

Positive Halogen Compounds. XIV. Reactions of *t*-Butyl Hypochlorite with Sulfides, Sulfoxides, and Acid Anhydrides¹

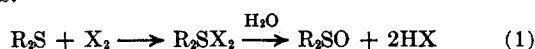
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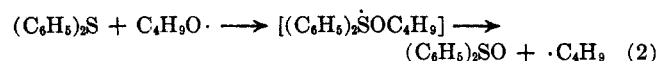
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t-Butyl hypochlorite reacts (2 moles) rapidly with diphenyl sulfide at room temperature to yield diphenyl sulfoxide and a mixture of products from the hypochlorite. The reaction is insensitive to light and air and does not induce chlorination of cyclohexane. A polar mechanism involving molecular chlorine and diphenylsulfur dichloride is suggested. Dimethyl sulfide is oxidized similarly to dimethyl sulfoxide, stabilized toward further oxidation as its HCl complex. Dimethyl sulfoxide alone, however, reacts rapidly with 3 moles of hypochlorite to give some derivative of trichloromethyl methyl sulfoxide, and more slowly with additional hypochlorite with C-S bond cleavage since CCl₄ is one of the products formed. *t*-Butyl hypochlorite undergoes an acetate-catalyzed reaction with acetic anhydride, apparently to give acetyl hypochlorite and *t*-butyl acetate. The former then decomposes to methyl chloride and CO₂. No evidence is found for the exchange of chlorine between *t*-butyl hypochlorite and acetic acid as proposed by Anbar and Dostrovsky. In fact, acetic acid inhibits the above anhydride exchange.

The oxidation of sulfides to sulfoxides by peroxy compounds or by autoxidation has been reviewed by Barnard, Bateman, and Cunneen,³ who propose a general polar mechanism for the reactions, except in the case of the oxygen-catalyzed oxidation by *t*-butyl hydroperoxide where involvement of *t*-butyl peroxy radicals has been suggested. Similarly, the oxidation of sulfides by halogens was early shown^{4,5} to involve rapid formation of a sulfur dihalide followed by hydrolysis.



Such reactions are reviewed by Ranky and Nelson⁶ and Szmant,⁷ and the hydrolysis scheme is supported by recent work by Mislow⁸ and Johnson and McCants.⁹ In contrast, the characteristic reaction of sulfides with alkoxy and acyloxy radicals apparently involves attack on α hydrogens when these are available, to give a variety of products depending on experimental conditions, but usually no sulfoxides.¹⁰ Recently, however, Gritter and Carey¹¹ have reported a small yield (1%) of diphenyl sulfoxide on heating diphenyl sulfide with di-*t*-butyl peroxide at 150°, which they take as evidence for a radical displacement on oxygen *via* an intermediate sulfonium radical (as is shown in eq 2),



analogous to the oxygen transfer *via* a phosphoranyl radical demonstrated in the reaction of alkoxy radicals with trivalent phosphorus compounds.¹² Higher yields

of sulfoxide (28–46%) were obtained in the reaction between *t*-butyl hypochlorite and diphenyl sulfide; as the process was reported to be accelerated by light, they propose a chain reaction involving eq 2 and 3.



Quite a different account of the hypochlorite-sulfide reaction has been given by Skell and Epstein¹³ who report that oxidation occurs at -78° *via* an intermediate alkoxy sulfonium salt (eq 4), subsequently decomposed.



They note that sulfoxides are converted to sulfones under these conditions, but that the intermediate salt is stable toward further hypochlorite. Their technique (which has not been published in detail) has been used by Johnson and McCants⁹ to oxidize 4-substituted thianes to the corresponding 1-oxides, obtaining products with a preferred *cis* stereochemistry.

Because of this contradiction and our interest in the chemistry of *t*-butyl hypochlorite, we have reinvestigated its reaction with diphenyl sulfide, dimethyl sulfide, and their corresponding sulfoxides, and find all to be polar, rather than radical processes. We also report results on another polar reaction of *t*-butyl hypochlorite, its exchange with acid anhydrides.

Diphenyl Sulfide.—We find that *t*-butyl hypochlorite (and also isopropyl and cumyl hypochlorites) reacts at room temperature with carefully purified diphenyl sulfide to yield diphenyl sulfoxide as the sole product from the sulfide. The reaction is rapid and exothermic, even in dilute solution, and is characterized by appearance of an intense transient yellow color which fades at completion of the reaction. Under the same conditions no reaction occurs between *t*-butyl hypochlorite and either diphenyl sulfoxide or diphenyl sulfone.

