

isocyanates and isothiocyanates. Phenyl isocyanate and *p*-bromophenyl isocyanate interact with diazomethane in cold ethereal solution to form the β -lactams of *N*-phenyl- β -alanine and *N*-(*p*-bromophenyl)- β -alanine.

Benzoyl isocyanate reacts vigorously with diazo-

methane to give in 68–70% yield 2-phenyl-4-oxazolone. With phenyl isothiocyanate, diazomethane forms a crystalline equimolar addition product, 5-anilino-1,2,3-thiadiazole. An electronic interpretation of the reactions is presented.

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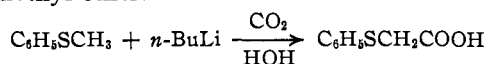
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Metalation of Some Sulfur-Containing Organic Compounds^{1a}

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Methyl phenyl sulfide was shown to undergo exclusive lateral metalation² with *n*-butyllithium in diethyl ether.



Under corresponding conditions nuclear metalation³ is effected with both diethylbarium and diethylstrontium to give metalation products which yield on carbonation, *o*-methylmercaptobenzoic acid. Metalations of methyl phenyl sulfide with other reagents are now reported. To determine the generality of the lateral metalation with *n*-butyllithium, a number of aryl methyl sulfides and higher-alkyl aryl sulfides were studied.

lithium in ether, *n*-butyllithium in petroleum ether (b. p. 28–38°) and phenylsodium in benzene gave lateral metalation (Table I). The rate of reaction was especially slow in petroleum ether. Lateral metalation also occurred with *n*-butyllithium at 150° in the absence of solvent. Under corresponding conditions at 150–155°, *n*-butylmagnesium bromide gave a nuclear metalation since *o*-methylmercaptobenzoic acid was isolated subsequent to carbonation. Thus, ortho-nuclear substitution was effected by metalating agents of the Group II metals, magnesium, barium³ and strontium³ but lateral metalation by the metalating agents of the Group I metals, lithium and sodium. Anisole also gives ortho-

TABLE I

METALATION OF METHYL PHENYL SULFIDE

Metalating agent ^a	Time, hr.	Temp., °C.	Solvent	Acid ^b yield, %	Thiophenol yield, %	Recovered sulfide, %
Sodium	18	25–28	Ether	3.9	20.9	52.4
Sodium	18	25–28	Benzene	Trace ^c	Trace ^c	87.5
Mercuric acetate	9.5	95–100		36.6 ^d		
<i>n</i> -Butylmagnesium bromide	2	135–140	None ^e	42.0 ^f	Trace ^c	63.0
	5	150–155	None	0.2 ^g		67.0
Methylithium	20	34	Ether	0.12		84.0
<i>n</i> -Butyllithium	20	28–38	Pet. ether	Trace ^c		91.5
<i>n</i> -Butyllithium	168	28–38	Pet. ether	3.6	2.27	31.7
<i>n</i> -Butyllithium	3	130–150	None	Trace ^c	22.7	29.0
<i>n</i> -Butyllithium	1	To 150 ^h	None	21.2	10.0	52.2
Phenyllithium	16	34	Ether	9.2		37.0
Phenylsodium	5	Room	Benzene	8.9		44.4
Phenylcalcium iodide	46	34	Ether			78.5
	3.5	150–160	None		13.0	58.8

^a The mole ratio of metalating agent to sulfide was 1:1. ^b Phenylmercaptoacetic acid was isolated unless otherwise specified. The yield was calculated on sulfide introduced. ^c Traces were not identified. ^d The product was *p*-acetoxymercuriphenyl methyl sulfide. ^e The ether was distilled, prior to addition of the sulfide, until the desired temperature was reached, as measured by a thermometer in the liquid. ^f Valeric acid only was isolated. ^g The product was *o*-methylmercaptobenzoic acid. ^h The sulfide was added to the cooled residue, after distillation of the ether. The mixture was heated to 150° during thirty minutes and cooled during the next thirty minutes. ⁱ Benzoic acid only was isolated.

