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Thermal Rearrangement of Mixed Dithiocarbamic-Imidic Anhydrides*[1]

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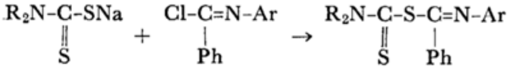
The various mixed dithiocarbamic-imidic anhydrides with the formula $R_2N\text{-}C(=S)\text{-}S\text{-}C(=N\text{-}Ph)\text{-}Ph$ (I) rearranged to thiobenzoyl-thioureas with the formula $R_2N\text{-}C(=S)\text{-}N(\text{-}Ph)\text{-}C(=S)\text{-}Ph$ (II) when kept at an elevated temperature in an inert solvent. This rearrangement was found to be reversible, and it followed first-order kinetics. The value of the forward rate constant (k_1) in *o*-dichlorobenzene at 100°C increased in the order: $R = CH_3 > C_2H_5 > n\text{-}C_3H_7 > n\text{-}C_4H_9$, and a good correlation between $\log k_1$ and σ^* for R was obtained. The rearrangement following mixture of $(CH_3)_2N\text{-}C(=S)\text{-}S\text{-}C(=N\text{-}Ph)\text{-}Ph$ and $(C_2H_5)_2N\text{-}C(=S)\text{-}S\text{-}C(=N\text{-}C_6H_5Cl\text{-}p)\text{-}Ph$ gave no crossed products. A probable reaction mechanism was proposed.

In an earlier paper,[1] the thermal rearrangement of *O*-aryl-*S*-(*N,N*-dimethyl-thiocarbamoyl)-*N*-arylthiolimidocarbonates to 1,1-dimethyl-3-aryl-3-(aryloxy-thiocarbonyl)-2-thioureas was reported. Since it was of interest to investigate further the scope of this kind of rearrangement, the thermal rearrangement of *N,N*-dialkyldithiocarbamic-*N*-(phenyl)benzimidic anhydrides with the formula $R_2N\text{-}C(=S)\text{-}S\text{-}C(=N\text{-}Ph)\text{-}Ph$ (I), which are similar to the thiolimidocarbonates mentioned above, was tested; moreover, the kinetics of the rearrangement for various compounds I ($R = CH_3$, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$) have been studied in order to establish a reaction mechanism.

Results and Discussion

Synthesis of Mixed Dithiocarbamic-Imidic Anhydrides (I). The various anhydrides were synthesized by the reaction of an appropriate sodium *N,N*-dialkyldithiocarbamate with a proper *N*-(aryl)benzimidoyl chloride (Eq. (1)):

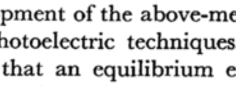


$$R_2N\text{-}\underset{\underset{\displaystyle S}{\|}}{C}\text{-}SNa + Cl\text{-}\underset{\underset{\displaystyle Ph}{|}}{C}\text{=N-Ar} \rightarrow R_2N\text{-}\underset{\underset{\displaystyle S}{\|}}{C}\text{-}S\text{-}\underset{\underset{\displaystyle Ph}{|}}{C}\text{=N-Ar} \qquad (1)$$

(I)

Data on their physical constants, *etc.*, are given in Table 1.

Thermal Rearrangement. In order to examine the possibility of the thermal rearrangement of I, a pale yellow solution of I in *o*-dichlorobenzene, containing 1 mg I/m*l*, was kept at 100°C. Upon being heated, the solution gradually turned deep yellow. In order to analyze the reaction products, the resulting solution was submitted to thin-layer chromatography on silica gel and separated into two kinds of compounds. One kinds of compounds were compounds I unchanged, while the others were newly-formed deep yellow substances (II). The results of elemental analysis showed that the composition of the compounds II was just the same as that of I. In the infrared spectrum of the compounds II, however, no $\nu_{C=N}$ at *ca.* 1620 cm^{-1} was observed, and a strong absorption band appeared at *ca.* 1510 cm^{-1}; this band may be assignable to the thioureido group.[2] On the basis of these data, it seems reasonable to assume that I gave rise to the same kind of rearrangement to thiolimidocarbonates as has been reported previously,[1] involving the migration of the thiocarbamoyl group, thus producing 1,1-dialkyl-3-aryl-3-(phenylthiocarbonyl)-2-thioureas (II) with the following structure:



$$R_2N-\underset{\underset{\displaystyle S}{\|}}{C}-\underset{\underset{\displaystyle Ar}{|}}{N}-\underset{\underset{\displaystyle S}{\|}}{C}-Ph$$

(II)

The compounds II formed by the thermal rearrangement of I are listed in Table 2.

