A Cyclic Sulfinate Ester. Preparation and Reactions of 1,2-Benzoxathian 2-Oxide

EDWIN N. GIVENS AND LYLE A. HAMILTON

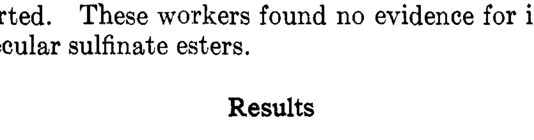
Research Department, Mobil Oil Corporation, Paulsboro, New Jersey

Received March 21, 1967

A cyclic sulfinate ester, 1,2-benzoxathian 2-oxide, has been prepared by chlorination of β-(*o*-hydroxyphenyl)-ethyl mercaptan. The structure was confirmed by several analytical methods. Peroxide oxidation to the known sultone, 1,2-benzoxathian 2,2-dioxide, agrees with the proposed structure. The instability of the product was evident from the necessary refrigerated conditions for storage. The importance of hydroxylic solvent is discussed. Acetic acid is a suitable solvent for the reaction, but more nucleophilic hydroxylic solvents such as methyl or *t*-butyl alcohol cause further oxidation to sultone products. New chlorinated sultones in the benzoxathian system were prepared and isolated from alcoholic solvent systems. The reactions were examined under a variety of conditions and a mechanistic interpretation of the reaction sequence is presented. Several intermediates are proposed in this reaction scheme to account for products and their distribution.

In contrast to the extensive literature on the preparation of cyclic sulfonate esters of sultones,[1] only three cyclic sulfinate esters have been reported.[2] We have prepared 1,2-benzoxathian 2-oxide (I) in good yield by chlorination of β-(*o*-hydroxyphenyl)ethyl mercaptan and have studied several of its reactions including oxidation and halogenation.

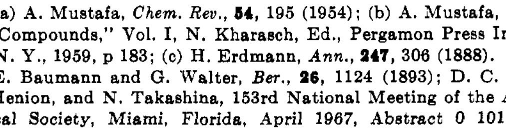
Chlorination of bivalent sulfur compounds has received attention recently as a synthetic method of preparing sulfinate esters.[3] Goethals and Verzele reported that 4,4-bis(hydroxymethyl)-1,2-dithiolane gives the 2,2-bis(hydroxymethyl)propane-1,3-disulfonic acid disultone in 20–25% yield (eq 1).[4] From 4-hydroxybutanethiol a 5–15% yield of butane sultone was isolated from its aqueous chlorination solution. The main product was 4-chlorobutanesulfonyl chloride. From the homologous tri-, penta-, and hexamethylenehydroxythiols only chloroalkanesulfonyl chlorides were reported. These workers found no evidence for intramolecular sulfinate esters.



(1)

Results

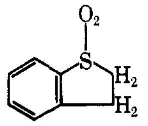
We have found that the addition of chlorine to a solution of β-(*o*-hydroxyphenyl)ethyl mercaptan in acetic acid at room temperature produced the cyclic sulfinate ester, 1,2-benzoxathian 2-oxide (I) (eq 2).



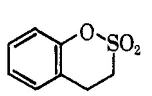
I

(2)

Elemental, infrared, nmr, and mass spectroscopic analysis of the product were in good agreement with the proposed structure. The isomeric 2,3-dihydrobenzothiophene 1,1-dioxide (II) was not the product since a sulfone band at 1300 cm^{-1} was absent in its infrared spectrum. In addition, the glpc retention times of I and an authentic sample of II differed. Peroxide oxidation of I gave the known sultone 1,2-benzoxathian 2,2-dioxide (III) reported previously by Truce and Hoerger.[5] The absence of any aromatic chlorine substitution was evident from the absence of chlorosultones.



II



III

Evidently a complicating side reaction seemed to limit the maximum yield of I to 45%. Acetyl chloride, a by-product from chlorine oxidation of mercaptans in acetic acid,[6] may have reacted with intermediate disulfide to give the bis[2-(2-acetoxyphenyl)ethyl] disulfide. Subsequent ester oxidation would give the corresponding sulfinic acid chloride which would have hydrolyzed to water-soluble acids during work-up. The competing esterification reaction was favored by reducing the rate of chlorine addition, thereby increasing the opportunity for esterification to occur. When the rate of chlorine addition was reduced threefold, only a trace of ether-soluble product was isolated which was consistent with maximum esterification.

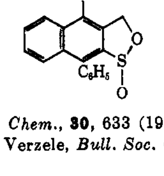
The instability of I was evident from its complete decomposition when stored overnight at room temperature, but at refrigerator temperatures it could be kept for several weeks without decomposition. Compound I was stable to short-path distillation and glpc analysis as determined by the infrared analysis of the vapor effluent.

