

Mechanisms of S_Ni Reactions.

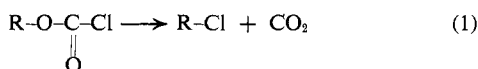
The Decomposition of Aralkyl Thiocarbonates¹

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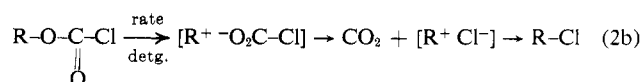
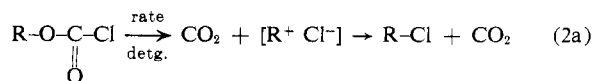
Thiocarbonates (ROCOSR', R = aralkyl) decompose to carbon dioxide and the corresponding sulfides (RSR') on being heated at elevated temperatures in inert solvents. The decomposition is clearly analogous to the decomposition of alkyl chlorocarbonates to alkyl chlorides and carbon dioxide,^{2,3} and study of the dependence of the rate of decomposition on both solvent and the nature of the aralkyl group shows that, like the chlorocarbonate decomposition, the reaction involves rate-determining formation of the aralkyl carbonium ion by heterolysis of the R-O bond. The rate of decomposition of a series of benzhydryl thiocarbonates, Ph₂CHOCOSR', varies markedly with R'. Of particular interest is the fact that the compound where R' equals phenyl decomposes more rapidly than would be expected from the decomposition rates of a series of S-alkyl thiocarbonates. This result seems most readily explained by a mechanism in which both the R-O and C-S bonds are broken in the rate-determining step. The possible implications for the mechanism of the chlorocarbonate decomposition and other S_Ni reactions are discussed.

The decomposition of alkyl chlorocarbonates (eq. 1) is one of the classic examples of an S_Ni reaction. The variation of the rate of decomposition with the nature



of the alkyl group^{2,3} and with solvent ionizing power² make it clear that the rate-determining step of the

bond is synchronous with (eq. 2a), or alternatively occurs subsequent to (eq. 2b), the fission of the R-O bond.



One way to obtain information pertinent to this point is to find a compound of the structure ROCOZR' which undergoes an analogous decomposition (ROCOZR' → RZR' + CO₂) and to investigate the influence of suitable changes in R' on its rate of decomposition. We have found that thiocarbonates of the structure ROCOSR' undergo thermal decomposition at elevated temperatures in a reaction (eq. 4) which is not only formally analogous to the chlorocarbonate decomposition but also shows a similar dependence on solvent ionizing power and structure of the R group. Accordingly, the thiocarbonate decomposition seems ideally suited for studies of the type outlined above. The present paper describes the results of studies of the variation of thiocarbonate decomposition rate with variation in R' and discusses the implications of those results as regards the general question of the timing of the various bond scissions involved in a typical S_Ni reaction.

Table I. Products of the Decomposition of Aralkyl Thiocarbonates

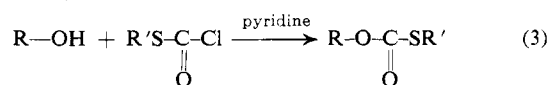
Thiocarbonate, } ROCOSR' } Solvent Temp., °C. Products ^a	R = (C ₆ H ₅) ₂ CH R' = C ₆ H ₅ C ₆ H ₅ CN 145	(C ₆ H ₅) ₂ CH C ₆ H ₅ CH ₂ C ₆ H ₅ CN 170	C_6H_5 $p\text{-ClC}_6\text{H}_4\text{CH}$ C ₆ H ₅ C ₆ H ₅ CN 145	C_6H_5 $p\text{-ClC}_6\text{H}_4\text{CH}$ CH ₃ C ₆ H ₅ CN 165	(C ₆ H ₅) ₂ CH C ₆ H ₅ C ₆ H ₅ Br 145
Carbon dioxide	1.01	0.94	0.95	0.95	1.00
RSR'	0.83	0.67	0.83	0.87	0.78
R'SSR'	0.02	<i>b</i>	<i>b</i>	<i>b</i>	0.02
R-R	0.07	<i>b</i>	<i>b</i>	<i>b</i>	0.02
ROH	0.00	0.07	0.00	0.00	0.00

^a Mole/mole of thiocarbonate. ^b None detected, but a small amount could possibly have been present.

reaction involves heterolysis of the R-O bond and formation of the alkyl carbonium ion R⁺. It has not been known, however, whether breaking of the C-Cl

Results

Synthesis of Thiocarbonates. The various thiocarbonates were all synthesized by reaction of the appropriate alcohol with the proper chlorothioformate (eq. 3). Data on their physical constants, etc., are given in Table V.



