TABLE III
PHOTODECOMPOSITION OF ADDITIONAL HYPOCHLORITES

				Yield, %		
[ROCl]	M	[Olefin]	M	Chloro alcohol	Tetrahydrofuran	Alcohol
1-Pentyl	1.16	*cis*-$C_2H_2Cl_2$	5.8	34[a]		
	1.12	*cis*-$C_2H_2Cl_2$	5.6		50[a]	
4-Phenyl-1-butyl	0.888	*cis*-$C_2H_2Cl_2$	4.44		56[a]	
2-Pentyl	1.15	*trans*-$C_2H_2Cl_2$	2.3		25.7 ± 0.4	43.5 ± 0.3
	0.91		4.55		40.1 ± 1.8	36.6 ± 1.8
	0.536		7.94		49.1	21.6
2-Hexyl	0.885	*cis*-$C_2H_2Cl_2$	4.43		89.0 ± 0.4[b]	6.7 ± 0.5
	0.663		6.63		82.7 ± 2.3[b]	5.3 ± 0.1

[a] Isolated product in preparative-scale experiments. [b] Equimolar mixture of cis and trans isomers.

TABLE IV
CONVERSION OF ALCOHOLS TO TETRAHYDROFURANS

Alcohol (or hypochlorite)	Yield, % ROCl	Yield, % $Pb(OAc)_4$[a]
1-Butyl	60	20
1-Pentyl	75	43
2-Pentyl	49	9.5
2-Hexyl	89	41
4-Phenyl-1-butyl	56	40–49
2-Methyl-2-pentyl	80[b]	10

[a] Reference 8. [b] Reference 2. No radical trap is required in the case of *tert*-hypochlorites.

rotary evaporator. Three vacuum distillations of the residue yielded 34% product, bp 67–68° (4 mm). The purity by glc was >95% and ir and nmr spectra consistent with the structure. The major impurity was 2-methyltetrahydrofuran formed during distillation and accounting for the low yield.

2-Methyltetrahydrofuran.—1-Pentyl hypochlorite (0.530 mol) (2 *M* solution in Freon-113) and 2.65 mol of *trans*-dichloroethylene were photolyzed at 0°. One-half of the reaction mixture was refluxed with 0.53 mol of 2,6-lutidine for 1 hr. Two fractional distillations yielded 11.7 g (51%) of 2-methyltetrahydrofuran, bp 68–70° (648 mm), purity by glc >98%. The other half of the reaction mixture was refluxed for 1 hr with 200 ml of 15% KOH in propylene glycol. Distillation yielded 11.1 g (49%) of 2-methyltetrahydrofuran.

2-Phenyltetrahydrofuran.—A mixture of 30.5 ml of 1.33 *M* 4-phenyl-1-butyl hypochlorite and 0.204 mol of *cis*-dichloroethylene was photolyzed at 0° (3 hr). The product was refluxed overnight with 91 ml of 5% KOH in methanol. Water was added and the mixture was extracted with three portions of ether. Fractional distillation yielded 3.36 g (56%) of 2-phenyltetrahydrofuran, bp 105–107.5° (15 mm), ir and nmr spectra consistent with structure. A higher boiling fraction (1.05 g) contained 59% of the furan by glc, indicating a total yield of 66%.

Registry No.—*n*-Butyl hypochlorite, 5923-22-8; *n*-pentyl hypochlorite, 35042-28-5; 4-chloro-1-pentanol, 35096-45-8; 2-methyltetrahydrofuran, 96-47-9; 2-phenyltetrahydrofuran, 16133-83-8.

Photosensitized Oxidation of Dialkyl Disulfides[1]

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Dialkyl disulfides are photooxidized in the presence of methylene blue sensitizer to the corresponding thiosulfinates. Quenching experiments indicate that singlet oxygen is the oxidant. A mechanism for the reaction, involving an adduct between the disulfide and singlet oxygen as an intermediate, is proposed. The implications of these results for the photodynamic effect are discussed.

By a variety of ways and particularly through the work of Foote and coworkers,[2] it has been amply demonstrated that the Kautsky[3,4] mechanism for photosensitized oxidation is a valid mechanism. According to this mechanism the photooxygenation occurs with excited singlet molecular oxygen as the oxidant. This demonstration has important implications both for organic chemistry and biological chemistry. In biological chemistry, photosensitized oxidation leading to pathological effects in organisms has been known as photodynamic action. Foote[5] and Hastings and Wilson[6] have pointed out that in some cases photodynamic action may also involve singlet oxygen. Indeed, Foote[7] has demonstrated that β-carotene efficiently quenches singlet oxygen and has suggested that the function of carotenoid pigments is to provide protective action against photodynamic damage.

