[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Cleavage of Sulfides and Sulfones by Alkali Metals in Liquid Amines.[1] I

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Several organic sulfides and sulfones have been cleaved in good yields to the hydrocarbon and mercaptan or sulfinic acid by sodium in liquid ammonia and/or lithium in methylamine. The direction of this cleavage has been established for a number of alkyl aryl and unsymmetrical diaryl sulfides and sulfones.

Reductive cleavages using sodium in liquid ammonia have been reported for both ethers and sulfides. Diaryl ethers are reported to give the corresponding phenol and aromatic hydrocarbon with the unsymmetrical diaryl ethers cleaving in the direction which gives the weakest acid.[2,3] Alkyl aryl ethers are cleaved in poor yields to the phenol and alkane,[4] while dialkyl ethers are unaffected. Lower molecular weight sulfides have been cleaved by this reagent to the corresponding mercaptan and alkane.[5,6]

The use of excess sodium often removes the sulfur entirely from the molecule as sodium sulfide,[7] and this fact has been used to advantage as the basis of a quantitative determination of sulfur.[8]

Good general methods for cleaving sulfones have been lacking, although fair success has been had with base-catalyzed cleavage[9] to produce the mercaptan and olefin. Aromatic sulfones are cleaved by sodium piperidide[10] to give a sulfinic acid and the corresponding N-arylpiperidine. Diaryl and alkyl aryl sulfones are reductively cleaved with sodium amalgam in boiling ethanol to give the sulfinic acid and the hydrocarbon,[11] and more recently, it has been shown[12] that diphenyl sulfone as well as diphenyl sulfide can be cleaved with triphenylsilyllithium. Other isolated instances of sulfone cleavage are known, usually under vigorous conditions,[13] and a rather complete review of the older literature has been given by Suter.[14]

We have found that sulfones and sulfides of various types are cleaved, usually in good yields, by the controlled addition of lithium in methylamine. Sodium in liquid ammonia is likewise effective for sulfides and for diaryl sulfones. Thus, lithium in methylamine cleaves dialkyl and diaryl sulfides to the hydrocarbon and the mercaptan. Alkyl aryl sulfides give the aromatic thiol and alkane upon cleavage with lithium in methylamine, while dialkyl sulfones yield the hydrocarbon and sulfinic acid, and alkyl aryl sulfones produce the aromatic hydrocarbon and aliphatic sulfinic acid. Diaryl sulfones are reductively cleaved to the thiol and hydrocarbon by lithium in methylamine, but the aromatic sulfinic acid and hydrocarbon are produced when sodium in liquid ammonia is used. The latter system fails to react with dialkyl and alkyl aryl sulfones and is, consequently, not as general a cleaving agent as lithium in methylamine. For this reason we have directed our attention primarily to the latter.

Lithium in methylamine has been extensively investigated as a reducing system for hydrocarbons,[15] and excellent reviews are available on alkali metal–amine systems in regard both to their reduction of hydrocarbons and their cleavages of ethers.[16,17] Apparently cleavages with such systems occur by release of electrons from the dissolving metal eventually to the compound being cleaved.[18] It is not readily apparent whether this requires the simultaneous addition of two electrons or the stepwise addition of single electrons since the products in either case would be those derived from the anion rather than the radical.[16]

To avoid the presence of excess reducing agent, it is necessary to employ a method of controlled addition of the metal to the solution of the substrate. This is accomplished conveniently by allowing the amine solvent containing the sulfide or sulfone to reflux through a thimble containing the metal. The metal is thus dissolved by the returning condensate and its speed of addition may be controlled by adjustment of the reflux rate.

Decyl sulfide with two equivalents of lithium gave a quantitative yield of decyl mercaptan (after acidification). Williams noted similar results with the sodium in ammonia cleavage of the lower molecular weight sulfides.[5] The other product of the cleavage was decane. Another dialkyl sulfide, dibenzyl sulfide, proved to be an exception to the general behavior of aliphatic sulfides, since even very slow addition of lithium gave mostly lithium sulfide (hydrogen sulfide on acidification) and toluene. This facile cleavage of a benzyl group has been previously observed and utilized in the protection and subsequent regeneration of a thiol group as during protein synthesis.[19] Furthermore, treatment of α-toluenethiol with one equivalent of lithium caused extensive reduction to lithium sulfide and toluene.