Metalation of Methyl Phenyl Sulfide.—The position substituted was conditioned by the metalating agent employed rather than by solvent or temperature. Methyl- and phenyl-

nuclear metalation with Grignard reagents.⁴ Phenylcalcium iodide failed to metalate methyl phenyl sulfide in ether or at 150–160° in the absence of solvent. This reagent did not metalate phenyl sulfide⁵ but did metalate dibenzothiophene in the 3-position.⁶ Mercuric acetate gave

(1a) Paper LXVI in the Series: "The Relative Reactivities of Organometallic Compounds"; the preceding paper with Gainer is in *THIS JOURNAL*, **71**, 2327 (1949).

(1b) Present address: Firestone Tire and Rubber Co., Akron, Ohio.

(2) Gilman and Webb, *THIS JOURNAL*, **62**, 987 (1940).

(3) Gilman, Haubein, O'Donnell and Woods, *ibid.*, **67**, 922 (1945).

(4) Challenger and Miller, *J. Chem. Soc.*, 894 (1938).

(5) Gilman and Bebb, *THIS JOURNAL*, **61**, 109 (1939).

(6) Gilman, Jacoby and Pacevitz, *J. Org. Chem.*, **3**, 120 (1938).

the *p*-acetoxymercuri- compound with methyl phenyl sulfide. The para substitution was proved by comparison of the bromomercuri- compound prepared from the acetoxymercuri- derivative and sodium bromide with that obtained from *p*-methylmercaptophenylmagnesium bromide and mercuric bromide. This orientation appears to be general for alkyl aryl and aryl ether types as both anisole⁷ and phenyl sulfide⁸ undergo *p*-mercuration.

Metalation of Other Aryl Methyl Sulfides.—*n*-Butyllithium in diethyl ether gave exclusive lateral metalation with each of the aryl methyl sulfides investigated as evidenced by the isolation of the corresponding arylmercaptoacetic acid on carbonation and hydrolysis (Table II). Identifications were completed by mixed melting point determinations with authentic specimens. Arrangement of the aryl radicals in order of decreasing yield of metalation product gives the series: phenyl-, *p*-tolyl-, α -naphthyl- > *p*-dimethylaminophenyl- > β -naphthyl- > *p*-chlorophenyl-.

TABLE II
METALATION OF ARYL METHYL SULFIDES BY *n*-BUTYLLITHIUM

Aryl group ^a	Time, hr.	Acid, ^b yield, %	Recovered sulfide, %
<i>p</i> -Tolyl	16	38.2	51.0
<i>p</i> -Chlorophenyl	5	5.8 ^c	^d
<i>p</i> -Dimethylaminophenyl	19	22.4 ^e	52.1
<i>p</i> -Dimethylaminophenyl	19	15.1	43.1
α -Naphthyl	5	35.4	^d
β -Naphthyl	20	11.7	85.0

^a The mole ratio of metalating agent to sulfide was 1:1. The reactions were performed in refluxing ether solution. ^b The corresponding arylmercaptoacetic acid was isolated in each case and identified by a mixed melting point determination with an authentic specimen. The yields, based on sulfide introduced, are for pure acid or acid melting within 1–2° of the pure compound, unless otherwise noted. In check runs the yields differ by less than 10%. The reaction time beyond about five hours is not critical since the yields of phenylmercaptoacetic acid from methyl phenyl sulfide were 43.5 and 35.2% in fifteen hours and 37.6 and 39.7% in five and four and one-half hours, respectively. ^c The crude acid melted at 99–100° or at 105° after two recrystallizations from petroleum ether (b. p. 60–68°). ^d The neutral fraction was not investigated. ^e The crude acid melted at 75–80° and at 85–86° after two recrystallizations from benzene.