Kinetics of the Rearrangement. Studies of the kinetics on the rearrangement for all the compounds I were successfully carried out by observing the development of the above-mentioned yellow color using photoelectric techniques. As a result, it was found that an equilibrium existed in these systems. The values of the equilibrium constants (K), given by the equation of $K = C_{II}/C_I$, where C_{II} and C_I are the concentrations of II and I respectively at the equilibrium, in *o*-dichlorobenzene at 100°C were 2.33 for I-1, 1.08 for I-2, 0.89 for I-3, and 0.82 for I-4, and fairly good first-order forward rate constants (k_1) were derived from the

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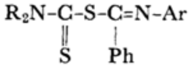
*[1] Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

[1] A. Kaji and K. Miyazaki, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 727 (1966).

[2] H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infra-red Determination of Organic Structure," Van Nostrand, New York (1949).

TABLE 1. MIXED DITHIOCARBAMIC-IMIDIC ANHYDRIDES

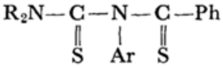


$R_2N-\underset{\underset{S}{\|}}{C}-S-\underset{\underset{Ph}{|}}{C}=N-Ar$

Compd. No.	R	Ar	Mp[a] °C	Appearance	Yield[b] %	Formula	Anal.[c] C(%) Found (Calcd)	H(%) Found (Calcd)	N(%) Found (Calcd)
I-1	CH_3	Ph	81—82	pale yellow needles[d]	66	$C_{16}H_{16}N_2S_2$	64.00 (64.00)	5.49 (5.33)	9.03 (9.33)
I-2	C_2H_5	Ph	91—92	pale yellow needles[d]	68	$C_{18}H_{20}N_2S_2$	65.60 (65.85)	5.39 (6.10)	8.39 (8.54)
I-3	n-C_3H_7	Ph	82—83	pale yellow prisms[e]	58	$C_{20}H_{24}N_2S_2$	67.10 (67.49)	6.30 (6.75)	7.77 (7.87)
I-4	n-C_4H_9	Ph	44—45	pale yellow needles[f]	55	$C_{22}H_{28}N_2S_2$	68.80 (68.75)	6.81 (7.28)	7.13 (7.28)
I-5	CH_3	4-Cl-C_6H_4	105—106	pale yellow needles[d]	65	$C_{16}H_{15}ClN_2S_2$	57.10 (57.40)	4.39 (4.49)	8.42 (8.39)
I-6	C_2H_5	4-Cl-C_6H_4	76—77	pale yellow needles[d]	70	$C_{18}H_{19}ClN_2S_2$	59.55 (59.59)	5.18 (5.24)	7.41 (7.72)

a) All melting points are uncorrected. b) Yield of the pure product.
c) All the compounds show a strong band at the region of *ca.* 1620 cm⁻¹ which may be assigned to $\nu_{C=N}$.
d) From ethanol-acetone. e) From ethanol. f) From methanol.

TABLE 2. 1,1-DIALKYL-3-ARYL-3-(PHENYLTHIOCARBONYL)-2-THIOUREAS



$R_2N-\underset{\underset{S}{\|}}{C}-\underset{\underset{Ar}{|}}{N}-\underset{\underset{S}{\|}}{C}-Ph$

Compd. No.	R	Ar	Mp[a] °C	Appearance	Anal.[b] Found C(%)	Found H(%)	Found N(%)
II-1	CH_3	Ph	159—160	deep yellow needles[c]	64.00	5.38	9.54
II-2	C_2H_5	Ph	136—137	deep yellow needles[c]	65.70	5.95	8.31
II-3	n-C_3H_7	Ph	123—124	deep yellow needles[c]	67.30	6.39	8.31
II-4	n-C_4H_9	Ph	108—109	deep yellow needles[d]	68.75	6.94	6.95
II-5	CH_3	4-Cl-C_6H_4	140—141	deep yellow needles[c]	57.10	4.40	8.14
II-6	C_2H_5	4-Cl-C_6H_4	139—140	deep yellow plates[c]	59.30	5.26	8.00

a) All melting points are uncorrected.
b) In each compound, the molecular formula and the theoretical values for the elements are equal to those of the corresponding starting compound I in Table 1.
c) From ethanol-acetone. d) From ethanol.

slopes of the straight lines obtained by plotting $x_e \cdot \ln(x_e/(x_e-x))$ against the time in min, where x and x_e are the concentrations of II at time t and at equilibrium respectively.