Contrary to Gritter and Carey,¹¹ we observe no effect of oxygen or irradiation, and, when the reaction is carried out in the presence of cyclohexane or methyl methacrylate, neither cyclohexyl chloride nor polymer are produced. All these results point to a polar, rather than a radical process, and this conclusion is further supported by a pronounced effect of solvent on rate. Reaction between 0.036 *M* sulfide and hypochlorite,

(13) P. S. Skell and M. F. Epstein, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 26N.

(1) Taken from the Ph.D. Thesis of M. J. Mintz, Columbia University, 1965. Support of this work by the National Science Foundation is gratefully acknowledged.

(2) National Science Foundation Predoctoral Fellow, 1961–1964.

(3) D. Barnard, L. Bateman, and J. I. Cunneen, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., 1961, p 194.

(4) K. Fries and W. Vogt, *Ann.*, **361**, 337 (1911).

(5) E. Fromm, *ibid.*, **396**, 75 (1913).

(6) W. Ranky and D. Nelson, ref 3, p 170.

(7) H. Szmant, ref 3, p 154.

(8) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **86**, 1452 (1964).

(9) C. R. Johnson and D. McCants, *ibid.*, **87**, 1109 (1965).

(10) L. Horner and E. Jurgens, *Ann.*, **602**, 135 (1957); C. Berglund and S. Lawesson, *Arkiv Kemi*, **20**, 225 (1963); G. Sosnovsky, *Tetrahedron*, **18**, 15 (1962).

(11) R. J. Gritter and D. J. Carey, *J. Org. Chem.*, **29**, 1160 (1964).

(12) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **81**, 1243 (1959); for additional examples, cf. C. Walling and M. Pearson "Topics in Phosphorus Chemistry," Vol. III, E. J. Griffith and M. Grayson, Ed., Interscience Publishers, Inc., New York, N. Y., 1966.

initially at room temperature, is complete in 5 sec in acetic acid, acetonitrile, and acetone, but requires 30 sec–1 min in benzene, 20–30 min in carbon tetrachloride, and 20–30 min in *n*-hexane and cyclohexane. In the latter solvents there is a pronounced induction period (15–20 sec in benzene, 15–25 min in cyclohexane) followed by rapid reaction.

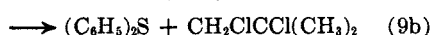
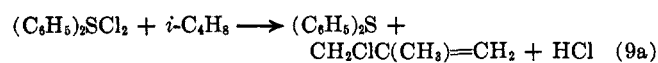
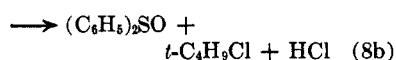
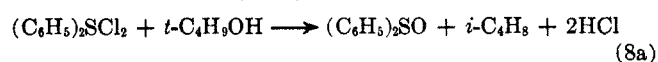
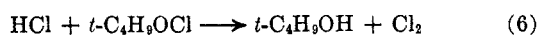
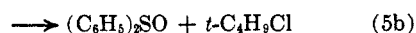
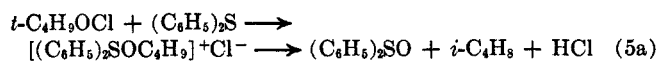
The formulation of Skell and Epstein (eq 4) implies a 1:1 stoichiometry for the reaction, but, at our temperatures, approximately 2 moles of hypochlorite are consumed/mole of sulfide oxidized. Further the decomposition of the hypochlorite yields a complicated mixture of products (Table I) of which *t*-butyl chloride and acetone, reported by Gritter and Carey,¹¹ are only minor compounds.

TABLE I
PRODUCTS FROM *t*-BUTYL HYPOCHLORITE-DIPHENYL
SULFIDE REACTION^a

Product	Yield, %
Diphenyl sulfoxide	94–100
HCl	Present
Isobutylene	Trace
<i>t</i> -Butyl chloride	8.4–13
Acetone	5–8
<i>t</i> -Butyl alcohol	38–47
Methallyl chloride	16–27
1,2-Dichloro-2-methylpropane	10–20
Isobutylene chlorohydrin	Trace

^a In benzene at room temperature, yields based on 2:1 stoichiometry.

Although our results clearly support a polar mechanism for the hypochlorite-sulfide reaction, they are inconsistent with the simple scheme indicated by Skell and Epstein for the reaction at -70° . A sequence which does account for the induction period, stoichiometry, and major products, however, is the following.