Higher-Alkyl Aryl Sulfides.—In marked contrast to the *methyl* aryl sulfides, the sulfides having higher-alkyl groups gave only *ortho* nuclear metalation, the corresponding *o*-alkylmercaptobenzoic acid being isolated (Table III). This orientation corresponds to that given by the oxygen ether types previously examined.⁹ In general, the lateral metalations proceeded to a greater extent than the nuclear metalations. Ethyl phenyl sulfide was not metalated by phenylcalcium iodide on refluxing in ether solution for sixty hours. Traces of sulfur-containing acids other

than the metalation acid were obtained from isopropyl and *n*-butyl phenyl sulfides with *n*-butyllithium. These melted at 154–156° and 79–80°, respectively, but were not identified.

TABLE III
METALATION OF HIGHER-ALKYL ARYL SULFIDES BY *n*-BUTYLLITHIUM

Sulfide ^a	Time, Metalation ^b hr.	Benzoic ^c acid, %	Recovered sulfide, %
Ethyl phenyl	15	7.7	51.5
	15	5.4	59.4
<i>n</i> -Propyl phenyl	20	6.9	54.5
Isopropyl phenyl ^d	20	9.0	65.0
	20	11.0	67.8 ^f
<i>n</i> -Butyl phenyl	19 ^g	6.2	57.0
	19 ^g	4.9	63.0
	18	6.4	64.0
Cyclohexyl phenyl	48	11.4 ^h	58.4
	24	8.5 ^h	60.5
Ethyl β -naphthyl	20	20.4 ⁱ	37.3

^a The mole ratio of sulfide to metalating agent was 1:1. The reactions were performed in refluxing ether solution. ^b The corresponding *o*-alkylmercaptobenzoic acid was isolated and identified by comparison with an authentic specimen, except in the last reaction. The yields are for pure acid based on sulfide introduced, unless otherwise noted. ^c The crude benzoic acid melted in the range 117–119°. ^d A small quantity (0.6 g.) of a crude acid isolated in this experiment probably contained benzoic acid. ^e The acid melted at 116–117° from petroleum ether (b. p. 60–68°) and was identified by comparison with a specimen from methyl thiosalicylate and isopropyl bromide in alcoholic potassium hydroxide. *Anal.* Calcd. for C₁₀H₁₂O₂S: S, 16.33. Found: S, 16.53. ^f The neutral fraction gave, from a one-tenth mole run, 1.25 g. of an unidentified oil, b. p. 174–176° (5–6 mm.), in addition to the recovered sulfide, b. p. 97–98° (20 mm.). ^g The *n*-butyllithium solutions used in these two experiments were filtered free of coarse particles but contained some finely divided solid. All other *n*-butyllithium solutions were filtered entirely free of solid. ^h The acid melted at 85–86° from petroleum ether (b. p. 60–68°) and was identified by a mixed melting point determination with a specimen from thiosalicylic acid and bromocyclohexane in alcoholic potassium hydroxide. *Anal.* Calcd. for C₁₁H₁₄O₂S: S, 13.56. Found: S, 13.71. The yield was based on material melting in the range 75–80°. ⁱ The yield was based on crude acid melting at 130–135°. Two recrystallizations from benzene raised the melting point to 157–158° where it remained unaltered after recrystallization from aqueous acetic acid. The acid was not identified. It contained sulfur but the neutral equivalent did not agree with the theoretical value for a monocarboxyethyl naphthyl sulfide.

Diphenyl Disulfide.—With *n*-butyllithium in ether there was obtained 4.3% of crude *o,o'*-dicarboxydiphenyl disulfide, 31.4% of *n*-butyl phenyl sulfide and 17.9% of recovered diphenyl disulfide. The same acid was isolated in a previously reported reaction with thiophenol.¹⁰

***p*-Bromophenyl Methyl Sulfide.**—In contrast to *p*-bromoanisole which is metalated by *n*-butyl-¹¹ and methylithium¹² to give 5-bromo-2-methoxy-

(7) Dimroth, *Ber.*, **35**, 2867 (1902).

