acid, m.p. 217–218° dec. (lit.[23] m.p. 178–179°). Characteristic bands in the infrared spectrum (KBr pellet) appeared at 2941, 2597, 1689, 1595, 1418, 1302, 1256, 989, 919, 855 (w), 825 (w), and 761 cm.$^{-1}$.

trans-**3-Chloro-2-methylacrylic acid** (VII) was prepared by the method of Ferris and Marks.[14] The n.m.r. spectrum in CCl_4 showed a quartet olefinic proton at δ 7.48 (J = 1.5 c.p.s.), a doublet methyl at δ 1.98 (J = 1.5 c.p.s.), and a singlet carboxyl proton at δ 12.7 in the ratio 1:3:1. The infrared spectrum showed characteristic peaks at 3077, 2985, 2865, 2632, 2564, 1709, 1631, 1429, 1391 (w), 1332, 1316 (w), 1267, 1175 (w), 1135, 1101 (w), 1013, 926, 866, 790, and 741 cm.$^{-1}$.

Acknowledgment.—The authors wish to thank Mr. C. B. Strow, Jr., who first measured the n.m.r. spectra of methyl *cis*-3-chloroacrylate and methyl *trans*-3-chloroacrylate.

The Base-Catalyzed Oxidation of Organic Sulfides with Molecular Oxygen[1a]

THOMAS J. WALLACE, HARVEY POBINER, FRANK A. BARON, AND ALAN SCHRIESHEIM

Esso Research and Engineering Company, Process Research Division, Exploratory Research Section, Linden, New Jersey

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The base-catalyzed autoxidation of α-sulfido carbanions has been investigated with several benzyl-type sulfides, aralkyl sulfides, and dialkyl sulfides. The observed rates of oxygen consumption were found to be dependent on sulfide structure, base strength, and the solvent. The results obtained suggest that the rate-determining step in these reactions is proton abstraction from the sulfide to form an α-carbanion which reacts rapidly with oxygen to produce both carboxylic and sulfonic acids. An anion-radical mechanism involving the formation of unstable α-hydroperoxide anions is proposed and discussed.

The oxidation of organic sulfides has been studied with a variety of oxidizing agents. Reagents such as nitric acid,[1] potassium permanganate,[1] chromic acid,[2] perbenzoic acid,[3] hydrogen peroxide,[4] manganese dioxide,[5] and periodate[6] produce sulfoxides, sulfones, and mixtures of sulfoxides and sulfones. Elegant work on the reactions of sulfides with hydroperoxides and the effect of hydrocarbon and hydroxylic solvents on such reactions has also been carried out.[7,8]

The radical-induced oxidation of organic sulfides with molecular oxygen in the liquid phase at moderate temperatures (45–75°) is reported to yield a complex mixture of products. The proposed mechanism of oxidation involves introduction of oxygen into the sulfide at the α-carbon atom followed by several secondary and competing reactions.[7] Alkyl and benzyl sulfides are resistant to oxidation by molecular oxygen in the absence of free-radical initiators.[9]

Recently, it has been demonstrated that polar solvents have a marked effect on the anionic oxidation of mercaptans[10–13] and weakly acidic hydrocarbons such as toluene.[14] Studies in the absence of oxygen have demonstrated that various sulfones, sulfoxides, sulfides, and disulfides are decomposed to olefins in the presence of potassium *t*-butoxide and a polar solvent.[15–17] Owing to the unreactivity of aliphatic and benzylic sulfides toward molecular oxygen in the absence of free-radical initiators, the base-catalyzed oxidation of these compounds has been investigated in the polar solvent, hexamethylphosphoramide (HMPA).