In other hydroxylic solvents, such as aqueous acetic acid, methyl alcohol, and *t*-butyl alcohol, the mercaptan was oxidized to sultones and disulfide. The sultones were identified as III, 6-chloro-1,2-benzoxathian 2,2-dioxide (IV), 8-chloro-1,2-benzoxathian 2,2-dioxide (V), and 6,8-dichloro-1,2-benzoxathian 2,2-dioxide (VI).

---

(1) (a) A. Mustafa, *Chem. Rev.*, **54**, 195 (1954); (b) A. Mustafa, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1959, p 183; (c) H. Erdmann, *Ann.*, **247**, 306 (1888).

(2) E. Baumann and G. Walter, *Ber.*, **26**, 1124 (1893); D. C. Dittmer, R. S. Henion, and N. Takashina, 153rd National Meeting of the American Chemical Society, Miami, Florida, April 1967, Abstract 0 101. These workers reported the isolation of a cyclic sulfinate ester from the thermal decomposition of a thiete sulfone.



(3) I. B. Douglass, *J. Org. Chem.*, **30**, 633 (1965).

(4) E. J. Goethals and M. Verzele, *Bull. Soc. Chim. Belges*, **74**, 21 (1965).

(5) W. E. Truce and F. D. Hoerger, *J. Am. Chem. Soc.*, **76**, 5357 (1954).

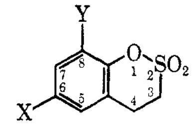
(6) I. B. Douglass and B. S. Farah, *Org. Syn.*, **40**, 62 (1960).

TABLE I

SULTONE DISTRIBUTION FROM CHLORINATION IN HYDROXYLIC SOLVENTS

Reactant	Solvent	Compn,[a] %	Cl_2/ reactant[b]	Yields, % Disulfide[c]	Yields, % Sultones[d]	Sultone distribn I	III	IV	V	VI
1. β-(*o*-Hydroxyphenyl)ethyl mercaptan	Water	20	3/1	58	31		18	33	13	37
	Acetic acid	80								
2. β-(*o*-Hydroxyphenyl)ethyl mercaptan	Water	20	1/1	100						
	Acetic acid	80								
3. β-(*o*-Hydroxyphenyl)ethyl mercaptan	*t*-Butyl alcohol		3/1	60	28		41	41	8	10
4. β-(*o*-Hydroxyphenyl)ethyl mercaptan	Methyl alcohol	8	3/1		42		58	25	9	8
	Acetonitrile	92								
5. β-(*o*-Hydroxyphenyl)ethyl disulfide	Acetic acid	70	3.6/1	65	35		2	28	14	56
	Methyl alcohol	30								
6. 1,2-Benzoxathian 2-oxide (I)	*t*-Butyl alcohol		2.5/1		84		1	2	3	93
7. 1,2-Benzoxathian 2-oxide (I)	*t*-Butyl alcohol		1.3/1		10	90	10	18	2	69
8. 1,2-Benzoxathian 2-oxide (I)	Methyl alcohol	8	2/1		55	8	...	7	...	93
	Acetonitrile	92								
9. 1,2-Benzoxathian 2,2-dioxide (III)	*t*-Butyl alcohol		4/1	No reaction			100			

[a] Volume per cent. [b] Mole ratio. [c] β-(*o*-Hydroxyphenyl)ethyl disulfide. [d] Includes III, IV, V, and VI.



III, X = H; Y = H
IV, X = Cl; Y = H
V, X = H; Y = Cl
VI, X = Cl; Y = Cl

Assignment of the chlorosultone structures was based largely on elemental, infrared, nmr, and mass spectroscopic analysis. From the nmr the following conclusions were drawn: IV has chlorine substitution in either the 6 or the 7 position, V has halogen located at either the 5 or 8 position, and VI has two *meta*-oriented hydrogen atoms. Final assignments had to be based largely on the expected *ortho–para* orienting effect on chlorination of probable *o*-alkylphenolic intermediates.[7] These intermediates and their role in the reaction sequence is dealt with more extensively below.