(1) (a) This research was supported by the National Science Foundation under grants G-19503 and GP-1975. (b) Part of this work has appeared in preliminary form: J. L. Kice and R. A. Bartsch, *Tetrahedron Letters*, 1693 (1963).

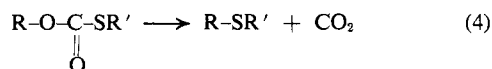
(2) K. L. Olivier and W. G. Young, *J. Am. Chem. Soc.*, **81**, 5811 (1959).

(3) K. B. Wiberg and T. M. Shryne, *ibid.*, **77**, 2774 (1955).

Table II. Kinetics of the Decomposition of Aralkyl Thiocarbonates

Thiocarbonate, ROCOSR'		Solvent	Temp., °C.	[ROCOSR'] ₀ , M	k ₁ × 10 ⁴ , sec. ⁻¹
R	R'				
(C ₆ H ₅) ₂ CH	C ₆ H ₅	C ₆ H ₅ CN	134	0.081	1.8
			145	0.066	4.6
		C ₆ H ₅ Br	145	0.088	0.18
				0.048	0.19
(C ₆ H ₅) ₂ CH	C ₆ H ₅ CH ₂	C ₆ H ₅ CN	155	0.088	0.45
			166	0.072	2.4
(C ₆ H ₅) ₂ CH	CH ₃	C ₆ H ₅ CN	166	0.053	2.4
				0.075	1.1
(C ₆ H ₅) ₂ CH	CH ₃ CH ₂	C ₆ H ₅ CN	166	0.061	1.2
				0.072	0.66
(C ₆ H ₅) ₂ CH	(C ₆ H ₅) ₂ CH	C ₆ H ₅ CN	166	0.050	0.66
				0.145	4.7
(C ₆ H ₅) ₂ CH	ClCH ₂ CH ₂	C ₆ H ₅ CN	166	0.086	4.7
				0.10	5.5
(C ₆ H ₅) ₂ CH	CH ₃ O ₂ CCH ₂	C ₆ H ₅ CN	123	0.13	7.4
			131	0.10	0.27
			139	0.10	0.60
			186	0.10	1.2
C ₆ H ₅ CH ₂ p-ClC ₆ H ₄ CH	C ₆ H ₅ C ₆ H ₅	C ₆ H ₅ CN	186	0.072	0.0042
		C ₆ H ₅ CN	146	0.087	2.4
C ₆ H ₅ p-ClC ₆ H ₄ CH C ₆ H ₅	CH ₃	C ₆ H ₅ CN	166	0.068	0.57
				0.055	0.65

Decomposition of Aralkyl Thiocarbonates. On being heated at elevated temperatures in inert solvents aralkyl thiocarbonates undergo decomposition with essentially quantitative evolution of carbon dioxide (eq. 4).



The appropriate organic sulfide can be isolated as the other major reaction product in yields ranging from 67–87% (Table I). Small amounts of other products were isolated in certain cases. These may result not only from side reactions involving the thiocarbonate but also from some breakdown of the aralkyl sulfide at the temperatures involved. In any event, Table I shows that in all five cases where a detailed product study has been made the principal course of the decomposition is that shown in eq. 4. We assume this is also true for the other aralkyl thiocarbonates whose decompositions have been investigated kinetically in the present work.