Results

The base-catalyzed oxidation of benzyl sulfide with molecular oxygen has been studied under a variety of conditions. In potassium *t*-butoxide–HMPA, benzyl sulfide yielded benzoic acid and stilbene as the reaction products at 23.5 and 80°. When potassium hydroxide was employed as the base in HMPA, the reaction products were benzoic acid and a trace of stilbene. In potassium *t*-butoxide–*t*-butyl alcohol media a low yield of benzoic acid was obtained after 22 hr. of oxidation at 80°. Specific reaction conditions employed and product yields obtained under these conditions have been summarized in Table I. Other suspected intermediates such as benzaldehyde, benzyl alcohol, α-toluenesulfonic acid, and benzyl sulfoxide could not be detected by the analytical methods employed. The rates of oxidation of benzyl sulfide under the above conditions are also included in Table I. Each rate of oxidation was calculated from the moles of oxygen consumed as a function of time during the initial stages of the reaction using the oxidation apparatus described in the Experimental section. When necessary, corrections for solvent oxidation were made. All rate plots obtained were similar to those shown in Figure 1. Initially, the oxidation is rapid and the moles of oxygen consumed are linear with time. As the reactions progressed oxygen consumption decreased as indi-

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[1a] NOTE ADDED IN PROOF.—For a preliminary account, see T. J. Wallace *et al.*, *Chem. Ind.* (London), 945 (1965).

(1) E. O. Beckmann, *J. prakt. Chem.*, **17**, 439 (1878).

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(13) T. J. Wallace, H. Pobiner, and A. Schriesheim, *J. Org. Chem.*, **29**, 888 (1964).

(14) T. J. Wallace, A. Schriesheim, and N. Jacobson, *ibid.*, **29**, 2907 (1964).

(15) T. J. Wallace, H. Pobiner, J. E. Hofmann, and A. Schriesheim, *J. Chem. Soc.*, 1271 (1965).

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TABLE I

RESULTS FROM THE BASE-CATALYZED OXIDATION OF BENZYL SULFIDE

Benzyl sulfide, mole	Base–Solvent (*M*, ml.)	Temp., °C.	Product(s) (% yield)	Time, hr.	$\frac{\text{Mole of } O_2}{\text{mole of } R_2S}$ min.$^{-1}$	Relative rate
0.05	KO-*t*-Bu–HMPA (2, 75)	80	C_6H_5COOH (43.4) $C_6H_5CH{=}CHC_6H_5$ (30.4)	20	0.150	3.57×10^3
0.05	KOH–HMPA[a] (2, 75)	80	C_6H_5COOH (52.5) $C_6H_5CH{=}CHC_6H_5$ (0.1)	24	0.006	1.42×10^2
0.05	KO-*t*-Bu–HMPA (2, 75)	23.5	C_6H_5COOH (27.9) $C_6H_5CH{=}CHC_6H_5$ (8.3)	26	0.058	1.38×10^3
0.5	KO-*t*-Bu-*t*-C_4H_9OH	80	C_6H_5COOH (1.31)	22	4.2×10^{-5}	1.00

[a] This base–solvent system is heterogeneous.

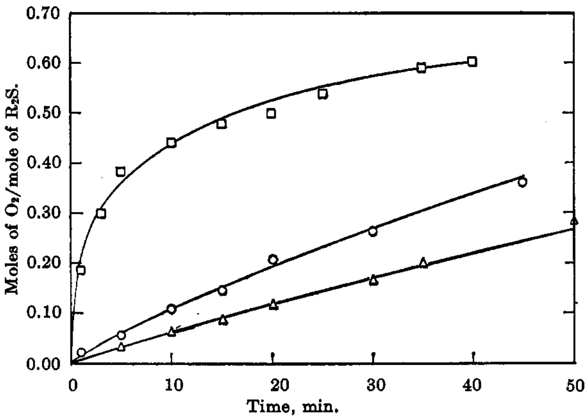


Figure 1.—Typical rate plots for the anionic oxidation of sulfides in HMPA: □, benzyl sulfide in KO-*t*-Bu–HMPA at 23.5°; ○, phenyl methyl sulfide in KO-*t*-Bu–HMPA at 80°; △, benzyl sulfide in KOH–HMPA at 80°.

cated. Each rate of benzyl sulfide oxidation has also been calculated relative to the rate in potassium *t*-butoxide–*t*-butyl alcohol at 80°. As indicated, the rate of oxidation of benzyl sulfide and the yield of benzoic acid is markedly dependent on the solvent. Regardless of the temperature or base employed oxidation in the polar solvent, HMPA, was 10^2 to 10^3 times faster than in potassium *t*-butoxide–*t*-butyl alcohol.

