pyrrolidone as solvents gave similar results, except that the latter solution jelled midway during the addition of water and stirring stopped. A 76.5% product yield was obtained nevertheless.

Reaction of $CF_3CCl{=}CCl_2$ with Zinc Dust in Formamide Solution.—The reaction was run as above, using 100 g. (0.5 mole) of 1,1,2-trichloro-3,3,3-trifluoropropene and 200 ml. of dry, redistilled formamide as the reaction solvent. The initial exothermic reaction commenced after about 5 min., low boiling material began to reflux shortly thereafter and condensation of trifluoropropyne and monochlorotrifluoropropene was observed in the trap. The reaction temperature dropped progressively to 60–65°, depending on the rate of addition of trichlorotrifluoropropene. Addition was completed in 1.5 hr. and the reaction mixture was stirred and refluxed for an additional 4 hr.; condensation rate of low boiling products in the trap had markedly decreased by this time. The reaction was worked up by distilling the intermediate boiling products into a Dry Ice–acetone cooled trap at slightly reduced pressure and combining these with the originally trapped product. Distillation of the combined product mixture through a 3-ft. center-rod column (condenser and receivers were cooled to −10°) gave the following fractions: (barometric pressure 702 mm.): $CF_3C{\equiv}CH$ (trap), 10.0 g., 21.3%, b.p −48° to −47°; $CF_3CCl{=}CH_2$,[6] 6.0 g., 9.2%, b.p. 13–15°; midcut, 3.2 g., 4.9%, b.p. 16° −50°, $n^{25}\text{D}$ 1.3511; $CF_3CCl{=}CHCl$ (*trans*-dichloro), 18.5 g., 22.6%, b.p. 51–52°, $n^{25}\text{D}$ 1.3638; mixed (*trans*) $CF_3CCl{=}CClH$ and $CF_3CH{=}CCl_2$, 8.1 g., 9.9%, b.p. 52–58°, $n^{25}\text{D}$ 1.3648; $CF_3CCl{=}CHCl$ (*cis*-dichloro), 5.0 g., 6.1%, b.p. 58°, $n^{25}\text{D}$ 1.3795; and $CF_3CCl{=}CCl_2$, 5.1 g., 5.1% (distillation residue). The material balance amounted to 78.9%. The three dichlorotrifluoropropenes are distinguishable by their proton n.m.r. spectra. 1,1-Dichloro-3,3,3-trifluoropropene, although not isolated from the *trans*-dichloro isomer is recognizable because of the relatively large coupling factor between the C-2 proton and the fluorines on the adjacent CF_3 group giving a quartet with widely separated peaks, $\tau = 3.85$, $J_{HF} = 6.4$. The *trans* isomer, b.p. 51–52°, exhibits a quartet which is well resolved although the peaks are close together, $\tau = 2.92$, $J_{HF} = 1.1$. The *cis* isomer, previously unreported, gives only a single broadened peak, $\tau = 3.35$, $J_{HF} < 0.2$, indicating extremely weak coupling between proton and the CF_3 fluorines. The infrared spectrum for the *cis* isomer shows a C=C absorption at 6.22 μ. The mass spectrum shows parent peaks at mass units of 164, 166, and 168 in the expected ratio of 9.6:6.2:1. Vapor phase chromatography indicated a minimum purity of 95%. The major contaminant was identified as 1,1-dichloro-3,3,3-trifluoropropene on the basis of parent peaks at 164, 166, 168, and the absence of mass 116 (CF_3CCl^+) in its mass spectrum.

Anal. Calcd. for (*cis*) $C_3HCl_2F_3$: C, 21.84; H, 0.61; Cl, 42.99; F, 34.56. Found: C, 21.66; H, 0.81; Cl, 40.65; F, 34.34.

New Catalysts for the Oxidation of Sulfides to Sulfones with Hydrogen Peroxide

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It has recently become of practical economic importance to have a method available for the oxidation of hydroxyl groups containing sulfides to the corresponding sulfones which eliminates secondary degradative oxidation reactions, gives good yields, simplifies product isolation and purification, and conserves reagents. The method described below using tungsten, molybdenum, and vanadium catalysts with hydrogen peroxide in water substantially meets these requirements.

