hydride (mp 87–89°, lit.[23] 92–93°). The deuterated compound (**2**) was prepared by reduction of dibenzoylethylene with lithium aluminum deuteride-d_4 99% D (Alfa Inorganics, mp 84–85°). Melting points are uncorrected. Infrared spectra were recorded on a Beckman IR 10 spectrophotometer, ultraviolet spectra on a Cary 15 spectrophotometer in cyclohexane, emission spectra on a Perkin-Elmer MPF-2A with phosphorescence attachment in an ether–isopentane–ethanol (EPA) glass, and mass spectra on a CEC 21-104 mass spectrometer with an ionization voltage of 15 eV. The structures assigned to **1** and **2** are in agreement with their ir, uv, nmr, and mass spectra.

Quantum Yields. Solutions 0.05 *M* in ketone and about 0.005 *M* in tetradecane internal standard were degassed and sealed under vacuum in 13 mm o.d. Pyrex tubes. The tubes were photolyzed on a merry-go-round apparatus at 25 ± 2° using a Hanovia 450-W medium pressure mercury lamp and a potassium chromate filter solution to isolate 3130-Å irradiation. Photolyses were carried to less than 10% except when dependence on extent of conversion was studied. The photolyzed solutions were analyzed for acetophenone formation and loss of starting material on a Hewlett-Packard 5750 dual flame gas chromatograph with a calibrated 5 ft × 1/8 in. column of 4% QF 1 and 1% Carbowax 20 M on Chromosorb G. Vpc traces were analyzed with a Gelman planimeter. Benzophenone–benzhydrol actinometers[24] were photolyzed simultaneously and analyzed at 3600 Å using a Beckman DU spectrophotometer with Gilford attachment Model 222. Variable-temperature studies employed the same apparatus immersed in a water bath thermostated to ±1°. Reported quantum yields are the result of multiple vpc analyses of one or more solutions, overall accuracy ±5%. Light intensities of approximately 5×10^{-6} Einstein $\mathrm{l.^{-1}\,sec^{-1}}$ were used in all cases.

Quenching Studies. Samples were prepared and analyzed as for quantum yield determination except that varying amounts of *trans*-piperylene (Chemical Samples) were added to the solutions. Five concentrations of piperylene, in addition to blanks containing no piperylene, were used for each Stern–Volmer plot.

Intersystem Crossing Quantum Yields. The method of Lamola and Hammond[25] was used. Degassed benzene solutions of 0.05 *M* acetophenone and **1** and **2** each 1.0 *M* in *cis*-piperylene (Chemical Samples) were irradiated for 6 hr at 3130 Å. Analysis for piperylene isomerization was on a 10 ft × 1/8 in. column of 25% sulfolane on Chromosorb P at 40°.

Mass Spectra Samples. Samples were prepared, degassed, irradiated for varying periods, and analyzed in the same way as for quantum yield determination. The benzene solutions were then washed twice with 10 ml of water and dried with magnesium sulfate, and the benzene was removed. The residue was recrystallized at 0° from chloroform–pentane and the crystalline product analyzed on a CEC 21-104 mass spectrometer with an ionization voltage of 15 eV. The molecular ion region was scanned several times for each sample and the isotopic composition calculated as an average value corrected for the natural abundance of ^{13}C.

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Mechanisms of SNi Reactions. Ion Pair Return in the Decomposition of Aralkyl Thiocarbonates[1a]

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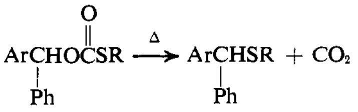
Abstract: On being heated at elevated temperatures in inert solvents *p*-chlorobenzhydryl S-alkyl or S-aryl thiocarbonates decompose to give carbon dioxide and a *p*-chlorobenzhydryl sulfide (eq 1). Use of both optically active and ^{18}O-labeled esters and recovery of the thiocarbonate remaining after partial decomposition show that this reaction is accompanied by some racemization of the thiocarbonate and also by equilibration of the ^{18}O label between the alkyl and acyl oxygens of the ester. Since other evidence indicates the involvement of ion pair intermediates in the decomposition, measurements of the rate of ^{18}O equilibration (k_{eq}) and of loss of optical activity (k_α) can be compared with rates of decomposition (k_{d}) to determine both the importance of ion pair return to reactants under various conditions and also the stereochemistry of the return process. The results reveal that the fraction of ion pairs undergoing return to thiocarbonate is somewhat larger in bromobenzene (89% for the S-phenyl ester) than it is for the same ester in the better ionizing solvent benzonitrile (77%), and also that in benzonitrile the percentage return from either the S-methyl or S-cyclohexyl ester is larger (90%) than for the S-phenyl compound. Although return with retention of configuration predominates for all three esters, it accounts for a smaller percentage of the total return in the case of the S-alkyl and cycloalkyl esters, return with racemization being almost nonexistent for the S-phenyl ester. The significance of these results and their interpretation in terms of both current theories of ion pair behavior and the mechanism (eq 2) of the thiocarbonate decomposition are discussed.

On being heated in inert solvents at 130–170° aralkyl thiocarbonates (**1**) undergo decomposition to an aralkyl sulfide and carbon dioxide (eq 1).[2] The dependence of the rate of this reaction on solvent ionizing power and on the structure of the aralkyl group indicates that the reaction involves heterolysis of the aralkyl–O bond and ion pair intermediates.[2] Furthermore, the variation in the rate of decomposition with



$$\underset{\mathrm{Ph}}{\mathrm{ArCH}}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{SR} \xrightarrow{\Delta} \underset{\mathrm{Ph}}{\mathrm{ArCH}}\mathrm{SR} + \mathrm{CO_2} \qquad (1)$$

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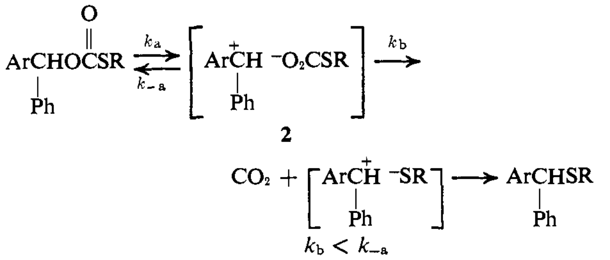
(1) (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. (b) To whom inquiries should be addressed at the Department of Chemistry, University of Vermont, Burlington, Vt. (c) Participant, National Science Foundation Research Participation for College Teachers Program, Summer 1967.