Oxidation of other benzyl-type sulfides was investigated in potassium *t*-butoxide–HMPA at 80°; specific reaction conditions employed, product yields obtained, and individual rates of oxidation are summarized in Table II. Each rate has been calculated relative to that observed for toluene. Benzyl phenyl sulfide and benzyl methyl sulfide yielded benzoic acid plus benzenesulfonic acid and methanesulfonic acid, respectively. Bis(α-phenylethyl) sulfide yielded benzoic acid and a polymeric material. 9-Fluorenyl sulfide was oxidized to fluorenone. All rates of oxidation followed the expected ease of carbanion formation for this series of compounds.

In order to obtain further information on the rate-determining step in these reactions the oxidation of other representative types of sulfides, *i.e.*, those which lack benzylic hydrogens, was investigated in potassium *t*-butoxide–HMPA at 80°, and these results are summarized in Table III. In all reactions the ratio of base to sulfide was 3. *t*-Butyl sulfide and phenyl sulfide did not oxidize under these reaction conditions. Phenyl methyl sulfide was oxidized to benzene sulfonic acid and carbon dioxide, *n*-butyl sulfide yielded butyric acid and 1-butanesulfonic acid, and tetramethylene sulfide yielded succinic acid and small amounts of other unidentified acidic and carbonyl containing compounds. Oxidation of these sulfides was not possible in potassium *t*-butoxide–HMPA at 23.5° and potassium hydroxide–HMPA at 80°. The rates of oxidation for these sulfides are also included in the table and have been calculated relative to the rate obtained for toluene under these conditions. Benzyl sulfide is also included for comparative purposes. This order of reactivity persists in potassium *t*-butoxide–HMPA at 80°: benzyl sulfide > toluene > phenyl methyl sulfide > tetramethylene sulfide > *n*-butyl sulfide >> *t*-butyl sulfide or phenyl sulfide.

Discussion

As previously indicated, in the absence of radical initiators autoxidation of alkyl, aryl, and aralkyl sulfides does not proceed at any measurable rate. Further, oxidation to acidic materials does not occur readily under any conditions. For the purpose of clarity, the present results will be discussed in terms of the rate-determining step, possible mechanisms by which the products can form, and finally, the role of the solvent.

An examination of the data in Table III indicates that the relative ease of sulfide oxidation follows the order benzyl sulfide > phenyl methyl sulfide > *n*-butyl sulfide > tetramethylene sulfide, which is consistent with a rate-determining step involving proton abstraction from the sulfide (eq. 1) to form the most stable

$$RCH_2{-}S{-}CH_2R + B^- \underset{}{\overset{\text{slow}}{\rightleftharpoons}} R\overset{-}{C}H{-}S{-}CH_2R + BH \quad (1)$$

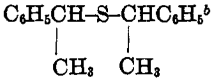
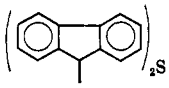
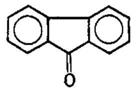
carbanion and subsequent rapid reaction of the α-carbanion with oxygen to yield the product (eq. 2).

$$R\overset{-}{C}H{-}S{-}CH_2R + O_2 \xrightarrow{\text{fast}} \text{products} \quad (2)$$

The same trend persists with the various benzyl-type sulfides listed in Table II. 9-Fluorenyl sulfide, which forms the most stable benzylic carbanion, consumes oxygen about four times as rapidly as bis(α-phenylethyl)

TABLE II

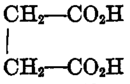
OXIDATION OF OTHER BENZYL SULFIDES[a]

Sulfide (mole)	Product(s)	% yield	Time, hr.	$\frac{\text{Mole of } O_2}{\text{Mole of } R_2S}$ min.$^{-1}$	Rate relative to toluene
$C_6H_5CH_2$–S–C_6H_5	C_6H_5COOH	62	23	0.145	6.30
	$C_6H_5SO_3H$	44			
	C_6H_5SH	32			
$C_6H_5CH_2S$–CH_3 (0.05)	C_6H_5COOH	77	67	0.083	3.61
	CH_3SO_3H	73			
 $C_6H_5CH(CH_3)$–S–$CH(CH_3)C_6H_5$[b] (0.05)	C_6H_5COOH	37	26	0.063	2.74
 (0.0013)		31	68	0.225	9.79
$C_6H_5CH_2$–S–$CH_2C_6H_5$	c	c	c	0.150	6.52
$C_6H_5CH_3$[d] (0.05)	C_6H_5COOH	48	24	0.023	1.00

[a] In 2 M KO-t-Bu–HMPA at 80°. [b] A polymeric material containing carbonyl linkages was also formed. [c] See Table I. [d] The oxidation of toluene under these conditions was initially studied by J. E. Hofmann and co-workers and will be reported on in detail in the near future.