A large variety of methods for oxidation of sulfides to sulfones has been reported in the literature.[2–4] The desired products are obtained in a wide range of yield, purity, ease of experimental manipulation, and economic applicability. The oxidation of sulfides to sulfones is most generally carried out utilizing 30% hydrogen peroxide in glacial acetic acid. The intermediate sulfoxide is formed readily but the sulfone reaction is slower, generally requiring heat. There are several variations in procedure. An excess over the two moles of hydrogen peroxide needed to satisfy the stoichiometry of the reaction is slowly added with cooling. The mixture is allowed to react at room temperature overnight to form the sulfoxide, and then warmed on a steam bath to give the sulfone. Alternatively, the reaction solution is refluxed for at least one half hour after the hydrogen peroxide addition. The hydrogen peroxide can in some cases be added directly to the refluxing glacial acetic acid solution. In preliminary work on the oxidation of hydroxyethyl sulfides, it was often found that acetic acid esters contaminated the sulfone product. Yields often were not so high as subsequently attained by the new method. It also was found in the case of 2-sulfonylethanols that the use of neutralizing bases during product isolation and purification to remove acetic acid residues resulted in at least some catalyzed dehydration to vinyl sulfones. Very water-soluble products requiring neutralization of acetic acid before removal of water for isolation gave products containing a great amount of acetate salts.

Also in preliminary work, it was found that reactions of 2-thioethanols with hydrogen peroxide in water alone without catalyst required reflux in the presence of a large excess of hydrogen peroxide for a long period (0.5–1 day) to give impure sulfones in poor yields.[5]

The described drawbacks in the use of hydrogen peroxide are eliminated by the use as catalysts of inorganic compounds of tungsten, molybdenum, or vanadium in dissolved or colloidal form in aqueous solutions without the use of glacial acetic acid. The metals are in their highest oxidation state. This improvement is particularly useful for the preparation of 2-sulfonylethanols but has much wider applicability.[6–8]

Generally, the subject reactions are carried out at 60–75° by adding 31% hydrogen peroxide (with efficient stirring) to the molybdenum, vanadium, or tungsten catalyst containing aqueous mixture at such a rate that the peroxide concentration is kept low. The very rapid preferential oxidation of sulfides and sulfoxides at low hydrogen peroxide concentration and moderate temperature, in effect, eliminates the loss of

[1] Deceased, June 5, 1960.

[2] C. M. Suter, "Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 660–667.

[3] A. Schoberl and A. Wagner, "Methoden Der Organischen Chemie," Vol. 9, E. Müller, ed., Georg Thieme Verlag, Stuttgart, 1955, pp. 211–215, 227–231.

[4] E. Emmet Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 2, Chemical Publishing Co., Inc., New York, N. Y., 1960, pp. 64–66.

[5] Improved but not best yields can be obtained by the use of small amounts of sequestering agents such as ethylenediaminetetracetic acid which apparently inhibit the secondary oxidation reactions.

[6] H. B. Freyermuth, H. S. Schultz, and S. R. Buc, U. S. Patent 3,005,-852 (October 24, 1961) (assigned to General Aniline and Film Corp.).

[7] H. S. Schultz, S. R. Buc, and H. B. Freyermuth, U. S. Patent 3,006,-962 (October 31, 1961) (assigned to General Aniline and Film Corp.).

[8] S. R. Buc, H. B. Freyermuth, and H. S. Schultz, U. S. Patent 3,006,-963 (October 31, 1961) (assigned to General Aniline and Film Corp.).

hydrogen peroxide due to catalyzed and uncatalyzed decomposition. The conversion to undesired byproducts resulting from secondary oxidation of sensitive groups such as hydroxy groups is almost completely eliminated under these reaction conditions. In most cases, only the stoichiometric amount of hydrogen peroxide is required to complete the conversion from sulfide to sulfone. With good stirring, sulfides of limited water solubility can be oxidized in satisfactory fashion. In case of extreme insolubility of the starting material, water-miscible solvents such as an alkanol or dioxane may be added. The sulfoxide is generally much more water soluble than either the corresponding sulfide or sulfone. This fact can usually be used to judge at what point the reaction is mainly in the sulfoxide stage.