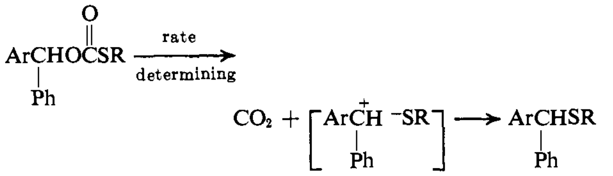
(2) J. L. Kice, R. A. Bartsch, M. A. Dankleff, and S. L. Schwartz, *J. Amer. Chem. Soc.*, **87**, 1734 (1965).

the nature of the thioalkyl group is such as to suggest that the carbonyl–sulfur bond is being broken, and RS on its way to becoming RS^-, in the transition state of the rate-determining step.[2] These particular results are compatible with either the mechanism in eq 2, in which the aralkyl–oxygen and carbonyl–sulfur bonds are broken in two successive steps, or with the alternative shown in eq 3, in which the two bonds



$$\underset{\mathrm{Ph}}{\mathrm{ArCH}}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{SR} \underset{k_{-a}}{\overset{k_a}{\rightleftarrows}} \underset{\mathbf{2}}{\left[\underset{\mathrm{Ph}}{\mathrm{Ar\overset{+}{C}H}}\ {}^{-}\mathrm{O_2CSR}\right]} \xrightarrow{k_b} \mathrm{CO_2} + \left[\underset{\mathrm{Ph}}{\mathrm{Ar\overset{+}{C}H}}\ {}^{-}\mathrm{SR}\right] \longrightarrow \underset{\mathrm{Ph}}{\mathrm{ArCH}}\mathrm{SR} \quad (2)$$

$$k_b < k_{-a}$$

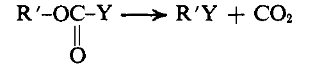


$$\underset{\mathrm{Ph}}{\mathrm{ArCH}}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{SR} \xrightarrow[\text{determining}]{\text{rate}} \mathrm{CO_2} + \left[\underset{\mathrm{Ph}}{\mathrm{Ar\overset{+}{C}H}}\ {}^{-}\mathrm{SR}\right] \longrightarrow \underset{\mathrm{Ph}}{\mathrm{ArCH}}\mathrm{SR} \quad (3)$$

are broken in a single step. However, the fact that in benzonitrile optically active *p*-chlorobenzhydryl S-methyl thiocarbonate (**1a**, Ar = $p\text{-}ClC_6H_4$, R = CH_3) racemizes several times faster than it decomposes to sulfide and CO_2 allows one to conclude that the correct mechanism must be the one in eq 2.[3] Thus, provided return of $[ArPhCH^+\ {}^-O_2CSR]$ ion pairs to thiocarbonate is both considerably faster than their loss of carbon dioxide (*i.e.*, $k_{-a} > k_b$) and does not occur with complete retention of configuration, the mechanism in eq 2 can easily account for the fact that **1a** racemizes faster than it decomposes. On the other hand, the mechanism in eq 3 cannot explain how the thiocarbonate can racemize prior to decomposition.

Establishment of eq 2 as the mechanism for the thermal decomposition of **1** establishes that ion pair return is occurring during the decomposition. While the phenomenon of ion pair return has been observed as an adjunct to certain solvolytic reactions,[4–7] and in certain isomerizations,[8–10] such as those of thiocyanates to isothiocyanates[8] and sulfinates to sulfones,[9] the thiocarbonate decomposition is the first example of ion pair return to *reactants* in an SNi reaction.

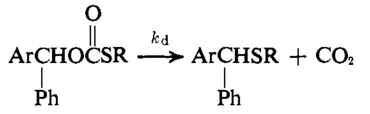
In most of the systems where ion pair return has been studied previously[4–7] the fraction of return is dictated by a competition between the return reaction and the reaction of the ion pair with solvent (solvolysis). In the others[8–10] the fraction of return to original reactants is controlled by the relative nucleophilicity toward the carbonium ion of the two "teeth" of the ambident anion of the ion pair. The thiocarbonate decomposition differs from both of these in that in this case the fraction of return to reactants is determined by a competition between return (step k_{-a}) and decomposition of the initial anion, $RSCO_2^-$, into RS^- and carbon dioxide (step k_b). The factors determining what fraction of the total ion pairs will undergo return are therefore different than in the systems investigated by others,[4–10] and this leads one to hope that a study of the details of ion pair return in both eq 2 and in related SNi reactions of the general type shown in eq 4 can contribute something to the better understanding of ion pair recombination phenomena in general. The present paper describes our initial studies in this area.



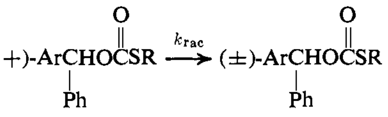
$$\mathrm{R'\text{-}O\underset{\underset{\mathrm{O}}{\|}}{C}\text{-}Y} \longrightarrow \mathrm{R'Y + CO_2} \quad (4)$$

Results

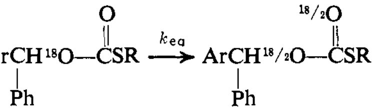
With the aid of optically active and suitably ^{18}O-labeled substrates one can measure the rate of each of the following processes for a thiocarbonate decomposition. One can also investigate the stereochemistry



$$\underset{\mathrm{Ph}}{\mathrm{ArCH}}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{SR} \xrightarrow{k_d} \underset{\mathrm{Ph}}{\mathrm{ArCH}}\mathrm{SR} + \mathrm{CO_2} \quad (5)$$



$$(+)\text{-}\underset{\mathrm{Ph}}{\mathrm{ArCH}}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{SR} \xrightarrow{k_{rac}} (\pm)\text{-}\underset{\mathrm{Ph}}{\mathrm{ArCH}}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{SR} \quad (6)$$



$$\underset{\mathrm{Ph}}{\mathrm{ArCH}}{}^{18}\mathrm{O}\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{SR} \xrightarrow{k_{eq}} \underset{\mathrm{Ph}}{\mathrm{ArCH}}{}^{18/2}\mathrm{O}\text{—}\overset{^{18/2}\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{SR} \quad (7)$$

of the sulfide ArPhCHSR formed from the decomposition of optically active thiocarbonate.