TABLE III

SULFIDE OXIDATIONS[a]

Sulfide (mole)	Product(s) (% yield)	Time, hr.	$\frac{\text{Mole of } O_2}{\text{Mole of } R_2S}$ min^{-1}	Rate relative to toluene
C_6H_5–S–CH_3 (0.05)	$C_6H_5SO_3H$ (36.8) CO_2 (36.0)	46	0.0104	0.45
n-$(C_4H_9)_2S$ (0.05)	n-$C_4H_9SO_3H$ (8.5) n-$C_3H_7CO_2H$ (10.9)	45.5	0.0033	0.15
t-$(C_4H_9)_2S$ (0.05)	None	21	0	0
 (0.05)	 HO_2C–CH_2–CH_2–CO_2H (5–10)[b]	70	0.0056	0.21
$(C_6H_5CH_2)_2S$ (0.05)	c	c	0.150	6.52
$C_6H_5CH_3$ (0.05)	d	d	0.023	1.00

[a] In 2 M KO-t-Bu–HMPA at 80 ± 0.5°. [b] This figure is only approximate owing to the complex nature of the reaction. [c] See Table I. [d] See Table II.

sulfide. The latter would be expected to form the least stable benzylic carbanion. The different rates of oxidation for benzyl sulfide at 80° in HMPA (Table I) also substantiate the proposed rate-determining step since the rate of oxidation in the presence of potassium t-butoxide is 25 times greater than that observed when potassium hydroxide was employed as the base. Aliphatic sulfides, which have less acidic α-carbon–hydrogen bonds, could not be oxidized in the presence of potassium hydroxide.[18] This codependence of the rate of oxidation on sulfide structure and base strength are in reasonable agreement with the rate-determining step proposed.

The unreactivity of t-butyl sulfide and phenyl sulfide toward oxygen is in agreement with the above conclusions and suggests that reaction between the carbanion and oxygen (eq. 2) occurs predominantly at the α-position. This is also consistent with recent studies in these laboratories on base-catalyzed elimination of sulfides in potassium t-butoxide–DMSO.[17] DMSO (ε 46) is considerably more polar than HMPA (ε 34); thus, carbanion reactions should proceed more readily in DMSO. However, n-butyl sulfide and t-butyl sulfide gave only 3.4 and 11.6% yields of their respective β-elimination products, i.e., butenes and isobutylene, after reaction periods of about 100 hr. in DMSO. Thus, the unreactivity of t-butyl sulfide and the failure to observe β-carbanion oxidation products in any appreciable quantity from the other aliphatic sulfides oxidized in HMPA is not surprising. These results do emphasize the importance of d-orbital stabilization by the adjacent divalent sulfur group in regard to the ease of anion formation from the sulfide in question.

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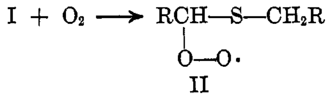
(18) A competing reaction involving β-elimination could also contribute to the results observed. See ref. 16 and 17.

Although the results are consistent with oxygen reacting with an α-sulfide anion, the exact mode by which this occurs and the subsequent steps involved can only be speculated upon based on the major products formed. Since the oxidation of all sulfides proceeded rapidly (see Figure 1 for representative rates), initial oxidation probably involves formation of the α-radical from the anion by electron transfer to oxygen (eq. 3 and 4). The resulting radicals can then react

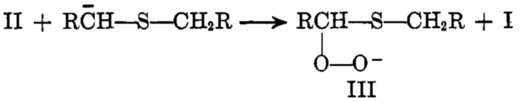
$$\mathrm{R{-}\bar{C}H{-}S{-}CH_2R + O_2 \longrightarrow \underset{I}{R{-}\underset{\cdot}{C}H{-}SCH_2R} + O_2^{\cdot-}} \qquad (3)$$

$$\mathrm{2R\bar{C}H{-}S{-}CH_2R + O_2 \longrightarrow 2R\dot{C}H{-}S{-}CH_2R + O_2^{2-}} \qquad (4)$$