Here Skell's sulfonium chloride is initially formed (perhaps reversibly) during the induction period, but in part, at least, breaks down to liberate HCl, which reacts rapidly with hypochlorite to liberate molecular chlorine. Chlorine, in turn, adds immediately to the sulfide to yield diphenylsulfur dichloride and the balance of the reaction proceeds through this intermediate and is autocatalyzed by the continued generation of HCl.¹⁴

Several observations support the above scheme, although it has certainly not been validated in detail.

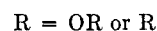
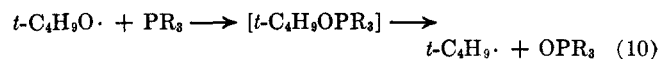
(14) Pyridinium hydrochloride is evidently as effective as HCl in liberating chlorine, since the over-all reaction proceeds rapidly in the presence of pyridine. The only significant change in products is a reduction in the yield of *t*-butyl chloride.

The transient yellow color corresponds qualitatively to that of solutions of the dichloride, which, when prepared independently, reacts immediately with *t*-butyl alcohol and simple olefins as indicated (evidently the olefin reaction is faster, since little isobutylene but substantial *t*-butyl alcohol remain at the end of the reaction). The origin of the acetone is obscure, but it may result from an alternative breakdown of the first adduct, analogous to that of *t*-butyl persulfonates.¹⁵

An additional and rather surprising observation must also be accommodated by the scheme, this is that the over-all reaction is strongly retarded by the addition of olefins such as cyclohexane or 2-methyl-2-butene.

The olefin is consumed, since very small quantities act simply to prolong the induction period, and they appear to trap intermediate addition products. In benzene, cyclohexene is converted to 1,2-dichlorocyclohexane and 3-chlorocyclohexene (2.5:1), and reaction with diphenylsulfur dichloride gives the same products in about the same ratio. Chlorine, in contrast, yields almost exclusively 1,2-dichlorocyclohexane. *trans*-Dichloroethylene and trichloroethylene, which we find do not react readily with diphenylsulfur dichloride, have no effect on the hypochlorite oxidation.

Finally, regardless of details of mechanism, data in the literature strongly support the probability of a polar rather than a radical path for the hypochlorite-sulfide reaction. As pointed out by Walling and Rabinowitz,¹² the known radical oxygen transfer process to phosphorus is exothermic by some 33 kcal/mole



since $D(\text{C}_4\text{H}_9\text{O}\cdot) = 89$ kcal/mole¹⁶ and $D(\text{R}_3\text{PO}) \cong 122$ kcal/mole (the value for POCl_3 ¹⁷). In contrast, Mackle¹⁸ gives $D[(\text{C}_6\text{H}_5)_2\text{SO}] = 89$ kcal/mole, making oxygen transfer here essentially thermoneutral. Consistent with this difference, the competition between eq 10 for triethyl phosphite and hydrogen abstraction in the presence of cyclohexane favors eq 11 by a factor of



600.¹⁹ In contrast, as noted previously, reactions of alkoxy radicals with sulfides containing α hydrogens leads to exclusive hydrogen abstraction.¹⁰ Even if Gritter and Carey's results with di-*t*-butyl peroxide are accepted as evidence for a marginal but real oxygen transfer, when we come to hypochlorite systems it is significant that the potentially more facile chain reaction between *t*-butyl hypochlorite and triphenyl phosphite is replaced by a fast polar reaction to give a phosphonium salt as shown by Denney and DiLeone.²⁰

Dimethyl Sulfide.—In methylene chloride or benzene solution dimethyl sulfide reacts rapidly with *t*-butyl hypochlorite, and, as in the case of diphenyl sulfide, the reaction appears insensitive to oxygen and light and does not induce the chlorination of cyclohexane. Evaporation of solvent leaves a high-boiling oily resi-

(15) P. D. Bartlett and B. J. Storey, *J. Am. Chem. Soc.*, **80**, 4954 (1958).

(16) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

(17) T. L. Cottrell, "The Strength of Chemical Bonds," Butterworth and Co. (Publishers) Ltd., London, 1954.

(18) H. Mackle, *Tetrahedron*, **19**, 1159 (1963).

(19) C. Walling and M. Pearson, *J. Am. Chem. Soc.*, **86**, 2262 (1964).