Kinetics of the Decomposition. For all the aralkyl thiocarbonates except benzhydryl S-carbomethoxymethyl thiocarbonate the kinetics of the decomposition can be followed by observing the disappearance of the infrared absorption band due to the carbonyl group of the thiocarbonate. Depending on the thiocarbonate, this occurs at 1705 to 1720 cm.⁻¹. When followed in this way the decompositions were found to exhibit good first-order kinetics over at least 75% reaction. With some of the slower runs there was a tendency for the rate to accelerate somewhat after this point, apparently due to catalysis of the decomposition by substances resulting from the breakdown of a small amount of the normal decomposition products. In these cases the rate constant was determined from the initial linear portion of the log *c* vs. time plot. Some typical runs are shown in Figure 1.

In the case of the S-carbomethoxymethyl ester an alternate procedure, employing measurement of the rate of evolution of carbon dioxide, was used to follow the reaction. A run using this procedure with benzhydryl S-phenyl thiocarbonate gave a rate constant identical with that obtained by the infrared method. The various kinetic results are summarized in Table II.

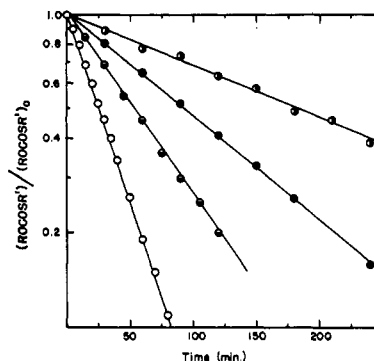


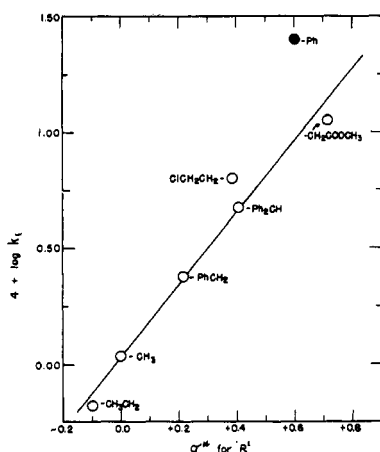
Figure 1. First-order plots of kinetic data for some representative thiocarbonate decompositions: ○, benzhydryl S-phenyl thiocarbonate, 0.060 M, 145°; ◐, benzhydryl S-benzyl thiocarbonate, 0.072 M, 166°; ●, benzhydryl S-methyl thiocarbonate, 0.061 M, 166°; and ○, benzhydryl S-ethyl thiocarbonate, 0.05 M, 166°.

Dependence of Rate on Solvent. The rate of decomposition of benzhydryl S-phenyl thiocarbonate was determined in bromobenzene and benzonitrile at 145°. As is evident from Table II, the rate is about 25 times greater in benzonitrile. This dependence of rate on solvent ionizing power seems comparable to that observed by Olivier and Young² for the chlorocarbonate decomposition.

Variation of Rate with Aralkyl Group. The variation of the rate of decomposition with nature of the aralkyl group was investigated for a series of aralkyl S-phenyl

Aralkyl group, R	Relative rates		
	Decompn. of ROSCSC ₆ H ₅ in C ₆ H ₅ CN at 186°	Solvolysis of RCl in HOAc at 25° ^a	Decompn. of ROCOCl in dioxane at 90° ^b
C ₆ H ₅ CH ₂ -	(1.0)	(1.0)	(1.0)
C ₆ H ₅ CH-	...	370	450
$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_6\text{H}_5\text{CH}- \\ \\ p\text{-ClC}_6\text{H}_4\text{CH}- \\ \\ \text{C}_6\text{H}_5 \end{array}$	2.6×10^4 1.2×10^{4c}	1.5×10^4 0.51×10^4

thiocarbonates, ROCOSPh. Table III shows their relative rates of decomposition at 186°, and for comparison, both the relative rates of acetolysis of a series of aralkyl chlorides and the relative rates of decomposition of two aralkyl chlorocarbonates. From these data it appears that the variation of the rate with the structure of the aralkyl group in the thiocarbonate



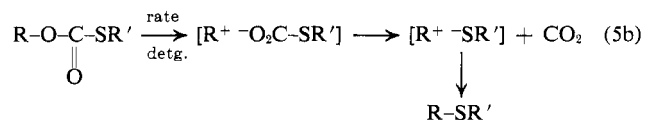
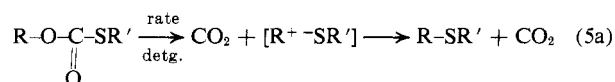
decomposition closely parallels that observed in the other two reactions. Taken together with the observed influence of solvent ionizing power, this seems to require that the rate-determining step of the aralkyl thiocarbonate decomposition, like the chlorocarbonate decomposition, involve formation of the aralkyl carbonium ion by heterolysis of the aralkyl-oxygen bond.

