

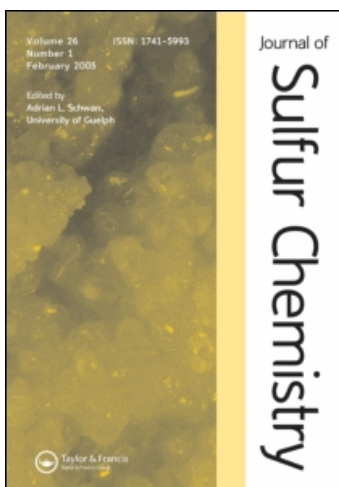
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Journal of Sulfur Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926081>

Researches on Organosulfur Compounds

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To cite this Article Tarbell, D. S.(1986) 'Researches on Organosulfur Compounds', Journal of Sulfur Chemistry, 6: 1, 1 – 11

To link to this Article: DOI: 10.1080/01961778608082489

URL: <http://dx.doi.org/10.1080/01961778608082489>

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RESEARCHES ON ORGANOSULFUR COMPOUNDS

D. S. TARBELL

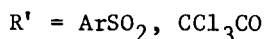
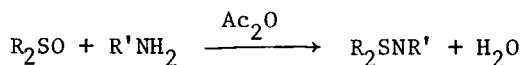
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U.S.A.*

(Received October 16, 1985)

Sulfur Reports occasionally invites chemists who have done outstanding research in sulfur chemistry throughout their careers to summarize their work informally. Such accounts afford them an opportunity to weave all of their research into a continuing story. Quite apart from the historical value, these accounts instructively suggest ways that research can develop, they point to areas that still deserve attention, and they stimulate ideas for addition by others of new chapters to the story. Prof. Tarbell was among the first to apply rigorous methods of physical organic chemistry to the study of organosulfur compounds. His account emphasizes an interest extending over more than 40 years in how sulfur compounds compare with their oxygen counterparts, as well as in a variety of other aspects such as sulfur in heterocycles and in biologically important compounds. Among the comparisons he describes are the Claisen and Fries rearrangements, aromatic substitution, cleavage of bonds to carbon, hydrogen bonding, and reactions of acid derivatives (especially of carbonic acid, where his work led to improved means now widely used of making *t*-BOC derivatives of amino acids). Prof. Tarbell, born in 1913, received the A.B., M.A. and Ph.D. degrees at Harvard University. After a year of postdoctoral work at the University of Illinois, in 1938 he joined the faculty of the University of Rochester, where he became Charles Frederick Houghton Professor of Chemistry in 1960. In 1967, he became Distinguished Professor of Chemistry at Vanderbilt University, where he now holds Emeritus status. He was selected to the National Academy of Sciences, U.S.A., in 1961 and has been the recipient of many other honors.

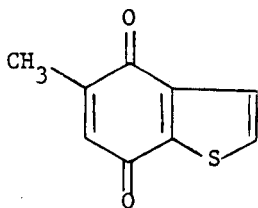
In about 50 of my research papers, organosulfur compounds have played a primary or a subordinate role. Many of the papers have reported investigation of the behavior of sulfur as compared with the oxygen analogs.

Our first paper on sulfur compounds involved the preparation of tetrahydrothiophene sulfoxide (then a considerable synthetic operation) to see if it would give any of the characteristic carbonyl reactions of cyclopentanone.¹ It did not, but it did react with sulfonamides or with amides of strongly acidic carboxylic acids such as trichloroacetamide and dichloroacetamide. Both these reactions were new ones, and the sulfilimines from acetamides were a new type of compound.

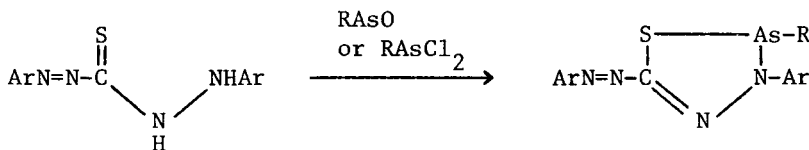


We extended the study of sulfilimines to the preparation of sulfanilamide derivatives which, however, showed no appreciable antibacterial activity.² We were not able to carry out further studies on sulfilimines because of World War II, although we did prepare some arsinimines derived from sulfanilamide.³