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(1) Abstracted from the Ph.D. Theses of David P. Tate and David N. Burdge.

(2) P. A. Sartoretto and F. J. Sowa, THIS JOURNAL, **59**, 603 (1937).

(3) F. C. Weber and F. J. Sowa, *ibid.*, **60**, 94 (1938).

(4) A. J. Birch, *J. Chem. Soc.*, 593 (1946); 102 (1947).

(5) F. E. Williams and E. Gebauer-Fuelnegg, THIS JOURNAL, **53**, 354 (1931); R. Adams and A. Ferretti, *ibid.*, **81**, 4939 (1959).

(6) R. C. Krug and S. Tocker, *J. Org. Chem.*, **20**, 1 (1955).

(7) C. A. Kraus and G. F. White, THIS JOURNAL, **45**, 775 (1923).

(8) F. J. Sowa, V. G. Arcadi and J. A. Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, **8**, 49 (1936).

(9) G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 705, 4004 (1930).

(10) W. Bradley, *ibid.*, 458 (1938).

(11) R. E. Dabby, J. Kenyon and R. F. Mason, *ibid.*, 4881 (1952).

(12) D. Wittenberg, T. C. Wu and H. Gilman, *J. Org. Chem.*, **23**, 1898 (1958).

(13) (a) D. T. Gibson, *J. prakt. Chem.*, [2] **142**, 218 (1935); (b) O. Jacobsen, *Ber.*, **20**, 900 (1887); (c) R. Otto and H. Ostrop, *Ann.*, **141**, 96 (1867); (d) R. Otto, *Ber.*, **18**, 248 (1885).

(14) C. M. Suter, "Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 681-683.

(15) R. A. Benkeser, *et al.*, THIS JOURNAL, **77**, 3230, 6042 (1955).

(16) A. J. Birch, *Quart. Revs.*, **4**, 69 (1950).

(17) G. W. Watt, *Chem. Revs.*, **46**, 317 (1950).

(18) W. C. Fernelius and G. W. Watt, *ibid.*, **20**, 195 (1937).

(19) V. du Vigneaud and G. Miller, *J. Biol. Chem.*, **116**, 469 (1936).

Symmetrical diaryl sulfides were cleaved smoothly with two equivalents of lithium in methylamine to give the hydrocarbon and thiophenol, both phenyl and *p*-tolyl sulfides giving nearly quantitative yields. Unsymmetrical diaryl sulfides were smoothly cleaved also, but the direction of cleavage is more complicated and is discussed below together with the corresponding unsymmetrical diaryl sulfones.

The alkyl aryl sulfides, phenyl decyl sulfide and mesityl decyl sulfide, cleaved in such a way that the thiophenol and aliphatic hydrocarbon were produced. In addition to decane, eicosane was formed in approximately 10% yield. This coupling was observed only in the alkyl aryl series.

Decyl sulfone was cleaved with two equivalents of lithium to give good yields of decane and lithium decyl sulfinate. Alkyl aryl sulfones are cleaved, with two equivalents of lithium, at the aromatic carbon–sulfur bond. Thus, decyl phenyl sulfone gave benzene and lithium decyl sulfinate.

Diaryl sulfones differ in that they are cleaved and, subsequently, reduced to the thiophenol. The intermediate sulfinate could not be isolated; even if less than equivalent amounts of lithium were employed in conjunction with slow addition rates, only unreacted sulfone and thiophenol were obtained. The corresponding sulfinates could be obtained, however, when two equivalents of sodium in liquid ammonia were used instead of four equivalents of lithium in methylamine. As previously stated, alkyl sulfones are unreactive toward sodium in liquid ammonia.

In an effort to obtain information which would aid in the elucidation of a mechanism(s), several unsymmetrical diaryl sulfides and sulfones were reductively cleaved with lithium in methylamine and the direction of cleavage established. It was hoped that there might be a relationship between the direction of cleavage and the σ-constants of the substituent groups. Although Sartoretto and Sowa[2] had noted such a correlation in their cleavage of unsymmetrical diaryl ethers with sodium in liquid ammonia, such a relation was not obvious in our cleavages of sulfides and sulfones.

