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An Acid-catalyzed Cleavage of Sulfoxides[1]

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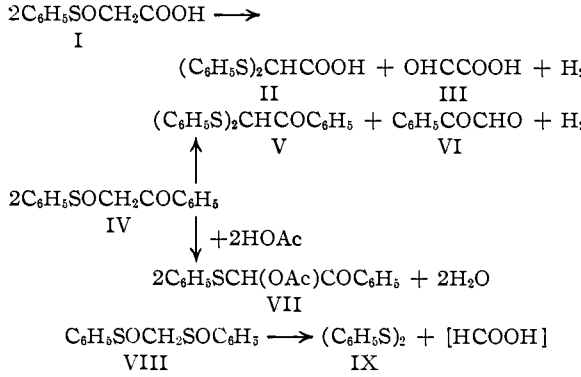
RECEIVED MARCH 27, 1961

The synthesis and characterization of a series of R-substituted mercapto-, sulfinyl-, sulfonyl-, bis-(mercapto)-acetic acids (where R = C_6H_5-, p-$CH_3C_6H_4$-, m-$CH_3C_6H_4$-, p-$(CH_3)_3CC_6H_4$-, p-ClC_6H_4-, p-$NO_2C_6H_4$-) and some related compounds are reported. The acid-catalyzed oxidation–reduction cleavage of α-sulfinyl acids, α-sulfinyl ketones and β-disulfoxides has been investigated and a mechanism is proposed.

Introduction

Preparatory to a study of their chelating tendencies, we have recently prepared a variety of bifunctional sulfoxides and sulfones. During the course of these preparations, usually carried out in acetic acid solution, we observed that oxidation of the appropriate thioethers led to anomalous products if the reaction mixtures were not kept cold. These anomalous products resulted because of the quite general instability of α-sulfinyl acids, α-sulfinyl ketones and β-disulfoxides in acid solution. In each case, an α-carbon atom was oxidized and sulfur reduced. Thus, phenylsulfinylacetic acid (I) gives bis-(phenylmercapto)-acetic acid (II) and glyoxylic acid (III); ω-phenylsulfinylacetophenone (IV) gives bis-(ω-phenylmercapto)-acetophenone (V) and phenylglyoxal (VI) or ω-phenylmercapto-(acetoxy)-acetophenone (VII); bis-(phenylsulfinyl)-methane (VIII) gives diphenyl disulfide and, presumably, formic acid.



Such reactions are by no means unknown. Since the first report by Smythe[2] of the ready cleavage of dibenzyl sulfoxide by dry hydrogen chloride, there have been reports of similar instabilities of sulfoxides in the presence of acids, varying from dilute mineral acids, through dry hydrogen halides, to mercuric chloride. Thus Pummerer,[3] Hilditch,[4] Larsson and Jönsson,[5] Hellström and Lauritzson[6] and Tananger[7] report instances of the disproportionation of various α-sulfinyl acids and esters under acidic conditions. Holmberg[8] reports similar reactions for a number of α-sulfinyl ketones. Among the more indirect evidence may be mentioned the work of Fitger,[9] Schöberl,[10] Barnett,[11] Hünig and Boes,[12] Bordwell and Pitt,[13] and Sosnovsky.[14] From these investigations, and those to be reported in the Experimental, the following generalizations may be made: (a) α-Sulfinyl acids, α-sulfinyl esters, α-sulfinyl ketones and β-disulfoxides disproportionate under a wide variety of acidic conditions to give products in which the sulfur atom has been reduced and the α-carbon atom oxidized. The oxidation–reduction products are formed in high yield.

(b) Acid catalysis is a necessary factor, since the sulfoxides may be recrystallized from aprotic solvents and ethyl phenylsulfinylacetate may even be distilled without decomposition.[3]

(c) For the disproportionation to occur at all, the carbon atom alpha to the sulfoxide must bear a hydrogen atom.[4,5,7]

(d) When the α-carbon also bears a strongly electron-withdrawing group, the reaction is greatly facilitated.[2–14] However, dibenzyl sulfoxide,[2] diisoamyl sulfoxide[4] and methyl 2-methylallyl sulfoxide[15] are reported to disproportionate readily. Aryl β-acylvinylsulfoxides appear to be stable.[16]

(e) In the arylsulfinylacetic acid series, the presence of a p-CH_3– group promotes the disproportionation whereas a p-NO_2– group retards it.[17]

(f) By means of acetic anhydride,[3] dry hydrogen halides,[3] thionyl chloride[13] or acetic acid, it is possible to convert some sulfoxides into esters of α-hydroxythioethers. Recently, Sosnovsky has reported[14] that peresters convert thioethers to esters of α-hydroxythioethers, a reaction which almost certainly goes through the sulfoxide. It is not yet known whether these compounds are formed intramolecularly or, more reasonably, whether they are formed by initial cleavage to mercaptan and the appropriate carbonyl compound, followed by hemithioacetal formation and subsequent esterification.