The oxidation of 2-phenylmercaptoethanol and the other compounds cited in the experimental section illustrate the results from some of the variations in experimental conditions. A tungstic acid-catalyzed reaction gave a 94.5% yield of a pure product using an essentially stoichiometric quantity of hydrogen peroxide while an uncatalyzed oxidation under similar conditions gave a 63.5% yield of an impure 2-phenylsulfinylethanol plus at least two products[9] resulting from degradation reactions.

The vanadium catalyst is satisfactory only in the pH range 1–2. During the course of the reaction, permanent and transient color changes are noted which can be interpreted in the light of literature description.[10] The active vanadium catalyst solution as initially prepared is a pale yellow and hazy solution. The color has been ascribed to a vanadyl salt (VO_2^+ or VO^{+3}). Increasing the acidity of a vanadate solution leads to the formation of vanadium pentoxide which has an isoelectric point at about pH 2.2. Vanadium pentoxide is polymeric and only slightly soluble in water. Vanadium pentoxide dissolves in hydrogen peroxide. Continued acidification yields monomeric vanadyl forms. Transient yellow and reddish color changes associated with peroxy vanadyl ions were observed during the course of the hydrogen peroxide addition. In view of these considerations, the haze which begins to form in the reaction solution when it is negative for hydrogen peroxide and which is cleared by hydrogen peroxide addition, is believed to be vanadium pentoxide. These observations suggest that the actual oxidizing agent is a peroxy form of tungstic, vanadic, or molybdic acid which might react much more rapidly with the sulfide or sulfoxide than hydrogen peroxide alone. The peroxy form of the catalyst then would be quickly regenerated by hydrogen peroxide.

Tungsten and molybdenum catalysts are operable over a broader pH range than the vanadium catalyst. The preferred pH is about 5–6, but satisfactory reactions have been carried out at about pH 3–8.

The mechanism of the oxidation of sulfides to sulfoxides and sulfones is apparently ionic and can be pictured in a manner analogous to the electrophilic reaction of per-acids on olefins[11,12] to form glycols and epoxides.

Experimental

2-Phenylmercaptoethanol was prepared by the procedure of Kirner and Richter[13] from sodium thiophenolate and ethylene chlorohydrin and then purified by fractional distillation, b.p. 116° (2 mm.), $n^{24.7}\text{D}$ 1.5900. Literature constants[13] are b.p. 115° (2 mm.) and $n^{20}\text{D}$ 1.5917.

Uncatalyzed Oxidation of 2-Phenylmercaptoethanol.—Sixty-five milliliters of distilled water and 30.8 g. (0.20 mole) of 2-phenylmercaptoethanol were charged into a reaction vessel to give a two layered mixture. The rapidly stirring mixture was heated to 65° and then 31% aqueous hydrogen peroxide was added slowly in several portions from a buret. Intermittent heating was needed to maintain the temperature at 65–70° since the reaction was only moderately exothermic. Starch–iodide paper was used to test when each portion of hydrogen peroxide had completely reacted before adding the next portion. A clear and homogeneous solution resulted after 70 min. when 19 ml. (0.19 mole) of hydrogen peroxide had reacted. This approximates the amount for conversion of sulfide to sulfoxide. Twenty milliliters (0.20 mole) more hydrogen peroxide solution was added within 15 min. After this point, continuous heating was needed to maintain the desired temperature. The mixture was cooled after 280 min. (total) to stop the reaction. The starch–iodide test was still positive. The pH of the cooled solution was 4.0. Sodium bisulfite (0.17 mole) was needed to back titrate the solution to a negative starch–iodide test. Addition of salt caused layer separation. After extraction with benzene, the extract was dried over anhydrous sodium sulfate and fractionally distilled using a short Claisen takeoff head. The main fractions weighing 21.6 g. distilled at 179–207° (1–4 mm.); $n^{25}\text{D}$ 1.5809–1.5848. These fractions were shown by infrared spectra to be essentially the same and to contain neither a sulfide nor a sulfone group. C, H, and S analyses of the fraction with b.p. 186–207° (1–2 mm.) and $n^{25}\text{D}$ 1.5809 gave the following result.