(20) D. B. Denney and R. R. DiLeone, *ibid.*, **84**, 4737 (1962).

due, which is apparently a dimethyl sulfoxide-HCl complex or salt since it yields HCl and dimethyl sulfoxide on hydrolysis. The molar ratio of components is evidently between 1:1 and 2:1 since its neutralization equivalent was found to be 170 (calcd for 1:1, 114.5). The nuclear magnetic resonance (nmr) spectra of the product in methylene chloride is also consistent with this view, showing a single peak 20 cps downfield from dimethyl sulfoxide (DMSO). Addition of DMSO shifts the single peak upfield, while addition of HCl to DMSO in methylene chloride produces a similar downfield shift, expected behavior for a system showing rapid exchange. Hydrogen bonding to sulfoxides and their basic properties are well known, and while the HCl complex was first proposed by Fromm as a double-bond addition product,⁵ it is now believed that proton attachment is to oxygen, $[R_2SOH^+]Cl^-$.⁶

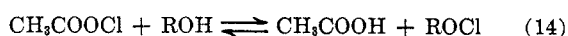
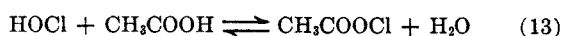
Although other products were not investigated in detail, *t*-butyl alcohol and a smaller amount of *t*-butyl chloride were detected, and we believe that the overall reactions follow qualitatively the same path as does that of diphenyl sulfide.

Dimethyl Sulfoxide.—Although formation of an HCl adduct of the sulfoxide protects dimethyl sulfide from oxidation beyond the sulfoxide state, DMSO itself in methylene chloride or in benzene reacts essentially instantaneously with *t*-butyl hypochlorite until 3 equiv have been added, and then more slowly with additional hypochlorite up to a total of 8–9 equiv. Again the reaction appears insensitive to light of air, fails to induce chlorination of cyclohexane, and yields *t*-butyl alcohol plus smaller amounts of HCl and *t*-butyl chloride. The oxidation product obtained with 3 equiv of hypochlorite shows a single nmr line downfield from DMSO, contains sulfur and chlorine, and yields chloroform on basic hydrolysis. The results are consistent with a trichloromethyl sulfoxide or sulfone, perhaps complexed with HCl, and it is plausible that we are dealing with a polar α halogenation similar to that observed by Bordwell and Pitts with other chlorinating agents.²¹ With further amounts of hypochlorite, carbon tetrachloride becomes a significant product, indicating that C-S bond cleavage of the intermediate now takes place.

The Reaction of *t*-Butyl Hypochlorite with Acid Anhydrides.—Another polar reaction of interest in hypochlorite chemistry is the exchange of chlorine between different derivatives of hypochlorous acid. Hypochlorite esters are conveniently made²² *via* the exchange between hypochlorous acid and alcohols (eq 12) for which Anbar and Dostrovsky report $K = 40$ in



water.²³ Exchange is acid and base catalyzed, and Anbar and Dostrovsky²³ interpret their results as showing specific catalysis by acetic acid, *via* formation of acetyl hypochlorite.



De la Mare and co-workers have also considered an acid-catalyzed formation of acetyl hypochlorite in dis-

cussing their work on aromatic substitution of chlorine by hypochlorous acid. In contrast to these reports, we have observed no change in the infrared or ultraviolet spectra of *t*-butyl hypochlorite in acetic acid,²⁴ and find that acetic acid exerts a solvent effect, but does not otherwise participate in *t*-butyl hypochlorite chlorination of a number of hydrocarbons. Specifically, no CO₂ is evolved as would be expected if acetyl hypochlorite participated in the chain.²⁵ Our results imply that, if the exchanges (eq 13 and 14) do occur, the equilibria must lie far to the left and right, respectively.²⁶

If the equilibrium (eq 14) is indeed unfavorable, it might be shifted to the left by carrying out exchange in the presence of acetic anhydride to remove alcohol, and we find that *t*-butyl hypochlorite and acetic anhydride in fact react slowly at room temperature in the dark and more rapidly in light to give *t*-butyl acetate, CO₂, and methyl chloride, the latter two products presumably by decomposition of acetyl hypochlorite as in the usual formulation of the Hunsdieker reaction.²⁷ Saturation of the system with sodium acetate increases reaction rate five- to tenfold. A further, very large, increase in the rate of the acetate-catalyzed reaction is observed by raising the temperature to 70°. The difference in rate between 0 and 70° is approximately 2000-fold, but may in part be due to greater solubility of sodium acetate at the higher temperature.