(1) Taken in part from the thesis submitted by William J. Kenney in partial fulfillment of the requirements of the M.S. Degree.

(2) J. A. Smythe, *J. Chem. Soc.*, **95**, 349 (1909).

(3) R. Pummerer, *Ber.*, **42**, 2282 (1909); R. Pummerer, *ibid.*, **43**, 1401 (1910).

(4) T. P. Hilditch, *ibid.*, **44**, 3583 (1911).

(5) E. Larsson and K. Jönsson, *ibid.*, **67B**, 1263 (1934).

(6) N. Hellström and T. Lauritzson, *ibid.*, **69B**, 2003 (1936).

(7) A. Tananger, *Arkiv. Kemi Mineral. Geol.*, **24A**, 10 (1947).

(8) B. Holmberg, *J. prakt. Chem.*, **141**, 93 (1934); B. Holmberg, *Arkiv. Kemi Mineral. Geol.*, **12A**, 28 (1938); **14A**, 9 (1940); **15A**, 20 (1942).

(9) P. Fitger, *Ber.*, **54**, 2952 (1921).

(10) A. Schöberl, *Ann.*, **507**, 111 (1933); A. Schöberl and H. Eck, *ibid.*, **522**, 97 (1936).

(11) J. Barnett, *J. Chem. Soc.*, 5 (1944).

(12) S. Hünig and O. Boes, *Ann.*, **579**, 23 (1953).

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

(14) G. Sosnovsky, *J. Org. Chem.*, **26**, 281 (1961).

(15) H. P. Koch, *J. Chem. Soc.*, 2892 (1950).

(16) N. K. Kochetkov and V. N. Vinogradova, *J. Gen. Chem. U.S.S.R.*, **27**, 2785 (1957).

(17) J. A. Walsh and D. A. Davenport, to be published.