The cleavage of diaryl sulfones by lithium in methylamine proceeds, not through the sulfide, but through the further reduction of the sulfinate anion to the thiolate anion. This was shown by the fact that three equivalents of lithium quantitatively reduced benzenesulfinic acid to the thiolate, while cleavage of diphenyl sulfone with less than four equivalents of lithium gave only the thiol and unreacted sulfone; no sulfide could be isolated. The fact that reduction of the sulfinate is faster than the original cleavage reaction was shown by treatment of equimolar amounts of benzenesulfinic acid and di-*p*-tolyl sulfone with three equivalents of lithium. Only benzenethiol was isolated and the sulfone was recovered unchanged. Sodium in liquid ammonia, however, also quantitatively reduces benzenesulfinic acid, and when an equimolar mixture of *p*-toluenesulfinic acid and di-*p*-tolyl sulfone was treated with three equivalents of sodium in ammonia three-fourths of the sulfinic acid and three-fourths of the sulfone were recovered. Some of the thiol was also isolated, suggesting that the reduction step and cleavage step are probably highly competitive reactions when sodium and ammonia are used.

Lithium-in-methylamine cleavages stop cleanly at the sulfinate in the case of aliphatic sulfones. In a separate attempt to reduce lithium decylsulfinate with two equivalents of lithium, no appreciable amount of the metal reacted. This may be due to the extremely low solubility of the decylsulfinate in the methylamine solvent.

A "rule of thumb" consistent with the observed facts for the aromatic compounds suggests that cleavage occurs to produce the least basic anion of the pair having the greatest difference in basicities. Thus, if the difference in basicity of $\mathrm{Ar'}\overset{\ominus}{\mathrm{S}}$ and $\mathrm{Ar}\overset{\ominus}{\mathrm{S}}$ is greater than the difference in basicity of $\overset{\ominus}{\mathrm{Ar'}}$ and $\overset{\ominus}{\mathrm{Ar}}$ then the cleavage proceeds so as to produce the most acidic thiol. If, on the other hand, the differences in basicities of the two possible carbanions is greater than that of the two possible thiolate or sulfinate anions then the production of the least basic carbanion would decide the direction of cleavage. This tentative hypothesis is consistent with the fact that the cleavage of alkyl aryl sulfides produces the aromatic thiol while the cleavage of the corresponding sulfone yields the aliphatic sulfinate. In the first instance, the difference in pK_a of benzenethiol and decyl mercaptan is about 5.3 units[20] while the difference in pK_a of decane and benzene is claimed to be considerably less, the range of pK_a for such simple hydrocarbons being only 37–40 (however, it should be noted that these values are at best only approximate estimations).[21] On the other hand, starting with the sulfones, the difference in pK_a of the cleavage products, benzenesulfinic acid and decanesulfinic acid, is probably about the same as the difference in pK_a of benzoic and decanoic acids,[22] the latter being only about 0.9 of a pK_a unit.[23] Since the difference in pK_a of benzene and decane probably approximates three pK_a units, production of the least basic carbanion (phenyl) and not the least basic sulfinate should control the direction of the cleavage.

With most of the unsymmetrical diaryl sulfides and sulfones studied so far, the differences, as might be expected, are not nearly so pronounced. For instance, the cleavage of *m*-tolyl phenyl sulfide produces the two thiols in a mole ratio which is nearly one to one. However, with *p*-anisyl phenyl sulfone, the difference in base strengths is apparently pronounced enough to force cleavage to proceed in only one direction. In this instance, the least basic carbanion would be the *p*-anisyl carbanion, at least based on the electronegative effect alone of the *p*-methoxy group.

A more critical examination of the "rule" could be made if the pK_a values of the various sulfinic acids and hydrocarbons were known more exactly.

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(20) J. Maurin and R. A. Paris, *Compt. rend.*, **232**, 2428 (1951).

(21) A. A. Morton, *Chem. Revs.*, **35**, 1 (1944).