In addition to photosensitization, a number of other methods for producing singlet oxygen have been described. Included are the reaction of sodium hypochlorite and hydrogen peroxide,[8] the use of a radiofrequency discharge in gaseous oxygen,[9,10] the reaction of bromine and hydrogen peroxide,[11] the decomposition of alkaline solutions of peracids,[11] the decomposition of photoperoxides,[12,13] the self-reaction of *sec*-butylperoxy

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radicals,[14] and the base-induced decomposition of peroxyacetylnitrate.[15]

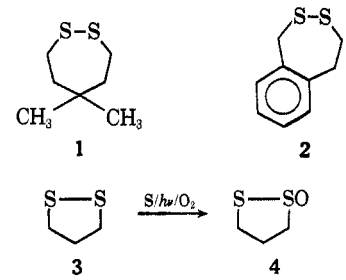
We have shown that certain exothermic reactions of ozone with organic compounds also give singlet oxygen.[16-19] These observations have important consequences for air pollution studies, since ozone continues to be regarded as an important and highly toxic air pollutant. Because many of these reactions occur under very mild conditions and offer a very convenient and efficient source of singlet oxygen, we have sought to use them to study the possible intervention of singlet oxygen in some photodynamic reactions.

One such exothermic reaction is that between ozone and triphenyl phosphite, first studied by Thompson,[20] and shown by us[16-18] to give singlet oxygen. We have recently found[21] that the triphenyl phosphite–ozone adduct reacts with simple dialkyl disulfides to produce thiolsulfinates and sometimes thiolsulfonates. These reactions were studied as models for photodynamic action in biological molecules containing the cystine residue.

Interpretation of these results requires consideration of the singlet oxygen mechanism previously observed[16-18] and a bimolecular mechanism involving the phosphite–ozone adduct and a disulfide molecule. This latter type of mechanism has been suggested for the reaction between the phosphite ozonide and tetramethylethylene[22] and for the corresponding reaction with *cis*- and *trans*-diethoxyethylenes.[23] Also, Koch has shown[24] that certain substrates can induce the decomposition of the phosphite ozonide *via* a bimolecular reaction, although this work cannot distinguish between a direct donation of the oxygen and the intervention of free singlet oxygen in the oxidation step. Thus, whether the ozonide will give singlet oxygen by unimolecular decomposition or perhaps *via* induced decomposition may depend upon substrate concentration in some cases.

To facilitate the interpretation of the results using the phosphite ozonide we have also subjected the disulfides to photosensitized oxidation. The only other reported case of attempted photooxidation of a noncyclic disulfide is that for diphenyl disulfide, which was found to be inert to these reaction conditions.[25] Among cyclic disulfides, **1** and **2** were also found to be inert to photosensitized oxidation[25] while **3** gives the corresponding cyclic thiolsulfinate **4**.[26]

On the other hand, there are a number of reports of



monosulfides being photooxidized to the corresponding sulfoxides.[25,27,28]

Results and Discussion

As indicated in Table I, photosensitized oxidation of the dialkyl disulfides leads to good yields of the corresponding thiolsulfinates. In the case of dimethyl disulfide the thiolsulfinate undergoes a thermal disproportionation reaction to thiolsulfonate and disulfide. Traces of thiolsulfonate were also evident in the diethyl disulfide case. This side reaction appears to be analogous to that observed for aryl thiolsulfinates[29-32] and alkyl thiolsulfinates[33] synthesized by nonoxidative processes. The thiolsulfonates are not further photooxidation products of the thiolsulfinates, since we have shown in a separate experiment that the thiolsulfinate from di-*tert*-butyl disulfide, for example, is not oxidized to thiolsulfonate under the reaction conditions.