TABLE I

	R	Yield, %	Recrystn. solvent	M.p., °C. Exptl.	M.p., °C. Lit.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Other, % Calcd.	Other, % Found	Neut. equiv. Calcd.	Neut. equiv. Found
				$RSH + ClCH_2CO_2H \xrightarrow{NaOH} RSCH_2CO_2H + NaCl + H_2O$									
X	C_6H_5-	100	H_2O	63.5	63.5[a]	...	...	..	..	....	....	168.2	168
XI	p-$CH_3C_6H_4$-	96	95% EtOH	88.5–90	.....	59.31	59.29	5.53	5.43	....	....	182.2	180
XII	m-$CH_3C_6H_4$-	90	95% EtOH	67–68	.....	59.31	59.57	5.53	5.70	....	....	182.2	183
XIII	p-t-BuC_6H_4-	84	Petr. eth.	58.5–59.0	.....	64.26	64.06	7.19	7.43	....	....	224.3	224
XIV	p-ClC_6H_4-	87	Petr. eth.	104–105	105[b]	...	...	..	..	....	....	202.7	204
XV	p-$O_2NC_6H_4$-	80	H_2O	149–151	156.7[c]	...	...	..	..	....	....	...	..
XVI	C_2H_5-	75	Distilled	Liquid	118[d,m]	...	...	..	..	....	....	120.2	119
				$RSCH_2CO_2H + H_2O_2 \xrightarrow[\text{cold}]{\text{acetic acid}} RS{-}CH_2CO_2H + H_2O$								
I	C_6H_5-	82	EtOAc–C_6H_6 (1:3)	112–113	112.5–113[a]	... 54.55	... 54.98	.. 5.09	.. 5.05	....	....	184.2 198.2	185 197
XVII	p-$CH_3C_6H_4$-	53	HOAc	105–106	.....	54.55	54.57	5.09	5.29	....	....	198.2	199
XVIII	m-$CH_3C_6H_4$-	59	HOAc	90–91	.....	59.98	60.00	6.71	6.99	....	....	240.3	238
XIX	p-t-BuC_6H_4-	79	Et_2O	125–126	.....	43.93	44.14	3.23	3.16	16.21[k]	16.05[k]	218.7	220
XX	p-ClC_6H_4-	54	Me_2CO	127.5–128	140–141[e]	41.93	42.06	3.08	3.36	6.11[l]	6.05[l]	229.2	232
XXI	p-$O_2NC_6H_4$-	74	Aq. Me_2CO	177.0–177.5									
				$RSCH_2CO_2H + 2H_2O_2 \xrightarrow{\text{acetic acid}} RS(=O)_2{-}CH_2CO_2H + 2H_2O$									
XXII	C_6H_5-	62	H_2O	111.5–112.5	110–110.5[a]	...	...	..	..	....	....	200.2	200
XXIII	p-$CH_3C_6H_4$-	98	H_2O	114–115	.....	50.42	49.99	4.69	4.87	....	....	214.4	211
XXIV	p-t-BuC_6H_4-	92	C_6H_6	128–128.5	.....	56.24	56.48	6.29	6.48	....	....	256.3	255
XXV	p-ClC_6H_4-	45	H_2O	120.5–121.5	122[f]	...	...	..	..	....	....	234.7	237
XXVI	p-$O_2NC_6H_4$-	44	Aq. Me_2CO	171–172	167[g]	...	...	..	..	....	....	245.2	251
				$2RSCH_2CO_2H \xrightarrow[\Delta]{\text{acid}} (RS)_2CHCO_2H + OHCCO_2H + H_2O$									
II	C_6H_5-	90	Aq. HOAc	101–103	104–106[h]	...	...	..	..	....	....	276.3	276
XXVII	p-$CH_3C_6H_4$-	82	Aq. HOAc	125–126	.....	63.13	62.83	5.38	5.25	....	....	304.4	303
XXVIII	p-t-BuC_6H_4-	87	Aq. HOc	121.5–122	.....	68.00	68.27	7.26	7.44	....	....	388.6	388
XXIX	p-ClC_6H_4-	76	HOAc	180.5–181	.....	48.69	48.58	2.92	3.14	20.53[k]	20.23[k]	345.3	341
				$(RS)_2CHCO_2H + 4H_2O_2 \xrightarrow[\Delta]{\text{acetic acid}} (RS)_2CH_2(=O)_2 + 4H_2O + CO_2$									
XXX	C_6H_5-	81	HOAc	119–120	118–119[i]	...	...	..	..	....	....	...	..
XXXI	p-$CH_3C_6H_4$-	81	HOAc	134–135	135[j]	...	...	..	..	....	....	...	..
XXXII	m-$CH_3C_6H_4$-	..	HOAc	89–90	.....	55.56	55.81	4.97	4.85	....	....	...	..
XXXIII	p-t-BuC_6H_4-	95	Aq. EtOH	159.5–160	.....	61.71	61.64	7.07	7.04	....	....	...	..
XXXIV	p-ClC_6H_4-	..	Aq. EtOH	190.5–191	.....	42.73	42.98	2.76	2.78	19.41[k]	19.35[k]	...	..
XXXV	C_2H_5-	>85	Aq. HOAc	102–103	104[d]	...	...	..	..	....	....	...	..

[a] H. D. Crockford and T. B. Douglas, *J. Am. Chem. Soc.*, **56**, 1472 (1934). [b] H. Gilman and F. J. Webb, *ibid.*, **71**, 4062 (1949). [c] O. Behaghel, *J. prakt. Chem.*, 114, 287 (1926). [d] H. Bohme, *Ber.*, **69B**, 1610 (1936). [e] K. Fries and G. Schürmann, *ibid.*, **47**, 1200 (1914). [f] J. Troeger and C. Budde, *J. prakt. Chem.*, [2] **66**, 146 (1902). [g] A. V. Sunthankar, B. D, Tilak and K. Venkataraman, *Proc. Indian Acad. Sci.*, **38A**, 23 (1953). [h] R. Otto and J. Troger, *Ber.*, **25**, 3426 (1892). [i] R. L. Shriner, H. C. Struck and W. J. Jorison, *J. Am. Chem. Soc.*, **52**, 2060 (1930). [j] E. Fromm, A. Foster and B. v. Scherschwitzki, *Ann.*, **394**, 348 (1912). [k] Chlorine, %. [l] Nitrogen, %. [m] B.p. (11 mm.).