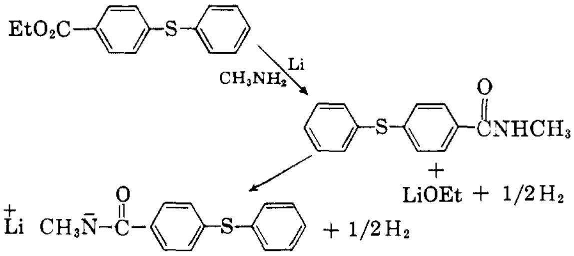
(22) R. R. Coats and D. T. Gibson, *J. Chem. Soc.*, 445 (1940).

(23) L. F. Fieser and M. Fieser, "Textbook of Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1950, pp. 157, 524.

In opposition to this approach Birch[13] has pointed out, in reference to the cleavage of ethers by sodium in ammonia, that "the greater part of the energy of the transition state will be consumed by the carbon system" since the hydrocarbon is a much weaker "acid" than the phenol or alcohol portion. It is quite obvious, in any event, that a detailed explanation cannot be developed with the present facts available. Further work is being done along these lines.

During the cleavage of unsymmetrical diaryl sulfides and sulfones, a number of products was obtained which indicated the occurrence of other reactions. Thus, the anisole produced in the cleavage of the anisyl phenyl sulfides and sulfones was further cleaved, as evidenced by the detection of phenol among the reaction products. This cleavage of anisole to produce phenol by lithium in methylamine has been previously noted by Benkeser and co-workers.[16] Further, 3- and 4-methylcyclohexenes[24] were noted when the tolyl compounds were cleaved. Cyclohexene was also detected in most instances. Such reductions of aromatic hydrocarbons by this system are well known.[15] The detection of N-methylaniline in several of the cleavage reactions indicated the probable formation of lithium methylamide during the course of the reaction and its subsequent attack upon the unreacted substrate. Such a displacement has an analogy in Bradley's[10] work on the cleavage of diaryl sulfones with sodium piperidide to produce the N-arylpiperidine.

When *p*-carbethoxyphenyl phenyl sulfide was cleaved with lithium in methylamine, *p*-phenylmercapto-N-methylbenzamide was formed as expected, but this compound was recovered largely unchanged. Failure of this compound to cleave may have been due to formation of the salt of the amide.[18]



When *m*-chlorophenyl phenyl sulfone was cleaved with lithium in methylamine only benzenethiol could be identified; the absence of chlorine-containing products suggests that the halogen–carbon bond may be more labile than the carbon–sulfur bond to this reducing system.

Experimental[25]

Preparation of Decyl Sulfide.—One mole of sodium (23 g.) was dissolved in one liter of absolute ethanol and 174 g. (1.00 mole) of decyl mercaptan was added. To this solution was added slowly, with stirring, 221 g. (1.00 mole) of decyl bromide and the reaction mixture was refluxed gently overnight. The sodium bromide was filtered off and the ethanol evaporated to yield the crude sulfide, which was purified by distillation, b.p. 155–160° (0.1 mm.), m.p. 27° (literature[26] m.p. 27°), yield 241 g. (76%).

TABLE I

CLEAVAGE PRODUCTS OF R–S–R′

Compound	Mercaptan (% yield)	Hydrocarbon (% yield)
R,R′ = n-$C_{10}H_{21}$	n-$C_{10}H_{21}SH$ (86)	n-$C_{10}H_{22}$ (85)
R,R′ = $C_6H_5CH_2$	None isolated	$CH_3C_6H_5$ (22)
R = n-$C_{10}H_{21}$	C_6H_5SH (87)	n-$C_{10}H_{22}$ (71)
R′ = C_6H_5		n-$C_{20}H_{42}$ (21)
R = n-$C_{10}H_{21}$	2,4,6-$(CH_3)_3C_6H_2SH$ (78)	n-$C_{10}H_{22}$ (74)
R′ = $(CH_3)_3C_6H_2$		n-$C_{20}H_{42}$ (21)
R,R′ = C_6H_5	C_6H_5SH (80)	C_6H_6[a]

[a] Not isolated.