In all the work in the present paper the aralkyl group of the thiocarbonate has been *p*-chlorobenzhydryl (Ar = $p\text{-}ClC_6H_4$). The required optically active and ^{18}O-labeled thiocarbonates were prepared by reaction of optically active and ^{18}O-labeled *p*-chlorobenzhydrol, respectively, with the appropriate chlorothiol formate, RSCOCl.

The rate constant for eq 7, k_{eq}, was determined by partially decomposing samples of the labeled thiocarbonate, recovering the undecomposed thiocarbonate, reducing it with lithium aluminum hydride, and then determining the ^{18}O content of the *p*-chlorobenzhydrol isolated from this reduction. Control experiments showed that the ^{18}O content of the ether oxygen of the thiocarbonate could be reliably determined by this procedure.

In all of the cases studied in the present paper the aralkyl sulfide formed as one of the products of the decomposition was optically inactive. To measure k_{rac}, the rate constant for eq 6, we measured k_α, the first-order rate constant for loss of optical activity

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(3) J. L. Kice and M. A. Dankleff, *Tetrahedron Lett.*, 1783 (1966).

(4) (a) H. L. Goering, R. G. Briody, and J. F. Levy, *J. Amer. Chem. Soc.*, **85**, 3059 (1963); (b) H. L. Goering and J. F. Levy, *ibid.*, **86**, 120 (1964); (c) H. L. Goering and J. F. Levy, *ibid.*, **84**, 3853 (1962); H. L. Goering and S. Chang, *Tetrahedron Lett.*, 3607 (1965).

(5) (a) A. F. Diaz and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 1318 (1966); (b) E. H. White and C. A. Elliger, *ibid.*, **89**, 165 (1967).

(6) (a) H. L. Goering and E. C. Linsay, *ibid.*, **91**, 7435 (1969); (b) H. L. Goering and J. T. Doi, *ibid.*, **82**, 5850 (1960); (c) H. L. Goering, J. T. Doi, and K. D. McMichael, *ibid.*, **86**, 1951 (1964).

(7) (a) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958); (b) D. J. Cram, *ibid.*, 74, 2129 (1952); (c) S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952); (d) W. G. Young, S. Winstein, and H. L. Goering, *ibid.*, 73, 1958 (1951).

(8) A. Fava, A. Iliceto, A. Ceccon, and P. Koch, *ibid.*, **87**, 1045 (1965); A. Iliceto, A. Fava, U. Mazzucato, and O. Rossetto, *ibid.*, **83**, 2729 (1961).

(9) E. Ciuffarin, M. Isola, and A. Fava, *ibid.*, **90**, 3594 (1968); D. Darwish and E. A. Preston, *Tetrahedron Lett.*, 113 (1964).

(10) S. G. Smith, *ibid.*, 979 (1962); S. G. Smith and J. P. Petrovich, *J. Org. Chem.*, 30, 2882 (1965).

by the solution during the decomposition of optically active thiocarbonate, and then took advantage of the fact that under the present conditions k_α is related to k_{rac} and k_d in the following manner: $k_\alpha = k_{rac} + k_d$.

First-order rate constants for the decompositions, k_d, were determined by following the infrared absorption band due to the carbonyl group of the thiocarbonate in the manner described previously.[2]

Figure 1, which shows plots of the data for a representative kinetic run of each type with **1a** in benzonitrile at 145°, indicates the sort of precision associated with the determination of k_{eq}, k_α, and k_d.

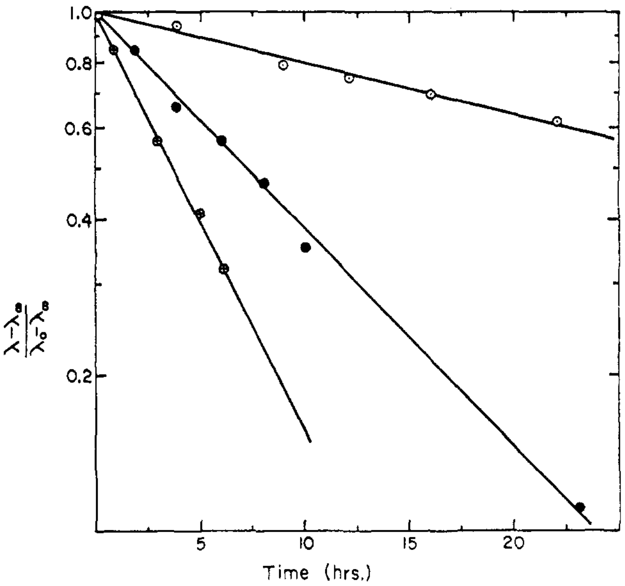
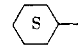
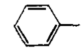
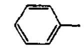


Figure 1. Rates of decomposition, ^{18}O equilibration, and loss of optical activity for *p*-chlorobenzhydryl S-methyl thiocarbonate in benzonitrile at 145°: ○, rate of decomposition, λ = (thiocarbonate); ●, rate of loss of optical activity, λ = rotation at 400 mμ; ⊕, rate of ^{18}O equilibration, λ = atom % ^{18}O in alkyl oxygen of thiocarbonate.

In the present work values of k_{eq}, k_α, and k_d were obtained in benzonitrile for three different *p*-chlorobenzhydryl thiocarbonates, the S-methyl (**1a**), S-phenyl (**1b**, R = C_6H_5), and S-cyclohexyl (**1c**, R = C_6H_{11}) esters, and k_d and k_{eq} were also measured for two of these esters, the S-methyl and S-phenyl compounds, in the less polar solvent bromobenzene. The various results are summarized in Table I.

