l* of dry toluene, 1 mol of dry pyridine was added gradually under vigorous agitation. The temperature was kept at 20—30°C during the reaction period of 2 hr. Then, the reaction mixture was filtered and the solvent was removed under reduced pressure.[*4] The residue was fractionated, and the product was obtained in a high yield: phenyl-, colorless oil, bp 110°C/21 mmHg (lit,[3d] bp 104°C/13 mmHg, bp 150°C/22 mmHg, bp 225—227°C/724 mmHg); *p*-nitrophenyl-, colorless needles (from *n*-hexane), mp 60.0—62.0°C.

***O*,*S*-Diaryl Dithiocarbonates (I).** The compounds I were prepared by three methods, A, B, and C. Method A was used most often. The results are listed in Table 1.

Method A. Example 1. *O*-(*p*-Nitrophenyl) *S*-(*p*-Methylphenyl) Dithiocarbonate (I-9). To a suspension of 3.54 g (0.02 mol) of potassium *p*-nitrophenolate in 25 m*l* of dry acetone at 0°C in an ice-water bath, there was added, all at once, 3.93 g (0.02 mol) of *p*-methylphenyl chlorodithioformate in 20 m*l* of dry acetone. The resulting mixture was then stirred for 1 hr, with the temperature kept at 5—10°C. Then the cooling bath was removed, and the reaction mixture was stirred for 2 hr at room temperature and poured into *ca.* 500 m*l* of cold water. In this way 5.85 g (96%) of pale yellow crystals with mp 97—99°C was obtained. Recrystallization from ethanol gave 4.40 g (72%) of pale yellow prisms with mp 103.0—103.5°C.

Example 2. *O*,*S*-Diphenyl Dithiocarbonate (I-3). To 50 m*l* of cooled absolute ethanol, there was added, in small portions, 3.9 g (0.1 mol) of potassium. After hydrogen evolution had ceased, 9.4 g (0.1 mol) of phenol was added. The resulting solution was then added gradually with continuous stirring to a cooled solution of 18.9 g (0.1 mol) of phenyl chlorodithioformate in 50 m*l* of absolute ethanol in an ice-water bath, with the temperature kept at 5—10°C. After the addition had been completed, stirring was continued an additional hour at a temperature below 10°C. The reaction mixture

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7) a) K. B. Wiberg and B. I. Rowland, *J. Amer. Chem. Soc.*, **77**, 2205 (1955); b) J. W. Schulenberg and S. Archer, "Organic Reactions," Vol. 14, p. 1 (1965).

8) a) A. Schönberg and L. Vargha, *Ber.*, **63**, 178 (1930); b) A. Schönberg, L. Vargha and W. Paul, *Ann.*, **483**, 107 (1930); c) H. R. Al-Kazimi, D. S. Tarbell and D. Plant, *J. Amer. Chem. Soc.*, **77**, 2479 (1955); d) D. H. Powers and D. S. Tarbell, *ibid.*, **78**, 70 (1956); e) H. Kwart and E. R. Evans, *J. Org. Chem.*, **31**, 410 (1966).

9) a) J. D. Edwards and M. Pianka, *J. Chem. Soc.*, **1965**, 7338; b) M. S. Newman and H. A. Karnes, *J. Org. Chem.*, **31**, 3980 (1966); c) K. Miyazaki, *Tetrahedron Lett.*, **1968**, 2793; d) H. M. Relles and G. Pizzolato, *J. Org. Chem.*, **33**, 2249 (1968).

[*3] All boiling and melting points are uncorrected.

10) H. C. Godt, Jr., and R. E. Wann, *J. Org. Chem.*, **26**, 4047 (1961).

11) A. F. McKay, D. L. Garmaise, G. Y. Paris, S. Gelblum and R. J. Ranz, *Can. J. Chem.*, **38**, 2042 (1960).

[*4] At this step, *p*-nitrophenyl chlorothiolformate was solidified.

was then poured into *ca.* 1000 m*l* of cold water; orange crystals with mp 39.0—40.5°C were thus afforded quantitatively. Recrystallization from ethanol gave 17.7 g (72%) of pale yellow plates with mp 42.5—43.0°C.

In this method, when phenyl chlorodithioformate was added to a solution of potassium phenolate in ethanol, diphenyl trithiocarbonate and diphenyl thionocarbonate were obtained, but the compound I-3 was not obtained.

Method B. This method worked well with phenols bearing electron-withdrawing substituents.