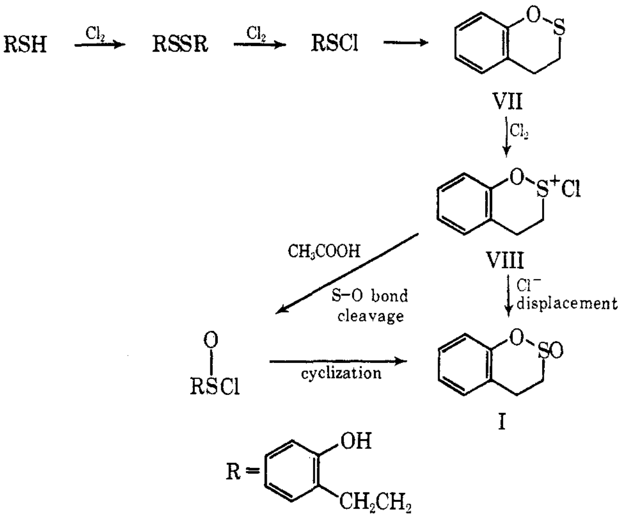
The oxidation of I with chlorine in alcoholic solvents gave the same sultones as produced from the mercaptan, but in different ratios (Table I). The same products suggested that I may be an intermediate in the mercaptan oxidation in alcohols.

Discussion

The study was extended to ascertain the reaction mechanisms involved. By using various solvents and altering the concentrations of reactants (Table I), we were able to make several inferences regarding the individual reaction steps.

Oxidation of Mercaptan in Acetic Acid.—The chlorine oxidation of the mercaptan in acetic acid probably goes first to the disulfide[8] (Scheme I). When additional chlorine in excess of 0.5 mole equiv of mercaptan is added, the disulfide is cleaved to form the sulfenyl chloride.[9] But the absence of the typical color generally developed in such reactions suggested that the sulfenyl chloride reacts immediately after formation. One possible reason for this *abnormal* reaction may be an intramolecular hydroxyl–sulfenyl chloride interaction leading to a cyclic sulfenate ester VII. Further sulfur oxidation of VII would lead ultimately to I.

SCHEME I



One possible sequence of steps to explain this reaction process involves formation of a chlorine addition intermediate VIII. This would be susceptible to reaction with acetic acid which could displace from sulfur either the oxygen or the chlorine atom.[10] Chloride ion displacement would lead directly to I while phenoxide ion displacement would give the sulfinyl chloride. Subsequent ring closure of the sulfinyl chloride would form I. The cyclization step should be fast based on the rapidity of analogous intermolecular esterifications in aliphatic systems.[3]

Concomitant aromatic ring chlorination is at most only a very minor process. Although phenols chlorinate very rapidly, the absence of ring chlorination in I cannot exclude the possibility of the existence of phenolic intermediates in this reaction. Other workers have shown that only minor ring chlorination of phenols occurs when sulfur compounds such as mercaptans, disulfides, or sulfenyl chlorides are present.[11]

Stability of I in Chlorine–Acetic Acid Solution.—The inactivity of I to further oxidation in chlorine–acetic acid differs from the reactivity of alkyl sulfinate esters.

---

[7] A. Campbell and D. J. Shields, *Tetrahedron*, 211 (1965).

[8] I. B. Douglass, B. S. Farah, and E. G. Thomas, *J. Org. Chem.*, **26**, 1996 (1961).

[9] See ref 1b, p 351.

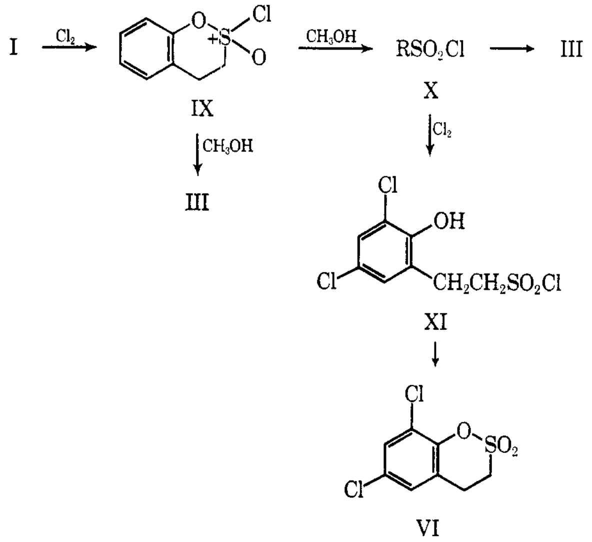
[10] H. Kwart and E. N. Givens, unpublished results.

[11] R. T. Wragg, *J. Chem. Soc.*, 5482 (1964); D. Delfs and K. Wedemeyer, German Patent 1,063,177 (1959); *Chem. Abstr.*, **55**, 15420*g* (1961).