H. Dam, the discoverer of vitamin K, spent the war years at the Rochester Medical School and we became interested in vitamin K analogs after making his acquaintance. We therefore synthesized an isostere of the active vitamin K compound, 2-methyl-1,4-naphthoquinone. The isostere, 5-methyl-4,7-thionaphthenequinone, showed only slight vitamin K activity.⁴ Attempts to prepare the 6-methyl isomer were unpromising.⁵



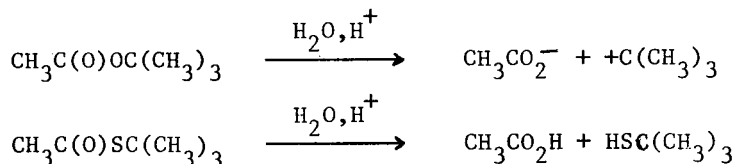
My research in WWII, under a contract with the National Defense Research Committee, was directed to methods of detection of toxic gases. We synthesized a series of substituted thiocarbazones,⁶ which had been found by others to be sensitive detectors of dichloroarsines or arsine oxides. We showed by a quantitative spectrophotometric study that one molecule of an arsine or its oxide reacted with one molecule of thiocarbazono,⁷ probably forming a cyclic structure as indicated. This method could be made quantitative.



During the synthesis of the thiocarbazones, we wished to know if ArSH groups could be formed by acid cleavage of ArSCH₃ groups, analogous to the acid splitting of ArOCH₃ to ArOH. We could not undertake a serious study of this problem until the end of World War II, when we found that cleavage of C₆H₅SCH₂C₆H₅ by proton acids was very slow and incomplete; with the Lewis acid AlBr₃ in C₆H₅Cl solution, on the other hand, the cleavage was rapid and quantitative and showed first order kinetics in the sulfide.⁸ This paper was the first in a series designed to show how oxygen compounds differ from their sulfur analogs in the rate of cleavage of the C—O compared to the C—S bond. We wrote a comprehensive review with 460 references on the cleavage of the carbon-sulphur bond in divalent sulfur compounds as background for further research.⁹

Further work showed that phenyl alkyl and phenyl aralkyl sulfides were cleaved by Lewis acids much more slowly than the corresponding ethers,¹⁰ although the order of relative reactivity was the same as that of the ethers: (C₆H₅)₃C > (C₆H₅)₂CH > C₆H₅CH₂ and (CH₃)₃C > (CH₃)₂CH > CH₃. Benzyl phenyl ether with AlBr₃ in C₆H₅Cl gave an extremely rapid cleavage, accompanied by nuclear benzylation and reaction with solvent, in sharp contrast to the corresponding sulfide.¹¹ We found that 4- or 2-brominated thiophenols reacted with benzene, chlorobenzene or toluene with AlBr₃ as catalyst to give XC₆H₅SC₆H₄R + HX, where X is 2- or 4-Br and R is H, Cl or CH₃. We presented a mechanism for this unexpected reaction.¹²

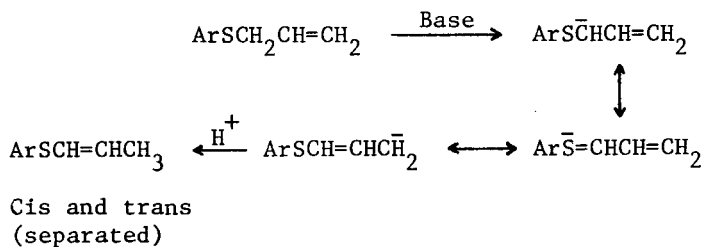
In two papers we measured the acid and base catalyzed hydrolysis of acetate, CH_3COOR and the thiol esters, CH_3COSR , as a function of R.^{13,14} *t*-Butyl acetate hydrolyzes under acid conditions with kinetics in agreement with alkyl-oxygen cleavage. The corresponding thiol esters hydrolyzes entirely by acyl-thiol cleavage, with no *t*-butyl carbocation formation.



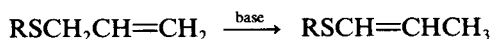
This contrast emphasizes the general tendency of carbon-sulfur bonds to split less rapidly than carbon-oxygen bonds. The acid-catalyzed hydrolysis of trityl thiolacetate, $\text{CH}_3\text{COSC}(\text{C}_6\text{H}_5)_3$, does give alkyl-sulfur cleavage, at a measurable rate, but the corresponding benzyl ester gives no alkyl-sulfur fission.¹⁴ The oxygen ester, $\text{CH}_3\text{COOC}(\text{C}_6\text{H}_5)_3$, is hydrolyzed instantly (presumably solvolyzed) even in neutral solution. These observations support the generalization above; the activation parameters for the acid-catalyzed reactions are consonant with this difference.