Mechanisms for these reactions and their possible relationship to the recently much-investigated reactions of dimethyl sulfoxide with alkyl halides[18] and tosylates[19] will be suggested in the Discussion.

Experimental

Most of the experimental data[20a,b] are summarized in Table I. The general methods were as follows.

Preparation of Mercaptoacetic Acids.—To 0.5 mole of purified thiol (all commercial products except p-NO_2-C_6H_4SH which was made by the method of Price and Stacy[21]) in 1.05 moles of aqueous sodium hydroxide was added 0.55 mole of chloroacetic acid. After refluxing for 2 hours and subsequent acidification, the acids were filtered and recrystallized from the solvents specified in Table I. Ethylmercaptoacetic acid (XVI) was isolated by continuous extraction of its aqueous solution with ether followed by distillation under reduced pressure.

Preparation of Sulfinylacetic Acids.—Equimolecular amounts of 30% by weight hydrogen peroxide and mercapto-acid were mixed in redistilled acetic acid, the temperature being kept at 0° for several hours. On concentration, the sulfinylacetic acids crystallized. They were recrystallized with the minimum amount of heating.

Preparation of Sulfonylacetic Acids.—One mole of mercaptoacetic acid in redistilled acetic acid was oxidized with slightly more than two moles of 30% by weight hydrogen peroxide, the temperature being kept at 0° for several hours and then allowed to warm to room temperature. In the case of the p-Cl- and p-NO_2- compounds, the reaction mixture was then heated at 70° for 1 hour. Removal of the solvent by distillation gave the crude acid. The rather poor yields for some of these preparations were caused by the difficulties encountered in purifying the crude material, formed in close to quantitative amounts.

(18) N. Kornblum, J. W. Powers, G. J. Anderson, W. J. Jones, O. Levand and W. M. Weaver, *J. Am. Chem. Soc.*, **79**, 6562 (1957); N. Kornblum, W. J. Jones and G. J. Anderson, *ibid.*, **81**, 4113 (1959); I. M. Hunsberger and J. M. Tien, *Chemistry & Industry*, 88 (1959).

(19) N. Kornblum, W. J. Jones and G. J. Anderson, *J. Am. Chem. Soc.*, **81**, 4113 (1959); H. R. Nace and J. J. Monagle, *J. Org. Chem.*, **24**, 1792 (1959); M. M. Baizer, *ibid.*, **25**, 670 (1960).

(20) (a) All melting points are uncorrected. All equivalent weights were determined in water (or acetone–water) to a phenolphthalein endpoint. All yields are of pure materials. (b) Microanalyses are by Dr. C. S. Yeh and Mrs. I. Groten of this department and by Galbraith Microanalytical Laboratories, Knoxville, Tenn. The infrared spectra are by Mrs. W. Dilling.

(21) C. C. Price and G. W. Stacy, *J. Am. Chem. Soc.*, **68**, 498 (1946).

The Cleavage of Sulfinylacetic Acids.—The sulfinylacetic acids were dissolved in redistilled acetic acid and refluxed overnight. With the *p*-Cl- and *p*-NO_2- compounds, warming with 6 *N* sulfuric acid was found to be more effective than refluxing with acetic acid. On removal of the solvent, the products were washed with water and recrystallized. The glyoxylic acid in the wash water was identified as the 2,4-dinitrophenylhydrazone and also as the semicarbazone. By using an aliquot and weighing the derivative, the yields of glyoxylic acid were shown to be considerably higher than those reported in Table I, which are based on the amount of purified bis-(mercapto)-acetic acid obtained. In the case of the *p*-NO_2- compound, no bis-(*p*-nitrophenylmercapto)-acetic acid was obtained but instead the corresponding disulfide (m.p. 181°) was isolated in moderate yield. The cleavage product of *m*-tolylsulfinylacetic acid (XVIII), presumably the expected bis-(*m*-tolylmercapto)-acetic acid, was obtained only as an intractable oil. On oxidation with excess hydrogen peroxide in acetic acid solution, this oil yielded the expected bis-(*m*-tolylsulfonyl)-methane (XXXII).

Preparation of Bis-(sulfonyl)-methanes.—The bis-(mercapto)-acetic acids obtained from the oxidation-reduction cleavage of the phenylsulfinylacetic acids were refluxed in redistilled acetic acid with an excess of 30% by weight of hydrogen peroxide. After several hours, the solvent was removed and the crude product washed with water. Recrystallization from the solvent specified gave the yields cited in Table I. The yield reported for bis-(ethylsulfonyl)-methane (XXXV) is the over-all one from ethylmercaptoacetic acid (XVI) since the intermediate compounds were not isolated.