These compounds readily form sulfonyl chlorides under similar conditions.[3] The differing reactivities may be accounted for on the basis of the relative stability of the aryl–oxygen bond to nucleophilic substitution as compared to the alkyl–oxygen bond. Chlorine addition to I probably forms an alleged addition complex IX. The fact that more than 1 equiv of chlorine is required before the typical greenish color appears supports such an intermediate complex. Apparently the electron pair on the sulfur atom is available for complexing the chlorine thereby forming a colorless intermediate IX which can be reversed to I.

Oxidation of I in Alcohols.—In more nucleophilic solvents, I produces sultones. Apparently, alcohols can react with the intermediate IX breaking either the oxygen–sulfur or the chlorine–sulfur bond (Scheme II).

Scheme II



Displacement of chloride ion gives III directly while phenoxide ion displacement gives β-(o-hydroxyphenyl)-ethanesulfonyl chloride (X). Ring chlorination of X follows to produce intermediates such as XI. Subsequent cyclization to chlorosultones would explain how aromatic ring chlorination can occur prior to the product-forming step. This is consistent with results from a control experiment in which III was found to be inert to chlorine in alcohol.

Initially, the existence of I as an intermediate in the chlorine oxidation of mercaptan was suspect. However, the sultone distributions from the mercaptan and I were quite different. The latter produced dichlorosultone VI almost exclusively while mercaptan gave mostly sultone (III) and monochlorosultones (IV, V). Also, since I was not present from the reaction with the mercaptan, the disulfide seems to go to sultone (or sulfonyl chloride) much more rapidly than disulfide itself will react.

Sultone Distribution.—An explanation for the difference in distribution of products can be found by comparing the relative rates of the competing reactions. When I is the reactant, the sulfonyl chloride (X) competes with I for available chlorine. Evidently ring chlorination of the sulfonyl chloride is much faster than the S-chlorine oxidation of I since the dichlorosultone predominates even in presence of limited chlorine (run 7). It also follows that the subsequent ring cyclization step must be much slower than the ring chlorination reaction.

For the mercaptan, the disulfide is formed first, which on further chlorine oxidation goes directly to sulfonyl chloride X in a series of rapid steps, each more rapid than the disulfide reaction itself. Then disulfide and sulfonyl chloride X compete for available chlorine. In this case, however, the disulfide competes more favorably with sulfonyl chloride than I since sultone III and monochlorosultones were the main products.

An experiment designed to test this idea was performed. The conditions were set up so that a large excess of chlorine was available in the limited presence of disulfide. The disulfide was added slowly to a chlorine solution and the product was found to be primarily dichlorinated product (run 5). Indeed, by using controlled conditions the yields of mono- and dichlorosultones may be altered by taking advantage of these competing reactions.

Experimental Section[12]

β-(o-Hydroxyphenyl)ethyl Mercaptan.—β-(o-Methoxyphenyl)-ethanol was prepared in 53% yield by the addition of ethylene oxide to the Grignard of o-bromoanisole in tetrahydrofuran.[13] The cyclization of β-(o-methoxyphenyl)ethanol was accomplished by refluxing in acetic acid with 47% hydrobromic acid.[14] Distillation at atmospheric pressure gave 2,3-dihydrobenzofuran. By the method of Frank and Smith,[15] a solution of 41.0 g (0.344 mole) of 2,3-dihydrobenzofuran in 160 ml of acetic acid was refluxed with 160 ml of 47% hydrobromic acid for 1 hr. To the hot solution was added 47 g (0.62 moles) of thiourea and the mixture refluxed overnight. After cooling, the reaction mixture was made strongly basic with sodium hydroxide. After refluxing for 2.5 hr, the reaction mixture was cooled and extracted with ether to remove unreacted 2,3-dihydrobenzofuran. After acidifying to pH 5 with hydrochloric acid, the oily layer was extracted with ether, washed with 10% sodium bicarbonate, dried, and distilled (bp 116–117° (0.3 mm), 36.7 g, 69% yield).

Anal. Calcd for $C_8N_{10}OS$: C, 62.31; H, 6.54; S, 20.73. Found: C, 61.80; H, 6.52; S, 20.80.

The infrared spectrum[16] showed major bands at 3420, 1230, 1100, and 750 cm^{-1}.

1,2-Benzoxathian 2-Oxide (I).—To a vigorously stirred solution of 4.0 g (26.0 mmoles) of β-(o-hydroxyphenyl)ethyl mercaptan in 100 ml of glacial acetic acid at room temperature was added rapidly 3.7 g of chlorine. The reaction mixture was stirred for 10 min and the solvent evaporated under reduced pressure using a maximum temperature of 60°. The residue was dissolved in ether and dried after washing successively with water, 10% sodium bicarbonate, and again with water. The ether was evaporated leaving an oil (3.2 g, 85% I by glpc). The oil was distilled through a short-path still (bp 120–140° (0.05 mm), 2.15 g, 49% yield).