(8) Sachs and Ott, *ibid.*, **59**, 171 (1926).

(9) Ref. 5; see also later papers in this series.

(10) Gilman, Arntzen and Webb, *J. Org. Chem.*, **10**, 374 (1945).

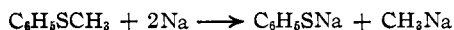
(11) Gilman, Langham and Jacoby, *THIS JOURNAL*, **61**, 106 (1939).

(12) Langham, Brewster and Gilman, *ibid.*, **68**, 545 (1941).

benzoic acid, *p*-bromophenyl methyl sulfide gave interconversion with *n*-butyllithium and chiefly coupling with methylithium, the reaction products being, respectively, *p*-methylmercaptobenzoic acid and methyl *p*-tolyl sulfide. *p*-Bromophenyl methyl sulfide failed to form an organolithium compound in ether and was quantitatively recovered.

Methyl Phenyl Selenide.—Like phenyl selenide,⁵ methyl phenyl selenide was cleaved by *n*-butyllithium in refluxing ether. On carbonation, 28.4% of benzoic acid and 25.6% of *n*-butyl methyl selenide were obtained. Amylsodium in petroleum ether (b. p. 28–38°) gave a 25% yield of benzoic acid after four hours at room temperature. Only a trace of acidic material was isolated on carbonating a mixture of methyl phenyl selenide and sodium sand in petroleum ether (b. p. 28–38°) after four hours of stirring at room temperature.

Cleavage Reactions.—No appreciable cleavage occurred when the aryl methyl sulfides were refluxed with *n*-butyllithium in diethyl ether for periods of time up to twenty hours. Noticeable cleavage resulted from more strenuous conditions of time and temperature. In each case the *methyl* group was eliminated with the formation of thiophenol. Refluxing of methyl phenyl sulfide with *n*-butyllithium in petroleum ether (b. p. 28–38°) for one hundred and sixty-eight hours gave 2.27% of thiophenol. Increased yields of thiophenol (10–22.7%) were obtained from methyl phenyl sulfide and *n*-butyllithium and phenylcalcium iodide at temperatures up to 160° in the absence of solvent. On carbonating a mixture of sodium sand and methyl phenyl sulfide which had been stirred eighteen hours at room temperature, there was isolated 20.9% of thiophenol and 3.5% of phenylmercaptoacetic acid. It is possible that the metalating agent was methylsodium.



Ethyl, *n*-propyl, *n*-butyl and cyclohexyl phenyl sulfides, unlike the aryl methyl sulfides, were cleaved by *n*-butyllithium in refluxing ether with elimination of the *alkylmercapto* group and formation of benzoic acid in addition to the metalation acid. No thiophenol was found. The *alkylmercapto* residue was isolated only from the reaction of *n*-butyllithium with *n*-butyl phenyl sulfide which gave 6.5% of *o*-(*n*-butylmercapto)-benzoic acid, 1.2% of benzoic acid and 1.0% of butyl mercaptan (as the lead salt).¹³ An exception was the reaction of isopropyl phenyl sulfide with *n*-butyllithium from which no benzoic acid was isolated in spite of a careful search. *n*-Butyl phenyl sulfide was cleaved in two ways by lithium metal in refluxing ether to yield on carbonation 11.9% of benzoic acid, 20.5% of thiophenol, 0.24% of *o*-(*n*-butylmercapto)-benzoic acid and 18.1% of recovered *n*-butyl phenyl sulfide. A trace of an acid

(13) Wertheim, *THIS JOURNAL*, **51**, 3661 (1929).