Preparation of Alkyl Aryl Sulfides.—Decyl phenyl sulfide was prepared by the slow addition of 155 g. (0.70 mole) of decyl bromide to 77 g. (0.70 mole) of benzenethiol in a sodium ethoxide solution prepared from 16.1 g. (0.70 mole) of sodium and 500 ml. of absolute ethanol. The reaction mixture was stirred until it cooled to room temperature. The resulting solution was filtered and distilled, the sulfide distilling at 165–170° (0.5 mm.), yield 162 g. (92%). The sulfone boiled at 180° (0.4 mm.).

Anal. Calcd. for $C_{16}H_{26}O_2S$: C, 68.15; H, 9.23. Found: C, 67.61; H, 9.30.

Decyl mesityl sulfide was prepared in the same manner in 90% yield. It had a b.p. 145° (0.2 mm.), and its sulfone melted at 31°.

Anal. Calcd. for $C_{19}H_{32}O_2S$: C, 70.00; H, 10.03. Found: C, 70.17; H, 10.01.

Preparation of Diaryl Sulfides.—These sulfides were prepared by the so-called Ziegler method from the diazonium salt of the appropriate amine and a solution of benzenethiolate in water held at 70–80°. In a typical preparation, 61.5 g. (0.5 mole) of *m*-anisidine[27] was converted into its hydrochloride with 118 g. of concentrated hydrochloric acid. A suspension of the hydrochloride was diazotized at 0° with 34.5 g. (0.5 mole) of sodium nitrite in the minimum amount of water. After diazotization was complete, the solution was neutralized with cold, saturated sodium acetate, filtered, and added dropwise to a stirred solution of 66.0 g. (0.60 mole) of benzenethiol in 200 ml. of water containing 32.0 g. (0.70 mole) of sodium hydroxide. This solution was maintained at 75–80° during the addition. There was a vigorous reaction, accompanied by the evolution of nitrogen, with each addition of the diazonium solution. After addition was complete, the stirred reaction mixture was heated to 95° for one hour, cooled, and the crude sulfide extracted with benzene. The benzene layer was dried over anhydrous sodium sulfate, and the benzene evaporated on the steam-plate. The crude sulfide was distilled once without fractionation and once through an externally heated, one-foot Widmer column. The yield of purified *m*-anisyl phenyl sulfide was 60.0 g. (55.5%). All of the sulfides were identified by conversion to the corresponding sulfones.

Preparation of Sulfones.—With the exception of mesityl sulfones,[28] all of the sulfones were prepared by oxidation of a glacial acetic solution of the sulfide with 30% hydrogen peroxide. In a typical oxidation 17 g. (0.066 mole) of *p*-carbethoxyphenyl phenyl sulfide was dissolved in 110 ml. of glacial acetic acid and refluxed for one hour with 130 ml. of 30% hydrogen peroxide (approximately 2.2 ml./meq. of sulfide). The oil which separated on cooling was induced to crystallize by scratching the walls of the flask. One recrystallization from ethanol–water gave 18 g. (94%) of pure sulfone, m.p. 65.5–67.5°.

Anal. Calcd. for $C_{15}H_{14}O_4S$: C, 62.05; H, 4.86. Found: C, 61.94; H, 4.84.

m-Anisyl phenyl sulfone is also previously unreported in the literature; m.p. 88–90°.

Anal. Calcd. for $C_{13}H_{12}O_3S$: C, 62.90; H, 4.87. Found: C, 63.08; H, 4.82.

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(24) The authors are indebted to Dr. R. A. Benkeser for furnishing authentic samples of these compounds for the purpose of comparison.

(25) All melting points are uncorrected.

(26) M. S. Kharasch and A. F. Zavist, This Journal, **73**, 964 (1951).

(27) Prepared by the reduction of *m*-nitroanisole over PtO_2 catalyst at 45 p.s.i. of hydrogen.

(28) H. Meyer, *Ann.*, **433**, 341 (1933).