Although kinetics have not been studied in detail, acetate catalysis suggests a simple displacement on hypochlorite chlorine by acetate- and base-catalyzed removal of *t*-butyl alcohol by esterification by the anhydride, while for the uncatalyzed reaction a cyclic transition state between anhydride and hypochlorite is attractive. Interestingly, while dilution of the system with ethyl acetate retards CO₂ evolution only moderately, both catalyzed and uncatalyzed reactions are inhibited by acetic acid. While this is further evidence for the absence of direct acetic acid-hypochlorite exchange, it is not predicted by any of the equilibria previously discussed and implies that the exchange processes are more complicated than indicated above.²⁸

Reaction with trifluoroacetic anhydride is more rapid, as might be expected, and shows catalysis by trifluoroacetate and inhibition by trifluoroacetic acid. Products were identified as *t*-butyl trifluoroacetate, CO₂, and another volatile material, presumably CF₃Cl. Very little CO₂ evolution was observed in propionic or butyric anhydrides, a surprising result since hydrolysis rates of these anhydrides are similar to that of acetic acid, but one which may simply reflect bulk dilution and a less polar medium since the acetic anhydride reaction is significantly retarded by dilution with ethyl acetate.

(24) A. Padwa, unpublished results from these laboratories.

(25) P. Wagner, Ph.D. Thesis, Columbia University, 1963.

(26) On the other hand, *t*-butyl hypochlorite exchanges chlorine readily with amides and amines, and is a convenient reagent for preparing N-halo compounds; thus, for nitrogen compounds



(27) C. V. Wilson, *Org. Reactions*, **9**, 332 (1957).

(28) Anbar and Dostrovsky's conclusion about exchange is actually based solely on their demonstration of general acid-base catalysis in which acetic acid and acetate were particularly effective. This is certainly not a compelling argument and the ambiguities involved in identifying the exact structures of transition states in such cases are well known; cf. R. Breslow, "Organic Reaction Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 2.

(21) F. G. Bordwell and B. M. Pitts, *J. Am. Chem. Soc.*, **77**, 572 (1955).

(22) F. D. Chattaway and O. G. Backeberg, *J. Chem. Soc.*, **1928**, 2999.

(23) M. Anbar and I. Dostrovsky, *ibid.*, 1094 (1954).

Experimental Section

Materials.—Solvents were dried and distilled in the usual manner, and physical constants were checked against those in the literature. **Hypochlorites** were prepared as in previous papers in this series. **Diphenyl sulfide** (Eastman White Label) was purified by heating for 1 hr with aqueous NaOH and zinc dust to remove disulfide, dried, and distilled. **Dimethyl sulfide** was commercial material, redistilled (bp 37.5–38°). **Dimethyl sulfoxide** was dried over sodium sulfite and distilled from calcium hydride under vacuum.

Reaction of Diphenyl Sulfide with *t*-Butyl Hypochlorite.—In a series of reactions, 1 equiv of *t*-butyl hypochlorite was added dropwise to a solution of 0.1–1.0 g of diphenyl sulfide in a stirred flask. An intense yellow color appeared within a few seconds of the initial addition and faded on completion of the run. Evaporation of solvent in higher concentration experiments and addition of hexane yielded diphenyl sulfoxide, mp 70° on recrystallization, yield $45 \pm 2\%$ /mole hypochlorite, essentially quantitative on the basis of sulfide consumed, determined by gas-liquid partition chromatography (glpc). Yields of products from hypochlorite were determined by glpc vs. calibrated standards for several runs (Table I). In every case products were collected and identified by infrared or nmr spectra.

Experiments with cumyl and isopropyl hypochlorites were carried out similarly and gave comparable yields of sulfoxide. On the other hand, no reaction was observed with diphenyl sulfoxide or sulfone on standing for 48 hr.

Rate Measurements.—Hypochlorite and sulfide (0.54 mmole each) were added to 15 ml of solvent at room temperature and the time required for disappearance of yellow color or oxidizing power was noted. Results, as described above, showed no difference under nitrogen or oxygen, in the dark or irradiated with a 100-w incandescent lamp. Runs in the presence of 1.5 *M* cyclohexane showed no cyclohexyl chloride, and runs with 2 *M* methyl methacrylate showed no polymer.