melting at 270°, after recrystallization from ethanol, was also found but was not identified. The formation of *o*-(*n*-butylmercapto)-benzoic acid was probably due to a metalation by phenyllithium formed in the cleavage reaction. The formation of a trace of benzoic acid has been observed in the reaction of phenyl *n*-tetradecyl sulfide with *n*-butyllithium.¹⁴

Experimental

Sulfides.—The methyl and ethyl sulfides were generally prepared from the corresponding sulfate and aryl mercaptan in aqueous alkali. *n*-Propyl, isopropyl, *n*-butyl and cyclohexyl phenyl sulfides were prepared from the corresponding halide and thiophenol in alcoholic potassium hydroxide solution.¹⁵ The boiling points and refractive indices agreed with the reported values.

General Procedure.—The metalations were performed according to procedures reported earlier.¹⁶ The organolithium, -calcium and -magnesium reagents were filtered free of solid before use. The metalation reactions were worked up, following carbonation on Dry Ice, by acidification of the mixture and extraction with ether. The ether layer was successively extracted with 8% sodium bicarbonate solution and 10–20% potassium hydroxide solution. The neutral fraction was recovered from the ether layer after drying over anhydrous sodium sulfate. The two aqueous extracts were acidified and the precipitates recovered by filtration or extraction. Benzoic acid was separated from the metalation acid by fractional crystallization from petroleum ether (b. p. 60–68°) or was isolated by ether extraction of the filtrate from the acidified bicarbonate extract.

Diphenyl Disulfide.—A solution of *n*-butyllithium prepared from 0.2 mole of *n*-butyl bromide and 0.4 g. atom of lithium in 200 ml. of ether, was treated with 10.9 g. (0.05 mole) of diphenyl disulfide, refluxed for twenty hours and carbonated on Dry Ice. In the usual manner there was isolated 0.65 g. of crude *o,o'*-dicarboxydiphenyl disulfide. The pure white compound was obtained after several recrystallizations from ethanol and acetic acid-water mixtures; m. p. 302–305° (microscope stage).

Anal. Calcd. for $C_{14}H_{10}O_4S_2$: neut. equiv., 153. Found: neut. equiv., 156.

The methyl ester, prepared from the acid and diazomethane, melted at 131–132° after one recrystallization from ethanol.¹⁷

Distillation of the neutral fraction gave 5.2 g. (31.4%) of *n*-butyl phenyl sulfide; b. p. 96–98° (4 mm.), n_D^{20} 1.5458.¹⁶ The distillation residue was recrystallized from ethanol to yield 1.95 g. (17.9%) of diphenyl disulfide identified by a mixed melting point determination.

***p*-Acetoxymercuriphenyl Methyl Sulfide.**—A mixture of 12.4 g. (0.1 mole) of methyl phenyl sulfide and 15.0 g. (0.05 mole) of mercuric acetate was stirred and heated on a steam-bath for nine and one-half hours and allowed to stand overnight. The white solid which formed was recrystallized from ethanol to give 6.7 g. of *p*-acetoxymercuriphenyl methyl sulfide; m. p. 183–184°, yield 36.6%. The constant melting point from ethanol was 184°.

Anal. Calcd. for $C_9H_{10}O_2SHg$: Hg, 52.40. Found: Hg, 52.84, 52.78.

***p*-Bromomercuriphenyl Methyl Sulfide.**—To an ethanol solution of 1.0 g. (0.0027 mole) of *p*-acetoxymercuriphenyl methyl sulfide was added 0.32 g. (0.0027 mole) of potassium bromide in 100 ml. of aqueous ethanol. The resulting precipitate weighed 0.93 g. (85.5%) and was purified by Soxhlet extraction with chloroform; m. p. 268–269°.

(14) F. W. Hoyt, Doctoral Dissertation, Iowa State College.

(15) Ipatieff, Pines and Friedman, *THIS JOURNAL*, **60**, 2731 (1938); Gilman and Heck, *ibid.*, **50**, 2223 (1928).

(16) See references 2, 3, 5 and 6.