Figure 1 shows the slopes of the straight lines obtained by plotting $x_e \cdot \ln(x_e/(x_e-x))$ *vs.* the time: the results are summarized in Table 3.

From these data, it is observed that the change of the reaction rate closely parallels the structure of the alkyl group in compound I. Figure 2 shows the slope of the straight line obtained by plotting $3+\log k_1$ *vs.* σ^* for R.

TABLE 3. FIRST-ORDER FORWARD RATE CONSTANTS (k_1) OF THE REARRANGEMENTS OF I TO II AT 100°C[a]

Compd. No.	$k_1 \times 10^2$ (min⁻¹)	Relative rates
I-1	3.00	(1)
I-2	1.41	0.47
I-3	1.17	0.39
I-4	0.92	0.31

a) For all runs, solvent: *o*-dichlorobenzene; concentration: 1 mg I/m*l*.

It is now desirable to determine whether the reaction is intermolecular or intramolecular in order to ascertain the mechanism of the rearrangement of I to II. If the reaction is supposed to be an intermolecular mechanism such as Scheme 1, the order of k_1 should be contrary to the experimental results shown in Table 3, because the polar

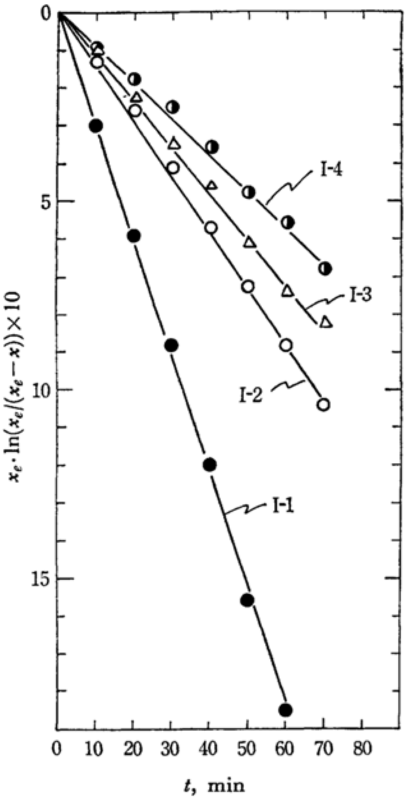


Fig. 1. The slopes of the straight lines obtained by plotting $x_e \cdot \ln(x_e/(x_e-x)) \times 10$ vs. time (min)

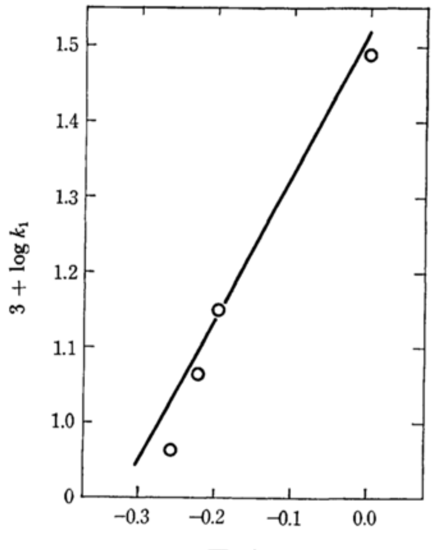
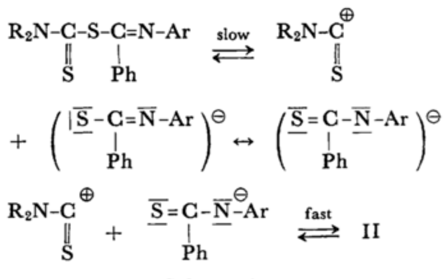


Fig. 2. The slope of the straight line obtained by plotting $3 + \log k_1$ vs. σ^*.

substituent constants (σ^*) of the alkyl group are 0.00 for CH_3, −0.10 for C_2H_5, −0.115 for *n*-C_3H_7, and −0.13 for *n*-C_4H_9[3]; thus, the stability of the *N,N*-dialkyl-thiocarbamoyl cation, which contributes to the reaction rate, should be increased in the order of $R = n\text{-}C_4H_9 > n\text{-}C_3H_7 > C_2H_5 > CH_3$.