Preparation of ω-Phenylmercaptoacetophenone.—ω-Phenylmercaptoacetophenone was prepared by the method of Delisle,[22] equimolecular amounts of sodium ethoxide, thiophenol and ω-bromoacetophenone being mixed in ice-cold absolute ethanol. After 2 hours the reaction mixture was allowed to stand at room temperature for 12 hours. The solvent then was removed *in vacuo* and the residue washed free of sodium bromide with cold water. Recrystallization from ethanol gave a 61% yield of beautifully formed, white needles, m.p. 53–54° (lit.[22] 52–53°); infrared absorption (CCl_4): 1670, 1264 cm.$^{-1}$; 2,4-dinitrophenylhydrazone recrystallized from (1:1) ethanol-ethyl acetate, as brilliant, brick-red needles, m.p. 150.0–150.5°.

Anal. Calcd. for $C_{20}H_{16}N_4O_4S$: C, 58.82; H, 3.95; N, 13.72. Found: C, 58.88; H, 3.62; N, 13.49.

If the above reaction mixture is refluxed, then bis-(ω-phenylmercapto)-acetophenone (V) is formed. Recrystallization from glacial acetic acid gives m.p. 98.5–100° (lit.[23] 99–100°); infrared absorption ($CHCl_3$): 1688, 1270 cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{16}OS_2$: C, 71.40; H, 4.79; S, 19.06. Found: C, 71.30; H, 4.81; S, 19.25.

Preparation of Bis-(ω-phenylsulfonyl)-acetophenone.—Oxidation of bis-(ω-phenylmercapto)-acetophenone (V) in glacial acetic acid with excess 30% by weight hydrogen peroxide gave a 61% yield of bis-(ω-phenylsulfonyl)-acetophenone. Recrystallization from acetic acid gave m.p. 182–183°; infrared absorption (Nujol): 1688, 1333, 1275, 1178, 1155, 849, 755 cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{16}O_5S_2$: C, 59.98; H, 4.03; S, 16.02; neut. equiv., 400.4. Found: C, 59.71; H, 4.23; S, 16.13; neut. equiv., 401.

Preparation of ω-Phenylsulfinylacetophenone (IV).—ω-Phenylmercaptoacetophenone (0.04 mole) was dissolved in 50 ml. of acetic acid, cooled to 0° and oxidized with an exact equivalent of 30% by weight hydrogen peroxide, added dropwise. After standing at room temperature for 12 hours, the solvent was removed under reduced pressure to yield a yellow oil. Effecting crystallization of this oil proved difficult. All traces of acetic acid had to be removed and the ethereal extract very thoroughly dried with anhydrous sodium sulfate before the sulfoxide precipitated. Trituration of the sulfoxide with water, filtration and vacuum drying over phosphorus pentoxide gave a 60% yield of a white powder, m.p. 76–77°; infrared absorption ($CHCl_3$): 1685, 1276, 1047 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{12}O_2S$: C, 68.83; H, 4.95. Found: C, 68.73; H, 5.00.

Oxidation of this sulfoxide with an excess of 30% by weight hydrogen peroxide in cold acetic acid, followed by removal of the solvent and recrystallization from 95% ethanol, gave a 53% yield of ω-phenylsulfonylacetophenone, m.p. 92–93°. Mixed melting point with an independently synthesized sample[24] showed no depression; infrared absorption ($CHCl_3$): 1690, 1328, 1274, 1157 cm.$^{-1}$.

Preparation of ω-Phenylmercapto-(acetoxy)-acetophenone (VII).—Refluxing of ω-phenylsulfinylacetophenone (IV) in glacial acetic acid for 11 hours, removing the solvent under reduced pressure, extraction from aqueous suspension with ether, evaporation of the ether and subsequent recrystallization from isopropyl alcohol and drying *in vacuo* gave a 45% yield of fluffy, white needles, m.p. 65.0–66.0°; infrared absorption (CCl_4): 1770, 1715, 1370, 1225, 1050 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{14}O_3S$: C, 67.10; H, 4.93; S, 11.20. Found: C, 67.00; H, 4.84; S, 11.18.