Table IV. Rate of Decomposition of $(\text{C}_6\text{H}_5)\text{CHOCOSR}'$ in Benzonitrile at 166°

R'	$k_1 \times 10^4$, sec. ⁻¹	Relative rate
CH ₃ CH ₂ -	0.66	0.60
CH ₃ -	1.1	(1.0)
C ₆ H ₅ CH ₂ -	2.4	2.2
(C ₆ H ₅) ₂ CH-	4.7	4.3
ClCH ₂ CH ₂ -	6.3	5.7
CH ₃ OOCCH ₂ -	11	10
C ₆ H ₅ -	25	23

Discussion

Analogous to eq. 2a and 2b, one can envisage two possible mechanistic extremes for the thiocarbonate decomposition. In one of these (eq. 5b) the rate-determining step involves heterolysis of *only* the R-O bond. In the other (eq. 5a) heterolysis of the car-



bonyl-sulfur bond is synchronous with the fission of the R-O bond. With either mechanism one would expect that the rate of decomposition of ROCOSR' should increase systematically with an increase in the electron-withdrawing character of R', since the greater the electron-withdrawing inductive effect of R' the better it can help to stabilize the negative charge on the anionic fragment of the incipient ion pair. The results in Table IV and Figure 2 are in accord with this expectation. Furthermore, the good correlation between $\log k_1$ and σ^* for the various alkyl and aralkyl substituents, despite their varied steric requirements, argues that for the R' groups in Table IV the steric bulk of R' has no significant influence on decomposition rate. Thus the deviation of the data for the S-phenyl ester from the $\log k_1$ - σ^* correlation for the remaining esters apparently cannot be ascribed to a steric effect.

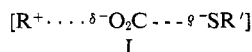
However, if the mechanism of the decomposition involves heterolysis of the carbonyl-sulfur bond in the rate-determining step, as in eq. 5a, the positive deviation of the S-phenyl ester data is understandable, because the phenyl group, unlike the other substituents in Table IV, can stabilize the R'S⁻ anion not only inductively but also by resonance.

(4) The σ^* values for all the substituents except $\text{CH}_3\text{OOCCH}_2-$ were taken directly from the table given by Taft.⁵ For $\text{CH}_3\text{OOCCH}_2-$ the value⁵ for $\text{CH}_3\text{OOC}-$ was divided by 2.8.

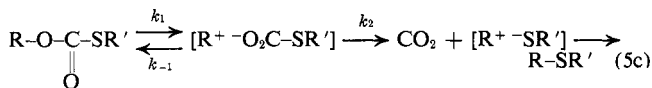
(5) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13, p. 619.

Convincing evidence for the ability of phenyl to stabilize a mercaptide ion in this manner has already been provided by the results of Kreevoy, *et al.*,⁶ on the acidity of a series of mercaptans. They found an excellent correlation between pK_a for $R'SH$ and σ^* for R' for a large number of alkyl and aralkyl mercaptans. However, thiophenol ($R' = \text{phenyl}$) was 1.6 pK units more acidic than expected from the pK_a - σ^* correlation line for the other mercaptans. Although this enhancement of acidity is less than found for phenol *vis-à-vis* alcohols, it is still significant, and as Kreevoy, *et al.*,⁶ pointed out, it must almost certainly be due to stabilization of the mercaptide ion by delocalization of the negative charge into the ring.