The rate of disproportionation observed in the dimethyl case is faster than that observed for an authentic sample of thiolsulfinate synthesized by a nonoxidative procedure. The presence of a small impurity peak in the nmr coupled with the observation that addition of a trace of pyridine decreased the rate to that of the authentic sample suggests that a small amount of an acidic impurity is responsible for the observed differ-

TABLE I

RESULTS OF PHOTOSENSITIZED OXIDATION OF VARIOUS DIALKYL DISULFIDES

		Reaction conditions			Yield,[b] %	
Registry no.	Substrate RSSR R =	Time, min	Temp,[a] °C	Oxygen absorbed per mole of disulfide	RSSR O	RSSR O_2
110-06-5	$(CH_3)_3C$	215	0	0.551	75[c]	0
882-33-7	C_6H_5	53	0	0	0	0
624-92-0	CH_3	135	0	0.56	60	13
	CH_3	60	25	0.4	69	8
110-81-6	C_2H_5	205	0	0.514	48.7[c]	Trace
629-19-6	CH_3CHCH_3	352	17-21[d]	0.454	73	
	$(CH_3)_3C$	271	13-17[d]	0.620	63[c]	
	$(CH_3)_3$[e]	270	15-20[d]	0.04	2.3	0
	$(CH_3)_3C$[f]	270	15-17[d]	0.113	3.1	0

[a] Bath temperature unless otherwise stated. [b] Determined by gpc analysis using an internal standard. [c] Isolated yield. [d] Reaction mixture temperature. [e] In the presence of a 3 molar excess of DABCO. [f] In the presence of an equimolar amount of DABCO.

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ence in disproportionation rates. Distillation of the crude thiolsulfinate leads to no improvement in this situation, presumably because of further decomposition of the unstable thiolsulfinate.

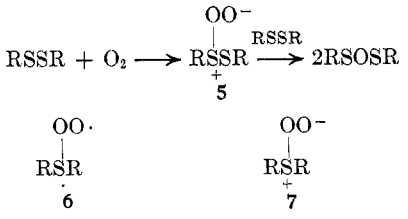
Kice and coworkers[34] have shown that the acid-induced disproportionation of aryl thiolsulfinates is catalyzed by sulfide. The mechanism given for this reaction calls for a rate-determining nucleophilic attack of the sulfide on the protonated thiolsulfinate. Operation of a similar mechanism in the present work, where disulfide acts as the nucleophile and a trace impurity acts as the acid, could explain the observed relative stability of the thiolsulfinate products toward the disproportionation process. Thus methyl methanethiolsulfinate is most troublesome, presumably because the S–S bond is most susceptible toward nucleophilic attack. On the other hand, *tert*-butyl *tert*-butanethiolsulfinate is formed and retained without contamination by the disproportionation product thiolsulfonate because steric factors make it highly resistant to nucleophilic attack.[35]

The products of these reactions therefore are the same as those obtained[21] when the triphenyl phosphite ozonide is used. As reported previously,[25] we have found that diphenyl disulfide is not oxidized under the conditions used.

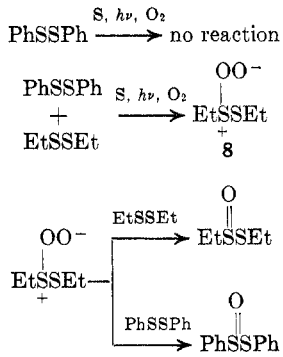
Evidence that the oxidations involve singlet oxygen comes from the observation (Table I) that the oxidation of di-*tert*-butyl disulfide can be essentially prevented, or severely retarded, in the presence of a 3 *M* excess or an equimolar amount, respectively, of the known[36] singlet oxygen quencher, 1,4-diazabicyclo-[2.2.2]octane (DABCO).

The oxidation reaction does not involve cleavage of the disulfide bond. When di-*tert*-butyl disulfide and diisopropyl disulfide were cooxidized, no mixed thiolsulfinate (*e.g.*, *tert*-butyl isopropanethiolsulfinate) was formed along with the *tert*-butyl and isopropyl thiolsulfinates.

The reaction presumably proceeds *via* the formation of an intermediate zwitterion **5** from the disulfide and singlet oxygen, which can then react further with another molecule of disulfide to give two molecules of thiolsulfinate. This mechanism is analogous to that invoked to explain the photosensitized oxidation of sulfides. In that case, the intermediate was formulated as **6** by Schenck and Krauch,[37] although the alternative formulation **7** given by Foote, *et al.*,[27,28] is more attractive.