(17) List and Stein, *Ber.*, **31**, 1670 (1898), report a melting point of 130.5° and Gattermann, *ibid.*, **32**, 1151 (1899), gives a melting point of 134°.

A mixed melting point determination with a specimen prepared from *p*-methylmercaptophenylmagnesium bromide and mercuric bromide showed no depression.

Anal. Calcd. for C_7H_7SHgBr : Hg, 49.68. Found: Hg, 49.64.

***p*-Dimethylaminophenyl Methyl Sulfide.**¹⁸—To a solution of 5.1 g. (0.22 g. atom) of sodium in 100 ml. of liquid ammonia was added slowly, with stirring, 33.4 g. (0.1 mole) of bis-(*p*-dimethylaminophenyl) disulfide (prepared from the Grignard reagent and sulfur). A further small quantity of the disulfide was added to discharge the blue color, the solution being pink at the end. Dropwise addition of 28.4 g. (0.2 mole) of methyl iodide in 30 ml. of ether resulted in the formation of a white precipitate. After the ammonia had evaporated the residue was partitioned between water and ether. Evaporation of the dried ether layer followed by distillation gave 26.4 g. (79%) of *p*-dimethylaminophenyl methyl sulfide, b. p. 159–160° (20 mm.).

***p*-Dimethylaminophenylmercaptoacetic Acid.**—To 1.67 g. (0.005 mole) of bis-(*p*-dimethylaminophenyl) disulfide in 75 ml. of liquid ammonia was added 0.23 g. (0.01 g. atom) of sodium followed by 0.95 g. (0.005 mole) of chloroacetic acid in 50 ml. of liquid ammonia. The ammonia was allowed to evaporate and the pink solid residue neutralized and extracted with ether. Evaporation of the dried ether solution gave the required acid, m. p. 85°, after recrystallization from benzene. The mixed melting point determination with the acid obtained by metalating *p*-dimethylaminophenyl methyl sulfide showed no lowering.

Anal. Calcd. for $C_{10}H_{13}O_2NS$: N, 6.63. Found: N, 6.66.

Methyl Phenyl Sulfide and Sodium.—A mixture of 12.4 g. (0.1 mole) of methyl phenyl sulfide and 2.5 g. (0.11 g. atom) of sodium sand in 75 ml. of diethyl ether was stirred for eighteen hours at room temperature (25–28°) prior to carbonation on Dry Ice. The reaction was worked up in the usual way to give 0.40 g. of phenylmercaptoacetic acid by precipitation and 0.25 g. of the same acid by extraction of the filtrate; m. p. 61–63°, yield 3.9%. By extraction with potassium hydroxide solution there was isolated 2.3 g. (20.9%) of thiophenol; b. p. 84–85° (50 mm.), n^{20}_D 1.5850. The recovered methyl phenyl sulfide amounted to 6.5 g. or 52.4%.

***n*-Butyl Phenyl Sulfide and Lithium.**—To a suspension of 1.38 g. (0.2 g. atom) of lithium cut in small pieces (1–2 mm. square) in 50 ml. of ether was added 16.6 g. (0.1 mole) of *n*-butyl phenyl sulfide in 25 ml. of ether. The mixture was stirred at room temperature for seven hours and then refluxed for thirty-six hours before carbonation on Dry Ice. Acidification of the bicarbonate extract gave 2.7 g. of acidic material, melting at 90–100°. Extraction with petroleum ether (b. p. 60–68°) separated an insoluble substance (unidentified) weighing 0.03 g. and melting at 270° after recrystallization from ethanol-water. The petroleum ether-soluble portion was fractionally crystallized to give 1.3 g. (10.6%) of benzoic acid and 0.05 g. (0.24%) of *o*-(*n*-butylmercapto)-benzoic acid both of which were identified by mixed melting point determinations. An additional 0.15 g. (1.3%) of benzoic acid was isolated by ether extraction of the original aqueous filtrate. The potassium hydroxide extract on acidification and distillation yielded 2.25 g. (20.5%) of thiophenol. Three grams (18.1%) of the starting material was recovered.