The observed deviation of the S-phenyl ester point in Figure 2 thus speaks strongly for a mechanism for the thiocarbonate decomposition involving at least partial heterolysis of the carbonyl-sulfur bond in the rate-determining step. In this connection, however, one should note that a plot of $\log k_1$ for thiocarbonate decomposition rate vs. pK_a of $R'SH$ (Figure 3) shows that the phenyl group does relatively less to enhance the decomposition rate of $ROCOSC_6H_5$ than it does to enhance the acidity of C_6H_5SH . One possible interpretation of this result is to assume that in the thiocarbonate transition state the breaking of the carbonyl-sulfur bond lags somewhat behind the cleavage of the aralkyl-oxygen bond, with the result that part of the developing negative charge resides on the oxygens. The transition state for the thiocarbonate decomposition (I) would then be pictured as



The observed solvent and structural effects could also be accommodated by a mechanistic sequence of the form



where $k_2 < k_{-1}$. Distinction between this mechanism and eq. 5a should be possible through determination of whether or not partial decomposition of carbonyl-labeled $ROCOC^{18}SR'$ leads to any equilibration of the oxygen label in the recovered undecomposed thiocarbonate. In any event, in contrast to eq. 5b, both eq. 5a and 5c involve fission of the C-S bond in the rate-determining step.

The present results thus indicate that, regardless of the specific timing involved, both the R-O and C-S bonds are effectively broken by the time the transition state of the rate-determining step of the thiocarbonate decomposition is reached. Naturally this does not necessarily require that a similar situation prevails in the chlorocarbonate decomposition. However, when the present results are taken together with the recent study of Rhoads and Michel,⁷ wherein those authors found strong evidence for cleavage of more than one bond in the rate-determining step of the decomposition of aralkyl chloroglyoxalates (eq. 6), they certainly suggest that equivalent mechanisms involving a transition

(6) M. M. Kreevoy, E. T. Harper, R. E. Duvall, H. S. Wilgus, III, and L. T. Ditsch, *J. Am. Chem. Soc.*, **82**, 4899 (1960).

(7) S. J. Rhoads and R. E. Michel, *ibid.*, **85**, 585 (1963).

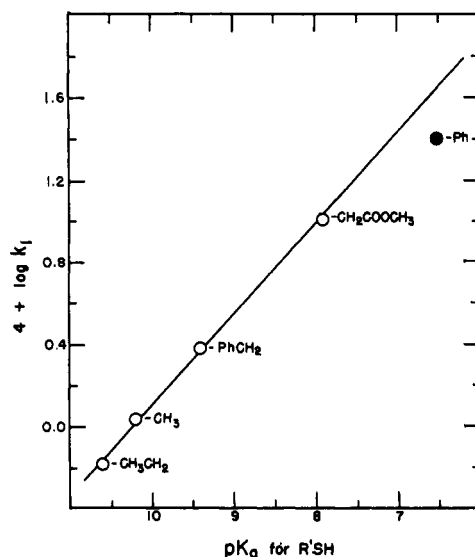
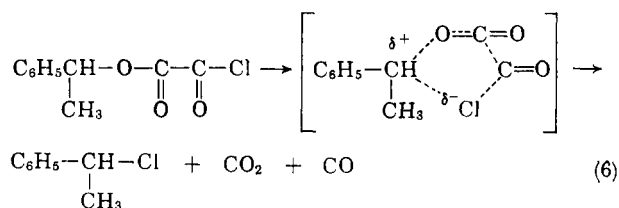


Figure 3. $\log k_1$ for benzhydryl thiocarbonates $Ph_2CHOCOSR'$ vs. K_{ap} for $R'SH$.

state for the rate-determining step where both R-O and C-Cl bonds are broken are probably a more accurate representation of the mechanism of the chloro-



carbonate decomposition than is eq. 2b. It would also appear that mechanisms involving at least partial scission of more than one bond in the rate-determining step may be a quite general phenomenon in S_Ni reactions.