Our early work on the kinetics and mechanism of the Claisen rearrangement of aryl allyl ethers led us to an examination of the behavior of aryl allyl ethers.¹⁵ We found that heating allyl sulfides gives entirely different products from the oxygen analogs, leading to cleavage and unexpected rearrangement products, emphasizing again the contrast between oxygen and sulfur analogs.¹⁶

During this work, we observed the acidifying effect of sulfur on an adjacent CH_2 group,¹⁷ an effect not found in the oxygen analogs.

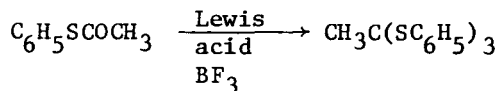


The isomerization is undoubtedly due to the stabilization of the negative charge of the intermediate carbanion by the sulfur. We separated the *cis* and *trans* forms of $\text{C}_6\text{H}_5\text{SCH}=\text{CHCH}_3$ by chromatography of their sulfilimines. We had previously found that sulfilimines can be readily converted to the corresponding sulfides by hydrogenolysis with hydrogen and palladium catalyst,¹⁸ a useful way of purifying liquid sulfides. We showed that the basic isomerization

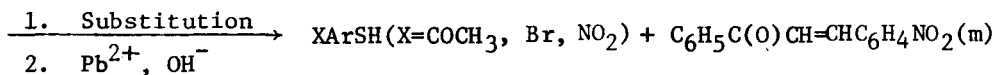
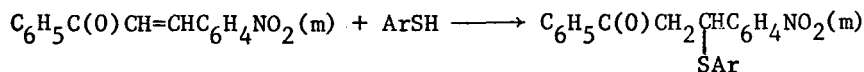


does involve a carbanion intermediate by demonstrating deuterium incorporation in the propenyl sulfide when EtOD is the solvent.¹⁹ Mass spectroscopy showed deuterium uptake.

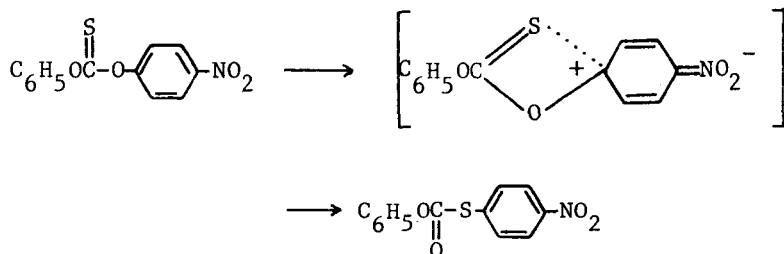
Sulfur attached to an aromatic ring makes substitution in the aromatic ring slower,^{8,11,16} compared to the oxygen analog. We found another striking example of this effect in a study of the Fries reaction on esters of thiophenols;²⁰ no Fries reaction occurs, but a phenyl trithioorthoacetate is formed. We found no evidence of a Fries reaction using other aryl thioesters.



Because of the observed difficulty of acylating an aromatic ring carrying a thiol substituent, we developed a route for preparing some substituted thiophenols,²¹ as indicated below. Addition to the conjugated ketone is rapid, only the Ar group undergoes substitution, and the free thiophenol is readily liberated by basic lead acetate.



We had noted the Schönberg rearrangement of thioncarbonates to thiolcarbonates in our review article,⁹ and we investigated this reaction as a route to some thiophenols we wanted for other work.²² We found that the reaction was faster with electron withdrawing groups *ortho* or *para* to oxygen, and we suggested that the rearrangement was a nucleophilic displacement going through a four-membered cyclic transition state.



We supported this mechanism by a kinetic study of the rearrangement of (*p*-ClC₆H₄O)₂C=S to *p*-ClC₆H₄OC(O)SC₆H₄-*p*-Cl at 268 °C;²³ the reaction is first order and has an entropy of activation of -12.6 e.u.