***p*-Bromophenyl Methyl Sulfide and Methylithium.**—A solution of methylithium, prepared from 14.2 g. (0.1 mole) of methyl iodide and 1.38 g. (0.2 g. atom) of lithium in 100 ml. of ether, was filtered, concentrated and treated with 10.2 g. (0.05 mole) of *p*-bromophenyl methyl sulfide in 20 ml. of ether. The total volume was 85 ml. After fifteen minutes, a 5-ml. aliquot was removed and carbonated. The remainder was refluxed for twenty-two hours

before carbonation. Both portions were worked up in the same manner. The aliquot yielded only a trace of acidic material which was insufficient for investigation and 83.3% of recovered *p*-bromophenyl methyl sulfide. The main portion gave 5–10 mg. of *p*-methylmercaptobenzoic acid identified by a mixed melting point determination. Three fractions were obtained on distillation of the neutral fraction: (1) methyl phenyl sulfide (10.3%) boiling range, 80–87° (18 mm.); (2) methyl *p*-tolyl sulfide (14.1%) boiling range 96–100° (18 mm.); and (3) *p*-bromophenyl methyl sulfide, (5.9%) boiling range 115–120° (10 mm.). Each of the three fractions was identified by hydrogen peroxide oxidation to the corresponding sulfone and determination of the mixed melting point with an authentic specimen.

***p*-Bromophenyl Methyl Sulfide and *n*-Butyllithium.**—To the filtered solution of *n*-butyllithium prepared from 6.85 g. (0.05 mole) of *n*-butyl bromide and 0.70 g. (0.1 g. atom) of lithium in 100 ml. of ether, was added rapidly with stirring 5.08 g. (0.025 mole) of *p*-bromophenyl methyl sulfide in 50 ml. of ether. After fifteen minutes at room temperature, a 50-ml. aliquot was removed and carbonated on Dry Ice. By means of the usual procedures, there was isolated 1.23 g. (88%) of *p*-methylmercaptobenzoic acid¹⁹; m. p. 189.5–190°. The remainder of the reaction mixture was refluxed for seventeen hours before carbonation. There was isolated 6.1% of *p*-methylmercaptobenzoic acid and 18.3% of recovered sulfide.

Methyl Phenyl Selenide and *n*-Butyllithium.—Methyl phenyl selenide²⁰ was prepared from selenophenol and dimethyl sulfate in 80% yield; b. p. 89–90° (15 mm.), n^{25}_D 1.6060.

To the filtered solution of *n*-butyllithium prepared from 13.7 g. (0.1 mole) of *n*-butyl bromide and 1.40 g. (0.2 g. atom) of lithium in 100 ml. of ether was added 8.35 g. (0.05 mole) of methyl phenyl selenide in 25 ml. of ether. The solution was stirred for one-half hour at room temperature, refluxed for nineteen hours, carbonated on Dry Ice and worked up in the usual way. There was isolated 28.4% of benzoic acid, 25.6% of *n*-butyl phenyl selenide and 13.8% of recovered methyl phenyl selenide. The liquids were identified by boiling point and refractive index. When the reflux period was shortened to four hours, 21% of benzoic acid was obtained.

Methyl Phenyl Selenide and *n*-Amylsodium.—The metalating agent was prepared²¹ at ice-bath temperature from 10.6 g. (0.1 mole) of *n*-amyl chloride and 5.7 g. (0.25 g. atom) of sodium in 100 ml. of petroleum ether (b. p. 28–38°). Without removing the ice-bath, 8.35 g. (0.05 mole) of methyl phenyl selenide was added rapidly. No change was observed for about fifteen minutes, when the mixture changed from a black to a gray color and refluxed for a few minutes. When the refluxing ceased, the ice-bath was removed and the stirring continued for four hours at room temperature. The thick brown mixture was carbonated as usual. The mixture was worked up by means of the customary procedures to yield 1.92 g. (31.8%) of crude benzoic acid, m. p. 117–119°. In an attempt to crystallize the acid from water, 0.15 g. remained undissolved and was removed by filtration. The filtrate deposited 1.5 g. of benzoic acid; m. p. 120–121°, yield 25%. The insoluble material was organic in nature but did not melt at 280°. It was not identified.