Table I. Kinetics of the Decomposition of *p*-Chlorobenzhydryl Thiocarbonates[a]

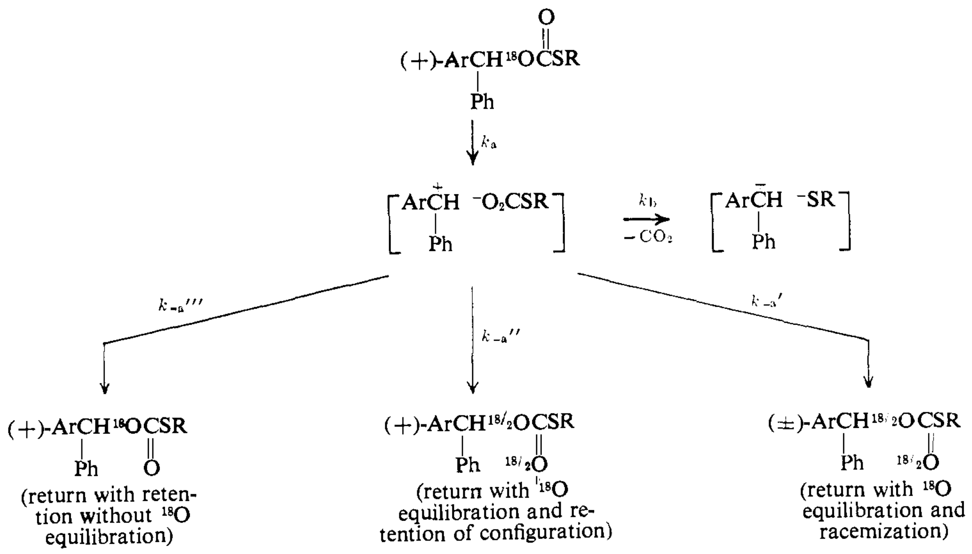
Solvent	Temp, °C	R in RS	$k_{eq} \times 10^5$, sec^{-1}	$k_\alpha \times 10^5$, sec^{-1}	$k_d \times 10^5$, sec^{-1}
PhCN	145	CH_3	5.1	2.6	0.65
			1.6	0.81	0.19
			75	28	22
PhBr	155	CH_3	4.4		0.28
	145		8.3		1.03

[a] Rate constants listed are average of several runs. Initial concentration of thiocarbonate, 0.09–0.40 *M*.

Discussion

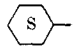
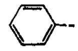
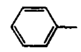
From Table I one sees that in each instance k_{eq} is considerably larger than k_d, the exact factor varying between 3 and 16. This means that in each system studied return of ion pair **2** to thiocarbonate (step k_{-a} in eq 2) is considerably faster than elimination of carbon dioxide from the anion $RSCO_2^-$ in the ion pair (step k_b), and that the majority of the ion pairs **2** formed by dissociation of the aralkyl–oxygen bond in the thiocarbonate simply undergo recombination. Only a small fraction go on to lose carbon dioxide and form the [$ArPhCH^+\ ^-SR$] ion pair, which then collapses to the aralkyl sulfide.

As is outlined in eq 8 ion pair return can have several different consequences as far as ^{18}O equilibration and retention of stereochemical configuration in the thiocarbonate are concerned. In the thiocarbonate de-



(8)

Table II. Behavior of Ion Pairs in the Decomposition of *p*-Chlorobenzhydryl Thiocarbonates

Solvent	Temp, °C	R in RS	k_b/k_{-a}'	k_b/k_{-a}''	k_{-a}''/k_{-a}'	$(k_{-a}' + k_{-a}'')/k_b$	% return to thiocarbonate[a]			% ion pairs losing CO_2[a]
							Total	With retention	With racemization	
PhCN	145	CH_3	0.33	0.20	1.6	7.8	89	55	34	11
			0.31	0.20	1.6	8.4	90	55	35	10
			3.7	0.32	11.5	3.4	77	71	6	23
PhBr	155	CH_3				15.7	94			6
	145					8.1	89			11

[a] Calculated omitting any ion pairs which undergo return to thiocarbonate without undergoing ^{18}O equilibration.

compositions under study it is clear, since k_α is always larger than k_d, that some of the ion pairs must be undergoing return to give racemic thiocarbonate (step k_{-a}'). Even more, however, must return with retention of configuration (step k_{-a}'') since k_{eq} is always considerably larger than k_{rac} ($k_{rac} = k_\alpha - k_d$). One must also keep in mind that some may also be undergoing return without ^{18}O equilibration (step k_{-a}'''). This process cannot, of course, be detected experimentally in the present system. When ^{18}O-labeled carboxylate esters were first used[4,6b,c] to detect ion pair return it was believed that all return occurred with ^{18}O equilibration. However, more recent results with several systems[5,11] indicate that this is not always the case, so that some return of the type represented by step k_{-a}''' could well be occurring undetected in the thiocarbonate reaction. We will have more to say about this point later in the discussion.

The rate constants in eq 8 are related to those in Table I in the manner shown

$$\left(\frac{k_b}{k_{-a}'}\right) = \frac{k_d}{k_\alpha - k_d} \tag{9a}$$

$$\left(\frac{k_b}{k_{-a}''}\right) = \frac{k_\alpha}{k_{eq} + k_d - k_\alpha} \tag{9b}$$

$$\frac{k_{-a}''}{k_{-a}'} = \left(\frac{k_{eq}}{k_\alpha - k_d}\right) - 1 \tag{9c}$$

$$\left(\frac{k_{-a}' + k_{-a}''}{k_b}\right) = \frac{k_{eq}}{k_d} \tag{9d}$$

Values for these ratios for the different systems studied are shown in Table II. We can also use the ratios in eq 9a–d to calculate just what percentage of the total ion pairs reacting by paths k_{-a}', k_{-a}'', and k_b follow each particular path. These data are also shown in Table II. Let us now discuss a number of aspects of the data in Table II.