Anal. Calcd. for $C_8H_{10}O_2S$: C, 56.44; H, 5.92; S, 18.81. Found: C, 56.42; H, 6.01; S, 18.91.

The main product is, therefore **2-phenylsulfinylethanol** in 63.5% yield.

Small amounts of higher boiling materials were obtained. The first (2 g.) was a liquid which had a saponification number of 150 mg. potassium hydroxide/g. and an infrared spectrum which indicated the presence of an ester group.

The second higher material was a solid (2.0 g.) that was recrystallized from methanol–water to give 0.25 g. melting at 62–64°. An infrared spectrum showed neither hydroxyl nor carbonyl absorptions but appeared similar to that expected for an aromatic hydrocarbon. A freezing point depression measurement in benzene gave a value for molecular weight of 246. Molecular weight calculated for $C_{14}H_{14}S_2$ is 246.

Anal. Calcd. for $C_{14}H_{14}S_2$: C, 68.24; H, 5.73; S, 26.03. Found: C, 68.18; H, 5.96; S, 25.24.

Literature m.p. values[14,15] reported in the range 65° to 69° confirm this compound to be **1,2-bis(phenylmercapto)ethane.**

Catalyzed Oxidation of 2-Phenylmercaptoethanol.—A *tungstic acid* catalyst solution was prepared by slurrying 0.20 g. (0.00080 mole) of $WO_3 \cdot H_2O$ in 65 ml. of distilled water and then dissolving it by adding a few drops of 50% sodium hydroxide to bring the pH to 11.3. The pH was then reduced to 5.6 with a few drops of glacial acetic acid to give a slightly translucent solution. This was immediately added into a 250-ml. round-bottomed, three-neck flask, followed by 30.8 g. (0.20 mole) of 2-phenylmercaptoethanol. The rapidly stirred heterogeneous mixture was heated to 63°. The heating mantle was removed and 19.9 ml. (0.199 mole) 31% hydrogen peroxide was slowly added dropwise in 23 min. After a total of 27 min. a starch–iodide test was negative. The reaction mixture required continuous cooling to keep the temperature in the 63–67° range. A clear solution resulted after 16.8 ml. of hydrogen peroxide had been added. Dropwise

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[9] One of these products was identified as 1,2-bis(phenylmercapto)-ethane. The occurrence of this product can be explained by hypothesizing a radical reaction initiated by a hydroxyl radical abstracting a hydrogen attached to the hydroxyl carbon. It is reasonable to assume the formation of some hydroxyl radicals by a Fenton reagent type mechanism (C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957) if there is a substantial concentration of hydrogen peroxide present for any length of time, and the main ionic reaction is slow.

[10] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Clarendon Press, Oxford, 1950, pp. 809–815.

[11] D. Swern, *J. Am. Chem. Soc.*, **69**, 1692 (1947).

[12] W. A. Waters, "Organic Chemistry," Vol. 4, H. Gilman, ed., John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 1162–1168.

[13] W. R. Kirner and G. H. Richter, *J. Am. Chem. Soc.*, **51**, 3409 (1929).

[14] W. Ewerlof, *Ber.*, 717 (1871).