Anal. Calcd for $C_8H_8O_2S$: C, 57.19; H, 4.80. Found: C, 56.61; H, 4.73.

The infrared spectrum[16] showed bands at 3050, 2910, 1590, 1490, 1450, 1410, 1205, 1170, 1145, 1125, 1110, 1100, 890, 820, 785, 760, 705, 690, and 650 cm^{-1}. Bands were absent between

---

[12] All melting points were obtained on a Fisher-Johns melting point block. The infrared spectra were determined with a Perkin-Elmer Model 337 grating infrared spectrophotometer. The nmr spectra were determined on a Varian Model A-60 nmr spectrometer at 60 Mc. The mass spectra presented here were obtained with a CEC Model 21-103 mass spectrometer at an ionizing potential of 70 ev. Analyses were performed by the Analytical Division, Mobil Oil Corp., Paulsboro, N. J. Magnesium sulfate was employed as drying agent. Gas–liquid partition chromatography was carried out with an F & M Model 810 gas chromatograph.

[13] E. Hardegger, D. Redlich, and A. Gal, *Helv. Chim. Acta*, **28**, 631 (1945).

[14] S. E. Cantor and D. S. Tarbell, *J. Am. Chem. Soc.*, **86**, 2908 (1964).

[15] R. L. Frank and P. V. Smith, *ibid.*, **68**, 2103 (1946).

[16] Determined as a neat liquid.

1300 and 1400 cm^{-1} in agreement with known sulfinate esters.[17] The nmr spectrum showed equal numbers of aromatic and aliphatic hydrogen atoms at 6.78–7.4 and 2.3–3.5 ppm, respectively. The glpc analysis[18] showed the retention time of the product differed from 2,3-dihydrobenzothiophene 1-dioxide (mp 89–91° (lit.[19] mp 91–92°, infrared). The mass spectrum had a strong molecular ion peak at m/e 168 with a base peak at m/e 120 corresponding to a loss of SO.

Peroxide Oxidation of I.—To a stirred solution of 0.3 g of 30% hydrogen peroxide in acetic acid was added 2.3 g of I. The solution was refluxed for 15 min, cooled, and poured over ice. The mixture was extracted with benzene. The benzene solution was successively washed with water, 10% sodium bicarbonate solution, again with water, and dried. The solid residue left after evaporating benzene was placed on an alumina column and eluted with benzene. The product was recrystallized from a benzene–hexane mixture, mp 108–109°. The product was further purified by glpc, mp 113–114° (lit.[5] mp 111–112°).

Anal. Calcd for $C_8H_8O_3S$: C, 52.17; H, 4.38; S, 17.41. Found: C, 52.28; H, 4.53; S, 17.1.

The mass spectrum had a molecular ion peak at m/e 184 with a strong fragment at m/e 120 corresponding to a loss of SO_2. The nmr spectrum in $CDCl_3$ showed equal numbers of aromatic and aliphatic hydrogen atoms at 6.83–7.5 and 3.34–3.6 ppm, respectively. The infrared spectrum[20] showed a strong doublet at 1360 and 1370 cm^{-1} corresponding to known sulfonates.[17] Other bands appear at 1600, 1500, 1460, 1180, 1140, 1090, 900, 810, and 760 cm^{-1}.

Chlorination of I in *t*-Butyl Alcohol.—Into a flask which contained 4.2 g (25 mmoles) of I in 100 ml of predried *t*-butyl alcohol at 30° there was added 1.78 g of chlorine. The flask was protected from stray light. After stirring several minutes, the solvent was removed under reduced pressure and the remaining oil dissolved in benzene. The benzene solution was chromatographed on alumina to give 2.9 g of solid product. Fractional crystallization followed by glpc separation[21] resolved the product into four components, III–VI, discussed below.

Chlorinations of I in *t*-butyl alcohol shown in Table I as runs 6–8 were made by the method described here for run 6. To a flask containing 0.40 g (2.4 mmoles) of I in 40 g of *t*-butyl alcohol was added 0.30 ml of chlorine. The reaction mixture was stirred 15 min and the solvent removed by vacuum distillation. The oil was dissolved in ether, washed with water, dried, and evaporated, leaving 0.5 g of product. The product analysis is shown in Table I.

1,2-Benzoxathian 2,2-Dioxide (III).—The melting point, glpc, and infrared spectrum are consistent with the sultone prepared by the peroxide oxidation of I.