The ratio $(k_{-a}' + k_{-a}'')/k_b$ gives the ratio of the total rate of return (excluding that occurring without ^{18}O equilibration) to the rate at which ion pairs lose CO_2. Because step k_b involves simply the conversion of one ion pair to another, it seems reasonable to assume that k_b for a given thiocarbonate will not depend to any important degree on solvent. Since both k_{-a}' and k_{-a}'' represent reactions in which an ion pair is converted to an uncharged covalent molecule, $(k_{-a}' + k_{-a}'')/k_b$ would therefore be expected to increase with a decrease in the ionizing power of the solvent used for the decomposition. That this does happen is seen from the fact (Table II) that $(k_{-a}' + k_{-a}'')/k_b$ is larger, by a factor of slightly more than 2, in bromobenzene than it is in the more polar solvent benzonitrile.

A change from bromobenzene to benzonitrile leads to a tenfold increase in the quantity $k_{eq} + k_d$. Provided k_{-a}''' is not too large compared to $k_{-a}' + k_{-a}''$, $(k_{eq} + k_d)$ should be approximately equal to k_a, the rate of ionization of the thiocarbonate to the ion pair. Thus we see that the rate of return of the ion pair to thiocarbonate appears to be significantly less dependent on solvent ionizing power (in a reverse sense, of course) than is the rate of ionization of the thiocarbonate to the ion pair. The ionization of the thiocarbonate is undoubtedly a highly endothermic process. According to Hammond's principle[12] the transition state for the thiocarbonate--ion pair reaction will therefore be much closer in structure to the ion pair than it is to the thiocarbonate. Since the transition state will accordingly have considerable ion pair character it is not surprising that the rate of return is considerably less sensitive to changes in solvent ionizing power than is the rate of the reverse reaction, the ionization of **1** to give the ion pair.

Table II reveals some interesting variations in the several rate constant ratios with a variation of the thioalkyl group from S-methyl to S-phenyl. Thus there is a 1.6-fold increase in (k_b/k_{-a}''), a sevenfold increase in (k_{-a}''/k_{-a}'), and over a tenfold increase in (k_b/k_{-a}'). Operationally what this means is that on going from the S-methyl to the S-phenyl ester there is a dramatic decrease (from 34 to 6%) in the fraction of ion pairs undergoing return with racemization, and that this decrease comes at the expense of an increase not only in the fraction undergoing loss of CO_2 (from 11 to 23%) but also in the fraction undergoing return with retention (from 55 to 71%).

The anion PhS^- has been shown[13] to receive some stabilization from resonance interaction of the negative charge with the aromatic ring. Because of this PhS^- should be more stable relative to $PhSCO_2^-$ than CH_3S^-

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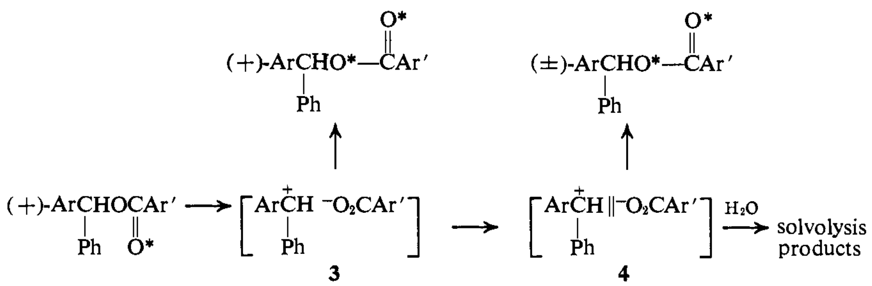
(11) H. L. Goering and R. F. Myers, *J. Amer. Chem. Soc.*, **91**, 3386 (1969).

(12) G. S. Hammond, *ibid.*, 77, 334 (1955).

(13) M. M. Kreevoy, E. T. Harper, R. E. Duvall, H. S. Wilgus, III, and L. T. Ditsch, *ibid.*, **82**, 4899 (1960).



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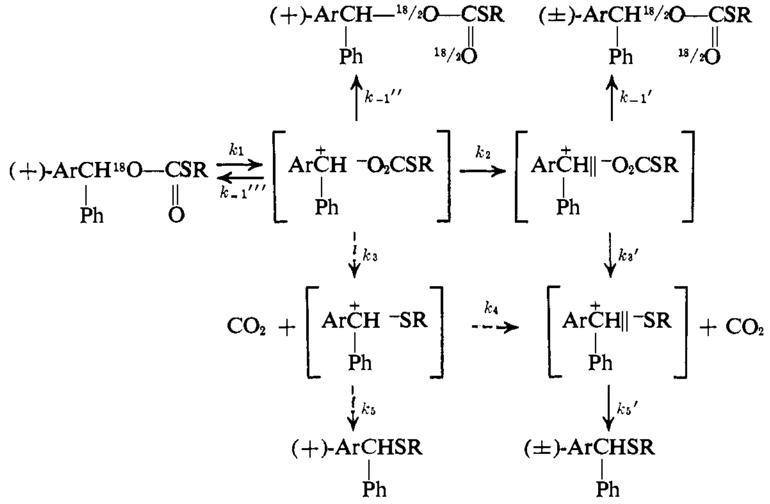

(11)

is relative to $CH_3SCO_2^-$. One would therefore expect that k_b for the S-phenyl thiocarbonate would be larger than k_b for the S-methyl ester. The decrease in $(k_{-a}' + k_{-a}'')/k_b$ of a factor of 2.3 and the increase in the fraction of ion pairs undergoing loss of CO_2 from 11 to 23% on changing from the S-methyl to the S-phenyl thiocarbonate are thus in line with the expected change in k_b on going from $CH_3SCO_2^-$ to $PhSCO_2^-$.

But why does this particular structural change lead to a large increase in (k_{-a}''/k_{-a}')? Certainly it is not due to the difference in the steric requirements of the methyl and the phenyl group, because the S-cyclohexyl ester, with an alkyl group of steric bulk comparable to phenyl, shows behavior which is, to all intents and purposes, identical with that of the S-methyl ester and very different from that of the S-phenyl compound. Frankly, we cannot say at this time that we really know the origin of the increase in (k_{-a}''/k_{-a}'), although we can offer some possible speculations. Before doing this, however, it will be helpful to recall briefly certain aspects of ion pair behavior that have emerged from other studies[4a,b] involving *p*-chlorobenzhydryl cations.