Scheme 1

Furthermore, the crossed products, such as II-2 and/or II-5, should be detected from the crossed reaction mixture of I-1 and I-6 if the rearrangement follows the intermolecular mechanism mentioned above. In order to ascertain this fact, the crossed reaction mixture obtained was compared with the specimens of II-2 and II-5 by thin-layer chromatography. However, the chromatograms of that reaction mixture eliminated the possibility of the formation of crossed products (Fig. 3).

Taking these results into consideration, it seems plausible to conclude that the rearrangement is not intermolecular, such as Scheme 1, but intramolecular.

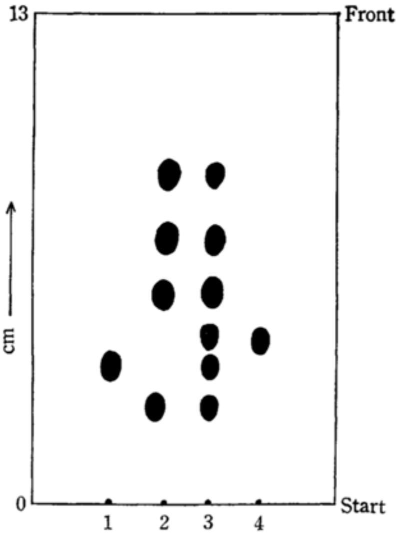


Fig. 3. Thin-layer chromatograms of the crossed reaction mixture.
1: II-5, 2: crossed reaction mixture, 3: mixture of I-1, I-6, II-1, II-2, II-5 and II-6, 4: II-2
Silica gel: WAKOGEL B-5F, Solvent: Benzene-*n*-Hexane-Glacial HOAc=10 : 4 : 0.1 (vol%), Detection: UV-ray

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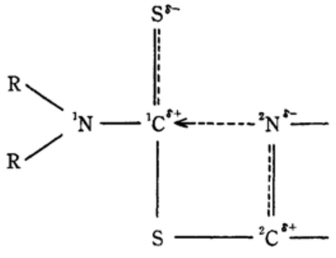
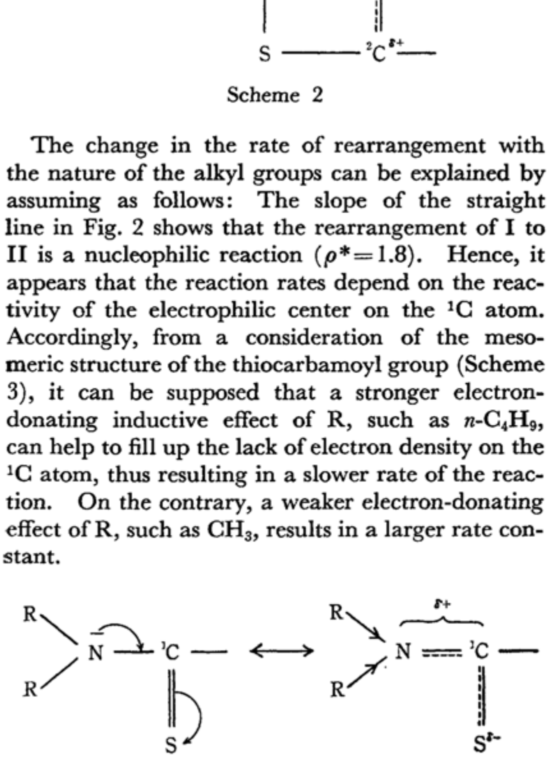
[3] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. Newman, ed., John Wiley and Sons, New York (1956), Chapter 13, p. 619.

Consequently, the four-membered cyclic structure (Scheme 2) which may be formed by a nucleophilic attack of the ^{2}N atom of the imidocarbonyl group on the ^{1}C atom of the thiocarbonyl group can be considered as an intermediate in the rearrangement.



Scheme 2

The change in the rate of rearrangement with the nature of the alkyl groups can be explained by assuming as follows: The slope of the straight line in Fig. 2 shows that the rearrangement of I to II is a nucleophilic reaction ($\rho^*=1.8$). Hence, it appears that the reaction rates depend on the reactivity of the electrophilic center on the ^{1}C atom. Accordingly, from a consideration of the mesomeric structure of the thiocarbamoyl group (Scheme 3), it can be supposed that a stronger electron-donating inductive effect of R, such as n-C_4H_9, can help to fill up the lack of electron density on the ^{1}C atom, thus resulting in a slower rate of the reaction. On the contrary, a weaker electron-donating effect of R, such as CH_3, results in a larger rate constant.