Example. *O*,*S*-Bis(*p*-nitrophenyl) Dithiocarbonate (I-11). To a cooled solution of 1.39 g (0.01 mol) of *p*-nitrophenol and 2.34 g (0.01 mol) of *p*-nitrophenyl chlorodithioformate dissolved 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.* 500 m*l* of cold water; 3.20 g (95%) of orange crystals with mp 160—164°C were thus obtained. Recrystallization from acetone-ethanol gave 2.12 g (63%) of orange prisms with mp 170.0—171.0°C.

Method C. Example. *O*,*S*-Diphenyl Dithiocarbonate (I-3). A mixture of 7.8 g (0.045 mol) of phenyl chlorothionoformate and 9.7 g (0.023 mol) of lead thiophenolate in 80 m*l* of dry benzene was heated under reflux for 6 hr. After cooling to room temperature, the reaction mixture was filtered and the solvent was removed under reduced pressure to give pale yellow crystals. Recrystallization from ethanol gave pale yellow plates with mp 42.5—43.0°C.

The synthesis of the compound I-11 by this method was attempted. As a result, it was found that, besides I-11, bis(*p*-nitrophenyl) trithiocarbonate and bis(*p*-nitrophenyl) thionocarbonate were formed in large quantities.

***S*,*S*-Diaryl Dithiocarbonates (II).** The compounds II were prepared by two methods, D and E. Method E was used most often because of its convenience. The data are shown in Table 2.

Method D. Example. *S*,*S*-Diphenyl Dithiocarbonate (II-3). A mixture of 0.86 g (0.005 mol) of phenyl chlorothiolformate and 1.1 g (0.0026 mol) of lead thiophenolate in 10 m*l* of dry benzene was heated under reflux for 24 hr. After it had then been cooled to room temperature, a white solid was removed by filtration; the filtrate was concentrated to dryness to yield 1.12 g (91%) of white crystals with mp 38—40°C. Recrystallization from ethanol gave white prisms with mp 41.5—42.0°C.

Method E. Example. *S*,*S*-Bis(*p*-nitrophenyl) Dithiocarbonate (II-11). Into a cooled solution of 1.55 g (0.01 mol) of *p*-nitrothiophenol and 2.18 g (0.01 mol) of *p*-nitrophenyl chlorothiolformate dissolved 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. The reaction mixture was poured into *ca.* 500 m*l* of cold water; 3.36 g (100%) of yellow crystals with mp 188—189°C was thus obtained. Recrystallization from benzene gave pale yellow needles with mp 191.5—192.5°C.

Thermal Rearrangement of I. The rearrangement of I was carried out at 200°C in a test tube without any solvent. That is, *ca.* 500 mg of I was placed in a test tube and heated to 200.5±0.1°C in a constant-temperature bath under a slow stream of nitrogen. On thin-layer chromatography on silica gel, it was shown that the compound I gradually underwent a change to another compound. When the compound I had changed completely, the reaction mixture was chromatographed on a silica gel column using a solvent mixture of benzene and *n*-hexane in order to isolate the product. After the solvent had been removed under reduced pressure, the product was recrystallized and identified by means of its IR spectrum and by a determination of melting-point and of a mixed-melting-point with an authentic sample.

Crossover Reaction. An equimolar mixture of I-3 and I-12 was heated in a test tube without any solvent at 230°C for 1 hr under a slow stream of nitrogen. The resulting mixture was then analyzed by thin-layer chromatography on silica gel with a solvent mixture of benzene-*n*-hexane (1 : 1). The chromatograms showed that II-3 and II-10 were produced. However, neither II-4 nor II-7 was detected.

Kinetic Measurements. The rates were followed by the ampoule technique. That is, approximately 30 mg of I was dissolved in diphenyl ether giving a final volume of 5 m*l*. This corresponds to about a 0.02M solution. About 1 m*l* of this solution was then transferred to each of four ampoules. These ampoules were flushed with nitrogen, sealed, and then immersed in a constant-temperature bath controlled to ±0.1°C. Ampoules were taken out from the bath at appropriate intervals and cooled immediately by immersion in cold water. From each run thus obtained, I and II were separated by thin-layer chromatography on silica gel with a solvent mixture of benzene and *n*-hexane and extracted with chloroform. The absorbance at the wavelength of the maximum absorption (Tables 1 and 2) was measured*[5] for the compounds thus isolated in order to determine the relative amounts of I and II. In all cases, a plot of the logarithm of C_t/C_0 against the time in sec, where C_t and C_0 are the concentrations of I at time t and time 0 respectively, 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 3. From these data, the rate constants were calculated (Tables 4, 5, and 6).

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