In examining the ion pair return accompanying the solvolysis of *p*-chlorobenzhydryl *p*-nitrobenzoate in aqueous acetone Goering and Levy[4b] found that their results could be best explained in terms of a mechanism involving two different types of ion pairs, one of which (**3**) underwent return strictly with retention of configuration, while return from the other (**4**) occurred with either considerable or complete racemization (eq 10). A mechanism involving two types of ion pair intermediates, one of which has lost its stereochemical memory and the other of which has not, could also be written for the thiocarbonate decomposition and is shown as eq 11.

Since none of the aralkyl sulfide formed in the thiocarbonate decompositions in Table I is optically active the reaction sequence of step k_3 followed by step k_5 plays no role in these decompositions. In view of the fact that in the decomposition of aralkyl chlorocarbonates, such as $PhC(CH_3)HOCOCl$, the aralkyl chloride product is formed with a high degree of retention of configuration,[14] we assume that the failure to isolate optically active product in the present decompositions must be due, *not* to the fact that k_4 is faster than k_5, but rather to the fact that k_3 is much slower relative to k_2 than is the case for the chlorocarbonate decomposition, as might be expected given the presumed greater stability of Cl^- relative to $ClCO_2^-$ as compared to RS^- *vs.* $RSCO_2^-$. Thus we do not believe that any of the reactions shown with dashed arrows in eq 11, *i.e.*, k_3, k_4, and k_5, play a significant role in the thiocarbonate decompositions we have studied, and we feel that analysis of the results in terms of the two types of ion pair mechanism should be attempted using only the other reactions in eq 11.

In terms of such an analysis k_d, k_α, and k_{eq} will be given by

$$k_d = k_1\left(\frac{k_2}{k_{-1}''' + k_{-1}'' + k_2}\right)\left(\frac{k_3'}{k_{-1}' + k_3'}\right) \quad (12a)$$

$$k_\alpha = k_1\left(\frac{k_2}{k_{-1}''' + k_{-1}'' + k_2}\right) \quad (12b)$$

$$k_{eq} = k_1\left(\frac{k_{-1}''}{k_{-1}''' + k_{-1}'' + k_2}\right) + k_1\left(\frac{k_2}{k_{-1}''' + k_{-1}'' + k_2}\right)\left(\frac{k_{-1}'}{k_{-1}' + k_3'}\right) \quad (12c)$$

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[14] K. B. Wiberg and T. M. Shryne, *J. Amer. Chem. Soc.*, 77, 2774 (1955).

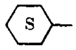
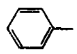
By suitable manipulation of these expressions it is possible to derive eq 13 and 14. The values of $(k_3'/$

$$(k_3'/k_{-1}') = \frac{k_d}{k_\alpha - k_d} \tag{13}$$

$$(k_2/k_{-1}'') = \frac{k_\alpha}{k_{eq} + k_d - k_\alpha} \tag{14}$$

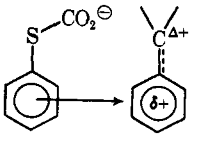
$k_{-1}')$ and (k_2/k_{-1}'') calculated for the various decompositions in benzonitrile from the data in Table I are shown in Table III.

Table III. Values of (k_3'/k_{-1}') and (k_2/k_{-1}'') for the Decompositions of *p*-Chlorobenzhydryl Thiocarbonates in Benzonitrile at 145°

R in RS	(k_3'/k_{-1}')	(k_2/k_{-1}'')
CH_3	0.33	0.85
	0.31	0.83
	3.7	0.41

One notes that (k_3'/k_{-1}') for the mechanistic scheme in eq 11 has the same value as (k_b/k_{-a}') in eq 8 (see Table II). As already discussed for k_b, the resonance stabilization of the negative charge in PhS^- means that this anion is going to be more stable relative to $PhSCO_2^-$ than CH_3S^- is relative to $CH_3SCO_2^-$, so that k_3' should be significantly larger for the S-phenyl ester than for the S-methyl compound. As far as k_{-1}' is concerned, the electron-attracting inductive effect of phenyl is going to mean that $PhSCO_2^-$ will be a somewhat more stable anion than $CH_3SCO_2^-$, so that k_{-1}' for the S-phenyl compound should be somewhat smaller than for the S-alkyl esters, although given the fact that the transition state for the k_{-1}' reaction is undoubtedly much closer to the ion pair in structure than it is to the thiocarbonate, the effect will undoubtedly be a small one. A change from R = CH_3 to R = C_6H_5 in $RSCO_2^-$ should therefore increase k_3' and slightly decrease k_{-1}'. The observed sizable increase in (k_3'/k_{-1}') is therefore readily understood.

In terms of the reaction scheme in eq 11 a change from $CH_3SCO_2^-$ to $PhSCO_2^-$ also results in a twofold *decrease* in (k_2/k_{-1}''). Since one might expect that, like k_{-1}', k_{-1}'' would be slightly smaller for the S-phenyl ester than for the S-methyl or S-cyclohexyl compounds, this would seem to suggest that there is some factor that causes the ion pair to "racemize" (step k_2) more slowly when the anion is $PhSCO_2^-$ than when it is either $CH_3SCO_2^-$ or cyclohexyl-SCO_2^-. One way that this might conceivably come about is if in the $[ArPhCH^+ \, ^-O_2CSPh]$ ion pair there were some weak π interactions between the phenyl group of $PhSCO_2^-$ and one of the rather electron-deficient aryl groups of the carbonium ion, *i.e.*



If such an interaction existed it could clearly reduce the rate of racemization of the ion pair. Although this proposal must be regarded at this stage as still highly speculative, one might note in its further defense that we have been unable to come up with any other plausible alternative that could cause a change from S-alkyl, or S-cycloalkyl, to S-aryl to lead to a significant decrease in k_2.[15]