6-Chloro-1,2-benzoxathian 2,2-Dioxide (IV).—The melting point after numerous recrystallizations from benzene–hexane mixtures was 133–135°.

Anal. Calcd for $C_8H_7ClO_3S$: C, 43.96; H, 3.22. Found: C, 43.87; H, 3.47.

The mass spectrum showed a strong molecular ion peak at m/e 218 with a main fragment peak at m/e 154 corresponding to a loss of SO_2. The infrared spectrum[20] showed sulfonate bands at 1390 and 1155 cm^{-1}.[17] Other bands appear at 1480, 1105, 910, 830, and 770 cm^{-1}. The very strong 830-cm^{-1} band suggests a 1,2,4 aromatic substitution. The nmr spectrum in C_6D_6 showed aromatic and aliphatic bands in a ratio of 3:4. The aliphatic band at 2.5 ppm is unresolved. The chemical shifts and coupling constants for an ABC spectrum of a 1,2,4 aromatic system were determined:[22,23] δ_A 6.39 ppm, δ_B 6.70, δ_C 6.53, J_{AB} = 8.9 cps, J_{AC} = 0.0 cps, J_{BC} = 2.4 cps. The ABC assignments are made to hydrogen atoms at either the 5-, 6-, and 8-ring positions, respectively, or to the 8, 7, and 5 positions, respectively.

8-Chloro-1,2-benzoxathian 2,2-Dioxide (V).—The melting point of the product after repeated recrystallization from benzene–hexane was 153–155°.

Anal. Calcd for $C_8H_7ClO_3S$: C, 43.96; H, 3.22. Found: C, 44.05; H, 3.32.

The mass spectrum showed a molecular ion peak at m/e 218 with a prominent fragment at m/e 154 corresponding to a loss of SO_2. The infrared spectrum[20] showed bands consistent with sulfonates at 1375 and 1150–1200 cm^{-1}.[17] Two other bands at 870 (s) and 790 cm^{-1} (m) are consistent with three adjacent hydrogen atoms on the aromatic nucleus. The nmr spectrum in C_6D_6 showed aromatic and aliphatic resonances in a ratio of 3:4. The aliphatic band at 2.38 ppm was unresolved. The chemical shifts and coupling constants for an ABC spectrum of three adjacent aromatic hydrogen atoms were determined:[22] δ_A 6.274 ± 0.003 ppm, δ_B 6.423 ± 0.003, δ_C 6.881 ± 0.002, J_{AB} = 7.64 ± 0.35 cps, J_{AC} = 1.98 ± 0.26 cps, J_{BC} = 7.93 ± 0.58 cps. Proton B is assigned to a ring position of either 6 or 7; A and C cannot unequivocally be assigned.

6,8-Dichloro-1,2-benzoxathian 2,2-Dioxide (VI).—The melting point after several recrystallizations from benzene–hexane was 125–126°.

Anal. Calcd for $C_8H_6Cl_2O_3S$: C, 37.96; H, 2.39. Found: C, 38.20; H, 2.61.

Mass spectroscopy showed a strong parent peak m/e 252 with a strong fragment at m/e 188 corresponding with a loss of SO_2. The infrared spectrum[20] showed bands at 1360 and 1155 cm^{-1} consistent with known sultones.[17] Other major bands were at 3430, 1450, 865, 840, 803, and 764 cm^{-1}. The nmr spectrum in $CDCl_3$ showed aromatic and aliphatic resonances in a 1:2 ratio. The aromatic AB pattern centered at 7.2 ppm (δ_{AB} 0.2 ppm, J_{AB} = 2.5 cps) is consistent with the hydrogen atoms located at either the 5,7 or 6,8 positions on the 1,2-benzoxathian nucleus. The fine structure of the aliphatic band centered at 3.5 ppm could not be resolved.

Chlorination of β-(*o*-Hydroxyphenyl)ethyl Mercaptan in Aqueous Acetic Acid (Run 1).—To a flask containing 2.0 g (13 mmoles) of β-(*o*-hydroxyphenyl)ethyl mercaptan in 75 ml of 20% aqueous acetic acid was added 2.8 g of chlorine. The reaction mixture was stirred for 15 min at room temperature and the solvent removed on a flash evaporator with a maximum temperature of 50°. The residual oil was taken up in ether and washed successively with water, 10% sodium bicarbonate solution, and again with water. After drying, the solvent was removed. In the infrared spectrum[24] the lack of an SH stretching vibration indicated the absence of mercaptan. The glpc pattern[18] and infrared spectrum were consistent with the presence of disulfide. The absence of reactant mercaptan in the product was further substantiated by the absence of the characteristic odor. The disulfide was removed from the product mixture by extracting in 10% sodium hydroxide solution. The base-insoluble product was analyzed by glpc[21] to give the product ratios shown in Table I. The disulfide yield was estimated by the weight difference before and after base extraction. Runs 2–4 were performed in a manner similar to run 1 described above except for differences in solvent or reactant ratios.