This proposed mechanism is supported by the data given in Table I, which indicates that approximately 0.5 mol of oxygen is absorbed per mole of disulfide. Further experimental support for the presence of **5** comes from experiments similar to those of Foote's[28] in which diphenyl disulfide is cooxidized with diethyl disulfide. In this case both disulfides are oxidized. Since diphenyl disulfide is otherwise inert to the conditions of photosensitized oxidation, it is presumably being oxidized by the zwitterion, **8**, produced from diethyl disulfide.



The observation that dialkyl disulfides are photooxidized to the corresponding thiolsulfinates suggests that photodynamic action in biological substrates containing the cystine residue could occur by a similar mechanism. The reported[38] very slow photooxidation of cystine in the presence of methylene blue may be due to the singlet oxygen quenching effect[39] of the free amino groups. Experiments to test this hypothesis are in progress. We have also found that a number of disulfides related to cystine are oxidized by singlet oxygen.[40]

The product thiolsulfinates are interesting themselves, since a large number of dialkyl thiolsulfinates have high antibiotic activity.[31,41,42] The nmr spectra of the thiolsulfinates and thiolsulfonates have several interesting features which will be discussed in detail elsewhere.

Experimental Section

Materials.—Commercial samples of dialkyl disulfides were purified immediately before use by distillation. Methylene blue and methanol used were Fisher reagent grade.

Apparatus.—The apparatus used was similar to that described in the literature.[43,44] A General Electric DWY 650-W lamp was used without filters. The lamp was operated at 90 V in order to reduce the heat generated.

Nmr Analyses.—Nmr spectra were recorded on a Varian Associates Model T-60 nmr spectrometer. The spectra were recorded in CCl_4 solution using TMS as internal standard unless otherwise indicated. Chemical shift values given are τ values.

Gpc Analyses.—Gpc analyses were carried out on a Hewlett-Packard Model 5750 gas-phase chromatograph using a 6-ft, 10% silicone rubber (UCW-98) on 45–60 mesh Chromosorb W column.

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General Procedure.—The methanolic solution of the disulfide was added to a filtered methanolic solution of methylene blue, and the solution was then photooxidized at the desired temperature until the oxygen uptake either stopped or became very slow. Reaction conditions and substrates used are listed in Table I. Products were analyzed by gpc or tlc. Preparative isolation of products was accomplished using gpc, tlc, and distillation. Examples of use of this general procedure are given below.

Photosensitized Oxidation of Di-*tert*-Butyl Disulfide.—A solution of 3.606 g (20 mmol) of di-*tert*-butyl disulfide in 140 ml of methanol was photooxidized in the presence of 0.05 g of methylene blue as sensitizer at a bath temperature of 0°. Oxygen uptake essentially stopped after 3.5 hr, when 252 ml (11.3 mmol) had been absorbed. Gpc analysis of the reaction mixture showed the presence of unreacted disulfide and *tert*-butyl-*tert*-butanethiolsulfinate. The reaction mixture was concentrated and then distilled[45] to give 2.8 g (75% yield) of the thiosulfinate, bp 45° (0.03 mm) [lit.[41] bp 30° (0.05–0.1 mm)]. The infrared spectrum of the product had absorptions at 3.38, 6.81, 6.88 (doublet), 7.34, 8.56, and 9.28 μ (S=O). The product had n^{21}D 1.5040 (lit.[46] n^{25}D 1.5060). The nmr spectrum showed two singlet absorptions at τ 8.47 and 8.68 which were assigned to the *tert*-butyl groups adjacent to the sulfoxy and ether sulfur groups, respectively. The thiosulfinate could also be isolated by preparative tlc on silica gel F of 1.75-mm thickness.

In a separate experiment di-*tert*-butyl disulfide was photooxidized at −68° with subsequent addition of dimethyl disulfide after the lamp had been turned off and the low temperature maintained. Analysis of this reaction mixture both at low temperature and at room temperature showed that the dimethyl disulfide had not been oxidized to methyl methanethiolsulfinate.

Several experiments were run to determine whether oxygen was evolved upon warmup of the oxidation mixture. Oxidation of 21.4 mmol of di-*tert*-butyl disulfide at −60, −70, and −85° until *ca.* 16 mmol of oxygen had been absorbed was followed by subsequent warmup and oxygen measurement. In all cases no evolved oxygen could be detected.