TABLE II

CLEAVAGE PRODUCTS OF R–SO_2–R′

Compound	Thiol or sulfinate (% yield)	Hydrocarbon (% yield)
R,R′ = n-$C_{10}H_{21}$	n-$C_{10}H_{21}SO_2Li$ (92)	n-$C_{10}H_{22}$
R,R′ = $C_6H_5CH_2$	$C_6H_5CH_2SO_2Li^a$	$CH_3C_6H_5$
R = n-$C_{10}H_{21}$ R′ = C_6H_5	n-$C_{10}H_{21}SO_2Li$ (95)	$C_6H_6^b$
R = n-$C_{10}H_{21}$ R′ = $(CH_3)_3C_6H_2$	n-$C_{10}H_{21}SO_2Li$ (80)	1,3,5$(CH_3)_3C_6H_3$ (55)
R,R′ = C_6H_5	C_6H_5SH (75), $C_6H_5SO_2Na^c$	$C_6H_6^b$
R,R′ = p-$CH_3C_6H_4$	p-$CH_3C_6H_4SH$ (100), p-$CH_3C_6H_4SO_3Na^c$ (85)	$CH_3C_6H_5^b$
R,R′ = $(CH_3)_3C_6H_2$	2,4,6$(CH_3)_3C_6H_2SO_2Na^c$	$(CH_3)_3C_6H_3^b$

[a] Identified as methyl benzyl sulfone. [b] Not isolated. [c] Product of sodium and ammonia cleavage; some C_6H_5SH also detected.

TABLE III

CLEAVAGE PRODUCTS OF R–$C_6H_4SC_6H_5$ AND R–$C_6H_4SO_2C_6H_5$

Compound R =	Thiols (mole %)	Other products identified
p-CH_3 Sulfide	p-$CH_3C_6H_4SH$ (28.9) C_6H_5SH (71.1)	Benzene, toluene, 3-methylcyclohexene,[a] 4-methylcyclohexene,[a] cyclohexene,[a] N-methylaniline
m-CH_3 Sulfide	m-$CH_3C_6H_4SH$ (51.2) C_6H_5SH (48.8)	Benzene, toluene, 4-methylcyclohexene,[a] cyclohexene[a]
p-CH_3O Sulfide	p-$CH_3OC_6H_5SH$ (0.0) C_6H_5SH (100)	Anisole, phenol, benzene,[a] cyclohexene[a]
m-CH_3O Sulfide	m-$CH_3OC_6H_4SH$ (3.9) C_6H_5SH (96.1)	Anisole, phenol, benzene,[a] cyclohexene,[a] N-methylaniline
p-CH_3 Sulfone	p-$CH_3C_6H_4SH$ (86.5) C_6H_5SH (13.5)	Benzene, toluene,[a] cyclohexene[a]
m-CH_3 Sulfone	m-$CH_3C_6H_4SH$ (36.9) C_6H_5SH (63.1)	Benzene, toluene, N-methylaniline
p-CH_3O Sulfone	p-$CH_3OC_6H_4SH$ (0.0) C_6H_5SH (100)	Anisole, phenol, benzene,[a] N-methylaniline
m-CH_3O Sulfone	m-$CH_3OC_6H_4SH$ (0.0) C_6H_5SH (100)	Anisole, phenol, benzene,[a] cyclohexene,[a] N-methylaniline
R–C_6H_4 = α-naphthyl Sulfide and sulfone	$C_6H_5SH^b$	Naphthalene

[a] Denotes presence of compound in a quantity much smaller than the others listed. [b] Determined by fractional distillation and not vapor-phase chromatography; amount of other thiol small if present at all.

Courtot and Frenkiel[29] reported a melting point of 109° for m-tolyl phenyl sulfone as opposed to our value of 124.5–125.5°.

Anal. Calcd. for $C_{13}H_{12}O_2S$: C, 67.23; H, 5.21. Found: C, 67.04; H, 5.33.