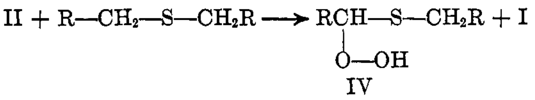
with oxygen by a free-radical chain reaction by one of two paths to form unstable α-peroxide ions. The predominance of step 6 or 7 as chain propagators cannot be resolved. The α-peroxide anion III would be stable under the present conditions in a manner similar to peroxy radicals or hydroperoxides (7) and can decompose in either a stepwise or concerted manner as shown. In either case, the resulting aldehydes and sulfenate ions (V) are highly unstable species[19] and they would be readily oxidized to carboxylic and sulfonic acids.



$$\mathrm{I + O_2 \longrightarrow \underset{\substack{|\\ O{-}O\cdot\\ II}}{RCH}{-}S{-}CH_2R} \qquad (5)$$

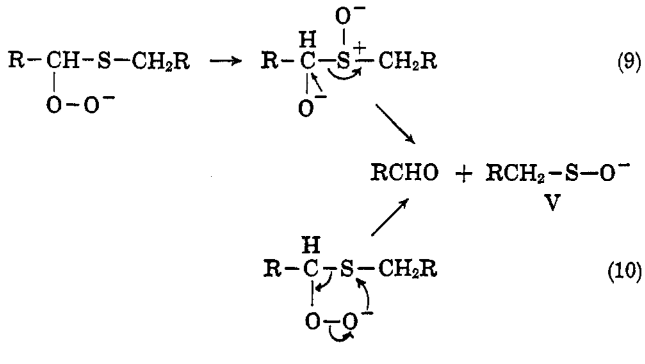


$$\mathrm{II + R\bar{C}H{-}S{-}CH_2R \longrightarrow \underset{\substack{|\\ O{-}O^-\\ III}}{RCH}{-}S{-}CH_2R + I} \qquad (6)$$

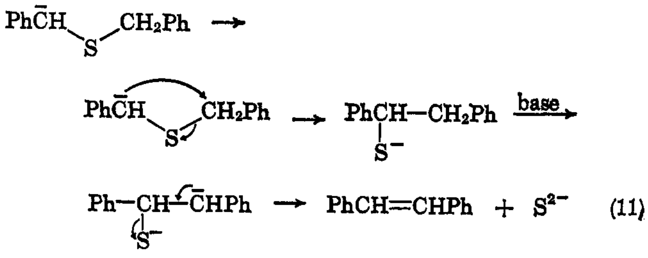


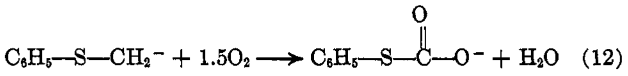
$$\mathrm{II + R{-}CH_2{-}S{-}CH_2R \longrightarrow \underset{\substack{|\\ O{-}OH\\ IV}}{RCH}{-}S{-}CH_2R + I} \qquad (7)$$

$$\mathrm{IV + B^- \longrightarrow III + BH} \qquad (8)$$

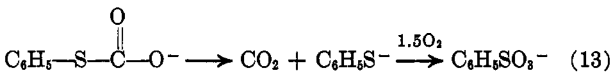


The formation of stilbene from benzyl sulfide is due to a competing reaction involving a carbanion rearrangement and subsequent β-elimination of sulfide ion. Details of this reaction and its generality with various benzyl-type sulfur compounds have recently been described.[15] In the oxidation of phenyl methyl sulfide formation of an unstable carboxylic acid from the initially formed α-carbanion and subsequent rapid decarboxylation and oxidation of the phenyl mercaptide ion to benzenesulfonic acid (eq. 12) is the most reasonable reaction path for the products observed.





$$\mathrm{C_6H_5{-}S{-}CH_2^- + 1.5O_2 \longrightarrow C_6H_5{-}S{-}\overset{\overset{\textstyle O}{\|}}{C}{-}O^- + H_2O} \qquad (12)$$



$$\mathrm{C_6H_5{-}S{-}\overset{\overset{\textstyle O}{\|}}{C}{-}O^- \longrightarrow CO_2 + C_6H_5S^- \xrightarrow{1.5O_2} C_6H_5SO_3^-} \qquad (13)$$