Photosensitized Oxidation of Diisopropyl Disulfide.—A solution of 3.115 g (20.7 mmol) of diisopropyl disulfide in 150 ml of methanol was photooxidized in the presence of 0.067 g of methylene blue at 17–21°. The reaction had essentially stopped when 210 ml (9.40 mmol) of O_2 had been absorbed. The reaction mixture was concentrated on the rotary evaporator to give an oily residue. Distillation of this residue gave isopropyl isopropanethiolsulfinate, bp ~37° (0.015 mm) [lit.[41] bp 25–30° (0.1 mm)]. The infrared spectrum had absorptions at 3.3, 7.2, 8.0, 8.7 and 8.8 (doublet), 9.2, 9.4, 9.6, 10.35, 11.35, and 12.6 μ. The nmr spectrum had absorptions at τ 8.65 (doublet, 6 H), a pair of overlapping doublets at 8.5 (6 H), and a pair of multiplets at 6.92 (1 H) and 6.45 (1 H). The yield as determined by gpc was 73%. Tlc analysis of a reaction mixture which had been standing for 2 days showed the presence of a small amount of isopropyl isopropanethiolsulfonate. This could be isolated using preparative tlc. It had infrared absorptions at 3.35, 6.8, 7.18, 7.29 (doublet), 7.52, 7.58 (doublet), 7.85, 8.6, 8.85, 9.45, 10.6, 11.35, 14.5, and 14.85 μ. The nmr spectrum consisted of a doublet at τ 8.62 (6 H, J = 7 Hz), a doublet at 8.55 (6 H, J = 7 Hz), and a pair of multiplets at 6.53 (2 H).

Photosensitized Oxidation of Diethyl Disulfide.—A solution of 2.937 g (24.7 mmol) of diethyl disulfide in 150 ml of methanol was photooxidized in the presence of 0.05 g of methylene blue. The bath temperature was 0°. Reaction was essentially complete after 3.5 hr, when 285 ml (12.7 mmol) of oxygen had been absorbed. The reaction mixture was concentrated and distilled and the thiolsulfinate was isolated by preparative tlc. The yield was 48.7%. The product had bp 33° (0.12 mm) [lit.[41] bp 52° (0.2–0.3 mm)] and n^{25}D 1.5203 (lit.[41] n^{25}D 1.524). The infrared spectrum had bands at 3.4, 6.9, 7.3, 7.85, 9.25, 9.75, 10.3, 12.85, and 13.2 μ. The nmr spectrum had two multiplets absorptions at τ 8.63 (3 H) and 8.55 (3 H) and a pair of multiplets centered at 7.0 (4 H).

Gpc and infrared analysis of the crude product showed the presence of the thiosulfonate, but there was not a sufficient quantity present to permit its isolation.

Photosensitized Oxidation of Dimethyl Disulfide.—A solution of 1.759 g (18.7 mmol) of dimethyl disulfide in 130 ml of methanol was photooxidized at room temperature in the presence of 0.1 g of methylene blue. After 1 hr, 162 ml (7.2 mmol) of oxygen had been absorbed and the reaction was essentially complete. The reaction mixture was analyzed by gpc using dodecane as an internal standard. It showed the presence of unreacted disulfide as well as methyl methanethiolsulfinate (69% yield) and methyl methanethiolsulfonate (8% yield). The thiolsulfinate was somewhat unstable to distillation, gpc, and tlc analysis. In some cases thiolsulfinate and thiolsulfonate were obtained by distillation for further analysis. In every case the thiolsulfinate underwent disproportionation to disulfide and thiolsulfonate while standing at room temperature. The thiolsulfinate had bp 28° (0.2 mm), distillate not pure [lit.[29] bp 56–56.5° (1.5 mm)], and $n^{24.5}$D 1.5305 (lit.[29] n^{17}D 1.5615). The thiolsulfonate had bp ~45° (0.001–0.005 mm) [lit.[47] bp 115° (13 mm)] and n^{28}D 1.5104 (lit.[47] n^{25}D 1.5112). The thiolsulfinate had nmr absorptions at τ 7.09 (singlet, 3 H) and 7.40 (singlet, 3 H). The thiolsulfonate had singlet absorptions at τ 7.35 (3 H) and 6.80 (3 H).

A comparison of the rate of disproportionation of the thiolsulfinate obtained with that for a sample of thiolsulfinate synthesized by a nonoxidation procedure indicated a higher rate in the present case. It is felt that this may be due to the presence of a trace impurity indicated by a small peak in the nmr spectrum. Addition of a small amount of pyridine decreased the rate of disproportionation to the rate for the authentic sample, perhaps suggesting that the trace impurity is acidic.