The cleavages of sulfides and sulfones were accomplished by the slow, controlled addition of a solution of lithium in methylamine or sodium in liquid ammonia to a solution of the sulfide or sulfone in methylamine or ammonia. To do this, the amine was refluxed through a thimble containing the calculated amount of lithium wire cut into small pieces. The thimble was placed in a holder situated between the reaction flask and the Dry Ice condenser and designed so that there could be a free flow of amine vapors around the thimble. The thimble itself consisted simply of a standard six-inch test-tube tapered at the bottom and fitted with a length of 6 mm. o.d. glass tubing sufficiently long enough to extend down into the neck of the reaction flask. This prevented the metal solutions from running down the walls of the flask. A small, loose plug of glass wool placed in the bottom of the thimble kept small pieces of the undissolved metal from dropping into the flask. It was found that magnetic stirring was quite satisfactory and the use of a magnetic stirrer with a build-in heating unit made possible increasing the reflux rate above that normal at room temperature.

In a typical cleavage, 19.5 g. (0.084 mole) of p-tolyl phenyl sulfone was placed in the 500-ml. reaction flask and approximately 300 ml. of methylamine was condensed into the flask. Dissolution was aided by stirring. The thimble containing 2.33 g. (0.336 g.-atom) of lithium metal was placed in its holder, and with rapid stirring, the amine was allowed to reflux, the condensate dropping into the thimble and carrying dissolved lithium back into the reaction flask. The deep blue lithium color was discharged immediately. After approximately one-half of the metal had been added, a deep red color appeared in the reaction flask (this was characteristic of most of the cleavages) which persisted until the end of the reaction. After all of the lithium had been added, the color was discharged by the careful addition of 20 ml. of methanol. The condenser was then removed and the amine allowed to evaporate overnight. Water (about 200 ml.) was added and the base-insoluble fraction extracted with ether. The constituents were examined either by fractional distillation or by vapor-phase chromatography.[30] The base soluble fraction was cooled, acidified with hydrochloric acid and the thiol mixture extracted with ether. The ether layer was dried over anhydrous sodium sulfate and the ether evaporated under a stream of N_2. The thiol mixture was then examined by either fractional distillation or vapor-phase chromatography. If the latter was used, the resulting curves were integrated by means of a compensating planimeter to obtain curves were integrated by means of a compensating planimeter to obtain the mole % of each thiol present. Constituents were identified by comparison of their retention times with those of authentic samples. If fractional distillation was used, the thiols were identified by means of their 2,4-dinitrothioethers and/or the corresponding sulfones.[31]

If a sulfinic acid was produced, it was isolated in the same manner and identified as such, or the reaction mixture, after treatment with methanol, was evaporated to dryness and

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[29] C. Courtot and J. Frenkiel, *Compt. rend.*, **199**, 558 (1934).

[30] A Perkin-Elmer model 154-C vapor fractometer was used for these measurements.

[31] (a) R. W. Bost, *et al.*, THIS JOURNAL, **54**, 1985 (1932); (b) **55**, 4956 (1933).

the crude lithium or sodium sulfinate washed with water, acetone and ether. It was then identified by conversion to its 2,4-dinitrophenyl sulfone[31b] or to the disulfone with dibromoethane.[32]

Attempted cleavage of *p*-carbethoxyphenyl phenyl sulfide was carried out as described above with two equivalents of lithium. The only identifiable product on workup was *p*-phenylmercapto-N-methylbenzamide, m.p. 101–102° after two recrystallizations from ethanol–water. Basic hydrolysis followed by acidification yielded *p*-phenylmercaptobenzoic acid, m.p. 173° (literature[33] 173° uncor.). This acid produced no depression of melting point in a mixture melting point determination with an authentic sample obtained by the basic hydrolysis of the original ester. Infrared showed the presence of characteristic amide absorption and the odor of methylamine was quite noticeable during the amide hydrolysis.

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LAFAYETTE, IND.

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[32] P. Allen, *J. Org. Chem.*, **7**, 23 (1942).

[33] W. S. Weedon and H. W. Doughty, *Am. Chem. J.*, **33**, 425 (1905).