In contrast to carboxylic acids, thioacids act as acylating agents for amines under mild conditions. We found that this reaction follows the equations:²⁴

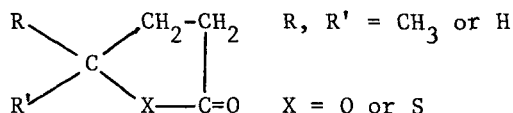
$$\text{Rate} = k [\text{C}_6\text{H}_5\text{COSH}] [\text{C}_6\text{H}_5\text{NH}_2]$$



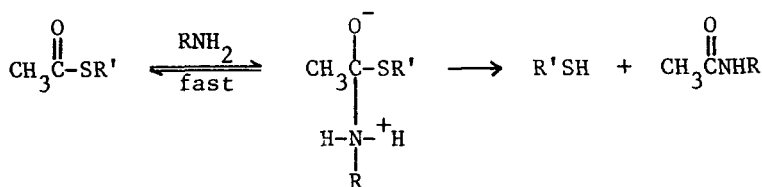
It proceeds at a measurable rate at 60 °C in chlorobenzene, but the same reaction with C_6H_5COOH does not go at a measurable rate at 100 °C. We attribute the difference between C_6H_5COSH and C_6H_5COOH to the strong hydrogen bonding in the latter to form a dimer, which has a heat of dissociation reported to vary from 8.7 to 21 kcal.

We supported the failure of sulfur compounds to hydrogen bond appreciably compared to the oxygen analogs by infrared studies, which showed that hydrogen bonding is negligible in determining the properties of $-SH$ compounds.²⁵ Later work by others has shown somewhat more hydrogen bonding than we observed, although we did find evidence for weak hydrogen bonding in RSH compounds by an NMR study.²⁶ The hydrogen bonding in $-OH$ compounds is very much stronger, however.

We studied the rate of the alkaline ring opening of three γ -lactones and the corresponding thiolactones in aqueous acetone.²⁷ The rates of hydrolysis show much smaller effects from increasing alkyl substitution around oxygen (or sulfur) than do the open chain acetates and thiolacetates.



At this time, in the early 1950's, biochemists discovered that coenzyme A, which plays a key role in metabolism, is an N-acylated derivative of β -aminoethanethiol. The S-acyl coenzyme rapidly transfers its acyl group to other substrates, in the presence of the appropriate enzyme. We wished to find out if the high reactivity of the S-acylcoenzyme A is related to its β -N-acyl structure. We studied spectrophotometrically the rate of aminolysis by *n*-butylamine of ethyl thiolacetate and the β -acetamino analog.²⁸ A detailed kinetic analysis shows that the aminolysis is in agreement with the following mechanism. The rates of aminolysis (and hydrolysis) of the two esters indicate little or no effect by a neighboring acetamino group on these rates. If acetylcoenzyme A is unusually reactive, the presence of the amide group on the β -carbon evidently is not the cause.

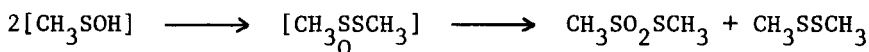
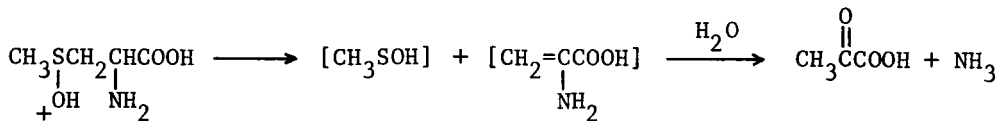


We examined the aminolysis of some further thiol esters more closely resembling acetylcoenzyme A in structure, with essentially similar results. Aminolysis, like hydrolysis, is catalyzed by both acids and bases. The reactivity of the thiol ester group does not vary much in going from ethyl thiolacetate to the more complex derivatives related to S-acetylcoenzyme A.²⁹

In some synthetic work on thiopyrones, we found that the infrared spectra of 1,4-thiapyrone, its hydrochloride and other derivatives show no frequency corresponding to normal carbonyl adsorption. These results are in agreement with other lines of evidence that the thiopyrone nucleus and thiopyrylium salts are resonance

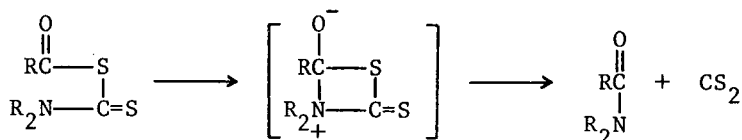
hybrids with little or no contributions from forms with a carbon-oxygen double bond.³⁰