Experimental Section

***p*-Chlorobenzhydrol-^{18}O.** 4-Chlorobenzophenone (150 g, 0.69 mol) was dissolved in a mixture of 700 ml of dioxane and 50 ml of ^{18}O-enriched water (~1.6 atom% ^{18}O) containing 0.1 ml of concentrated sulfuric acid, and the solution was heated at reflux for 24 hr. The major portion of the solvent was then removed by distillation, the residue dissolved in 200 ml of ether, and the ether solution dried over magnesium sulfate. After drying, the ether solution was added dropwise with stirring to a flask containing 15 g of lithium aluminum hydride and 200 ml of anhydrous ether. The mixture was stirred overnight at room temperature and then hydrolyzed by the addition of saturated ammonium chloride solution. The ether layer was washed several times with water and dried, and the ether removed under reduced pressure. The residue was recrystallized from hexane yielding 143 g (95%) of *p*-chlorobenzhydrol-^{18}O (1.42 atom % ^{18}O), mp 65°.

Resolution of *p*-Chlorobenzhydrol. The procedure used was a modification of that of Kenyon and Green.[16] *p*-Chlorobenzhydryl hydrogen phthalate[16] (27.8 g) and 29.9 g of brucine were dissolved in 140 ml of ethyl acetate. After being filtered, the solution was evenly divided between two 250-ml Erlenmeyer flasks. The flasks were then placed in an air-tight container and about 150 ml of cyclohexane was placed in the bottom of the container. The container was sealed and placed in the refrigerator. After about 3 weeks the crystals that had formed were removed by suction filtration. An additional crop of crystals could generally be obtained by returning the filtrates to the flasks and allowing them to stand in the container in the refrigerator for another 3-week period. The combined crops of crystals were dissolved in a minimal amount of acetone and decomposed with cold 3 *N* hydrochloric acid. Addition of a large volume of cold water (~200 ml) precipitated (+)-*p*-chlorobenzhydryl hydrogen phthalate. This was dissolved in ether, and the ether solution was extracted with 5% sodium bicarbonate solution. Acidification of the bicarbonate extract with dilute hydrochloric acid gave 3.5 g of purified product. This was dissolved in 50 ml of hot methanol, 5 ml of 40% sodium hydroxide solution was added, and the solution was heated on the steam bath for 15 min. After addition of 150 ml of water to the cooled solution, the mixture was extracted twice with ether and the ether extracts were dried over magnesium sulfate. After removal of the ether the residual oil was crystallized from hexane to give 1.3 g of partially resolved (−)-*p*-chlorobenzhydrol, mp 52–55°, $[\alpha]_D$ −4.40° (*c* 6, acetone). Other resolutions using the same procedure on occasion yielded alcohol having a specific rotation as high as −8.90°.

***p*-Chlorobenzhydryl S-Cyclohexyl Thiocarbonate.** Cyclohexyl chlorothiolformate, bp 61–62° (1 mm), was prepared in 57% yield

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(15) Another possible explanation of course is that our assumption that k_{-1}'' for $PhSCO_2^-$ is slightly smaller than k_{-1}'' for $CH_3SCO_2^-$ is wrong, and that the lower (k_2/k_{-1}'') for the S-phenyl ester actually is the result, not of a decrease in k_2, but rather of an increase in k_{-1}''. This could come about if there was a much larger fraction of return *without* ^{18}O equilibration from the first-formed ion pair in the S-alkyl cases than in the S-phenyl one. (As noted earlier, there is reason to believe from the results of other studies[5,11] that there could be some return without ^{18}O equilibration from the initial ion pair in the present decompositions.) The key question is whether a change from $CH_3SCO_2^-$ to $PhSCO_2^-$ as the anion would lead to as large a change in the ratio of (k_{-1}''/k_{-1}''') as would be required to explain the change in (k_2/k_{-1}'') on the basis of a change in k_{-1}''. The results of Diaz and Winstein[5a] would seem to indicate that in reactions involving $[Ph_2CH^+ \, ^-O_2CAr]$ ion pairs a change from $PhCO_2^-$ to *p*-$O_2NC_6H_4CO_2^-$ as the anion does *not* lead to any very appreciable decrease in the fraction of return occurring without ^{18}O equilibration. Since a change from benzoate to *p*-nitrobenzoate represents a change in anion stability which should be comparable to that involved on going from $CH_3SCO_2^-$ to $PhSCO_2^-$, this suggests that an explanation of our results in terms of a sizable variation in k_{-1}''/k_{-1}''' (and k_{-1}'') with change in the anion is less plausible than the one in terms of a change in k_2 that has been outlined.

(16) G. H. Green and J. Kenyon, *J. Chem. Soc.*, 751 (1950).

by reaction of phosgene with cyclohexyl mercaptan using a procedure analogous to that described[2] for the synthesis of benzyl and benzhydryl chlorothiolformates. Reaction of 2.2 g (0.012 mol) of the chlorothiolformate with 2.2 g (0.01 mol) of *p*-chlorobenzhydrol in 4 ml of benzene containing 0.9 g of pyridine for 6 hr at room temperature afforded the S-cyclohexyl thiocarbonate. The crude ester was purified by chromatography on alumina. The purified *p*-chlorobenzhydryl S-cyclohexyl thiocarbonate was an oil which resisted all attempts at crystallization even after further chromatography on alumina, but which appeared to be quite pure as judged by its spectral properties, elemental analysis, and behavior on thin-layer chromatography. *Anal.* Calcd for $C_{20}H_{21}ClO_2S$: C, 66.64; H, 5.86. Found: C, 66.75; H, 5.93.

Preparation of Optically Active and ^{18}O-Labeled *p*-Chlorobenzhydryl Thiocarbonates. The optically active and ^{18}O-labeled *p*-chlorobenzhydryl thiocarbonates were prepared from the appropriate alcohol by the same synthetic routes[2] used to prepare the analogous normal thiocarbonates.