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORY OF THE SOCONY MOBIL OIL CO., INC., AND THE WHITMORE LABORATORY OF THE COLLEGE OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE UNIVERSITY]

The Oxidation of Methylene and Methyl Groups by Sodium Hypochlorite[1]

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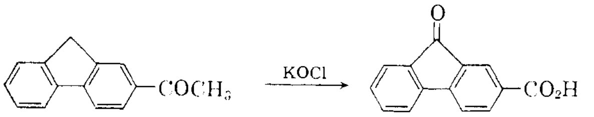
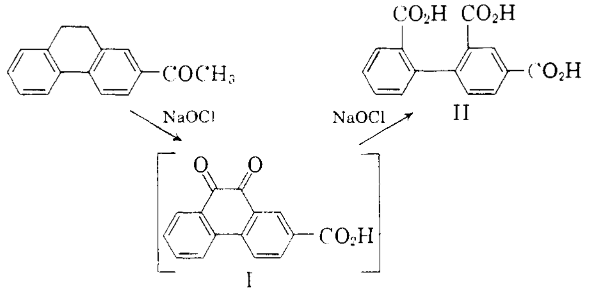
Methylene and methyl groups attached to an aromatic nucleus are readily oxidized by sodium hypochlorite when the nucleus also contains an acetyl group. The acetyl group seems to play a vital role in the oxidations, and a mechanism has been suggested to explain this. Sodium hypochlorite has been found to oxidize aromatic α-diketones such as benzil and 9,10-phenanthrenequinone.

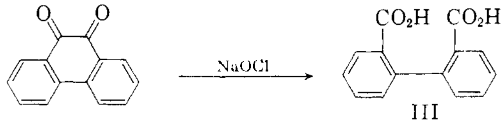
The oxidation of methyl ketones to carboxylic acids by means of alkaline hypohalite solutions is a well known and widely used technique. The reaction has been extended to higher alkylaryl ketones and alkylheterocyclic ketones.[3,4] Recently, Farrar has reported on the hypobromite oxidation of cyclic ketones to dicarboxylic acids.[5] The first report of the attack of hypohalite on a methylene group was that of Schiessler and Eldred.[6] They attempted to prepare fluorene-2-carboxylic acid by oxidizing 2-acetylfluorene, but instead obtained only fluorenone-2-carboxylic acid.



The present research was initiated when a similar anomalous oxidation was discovered. In attempting to prepare 9,10-dihydrophenanthrene-2-carboxylic acid from 2-acetyl-9,10-dihydrophenanthrene by oxidation with sodium hypochlorite (*p*H 12–13), an unexpected product was obtained. Analysis of the substance showed it to be 2,2′,4-tricarboxybiphenyl (II). The hypochlorite had oxidatively cleaved the 9,10-bond in the dihydrophenanthrene nucleus. When sodium hypochlorite solution with a *p*H of approximately 10 was used, the major oxidation product was the normal one, 9,10-dihydrophenanthrene-2-carboxylic acid. A small amount of the triacid was also produced.



It is interesting to note that the starting ketone differs from 2-acetylfluorene by only one methylene group. Considering the ketone obtained by Schiessler and Eldred, one might reasonably expect the quinone I to be an intermediate in the oxidation process. To test this hypothesis, 9,10-phenanthrenequinone was treated with sodium hypochlorite and converted in a 94% yield to diphenic acid (III). Benzil was oxidized to benzoic acid in 88% yield. These two experiments lend support to the suggestion that the phenanthrenequinone is an intermediate.



When 6-acetyltetralin was oxidized, an 18% yield of the normal product, tetralin-6-carboxylic acid, was obtained along with a 56% yield of a mixture of tricarboxylic acids. Upon separation, the acid obtained in lesser quantity was identified as 3-(2,4-dicarboxyphenyl)-propanoic acid (IV), while the predominant acid is believed to be the isomeric 3-(2,5-dicarboxyphenyl)-propanoic acid (V). The latter has not been reported previously.

p-Ethylacetophenone was converted to terephthalic acid in 95% yield. In order to determine

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(3) M. W. Farrar and R. Levine, THIS JOURNAL, **71**, 1496 (1949).

(4) R. Levine and J. A. Stephens, *ibid.*, **72**, 1642 (1950).

(5) M. W. Farrar, *J. Org. Chem.*, **22**, 1708 (1957).

(6) R. W. Schiessler and N. R. Eldred, THIS JOURNAL, **70**, 3958 (1948).