We made a quantitative study of the course of acid hydrolysis of S-methyl-L-cysteine sulfoxide, which supports the following mechanism.³¹

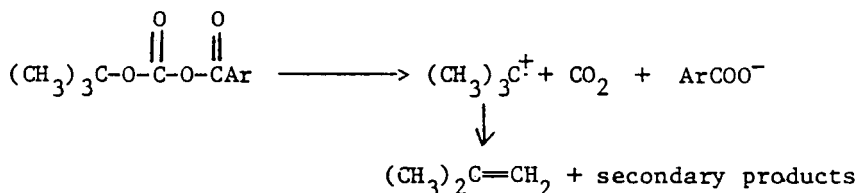


We studied the kinetics of the oxidation of a thiophenol derivative, $\text{C}_6\text{H}_4(\text{SH})\text{CH}_2\text{COOH}$, to the disulfide by hydrogen peroxide, using a spectrophotometric technique.³² With excess peroxide, the reaction is zero order; the rate is catalyzed by ferrous ion, and is inversely proportional to the square root of the hydrogen ion concentration. The results suggest that the reaction involves interaction of a heavy metal ion (in traces) with peroxide at the slow step. The addition of EDTA changes the kinetics. These interests led to a review with 29 references of the mechanism of oxidation of thiols to disulfides,³³ in connection with our experimental work.

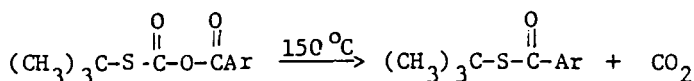
Some of our later research involved the mixed carboxylic-carbonic anhydrides $[\text{ROC}(\text{O})\text{OC}(\text{O})\text{R}^1]$ and related compounds, many of them sulfur compounds.³⁴ We studied the preparation of mixed carboxylic-dithiocarbamic anhydrides, and showed that they decompose to form amides, probably through a four-membered cyclic transition state.³⁵



We found that *p*-nitrobenzoic *t*-butylcarbonic anhydride decomposes with alkyl-oxygen cleavage to give carbon dioxide, isobutylene and various secondary products.³⁶

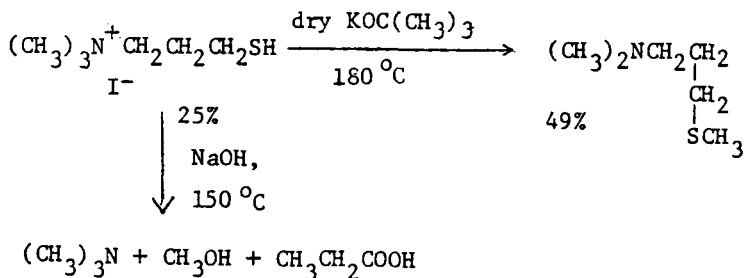


As expected from our earlier work, however, the corresponding sulfur compound gives no sulfur-alkyl cleavage, but forms the thiol ester in high yield.³⁷



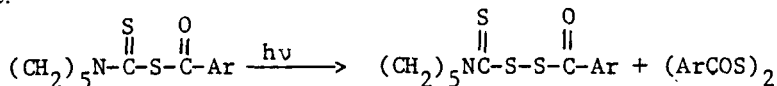
We prepared a series of aminothiols derived from 3-amino-1-propanethiol for examination as radiation-protective materials, and for other studies.³⁸ The syntheses were straightforward, in general, but we did describe in detail a useful electrolytic procedure for reducing disulfides in thiols in aqueous acid.

We expected that the quaternary aminothiol would readily form the S-methyl compound with base; it did so, but only under extremely drastic conditions.³⁹

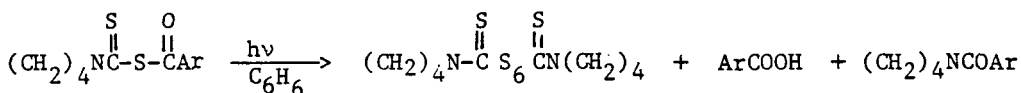


No trimethylene sulfide is found, but a polymer of $(\text{CH}_2\text{CH}_2\text{CH}_2\text{S})$ is present. We suggested a mechanism for the formation of the polymer.