In the case of each ^{18}O-labeled thiocarbonate the following experiment was carried out to demonstrate that synthesis of the thiocarbonate from the ^{18}O-labeled alcohol had not led to any loss of ^{18}O label and, more important, that all of the label was present in the alkyl oxygen of the thiocarbonate. A sample of the thiocarbonate was dissolved in ether and the solution was added to a mixture of excess lithium aluminum hydride in ether. The mixture was allowed to stir overnight and then was cautiously hydrolyzed by the addition of saturated ammonium chloride solution. After the hydrolysis, the ether layer was washed with water and then dried over either magnesium sulfate or Drierite. The ether was removed under reduced pressure and the residue was recrystallized from hexane. The *p*-chlorobenzhydrol so isolated was analyzed for ^{18}O content using the general type of procedure described by Doering and Dorfman.[17] In every case the oxygen-18 content of the *p*-chlorobenzhydrol isolated from the reduction of the thiocarbonate was identical within experimental error with the ^{18}O content of the starting alcohol used in the synthesis.

Specific rotations of the optically active thiocarbonates prepared by reaction of partially resolved (−)-*p*-chlorobenzhydrol ($[\alpha]_D$ −4.40°) with the appropriate chlorothiolformates were as follows: S-methyl ester, $[\alpha]_D$ +1.03° (*c* 6, acetone); S-phenyl ester, $[\alpha]_{363}$ +0.88° (*c* 6, hexane); S-cyclohexyl ester, $[\alpha]_{400}$ +2.3° (*c* 3.5, benzonitrile). Although the partially resolved S-phenyl ester was a solid with the same melting point as the corresponding racemic ester, the partially resolved S-methyl ester was an oil, rather than being crystalline like the racemic S-methyl ester, mp 62–63°. On standing for a long time it would slowly deposit crystals of the racemic ester, with a concomitant increase in the specific rotation of the remaining noncrystalline thiocarbonate and of the (−)-*p*-chlorobenzhydrol that was isolated after alkaline hydrolysis of samples of the thiocarbonate. That the noncrystalline partially resolved S-methyl thiocarbonate was indeed pure was demonstrated by thin-layer chromatography.

Kinetic Studies of the Thermal Decomposition of Thiocarbonates. The rates of decomposition of the thiocarbonates under various conditions were all measured using the infrared method described in an earlier publication.[2]

Kinetic Studies of the Equilibration of Alkyl and Acyl Oxygens in the Thiocarbonate Decomposition. A solution of the alkyl oxygen-labeled thiocarbonate was placed in the same type of apparatus used for the kinetic studies of the rate of decomposition and heated in a constant temperature bath. From time to time aliquots of the solution were removed and the solvent was stripped off at 1–2-mm pressure. The residue was then dissolved in ether and the ether solution was added to a mixture of excess lithium aluminum hydride in ether. The thiocarbonate was thereby reduced and the *p*-chlorobenzhydrol which was formed was isolated and purified in the manner already described. Its oxygen-18 content was then determined using the Doering and Dorfman[17] procedure. It was necessary to pyrolyze three or four consecutive portions (15–20 mg) of a given sample of *p*-chlorobenzhydrol before reproducible ^{18}O data were obtained for that particular sample. As long as this precaution was taken data of excellent precision and reproducibility were obtained. Without it the data were much less precise and reproducibility also suffered.

The ratio of mass 46 to mass 44 in the samples of CO_2 resulting from the pyrolyses was measured using a CEC residual gas analyzer.[18] The atom percentage of oxygen-18 in the *p*-chlorobenzhydrol, *P*, was then calculated using the following equation given by Doering and Dorfman[17]

$$P = \frac{0.00408R - 0.00204}{0.9959 + 0.00408R} \times 10^2$$

where

$$R = \frac{I_{46}/I_{44}}{I^\circ_{46}/I^\circ_{44}}$$

and I° represents the intensity of a particular mass peak in a sample of standard (or tank) carbon dioxide and I represents the intensity of the same mass peak in the sample of carbon dioxide from the pyrolysis of the *p*-chlorobenzhydrol sample.

The rate of ^{18}O equilibration between alkyl and acyl oxygens in the thiocarbonate was then determined by plotting log $(P - P_\infty)/(P_0 - P_\infty)$ *vs.* time, where P_0 = the atom per cent of oxygen-18 for a sample at $t = 0$ and $P_\infty = (P_0 + 0.204)/2$. The slope of the plot of log $(P - P_\infty)/(P_0 - P_\infty)$ *vs.* time is k_{eq}.

Kinetic Studies of the Rate of Loss of Optical Activity in the Thiocarbonate Decomposition. A solution of a partially resolved, optically active *p*-chlorobenzhydryl thiocarbonate in benzonitrile was placed in the same type of apparatus used for the kinetic studies of the rate of decomposition, and the apparatus was heated in a constant temperature bath. At appropriate time intervals aliquots of the solution were removed and their rotation at 400 mμ was determined using a Perkin–Elmer Model P-22 spectropolarimeter. This instrument can determine rotations to an accuracy of ±0.002°. Initial rotations of the solutions used were always at least 40 times this figure.

The rate of loss of optical activity, k_α, was determined from the slope of a plot of log α *vs.* time. The final rotations of the solutions were always zero, indicating that the reaction products are completely optically inactive.

In the case of the S-methyl ester it was shown by the following experiment that this was not due merely to racemization of the thiocarbonate prior to its decomposition. A sample of optically active *p*-chlorobenzhydryl S-methyl thiocarbonate ($[\alpha]_D$ +2.09°) was decomposed to the extent of about 10% in benzonitrile at 166°. The undecomposed thiocarbonate was separated from the *p*-chlorobenzhydryl methyl sulfide formed as the decomposition product by chromatography. Although the thiocarbonate had racemized to the extent of only about 30% during this period ($[\alpha]_D$ of the recovered thiocarbonate +1.46°), the aralkyl sulfide formed during the same period was optically inactive. This shows that even sulfide formed from optically active thiocarbonate is racemic.

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(17) W. von E. Doering and E. Dorfman, *J. Amer. Chem. Soc.*, **75**, 5595 (1953).

(18) We are indebted to Professor Thomas Koenig of the University of Oregon for the use of his instrument.