A 22% yield of bis-(ω-phenylmercapto)-acetophenone (V) also was isolated from this reaction of the sulfoxide.

Preparation of ω-Phenylsulfonyl-(acetoxy)-acetophenone.—ω-Phenylmercapto-(acetoxy)-acetophenone (VII) was dissolved in glacial acetic acid and oxidized with excess 30% by weight hydrogen peroxide at room temperature. Removal of the solvent under reduced pressure and then recrystallization from isopropyl alcohol gave a 48% yield of ω-phenylsulfonyl-(acetoxy)-acetophenone, as white needles, m.p. 93.0–94.5°; infrared absorption ($CHCl_3$): 1775, 1700, 1332, 1187, 1072 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{14}O_5S$: C, 60.36; H, 4.43; S, 10.06. Found: C, 60.31; H, 4.52; S, 10.10.

Acid-catalyzed Cleavage of Bis-(phenylsulfinyl)-methane (VIII).—Bis-(phenylsulfinyl)-methane (VIII) was prepared by the method of Shriner and Struck.[25] On refluxing in acetic acid for 48 hours (or heating with 6 *N* sulfuric acid for 24 hours) an 80% (or 77%) yield of diphenyl disulfide, recrystallized from acetic acid, m.p. 58.0–58.5°, was obtained. The identity of this compound was verified by its infrared absorption spectrum and mixed melting point. The other product, presumably formic acid, was not isolated.

Formation of Fe(III) and Cr(III) Chelates.—Chelates (or organic-solvent soluble salts) of phenylmercaptoacetic acid (X), phenylsulfinylacetic acid (I) and phenylsulfonylacetic acid (XXII) with both Fe(III) and Cr(III) were formed by the gradual addition of one mole of base to an aqueous solution of the components in the mole ratio of 3:1. The products were all singularly unattractive compounds which were difficult to obtain in an analytically pure form. Typical was the compound, $C_{24}H_{21}O_{12}S_2Fe$, which was formed by gradual addition of sodium hydroxide to an aqueous solution of phenylsulfonylacetic acid and ferric chloride. The compound was ruby-red, soluble in organic solvents and had no well-defined melting point.

Anal. Calcd. for $C_{24}H_{21}O_{12}S_2Fe$: C, 44.13; H, 3.24. Found: C, 44.29; H, 3.50.

In the case of the chromium compounds, it was necessary to heat the solution in order to cause reaction to occur.

When anhydrous ferric chloride was added to a solution of sodium ethoxide and bis-(phenylsulfinyl)-methane (VIII) [or bis-(phenylsulfonyl)-methane] in absolute ethanol, the precipitation of sodium chloride indicated that reaction had occurred but no pure compound could be isolated.

We do not intend to study these chelate compounds further.

Discussion

The products in these disproportionations can be rationalized if we assume the intermediate formation of mercaptan and the corresponding α-carbonyl compound. Then, we can have acid-catalyzed hemithioacetal (or hemithioketal) formation, followed by two competing reactions: with

(22) A. Delisle, *Ber.*, **22**, 309 (1899).

(23) F. Weygand and H. J. Bestmann, *Z. Naturforsch.*, **10b**, 296 (1955).

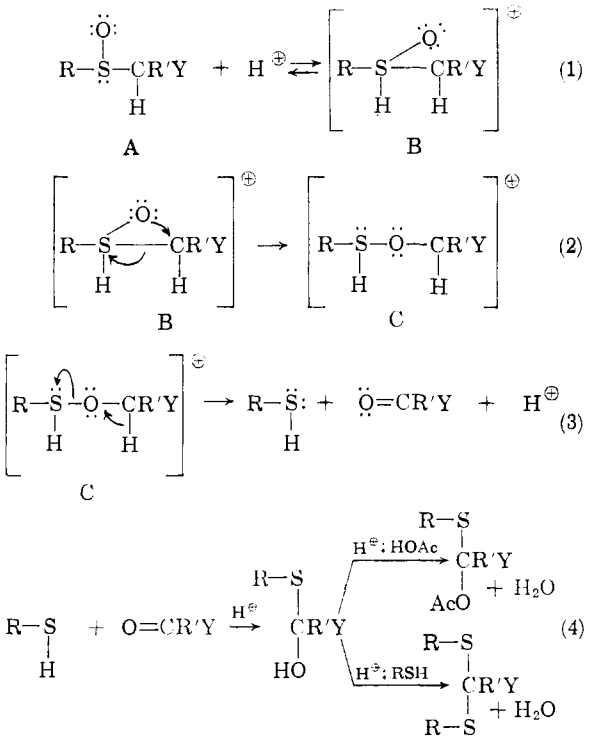
(24) R. H. Knospe, Ph.D. Thesis, Purdue University, January, 1955, p. 49.