Stoichiometry.—A solution of 1 g of diphenyl sulfide in 10 ml of benzene was titrated with *t*-butyl hypochlorite to the appearance of a permanent yellow color and persistence of oxidizing power. Five identical experiments required 2.16 ± 0.2 moles/mole of sulfide and yielded $97 \pm 2\%$ sulfoxide. Two similar experiments in 95% *t*-butyl alcohol required 2.00 moles and gave a 98% yield of sulfoxide.

Additives.—Since unpurified samples of diphenyl sulfide gave reaction mixtures in which an intense yellow color persisted for several hours, the effect of diphenyl disulfide on the reaction was examined briefly. Addition of a small amount of disulfide produced the lasting color (λ_{\max} 391 m μ) but no notable effect on rate or products.

Reactions in benzene containing pyridine were rapid and showed almost immediate precipitation of pyridinium hydrochloride. Products were the same as previously except that the yield of *t*-butyl chloride was reduced to 1–2%.

When hypochlorite (0.25 ml) was added to 0.3 g of diphenyl sulfide in 9 ml of benzene plus 1 ml of cyclohexene no immediate reaction was noted, and hypochlorite was still present after 2 hr. Substitution of 2-methyl-2-butene gave similar retar-

dation, but *trans*-dichloroethylene and trichloroethylene were without effect. A smaller amount of cyclohexene produced a long induction period, followed by reaction. Analysis of the products (glpc) showed 3-chloro-cyclohexene and 2,3-dichloro-cyclohexane (1:2.5) but no cyclohexene remaining.

Diphenylsulfur Dichloride.—The bright yellow solution of diphenylsulfur dichloride was prepared by passing chlorine into a solution of diphenyl sulfide in benzene as described by Fries and Vogt.⁴ It reacted immediately with *t*-butyl alcohol to give *t*-butyl chloride, and with cyclohexene to give 3-chlorocyclohexene and 1,2-dichlorocyclohexane (1:5), but showed no reaction with dichloro- or trichloroethylene. Reaction of molecular chlorine with cyclohexene in benzene gave a 1:100 ratio of the same products.

Reaction of Dimethyl Sulfide.—Dropwise addition of *t*-butyl hypochlorite to a 5% solution of dimethyl sulfide in benzene gave an immediate exothermic reaction both under air and nitrogen and in the dark or under illumination. Addition of cyclohexane yielded no cyclohexyl chloride. A similar reaction in methylene chloride was worked up by evaporating off solvent, and washing the residue with hexane. Nmr spectra and titration gave the results described in the text. Analysis of similar reaction mixtures (glpc) showed *t*-butyl alcohol and a little *t*-butyl chloride as the only other significant products.

Reaction of Dimethyl Sulfoxide.—Preliminary experiments in benzene similar to those described for dimethyl sulfide, showed a similar rapid reaction, insensitive to oxygen or light and no induced chlorination of cyclohexane. Addition of *t*-butyl hypochlorite, diluted with methylene chloride, to 3 ml of DMSO in 15 ml of methylene chloride showed essentially instantaneous reaction until 3 equiv had been added and a much slower reaction thereafter. Removal of solvent from a run to which 3 equiv had been added yielded a water-insoluble residue containing S and Cl with an nmr spectrum (CCl₄) showing a single peak 172 cps downfield from tetramethylsilane (TMS), and an infrared spectrum lacking the 1058, 1438, and 1308 cm⁻¹ bands of DMSO, but with a new band at 1113 cm⁻¹. Hydrolysis by stirring with 10% NaOH yielded chloroform, separated by glpc and identified by infrared and nmr spectra.

Reaction of *t*-Butyl Hypochlorite with Acid Anhydrides.—Small samples, typically 5 ml of anhydride and 1 ml of hypochlorite plus any additives, placed in sealed tubes, were allowed to react until hypochlorite color had faded, cooled, and opened. *t*-Butyl acetate, CO₂, and methyl chloride were determined by glpc, the last two using a silica gel column. When sodium acetate was used as a catalyst, approximately 20 mg was added, not all of which dissolved. Reactions at room temperature with acetic anhydride alone in the dark took several days for complete reaction; with sodium acetate, 36 hr; with sodium acetate at 70°, 30 min. Yields of products CO₂, methyl chloride, and ester were estimated as 30–75%, the highest yields being obtained at 70°.

Registry No.—*t*-Butyl hypochlorite, 507-40-4; diphenyl sulfide, 139-66-2; dimethyl sulfide, 75-18-3; dimethyl sulfoxide, 67-68-5.