[15] E. V. Bell and G. M. Bennet, *J. Chem. Soc.*, 3189 (1928).

hydrogen peroxide addition was resumed until a total of 35 ml. (0.35 mole) had reacted after a total of 63 min. Only intermittent cooling was needed after the sulfoxide state to maintain the temperature at 70–75°. Hydrogen peroxide was then added dropwise very slowly with slight heating to a total of 41 ml. (0.41 mole) over a further 65-min. period while testing with starch–iodide paper to find the point where there is slight excess over the theoretical stoichiometric amount (0.40 mole) of hydrogen peroxide needed to obtain the sulfone. The reaction was stopped when the last milliliter of hydrogen peroxide persisted for 15 min. Two layers formed on cooling, the pH of the water layer being 4.4. A trace of hydrogen peroxide was destroyed with 0.5 g. of sodium bisulfite. The reaction product was isolated and purified by dissolving the organic layer in benzene, extracting the aqueous layer with benzene, drying the combined extracts over anhydrous sodium sulfate and fractionally distilling to give 35.3 g. of **2-phenylsulfonylethanol** in 94.5% yield, b.p. 184° (4 mm.), $n^{24}D$ 1.5555. Literature constants[16] are b.p. 177° (2 mm.), $n^{11}D$ 1.5573. The structure was confirmed by infrared spectrum.

Anal. Calcd. for $C_8H_{10}O_3S$: C, 51.60; H, 5.41; S, 17.22. Found: C, 52.04; H, 5.57; S, 17.22.

A *vanadium* catalyst solution was prepared by dissolving 0.20 g. (0.0017 mole) of sodium orthovanadate (Na_3VO_4) in 65 ml. of distilled water. The pH of 12.5 was lowered to 1.8 by the addition of a few drops of dilute sulfuric acid to give a yellow solution. The catalyst solution was immediately added to a reactor with 30.8 g. (0.20 mole) of 2-phenylmercaptoethanol and heated to 67°. Hydrogen peroxide (31%) was added as before to the rapidly stirring mixture. The solution became clear after 16.2 ml. (0.162 mole) hydrogen peroxide had been added. Each time a drop of hydrogen peroxide entered the reaction solution, a momentary reddish color appeared which tended to persist when the addition rate was too fast. A negative starch–iodide test resulted when a pale yellow color was present. If there was no hydrogen peroxide present for a short time, a haze formed which was cleared by hydrogen peroxide addition. After the halfway point of the reaction had been reached, the temperature maintained itself spontaneously at 68–78° only when a relatively large excess of hydrogen peroxide was present. When a total amount of 39 ml. (0.39 mole) of hydrogen peroxide had been added over a 90-min. period, a negative starch–iodide test was obtained. The reaction was completed by adding 6 cc. more hydrogen peroxide in the course of another 65 min. At the end the solution had a reddish tinge; the pH was 1.3. Sodium bisulfite was added to destroy excess hydrogen peroxide. The The reaction product was isolated as before to give 31.8 g. (85%) of 2-phenylsulfonylethanol, b.p. 177–183° (3 mm.), $n^{25}D$ 1.5564–1.5570. This time employing ammonium metavanadate,[17] a second vanadium-catalyzed reaction was perfored by commencing at a pH of 5.45 and adding 18 ml. (0.18 mole) of hydrogen peroxide over a period of 42 min. A clear solution was obtained after this time which approximates the sulfoxide stage. The second reaction step did not proceed in a satisfactory fashion. The reaction was kept at 73–77° for a total reaction time of 298 min. The final pH was 4.4; no layering occurred on standing. The solution was salted and the product was isolated as before. Infrared spectra and C and H analyses on the distillation fractions showed the product to be a mixture of sulfoxide and sulfone.

Preparation of 3,3′-Sulfonyldipropionic Acid.—The preparation was carried out using a tungstic acid catalyst solution in water as described above by using 3,3′-thiodipropionic acid to react with essentially a stoichiometric amount of 31% hydrogen peroxide at 60° in the course of 2.5 hr. A white precipitate formed during the second half of the peroxide addition. After cooling to room temperature, the white solid was filtered, and dried in a vacuum at 80° to give a 91.3% yield, m.p. 222–224° (lit.,[18] m.p. 223–225°). The pH during the oxidation was approximately 3.

2,2′-Sulfonyldiethanol was prepared from 2,2′-thiodiethanol and hydrogen peroxide using a tungstic acid catalyst, prepared as already described, to give yields of 97–99%. A molybdic acid catalyst could be substituted for the tungstic acid under the same pH and temperature conditions to give similar results.