Chlorination of β-(*o*-Hydroxyphenyl)ethyl Disulfide in Methanol–Acetic Acid (Run 5).—The disulfide was prepared by adding 50 ml of a 0.0357 M solution of chlorine in acetic acid to 0.50 g (3.6 mmoles) of β-(*o*-hydroxyphenyl)ethyl mercaptan in acetic acid. The colorless disulfide solution was then added dropwise to 100 ml of methanol in 320 ml of 0.0357 M chlorine in acetic acid. The lightly tinted solution after stirring 10 min was poured into 2 l. of water and extracted with ether. The ether layer was washed with water before and after extracting with 10% sodium bicarbonate solution. The ether was evaporated and dried, leaving 0.6 g of oil. The oil was dissolved in ether and washed with 10% sodium hydroxide solution. After washing with water and drying, 0.2 g of oil remained. The glpc analysis[21] is reported in Table I.

---

(17) D. Darwish and E. A. Preston, *Tetrahedron Letters*, 113 (1964); L. T. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 22.

(18) A 12 ft × 0.25 in. o.d. column packed with silicone rubber SE-30 on Chromosorb W.

(19) F. G. Bordwell and W. H. McKellin, *J. Am. Chem. Soc.*, **72**, 1986 (1950); F. G. Bordwell, B. B. Lampert, and W. H. McKellin, *ibid.*, **71**, 1704 (1949).

(20) Determined as a suspension in a potassium bromide pellet.

(21) A 12 ft × 0.25 in. o.d. column packed with 5% nitrile silicone rubber XE-60 on Chromosorb W.

(22) Calculation of chemical shifts and coupling constants was performed on a 7040 computer using the LAOCOON II program of S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964). We wish to thank Dr. L. G. Alexakos for his assistance in performing these calculations.

(23) Weak signals required the use of a Varian C-1024 computer with the concomitant loss in resolution. The best computed values are presented.

(24) Determined as a Nujol mull.

Registry No.—I, 13428-10-9; III, 13422-27-0; IV, 13422-28-1; V, 13407-19-7; VI, 13422-27-2; β-(*o*-hydroxyphenyl)ethyl mercaptan, 13407-20-0.

Acknowledgment.—The authors are grateful to Drs. P. S. Landis and P. B. Venuto for generously reading and commenting on the original manuscript.

Reduction of Aromatic Compounds with Alkali Metals in Amine Solvents and in Aprotic Liquids Containing Ammonia

LYNN H. SLAUGH AND JOHN H. RALEY

Shell Development Company, Emeryville, California 94608

Received March 16, 1967

The properties of the alkali metals and mixtures thereof have been compared for the reduction of aromatic compounds in neat methylamine (and related media) at elevated temperatures, 60–190°. Like lithium, potassium and rubidium readily reduce benzene and alkyl-substituted benzenes to cyclic monolefins. While sodium is ineffective, sodium in the presence of small amounts of potassium or rubidium does reduce benzene. Potassium is considerably more selective than lithium for the synthesis of 1-alkylcyclohexenes from alkylbenzenes. The coproduct, potassium methylamide, readily isomerizes alkylcyclohexenes to an equilibrium distribution of the olefin isomers. Tetralin is reduced by potassium to a mixture containing $\geq 95\%$ $\Delta^{9,10}$-octalin. Aprotic liquids containing ammonia in quantities stoichiometric or less to the metal also are suitable media for the reduction of aromatic compounds.