As previously noted, the rate of oxidation decreased rapidly as the reactions progressed. Under purely radical conditions this has been attributed to the formation of sulfoxides and α-keto sulfides which act as inhibitors. Compounds such as sulfoxides and ketones are autoxidized more rapidly than sulfides under the present reaction conditions.[20] Thus, this is not the cause of the observed results. We feel that the decreased rate is due to base consumption by the acidic products formed in the initial stages of the reaction. This would decrease the ease of carbanion formation as the reactions progressed. The formation of water, carbon dioxide, and a sulfate ion would also have this effect. This is also in agreement with our earlier results on the oxidation of mercaptide ions in which it was observed that protic species inhibited the rate of oxidation in aprotic solvents.[11]

Finally, some statements on the effect of solvent in the present systems are apropos. The fact that oxidation in HMPA is 10^2 to 10^3 times faster than in t-C_4H_9OH is similar to our results on the oxidation of mercaptide ions and can be attributed to the fact that the base is deactivated by complexation with the protic species, t-C_4H_9OH. The effect of this on the transition state for RS^- oxidation has been considered in detail previously.[11] The marked solvent effect on the rate is also consistent with anionic intermediates being the active species.

Experimental

Reagents.—Bis(α-phenylethyl) sulfide, benzyl phenyl sulfide, and benzyl methyl sulfide were purchased from Columbia Organic Chemicals Co. Gas chromatographic analysis (F & M flame-ionization apparatus, Model 609, 2-ft. silicone rubber column, 30 wt. %, 0.25 in. in diameter, temperature programmed at 9°/min.) indicated they were at least 98% pure and they were used without further purification. 9-Fluorenyl sulfide was kindly supplied by P. M. G. Bavin of Smith Kline and French Laboratories, Herts, England. Benzyl sulfide (Aldrich Chemical Co.) was purified by recrystallization from a benzene–ethanol mixture (m.p. 48–49°). The following sulfides were purified by distillation through a 16-in. silvered column equipped with a tantalum-wire spiral: n-butyl sulfide (Matheson Coleman and Bell, b.p. 90° at 20 mm.), phenyl methyl sulfide (Evans Chemetics, Inc., b.p. 72° at 15 mm.), t-butyl sulfide (Aldrich Chemical Co., b.p. 70–72° at 70 mm.), tetramethylene sulfide (Matheson Coleman and Bell, b.p. 120–122°), and phenyl sulfide (Matheson Coleman and Bell, b.p. 142° at 0.5 mm.).

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(19) N. Kharasch, "Organic Sulfur Compounds," Vol. I, Pergamon Press Inc., New York, N. Y., 1961, Chapter 32.

(20) Details of these studies will be reported at a future date.

The distilled materials were found to be at least 98% pure when analyzed by gas chromatography. Potassium *t*-butoxide was obtained from the Mine Safety Appliance Co. as the sublimed material and stored continuously in a nitrogen drybox equipped with a moisture conductivity cell.

Solvent Purification.—*t*-Butyl alcohol (commercial grade) and hexamethylphosphoramide (Eastman Organic Chemicals) were purified by distillation over Linde 13X Molecular Sieves to remove any adsorbed water. The sieves had previously been conditioned by calcination at 400° for 4 hr. The solvents were stored continuously in a moisture-free drybox.

Oxidation Experiments.—All base–solvent systems were made up to the appropriate molarity under nitrogen in a heavy-walled Pyrex flask equipped with a side arm. The reactant was added to the reaction flask; the flask was sealed under nitrogen, removed from the drybox, and transferred to the oxidation apparatus. Oxygen was stored in a polyethylene balloon under 1-atm. pressure and passed through a wet-test meter and into a calcium chloride drying tower and finally through a water-cooled Friedrichs condenser and into the reaction flask containing the reaction mixture. The system was flushed with oxygen through the flask side arm, the side arm was sealed, and an equilibrium pressure was established. The reaction was initiated by stirring at 1300 r.p.m. The volume of oxygen consumed as a function of time was determined from the wet-test meter which allows an estimation of the volume of gas consumed to within ±1 cc. With this method, a constant oxygen partial pressure of 1 atm. was maintained above the system. All reactions were allowed to proceed until no apparent oxygen consumption was observed. This oxidation technique was recently described in greater detail.[21]