(25) R. L. Shriner and H. C. Struck, *J. Am. Chem. Soc.*, **52**, 2060 (1930).

mercaptan to give the thioacetal (or thioketal) or with solvent acetic acid to give the α-acetate of the hemithioacetal (or hemithioketal). It is known that such reactions occur readily under our experimental conditions and their mechanisms are well understood.

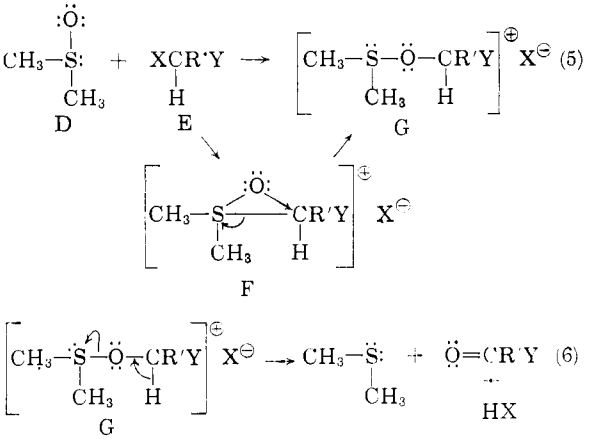
Our problem, therefore, reduces to the suggestion of a suitable mechanism for formation of mercaptan and the corresponding α-carbonyl compound from α-sulfinyl acids, α-sulfinyl esters, α-sulfinyl ketones and β-disulfoxides.

The general nature of the reaction, the acid catalysis, the effect of p-substitution on the rate of disproportionation in the arylsulfinylacetic acid series,[17] and the absence of iodine formation when the reaction is catalyzed by hydriodic acid,[3] all point to a heterolytic mechanism. Simple cleavage of the carbon–sulfur bond (with or without acid-catalysis) seems unlikely in view of the contrasting stability of the corresponding mercapto and sulfonyl derivatives. The following mechanism would seem to account in a reasonable manner for the experimental facts.



In A, where Y is any electron-withdrawing group, the oxygen atom is probably more basic than the sulfur atom, but the protonation of oxygen is barren of possibilities, while protonation of sulfur could lead to C *via* an SNi displacement reaction. This suggests a reason for the marked difference in stability of the sulfinyl as opposed to the mercapto and sulfonyl compounds. In the sulfoxides, there is a sulfur atom susceptible to protonation and an oxygen atom which might effect a nucleophilic displacement; in the sulfones, there is only a less basic[26] oxygen atom to displace on the carbon; in the mercapto compounds there is a sulfur to protonate but no oxygen atom to displace on the carbon. The stability of protonated sulfenic esters, of which C is a rather specialized example, is hard to gauge. Sulfenic esters are known and some of their reactions with acids have been summarized.[27] They are all, however, of the non-activated type (Y = H or R″) and their reactions may not necessarily parallel those of the present investigation. We intend to attempt the preparation of some activated sulfenic esters and to study their reactions with acids.

In the above scheme, it is conceivable that steps 2 and 3 blend into a synchronous process. Our belief that such is not the case is supported, in part, by an obvious parallel between this disproportionation reaction and that mentioned above between dimethyl sulfoxide and various alkyl halides and tosylates.



Compounds of type F and G are both known,[28] but it has not yet been established which is the primary product in the oxidation of activated alkyl halides E, to give dimethyl sulfide and the corresponding carbonyl compound. It is certainly suggestive that the halides which undergo oxidation most readily—benzylic bromides, phenacyl bromides and α-bromo acids and esters—are precisely those which are known to give cleavage in the analogous sulfinyl compounds.

(26) C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 2705 (1956); R. J. Gillespie and R. C. Passerini, *ibid.*, 3850 (1956); R. G. Laughlin, *J. Org. Chem.*, **25**, 864 (1960).

(27) N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Revs.*, **39**, 328 (1946).

(28) R. Kuhn, *Angew. Chem.*, **17**, 570 (1957); R. Kuhn and H. Trischmann, *Ann.*, **611**, 117 (1958); S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958).