Scheme 3

Experimental

Materials. Sodium *N, N*-dialkyldithiocarbamates were prepared by the known method.[4] *N*-Phenyl- and *N*-(4-chlorophenyl)benzimidoyl chloride were prepared by the usual method.[5]

Mixed *N,N*-Dialkyldithiocarbamic-*N*-(phenyl)-benzimidic Anhydrides (I). The following general method was employed for the synthesis of the various compounds I.

A solution of sodium *N,N*-dialkyldithiocarbamate (0.05 mol) in 50 m*l* of acetone was cooled in an ice bath to a temperature of between 5 to 10°C, after which the proper *N*-(aryl)benzimidoyl chloride (0.05 mol) was gradually stirred in. After the addition had been completed, the mixture was warmed to 40°C for 5 min. It was then cooled to room temperature and poured into *ca.* 150 m*l* of cold water, by which the desired product was obtained as a pale yellow oil and crystallized spontaneously on standing. Recrystallization from a suitable solvent gave pale yellow crystals. The data are shown in Table 1.

1,1-Dialkyl-3-aryl-3-(phenyl-thiocarbonyl)-2-thioureas (II). A solution of I in an inert solvent (toluene, chlorobenzene, *o*-dichlorobenzene, *etc.* may be used) was heated on a boiling water bath for one to five hours,[*2] after which the solvent was removed under reduced pressure. The crude product which remained was then purified by recrystallization or by chromatography on silica gel using as solvent benzene-*n*-hexane (2/1 v/v %).

Analytical Method. For the analysis of II in a mixture of I and II, it was advisable to use the absorbance at 452 mμ and to construct an absorbance-composition plot using a total concentration of the two components, I and II, of 100.0 mg/100.0 m*l* in *o*-dichlorobenzene. The calibration curves were obtained in this way. Since the rearrangement reactions were carried out at the same concentration, the composition of an unknown mixture could be determined by measuring the absorbance at 452 mμ and by reading the composition from the plot. The absorbance was determined with A. K. A. photo-electric-tube colorimeter (Kotaki-Seisakusho, Type No. 5-D).

Procedure for Kinetic Runs. To initiate a run, about 100 mg of I was weighed accurately. Next, in a 250 m*l* round-bottomed flask equipped with a sealed stirrer and a reflux condenser fitted with a calcium chloride drying tube, there was placed a suitable volume of *o*-dichlorobenzene (a G. R.-grade reagent was used after distillation) to make a solution of 100.0 mg I/100.0 m*l*; then the flask was immersed in a boiling water bath. When the inner temperature reached 100°C, the compound I already weighed was stirred into the flask. At appropriate intervals, a portion of the reaction mixture was taken out and cooled by immersion in cold water to room temperature. The absorbance was determined at 452 mμ, and the composition obtained from the plot. The data are shown in Fig. 1.

Equilibrium Constants (K). In the above run, the value of the equilibrium constant was derived from the analytical data of a reaction mixture heated until a constant absorbance was obtained. The values thus obtained were as follows:

$$C_{II\text{-}1}/C_{I\text{-}1}=70/30=2.33,\ C_{II\text{-}2}/C_{I\text{-}2}=52/48=1.08,$$
$$C_{II\text{-}3}/C_{I\text{-}3}=46.5/53.5=0.89,\ C_{II\text{-}4}/C_{I\text{-}4}=45/55=0.82$$

K Values Derived from Back Reactions. To confirm the K values obtained above, the following experiments were carried out: Pure accurately-weighed II (*ca.* 100 mg) was dissolved into *o*-dichlorobenzene to a concentration of 100.0 mg II/100.0 m*l*, after which the solution was heated on a boiling water bath. After 5 and/or 6 hr, a portion of the reaction mixture was

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[4] Houben-Weyl, "Methoden der organischen Chemie," **9**, Georg Thieme Verlag, Stuttgart (1955), p. 826.

[5] W. M. Lauer and C. S. Benton, *J. Org. Chem.*, **24**, 804 (1959); P. A. Smith and N. W. Kalenda, *ibid.*, **23**, 1599 (1958).

[*2] 1.5 hr for I-1, 2 hr for I-2, 3 hr for I-3, and 4 hr for I-4.

taken up and analyzed. The absorbances of the reaction mixture at the two intervals were equal, indicating the reaction to be equilibrium. The values of C_{II}/C_{I} measured by this method were 2.33 for II-1, 1.08 for II-2, 0.89 for II-3, and 0.82 for II-4; these values were equal to the K values derived from the corresponding forward reaction.

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