Experimental

Preparation of Thiocarbonates. The following general procedure was employed for the synthesis of the various thiocarbonates. A solution of 0.1 mole of the appropriate alcohol and 0.1 mole of pyridine in 40 ml. of benzene was placed in a three-necked flask which had been fitted with a reflux condenser and drying tube, a dropping funnel, and a stirrer. The solution was cooled in an ice bath and 0.1 mole of the proper chlorothiolformate was added dropwise with stirring. After the addition was complete the mixture was heated to reflux for 2 hr. It was then cooled to room temperature, and 50 ml. of ether was added. The ether-benzene layer was washed three times with water, the aqueous layer being discarded each time. The organic layer was then dried over sodium sulfate, and the solvent was removed under reduced pressure. The crude thiocarbonate was purified by chromatography on alumina, using benzene as eluent, followed by subsequent recrystallization from hexane or hexane-benzene mixtures. Table V summarizes the data on the physical properties, etc., of the various thiocarbonates involved in the present work.

Chlorothiolformates. Phenyl, ethyl, and methyl chlorothiolformates were a gift from the Stauffer

Table V. Preparation and Properties of Aralkyl Thiocarbonates

Thiocarbonate, ROCOSR'—		M.p., °C.	Yield, %	Formula	Analyses					
R	R'				Calcd., %			Found, %		
					C	H	S	C	H	S
(C ₆ H ₅) ₂ CH	C ₆ H ₅	87–88	55	C ₂₀ H ₁₈ O ₂ S	75.00	5.04	9.99	75.08	5.25	10.19
(C ₆ H ₅) ₂ CH	CH ₃	72–73	24	C ₁₅ H ₁₄ O ₂ S	69.74	5.46		69.77	5.44	
(C ₆ H ₅) ₂ CH	CH ₂ CH ₂	37–38	22	C ₁₈ H ₁₆ O ₂ S	70.56	5.92		70.43	5.92	
(C ₆ H ₅) ₂ CH	C ₆ H ₅ CH ₂	45–46	20	C ₂₁ H ₁₈ O ₂ S	75.41	5.44		75.51	5.49	
(C ₆ H ₅) ₂ CH	(C ₆ H ₅) ₂ CH	115–118	43	C ₂₇ H ₂₂ O ₂ S	78.99	5.40		78.67	5.27	
(C ₆ H ₅) ₂ CH	ClCH ₂ CH ₂	42–43	26	C ₁₆ H ₁₆ ClO ₂ S	62.65	4.93		62.65	5.32	
(C ₆ H ₅) ₂ CH	CH ₃ O ₂ CCH ₂	50–51	40	C ₁₇ H ₁₆ O ₄ S	64.54	5.10		64.65	4.78	
<i>p</i> -ClC ₆ H ₄ CH	C ₆ H ₅	95–96	26	C ₂₀ H ₁₆ ClO ₂ S	67.70	4.26		67.48	4.36	
<div style="text-align: center;">C₆H₅ <i>p</i>-ClC₆H₄CH</div>	CH ₃	62–63	24	C ₁₆ H ₁₄ ClO ₂ S	61.53	4.48		61.50	4.48	
<div style="text-align: center;">C₆H₅ C₆H₅CH₂</div>	C ₆ H ₅	59–60	20	C ₁₄ H ₁₂ O ₂ S	68.85	4.92	13.13	69.05	5.02	12.89

^a Yield of pure thiocarbonate. Yields of crude thiocarbonate considerably higher.

Chemical Co. They were fractionally distilled before use. *Benzyl chlorothiolformate* was prepared using a modification of Tilles' procedure.⁸ Phosgene (22.8 g.) was dissolved in 80 ml. of toluene. The mixture was kept at –20–0° and 20.0 g. of benzyl mercaptan was added dropwise. The mixture was stirred for 2 hr. at this temperature, warmed to room temperature, and allowed to stand overnight. Enough aqueous sodium hydroxide was added for the aqueous layer to remain basic to litmus. The toluene layer was then separated, the toluene was removed, and the residue was fractionally distilled, giving 23.5 g. (78%) of benzyl chlorothiolformate, b.p. 128–129° (12 mm.). *Benzhydryl chlorothiolformate* was prepared by the same method as benzyl chlorothiolformate. The residue after removal of the toluene was not distilled, but was used directly for the synthesis of the thiocarbonate. An 83% yield of the crude chlorothiolformate was obtained. The benzhydryl mercaptan required for its synthesis was prepared as previously described.⁹ *β-Chloroethyl chlorothiolformate* was synthesized by the procedure of Ringsdorf and Overberger,¹⁰ b.p. 57–60° (4–5 mm.).