Quantitative Determination of Products.—Quantitative analysis of all products and starting materials was carried out according to the method of Pobiner, Wallace, and Hofmann.[22] Two procedures were employed. One involves an extraction–ion-exchange–infrared procedure and the other an extraction–ultraviolet procedure. Both methods rely on initial homogenization with water and subsequent extraction with cyclohexane to remove the starting material. The latter removes any spectral interference during the determination of acidic products. The acidic products remain as their acid salts in the aqueous–HMPA phase and are subsequently liberated by acidification with hydrochloric acid. If the acid is aromatic, it can be quantitatively determined directly by ultraviolet spectroscopy from standard curves. If the acidic material is aliphatic or presents a weak ultraviolet absorption it is determined by the ion-exchange–infrared method. This involves treating the aqueous phase with Amberlite LA-2 anion-exchange resin. The free acid is extracted with CCl_4 and quantitatively determined by infrared spectroscopy. These methods were accurate to within 95–99% for all products isolated and identified.

Identification of Products.—The structure of the products reported have been confirmed by various methods following isolation by conventional techniques. These methods are summarized for each product. (a) Benzoic acid was identified by its characteristic infrared and ultraviolet spectra and its melting point (122–123°). (b) Stilbene was confirmed by its characteristic ultraviolet and infrared spectra and its melting point (124°). (c) Benzenesulfonic acid was confirmed by its characteristic ultraviolet and infrared spectra and the preparation of its phenylhydrazinium salt (m.p. 178–180°, lit.[23] m.p. 179°) according to the method of Latimer and Bost.[24] (d) Thiophenol was determined by its characteristic infrared and ultraviolet spectra. Quantitative data were obtained by potentiometric titration with standard silver nitrate solution. (e) Methanesulfonic acid was identified by its infrared spectrum and g.c. comparison to an authentic sample on the 2-ft. silicone rubber column described above. (f) Fluorenone was identified by infrared and ultraviolet comparison to an authentic sample of the ketone. (g) Carbon dioxide was determined by the infrared technique of Pobiner[25] which is both quantitative and qualitative. (h) 1-Butanesulfonic acid was identified by infrared comparison to an authentic sample and the preparation of its anilinium salt (m.p. 159–161°, lit.[26] m.p. 159–162°). (i) Butyric acid was determined by infrared comparison to an authentic sample. (j) Succinic acid was determined by infrared comparison to an authentic sample and its melting point (185°). In the oxidation of *n*-butyl sulfide and tetramethylene sulfide minor amounts of other products were formed but attempts to identify them were not successful. In many instances, attempts to detect sulfoxides and other reasonable intermediates were made. No evidence for the formation of such intermediates was found.

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A Convenient Method for the Preparation of Some Optically Active Allylic Alcohols[1]

DONALD B. DENNEY, ROGER NAPIER, AND ARTHUR CAMMARATA

School of Chemistry, Rutgers, The State University, New Brunswick, New Jersey

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Reaction of cyclic olefins such as cyclopentene, cyclohexene, and cyclooctene with *t*-butyl hydroperoxide and a copper salt of an optically active acid yields allylic esters. The esters can be converted into allylic alcohols by saponification or reduction with lithium aluminum hydride. In some cases optically active allylic alcohols have been obtained. The total asymmetric induction is not high but because of the high rotation of the optically pure materials substantial rotations are found.

The copper ion catalyzed reactions of *t*-alkyl peresters and diacyl peroxides with olefins yields allylically substituted esters.[2] The general mechanism for this reaction involves reduction of the peroxide by cuprous ion to give a radical and an anion from the peroxide. For example, *t*-butyl perbenzoate yields *t*-butoxy radicals, benzoate ion, and cupric ion. In the presence of a good hydrogen donor, hydrogen transfer often occurs and a new radical is generated. In general this radical is oxidized by cupric ion. The product of this oxidation varies according to the structure of the radical.

One of the most valuable applications of this reaction is the allylic substitution process which is exemplified by the reaction of a terminal olefin with *t*-butyl

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[2] For leading references, see J. K. Kochi, *Tetrahedron*, **18**, 482 (1962).