We found that the photolysis of the dithiocarbamic anhydride gives a new type of disulfide:⁴⁰



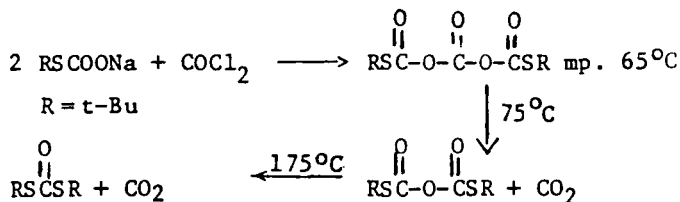
We suggested a free radical mechanism. Other analogs of the dithiocarbamic anhydride yielded complex polysulfides on photolysis.⁴¹



With the morpholine analog, a comparable compound with 13 sulfur atoms is formed. The methylamino analog decomposes thermally to the amide ArCONHCH_3 by a cyclic transition state.⁴²

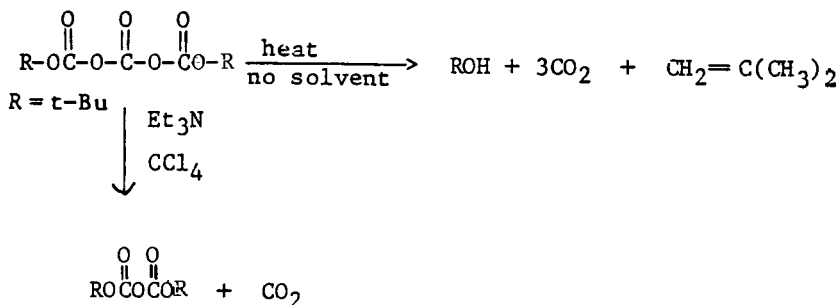
We measured rates of decomposition of the mixed anhydrides $\text{ArC}(\text{O})\text{OC}(\text{O})\text{SR}$, where R is isopropyl or *t*-butyl, by IR measurements. The reactions $\text{ArC}(\text{O})\text{OC}(\text{O})\text{SR} \rightarrow \text{ArC}(\text{O})\text{SR} + \text{CO}_2$ are first order, with a negligible amount of alkyl-sulfur cleavage. The rate is accelerated by nucleophiles, and the results are in agreement with earlier mechanisms of an ion chain reaction. We calculated activation parameters in several solvents.⁴³

We were surprised to isolate a new type of thiolcarbonate, di-*t*-butyl dithioltricarboxylate from the following reaction.⁴⁴

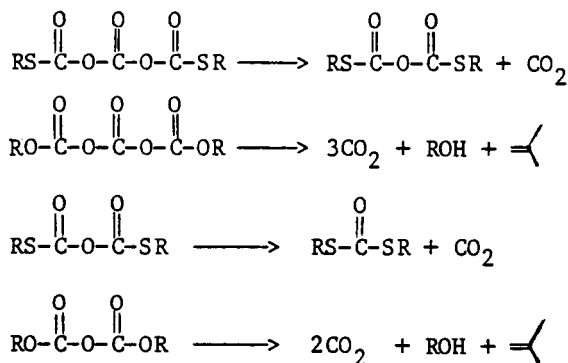


The dithioltricarbonate decomposes thermally in two stages, losing carbon dioxide to give the dicarbonate, which at higher temperatures loses a second molecule of carbon dioxide to give the monocarbonate.⁴⁴

We found that the corresponding oxygen compound, di-*t*-butyl tricarbonate, a crystalline compound like the dithiol compound, is readily accessible by a similar process.⁴⁵ This compound, heated above its melting point without solvent, fragments into 3 moles of CO₂, 1 mole of isobutylene, and 1 mole of *t*-butyl alcohol. This outcome emphasizes again the failure of *t*-butyl thiol compounds to form carbocations. Heating with triethylamine in CCl₄ gives a good yield of the dicarbonate.