Carbomethoxymethyl Chlorothiolformate. Methyl thioglycolate (23.3 g.) was dissolved in the minimum volume of ethanol and added with stirring to 41.8 g. of lead acetate trihydrate dissolved in 1:1 aqueous ethanol. The lead salt of the mercaptan precipitated immediately and was removed by filtration, washed three times with anhydrous ether, and dried. The dried salt (44.3 g.) was added in portions to 22.1 g. of phosgene in 100 ml. of dry toluene. The reaction mixture was kept at 0° for 2 hr. and then left overnight at room temperature. The excess phosgene was removed under reduced pressure, and the crude mixture was filtered to remove lead chloride. After removal of the toluene, the residue gave on distillation 25.3 g. (71%) of carbomethoxymethyl chlorothiolformate, b.p. 63° (1.0–1.2 mm.).

Product Studies of Thiocarbonate Decomposition. The reaction flask was the type previously used for study of the thermal decomposition of thiolsulfonates.¹¹

(8) H. Tilles, *J. Am. Chem. Soc.*, **81**, 714 (1959).

(9) J. L. Kice and F. M. Parham, *ibid.*, **82**, 6168 (1960).

(10) H. Ringsdorf and C. G. Overberger, *Makromol. Chem.*, **44**, 418 (1961).

(11) J. L. Kice, F. M. Parham, and R. M. Simons, *J. Am. Chem. Soc.*, **82**, 834 (1960).

Its outlet was connected to a trap filled with glass wool and cooled in an ice bath. This trap retained any solvent entrained by the nitrogen stream which was passed through the solution during the decomposition. After this trap came a tube filled with Drierite, to absorb any water produced during the reaction and swept out by the nitrogen, and after this came a U-tube filled with Ascarite. This was weighed after an initial nitrogen flush of the system, and at the end of the decomposition. The yield of carbon dioxide was estimated from the difference in these weights. The Ascarite tube was protected against back diffusion of air into the system by a pair of mineral oil traps of the type previously described.¹¹ The prepurified nitrogen used to sweep the reaction was first passed through two drying tubes and an Ascarite tube to remove any traces of moisture or carbon dioxide.

In a run, a weighed amount of the thiocarbonate was dissolved in the desired amount of solvent, and the solution was placed in the reaction flask. Nitrogen was passed through the solution for 1 hr. at room temperature. The solution was then heated in a constant temperature bath for the desired length of time, nitrogen being passed through the solution at a slow rate throughout the decomposition.

At the end of the decomposition the nonvolatile products were identified by removing the solvent under reduced pressure, separating the various products in the residue by chromatography on alumina, and identification of the chromatographic fractions by means of infrared and melting point comparisons with known samples. The results of the various product studies are shown in Table I.

Although the sulfides required as reference compounds for the benzhydryl thiocarbonate product studies were known compounds,^{9,11} *p*-chlorobenzhydryl methyl sulfide and *p*-chlorobenzhydryl phenyl sulfide had never been prepared. Their synthesis is outlined below.

p-Chlorobenzhydryl Phenyl Sulfide. Thiophenol was treated with *p*-chlorobenzhydryl chloride¹² following the exact procedure used by Kice and Parham⁹ for the preparation of benzhydryl phenyl sulfide. After recrystallization from alcohol, it melted at 56–57°.

(12) J. F. Norris and C. Banta, *ibid.*, **50**, 1804 (1928).

Anal. Calcd. for $C_{19}H_{15}ClS$: C, 73.41; H, 4.86. Found: C, 73.32; H, 4.89.

p-Chlorobenzhydryl Methyl Sulfide. *p*-Chlorobenzhydryl mercaptan¹³ was treated with methyl iodide in the same way as described⁹ for the synthesis of benzhydryl methyl sulfide. The initial product was an oil, which after some difficulty could be induced to crystallize from hexane, m.p. 31–32°.

Anal. Calcd. for $C_{14}H_{13}ClS$: C, 67.60; H, 5.27. Found: C, 67.71; H, 5.41.

Kinetic Studies of Thiocarbonate Decomposition.