Aromatic compounds in a suitable solvent are reduced readily by alkali metals,[1–4] alkaline earth metals,[3,5] and even by two rare earth elements, europium and ytterbium.[6] The course of the reaction is dependent upon the temperature, the metal, and the solvent. For example, benzene is reduced mainly to 1,4-cyclohexadiene by sodium in liquid ammonia at *ca.* −34°, provided a substance (alcohols, water, etc.) more acidic than ammonia is present.[1–4] On the other hand, added acids are not required and the product is exclusively cyclohexene when the reaction temperature is ~60–130°.[7] At the higher temperatures, the reduction can be stopped at the diene stage if lithium is used.[7] In refluxing ammonia, lithium is better than sodium for the conversion of certain aromatic compounds to dienes.[8] Benkeser and co-workers found low molecular weight monoamines, particularly methylamine and ethylamine, to be excellent media for reductions with lithium.[9–16] In neat monoamines, aromatic compounds are reduced to monoolefins[9,13,15] whereas in monoamine–alcohol solutions diolefins are obtained.[14] The isomeric distribution of monoolefins obtained from naphthalene or substituted benzenes is dependent upon the composition of mixed amine solvents.[13,15,16] Under certain conditions, lithium–monoamine reagents are strong enough to reduce isolated double bonds.[10,12] The most potent but least selective of the metal reagents thus far developed is lithium in ethylenediamine (reaction temperature, 90–100°).[17] The latter is useful for completely saturating ring systems and for the reduction of very inert materials.

In most cases, the above experiments were performed at the reflux temperature of the solvent. Since this temperature varies, it is difficult to sort out observed effects which are due to the intrinsic properties of the solvent or metal and effects which are due to temperature differences. We would like to report the results of an investigation wherein aromatic compounds were reduced by metals in neat amines or in aprotic media containing limited amounts of ammonia.[18] An autoclave system was used which made it possible to vary the conditions at will regardless of the boiling point of the solvent. The reducing capabilities of several alkali metals and alloys thereof have been compared. These comparisons are necessarily qualitative since the solubilities of the metals under the various conditions are not known.

Results and Discussion

An autoclave was charged with the aromatic hydrocarbon, alkali metal, and solvent and heated to the desired temperature (>25°). Stirring was applied with a paddle speed of 1000 rpm. The resultant organic product, excess solvent, and metal amide[19] were separated by distillation. In all cases, part of the metal reacted with the amine or ammonia solvent forming metal amides and hydrogen. This side reaction lowers the efficiency of metal utilization. In order to facilitate comparisons of the metals, the yields of products

---

(1) C. B. Wooster, U. S. Patent 2,182,242 (Dec 5, 1939); see also C. B. Wooster and K. L. Godfrey, *J. Am. Chem. Soc.*, **59**, 596 (1937).

(2) A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950).

(3) A. J. Birch, *ibid.*, **4**, 17 (1958).

(4) H. Smith, "Organic Reactions in Liquid Ammonia," Vol. 1, Part 2, Interscience Publishers, Inc., New York, N. Y., 1963.

(5) H. Boer and P. M. Duinker, *Rec. Trav. Chim.*, **77**, 346 (1958); P. Markov and C. Ivanoff, *Tetrahedron Letters*, No. 24, 1139 (1962).

(6) L. H. Slaugh, *Inorg. Chem.*, **6**, 851 (1967).

(7) L. H. Slaugh and J. H. Raley, *J. Org. Chem.*, **32**, 369 (1967). An autoclave was used for these experiments.

(8) A. L. Wilds and N. A. Nelson, *J. Am. Chem. Soc.*, **75**, 5360 (1953).

(9) R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *ibid.*, **77**, 3230 (1955).

(10) R. A. Benkeser, G. Schroll, and D. M. Sauve, *ibid.*, **77**, 3378 (1955).

(11) R. A. Benkeser, C. Arnold, Jr., R. F. Lambert, and O. H. Thomas, *ibid.*, **77**, 6042 (1955).

(12) R. A. Benkeser, J. J. Hazdra, R. F. Lambert, and P. W. Ryan, *J. Org. Chem.*, **24**, 854 (1959).

(13) R. A. Benkeser, R. K. Agnihotri, and M. L. Burrous, *Tetrahedron Letters*, No. 16, 1 (1960).

(14) R. A. Benkeser, M. L. Burrous, J. J. Hazdra, and E. M. Kaiser, *J. Org. Chem.*, **28**, 1094 (1963).

(15) R. A. Benkeser, R. K. Agnihotri, M. L. Burrous, E. M. Kaiser, J. M. Malland, and P. W. Ryan, *ibid.*, **29**, 1313 (1964).

(16) R. A. Benkeser and E. M. Kaiser, *ibid.*, **29**, 955 (1964).

(17) L. Reggel, R. A. Friedel, and I. Wender, *ibid.*, **22**, 891 (1957).

(18) Acids, such as water or alcohols, were not added.

(19) *Caution!* When ammonia is not present, alkyl-substituted metal amides (RNHM) are the coproducts of reduction. It has been our experience that substituted metal amides, such as potassium methylamide, are more reactive to the atmosphere than are the metal amides. Potassium methylamide may explode when exposed to air. Throughout the experiments, all air- and water-sensitive materials were manipulated in a drybox filled with nitrogen.