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[16] A. H. Ford-Moore, R. A. Peters, and R. W. Wakelin, *J. Chem Soc.*, 1754 (1949).

[17] N. V. Sidgwick, *loc. cit.*, p. 811 discloses that ortho-, pyro- or meta-vanadate in solution interconvert into the same form, the form being a function of salt and hydrogen ion concentration.

[18] R. Dahlbom, *Acta Chem. Scand.*, **5**, 690 (1951); *Chem. Abstr.*, **46**, 431 (1952).

Vinyl Derivatives of Metals. XVII. Radical Additions to B-Trivinyl-N-triphenylborazine[1]

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B-Trivinyl-N-triphenylborazine (I) has been shown to undergo radical-initiated copolymerization with other vinyl monomers, although homopolymerization was inhibited by steric interference by the phenyl groups attached to the nitrogen atoms.[3] We report here the addition of a number of reagents to the vinyl groups of I in the presence of radical initiators.

The radical addition of bromotrichloromethane and carbon tetrachloride to the dibutyl ester of vinylboronic acid has been reported.[4] In a similar manner, we were able to effect smooth addition of bromotrichloromethane and of carbon tetrabromide to the vinylborazine I in the presence of benzoyl peroxide.

$$3CX_3Br + [CH_2{=}CHBNC_6H_5]_3 \longrightarrow [CX_3CH_2CHBrBNC_6H_5]_3 \quad (X = \text{Cl and Br})$$

Isolation of the carbon tetrabromide adduct in the pure state was complicated by the tendency of this borazine to form relatively stable benzene and carbon tetrachloride solvates. Carbon tetrachloride and chloroform did not react with I at 100° in the presence of benzoyl peroxide. A reaction between I and carbon tetrachloride did occur at 140° when *t*-butyl peroxide was used as initiator, but no stable, crystalline product could be isolated. Attempted addition of $(CH_3)_3Si\text{-}CH{=}CHCBr_3$ to I in the presence of either peroxide also was unsuccessful.

Benzenethiol addition to I, initiated by benzoyl peroxide, also proceeded readily, giving $[C_6H_5SCH_2\text{-}CH_2BNC_6H_5]_3$. Addition of aliphatic mercaptans to vinylboronate esters had been recorded previously.[4]

The products of the reaction of I with anhydrous hydrogen bromide in the presence of benzoyl peroxide depended on the solvent used. In benzene the expected B-tris(β-bromoethyl)-N-triphenylborazine was obtained in good yield. In diethyl ether, on the other hand, complete rupture of the borazine ring system was observed, the only crystalline product isolated being anilinium bromide. The fate of the boron fragment of the ring was not established. This difference in behavior very likely is a reflection of the different states of HBr in these solvents, HBr being present essentially in the molecular form in benzene and as the strongly acidic oxonium salt in ether. The structure of the HBr-I adduct was shown to be $[BrCH_2CH_2BNC_6H_5]_3$. Its n.m.r. spectrum in the aliphatic region consisted of two triplets at 1.20 and 2.76 p.p.m. downfield from tetramethylsilane,[5] which is consistent with the —CH_2CH_2—

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[1] Part XVI: D. Seyferth and M. Takamizawa, *Inorg. Chem.*, to be published; also Part IV of the series "Borazine Derivatives."

[2] (a) Alfred P. Sloan Research Fellow; (b) Fellow of the M.I.T. School for Advanced Study, 1961–1962; on leave from the Shin-Etsu Chemical Industry Company, Ltd., Tokyo.

[3] J. Pellon, W. G. Deichert, and W. M. Thomas, *J. Polymer Sci.*, **55**, 153 (1961).

[4] D. S. Matteson, *J. Am. Chem. Soc.*, **82**, 4228 (1960).

[5] The n.m.r. spectrum was recorded in carbon tetrachloride solution using a Varian Associates A60 n.m.r. spectrometer.