Infrared Method. The apparatus used was of the same basic design as that employed by Kice and Bowers¹⁴ for kinetic studies of sulfinic acid disproportionation. Its principal feature is that it permits a sample to be removed without exposing the reaction solution to the external atmosphere.

A solution of the thiocarbonate was placed in the reaction flask, and a slow stream of nitrogen was passed through the solution for 1 hr. at room temperature to deaerate it. The reaction flask was then immersed in a constant temperature bath held at the desired temperature. A very slow stream of nitrogen was bubbled through the solution during the entire decomposition. Small samples were removed at convenient time intervals, including one infinity time sample removed after decomposition was complete.

The infrared absorption spectrum of these samples was then determined over the region 1800–1600 cm^{-1} . Earlier experiments with standard solutions of the various thiocarbonates in the reaction solvents employed had shown that the intensity of the thiocarbonate ester carbonyl band, which, depending on

the ester, occurs at frequencies from 1720 to 1705 cm^{-1} , followed Beer's law and that a plot of optical density vs. milligrams of thiocarbonate per milliliter of solution was satisfactorily linear.

Carbon Dioxide Evolution Method. An apparatus, similar to that employed for kinetic study of the thermal decomposition of thiosulfonates,¹¹ was used as the reaction flask. This permitted one to pass a stream of nitrogen through the solution throughout the decomposition. This nitrogen stream served to sweep the carbon dioxide evolved in the decomposition out of the reaction flask and into an apparatus for determination of carbon dioxide of the type described by Patchornik and Shalitin.¹⁵ In this apparatus the evolved carbon dioxide was trapped in an ethanol-dioxane-benzylamine solution (3:3:1) and determined by direct titration with a 0.08 *N* solution of sodium methoxide in methanol-benzene. Thymol blue (0.2% in dioxane) was used as indicator. Provided one avoids decompositions having very rapid rates, there is no difficulty in passing nitrogen through the reaction solution at a rate which keeps the time between the evolution of a molecule of CO_2 and its absorption in the ethanol-dioxane-benzylamine solution small enough so as not to interfere with accurate determination of the rate of decomposition of the thiocarbonate.

Purification of Solvents. Bromobenzene was purified as outlined in an earlier paper.¹¹ Benzonitrile was subjected to one additional purification step besides those previously described.¹¹ A slow stream of nitrogen was passed through the purified solvent while it was heated to 165° for 6 hr. This treatment served to remove a small amount of a slowly volatile carbonyl impurity which otherwise interfered seriously with the infrared procedure for following the kinetics.

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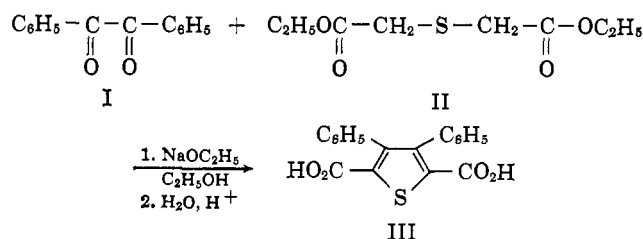
The Mechanism of the Hinsberg Thiophene Ring Synthesis^{1,2}

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Using conventional as well as O^{18} isotope techniques it has been shown that the reaction between α -diketones and thiodiacetates to yield thiophenes (Hinsberg condensation) is a Stobbe-type condensation proceeding via a δ -lactone intermediate.

More than 50 years ago Hinsberg³ first described the reaction between benzil (I) and diethyl thiodiacetate (II) to produce the thiophene ring system. The reaction, run essentially under Claisen-type conditions, was always worked up by diluting the alcoholic alkaline mixture with water, boiling for some time, and isolating the free dicarboxylic acid (III) thus formed.



The reaction proved to be quite general and Hinsberg,^{3,4} Backer and Stevens,^{5,6} Dimroth,^{7,8} and others⁹ have used the reaction to prepare thiophenes,

(1) Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963.

(2) Abstracted in part from the Doctoral Thesis of H. J. K.

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(9) D. E. Wolf and K. Folkers, *Org. Reactions*, **6**, 410 (1951).