Attempted Oxidation of Diphenyl Disulfide.—A solution of 3.19 g (15 mmol) of diphenyl disulfide in 145 ml of methanol was photolyzed in the presence of 0.06 g of methylene blue at a bath temperature of 0°. After 53 min of photolysis no oxygen had been absorbed.

Joint Photosensitized Oxidation of Di-*tert*-butyl Disulfide and Diisopropyl Disulfide.—A solution of 1.7 g (9.5 mmol) of di-*tert*-butyl disulfide and 0.752 g (5 mmol) of diisopropyl disulfide in 150 ml of methanol was photooxidized in the presence of 0.009 g of methylene blue at a bath temperature of 0°. Oxidation was continued for 50 min, at which time 88 ml (3.4 mmol) of oxygen had been absorbed. Gpc analysis of the reaction mixture showed the presence of unreacted disulfides as well as isopropyl isopropanethiolsulfinate and *tert*-butyl *tert*-butanethiolsulfinate and the isopropyl isopropanethiolsulfonate. No products of exchange reactions (*e.g.*, isopropyl *tert*-butanethiolsulfinate or *tert*-butyl isopropanethiolsulfinate) could be detected.

Photosensitized Oxidation of Di-*tert*-butyl Disulfide in the Presence of 1,4-Diazabicyclo[2.2.2]octane (DABCO).—A solution of 3.63 g (20 mmol) of di-*tert*-butyl disulfide in 100 ml of methanol was photooxidized in the presence of 0.82 g of methylene blue and 9.29 g (82.9 mmol) of DABCO. Gpc analysis of the reaction mixture showed a 2.35% yield of the thiolsulfinate. When the same reaction was repeated with 2.25 g (20 mmol) of DABCO present a 3.13% yield of the thiolsulfinate was obtained.

Attempted Photooxidation of Di-*tert*-butyl Thiolsulfinate.—A methanolic solution of 0.118 g (0.61 mmol) of *tert*-butyl *tert*-butanethiolsulfinate and 0.058 g of methylene blue was photolyzed at a bath temperature of 0°. After 70 min, there had been no oxygen uptake.

Joint Photosensitized Oxidation of Diphenyl Disulfide and Diethyl Disulfide.—A solution of diphenyl disulfide (6.50 g, 30 mmol), diethyl disulfide (0.70 g, 5.7 mmol), and methylene blue (0.059 g) in a mixture of benzene (75 ml) and methanol (125 ml) was photooxidized at room temperature for 165 min. Oxygen was bubbled through the reaction solution at a rate of 250 ml/min. Solvent was removed under reduced pressure and the residue (7.20 g) was analyzed by tlc on silica gel using CH_2Cl_2 as solvent. Ethyl ethanethiolsulfinate was separated and identified as described above. The presence of phenyl benzenethiolsulfinate and phenyl benzenethiolsulfonate was confirmed by comparing tlc R_f values with those of authentic samples prepared by oxidizing diphenyl disulfide with H_2O_2. Samples of phenyl benzenethiolsulfinate and phenyl benzenethiolsulfonate were separated from the reaction mixture by dry column chromatography on silica gel (Woelm, activity III, 3 in. flat diameter, 36 in. long). The products were identified by comparing infrared, nmr, and tlc R_f data with those of the authentic samples.

When the product phenyl benzenethiolsulfinate was subjected to glc analysis, only peaks corresponding to diphenyl disulfide

(45) We thank Mr. Daniel Kleypas for carrying out this experiment.
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(47) I. D. Douglas and B. S. Farah, *J. Org. Chem.*, **24**, 993 (1959).

and phenyl benzenethiolsulfonate were obtained. This glc disproportionation behavior was confirmed with an authentic sample of phenyl benzenethiolsulfinate.