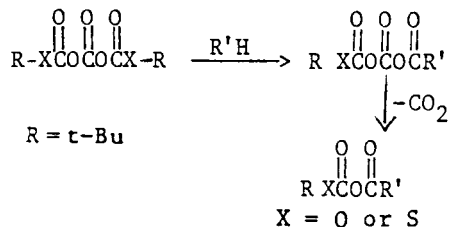
We studied the kinetics of decomposition of these novel compounds in some detail in chlorobenzene and decalin as solvents,⁴⁶ measuring the kinetics of the following reactions:



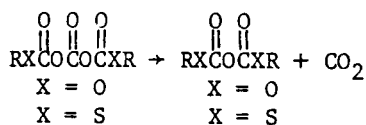
The decompositions, followed by IR measurements of the decrease of a carbonyl absorption band, give good first-order rate constants, allowing calculation of activation parameters. The reactions are much faster in chlorobenzene than in decalin, showing that the transition states have considerable ionic character. It appears from the activation parameters that the slow step is the same for oxygen and the sulfur compounds. The dicarbonate, ROC(O)OC(O)OR, and the monocarbonate, ROC(O)OR, are not intermediates in the decomposition of the corresponding tricarbonate. We conclude that an effect of triethylamine in arresting the decomposition of the oxygen tricarbonate at the dicarbonate stage is due to an association of the tertiary amine with the central

carbonyl group. This association in some way stabilizes the reactive intermediate long enough for the dicarbonate to form.

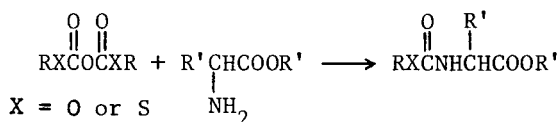
We found in a detailed study that amines, alcohols and pivalic acid, $((\text{CH}_3)_3\text{CCOOH})$ react with both tricarbonates at the central carbonyl group.⁴⁷



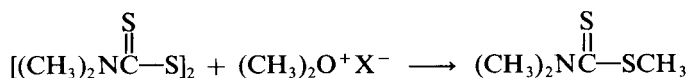
Because we had to prepare scores of batches of both tricarbonates and the dicarbonates from them by the action of tertiary amines, we published detailed procedures for these compounds in *Organic Syntheses*.⁴⁸ The dicarbonates can be obtained in satisfactory yields by heating the tricarbonates with tertiary amines.



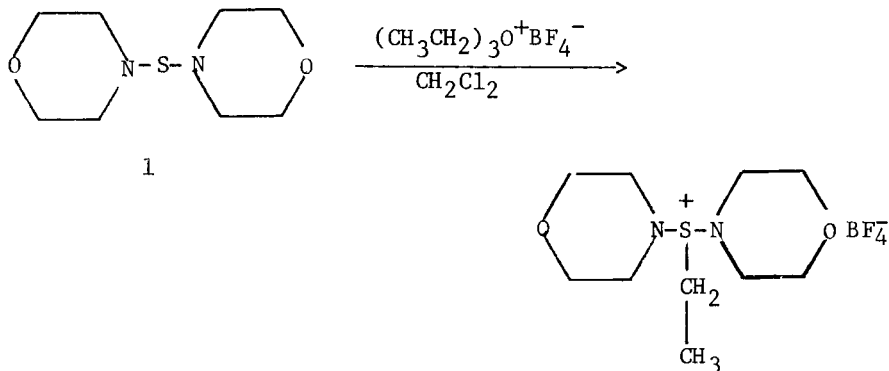
N-*t*-Butoxycarbonyl groups (*t*-BOC) have long been used for protecting primary amino groups during the synthesis of polypeptides from amino acid derivatives. Several reagents had been used to prepare the *t*-BOC compounds. Because we had both dicarbonates available, we studied their usefulness in the preparation of *t*-BOC and thiol *t*-BOC derivatives from amino acids and related compounds.⁴⁹ We found that the reactions indicated did proceed in high yields, under mild conditions, without racemization. As expected, the *t*-BOC groups are readily cleaved off by mild acid, which does not affect the thiol *t*-BOC, in agreement with our earlier work described above. The thiol *t*-BOC group can be removed by treatment with hydrogen peroxide in acetic acid. Thus these mechanistic studies of sulfur and oxygen compounds resulted in a practical method of making valuable reagents. Di-*t*-butyl dicarbonate has now largely superseded the explosive *t*-butoxycarbonyl azide as a reagent for making *t*-BOC derivatives of amino acids.



During extended studies which established the structure of the antibiotic fumagillin,⁵⁰ we studied several systems involving methoxonium ions as intermediates.⁵¹ This work led us to examine alkylation of dithiocarbamates by trimethyloxonium picrylsulfonate, which gives the product shown (the structure is proved by NMR and by an unambiguous alternative synthesis).⁵²



A novel resonance-stabilized sulfonium salt results from the alkylation of an amine sulfide with triethyloxonium fluoroborate; its structure is clear from its NMR spectrum.⁵³



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