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The Preparation and Reactions of Novel *O*-Acylhydroxylamines

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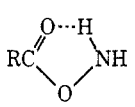
The new compounds *O*-pivaloyl-, *O*-(*p*-nitrobenzoyl)-, and *O*-(*m*-chlorobenzoyl)hydroxylamine as well as the previously prepared *O*-acetyl-, *O*-benzoyl-, and *O*-mesitoylhydroxylamines have been prepared in order to study their behavior with various nucleophiles. Because of the propensity of most *O*-acylhydroxylamines to isomerize to hydroxamic acids, attention was given to the bulky *O*-pivaloyl and *O*-mesitoyl compounds. *O*-Pivaloylhydroxylamine does transfer nitrogen to iodide ion (product is iodine), dibenzylamine (product is *N*,*N*-dibenzylhydrazine), and triphenylphosphine (product is iminotriphenylphosphorane). Nevertheless, olefins fail to react in the presence of *O*-acylhydroxylamines. Preferential isomerization of the *O*-acyl compounds to the corresponding hydroxamic acids occurs even when the highly substituted tetramethylethylene is treated with the bulky *O*-pivaloylhydroxylamine. Although *O*-mesitoylhydroxylamine does not isomerize, it decomposes to mesitoic acid when heated with or without an olefin (*cis*-3-hexene).

In an effort to develop a new and economical method for preparating N-unsubstituted aziridines from olefins, a study has been undertaken of the ability of *O*-acylhydroxylamines[1c] to transfer nitrogen. *O*-Acylhydroxylamines (**1**) are nitrogenous analogs of organic peracids (**2**) and, like the latter, have the potential to react with various nucleophilic regents. Nevertheless, there are surprisingly few reports of nucleophilic reactions on *O*-acylhydroxylamines and, indeed, few *O*-acylhydroxylamines have even been prepared and characterized.



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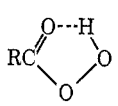

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There is only a meager amount of literature citing the attack of nucleophiles upon *O*-acylhydroxylamines. Treatment with potassium iodide liberates iodine (eq 1).[2] Also documented are the reactions of

$$1 + I^- \xrightarrow{H_2O} RCO_2H + [H_2NI] \xrightarrow{I^-,\ H_2O} NH_3 + I_2 \quad (1)$$

O-mesitoylhydroxylamine [*O*-(2,4,6-trimethylbenzoyl)-hydroxylamine] with secondary amines to give hydrazides,[3] and with sulfonamides to give sulfohydrazides.[4] *O*-acylhydroxylamines are known to rearrange to the thermodynamically more stable *N*-acyl compounds, hydroxamic acids. Since Jencks has found[5] that hydroxylamine often is acylated at the oxygen end of the molecule, this rearrangement must be at least partly responsible for the finding that direct acylation gives only the hydroxamic acid as an isolable entity. In order to minimize the isomerization of *O*-acylhydroxylamines, the carbonyl group must be protected by sufficient bulk in its vicinity. Carpino has shown[3] that such stability is imparted by a mesityl group. In the present work the *tert*-butyl group was relied upon to provide similar stability to the product.

Results and Discussion

If hydroxylamine is acylated initially upon its oxygen, and if the *tert*-butyl group provides the necessary stability to the O-acylated material, then treatment of hydroxylamine with pivaloyl chloride (trimethylacetyl chloride) should constitute a simple, direct procedure for the synthesis and isolation of *O*-pivaloylhydroxylamine. Although the *tert*-butyl group does provide some stability toward isomerization (see below), the reaction of pivaloyl chloride with hydroxylamine gave the *N*-pivaloylhydroxylamine (pivalohydroxamic acid) as the only product. Since the direct synthesis appeared inadequate, indirect methods were necessary.

The two procedures[6,7] that we followed to obtain new *O*-acylhydroxylamines both relied on initial addition of a blocking group upon the nitrogen of hydroxylamine, then O-acylation, and finally removal of the nitrogen block. For this study the known compounds *O*-benzoyl- and *O*-mesitoylhydroxylamine were prepared, as well as the new compounds *O*-pivaloyl-, *O*-(4-nitrobenzoyl)-, and *O*-(3-chlorobenzoyl)hydroxylamine. A variety of new compounds classified as intermediates in the synthetic procedures were also synthesized.[8]

We found that both the new and the reported "bulky" *O*-acylhydroxylamines do in fact suffer some decomposition. Solutions of *O*-pivaloylhydroxylamine in chloroform are stable at room temperature for longer than 1 month, but the neat free base does isomerize to pivalohydroxamic acid within hours at room temperature and over Dry Ice within 1 week. We found that *O*-mesitoylhydroxylamine has a tendency to revert to the carboxylic acid upon heating.

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(8) Attempts to carry some of these compounds through to *O*-acylhydroxylamines failed.