Since the amylnaodium in the foregoing experiment contained excess sodium metal, it seemed advisable to test the action of sodium on methyl phenyl selenide. Accordingly, a mixture of 3.4 g. (0.02 mole) of methyl phenyl selenide and 1.05 g. (0.045 g. atom) of sodium sand in petroleum ether (b. p. 28–38°) was stirred for four hours and carbonated by Dry Ice. Only a trace of a red oil was isolated by acidification of the bicarbonate extract.

Sulfones.—Attempts were made to metalate methyl and ethyl phenyl sulfones, phenyl sulfone and dibenzothio-

(19) Zincke and Jörg, *Ber.*, **43**, 3448 (1910).

(20) Baker and Moffitt, *J. Chem. Soc.*, 1722 (1930).

(21) Gilman and Pacevitz, *THIS JOURNAL*, **62**, 1301 (1940).

(18) Zincke and Jörg, *Ber.*, **42**, 3374 (1909), prepared this compound by another method.

phene-5-dioxide. As expected from the known reactions of sulfones with Grignard reagents,²² bicarbonate-soluble products were isolated in each case but only from methyl phenyl sulfone was the product identified. Here, *n*-butyllithium gave 47% of benzenesulfonylacetic acid and 45.5% of the sulfone was recovered. Ethyl phenyl sulfone reacted vigorously with ethylmagnesium bromide to yield on carbonation an acidic gum which was not identified. There was also separated a trace of an unidentified bicarbonate-insoluble but potassium hydroxide-soluble crystalline solid, m. p. 156°. The starting material was recovered to the extent of 61%. An unidentified acidic oil was also obtained from ethyl phenyl sulfone and *n*-butyllithium. This substance turned black on standing. Diphenyl sulfone reacted vigorously with *n*-butyllithium to give in low yield an acid melting at 200° after darkening from 120°. Attempts to purify this substance by recrystallization from a variety of solvents were unsuccessful.

(22) Ziegler and Connor, *ibid.*, **62**, 2596 (1940); Kohler and Tishler, *ibid.*, **57**, 217 (1935); Kohler and Potter, *ibid.*, **57**, 1316 (1935); **58**, 2166 (1936); Kohler and Larsen, *ibid.*, **57**, 1448 (1935); **58**, 1518 (1936).

An acidic gum was obtained from dibenzothiophene-5-dioxide and *n*-butyllithium following carbonation. All efforts to crystallize the product were unsuccessful.

Summary

1. Methyl aryl sulfides, in general, undergo lateral metalation with metalating agents of the Group I metals.
2. Methyl phenyl sulfide is metalated in the nucleus by *n*-butylmagnesium bromide.
3. Ethyl phenyl, *n*-propyl phenyl, isopropyl phenyl and *n*-butyl phenyl sulfides give *ortho*-nuclear metalation with *n*-butyllithium in diethyl ether.
4. Some cleavage reactions of alkyl phenyl sulfides with lithium and sodium metals and with *n*-butylmagnesium bromide and *n*-butyllithium have been examined.

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[CONTRIBUTION FROM THE GEORGE M. MOFFETT RESEARCH LABORATORIES, CORN PRODUCTS REFINING COMPANY]

Properties of the Fractions and Linear Subfractions from Various Starches

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There have been no critical standards by which to evaluate the purity and extent of degradation of the fractions from various starches. As a consequence, doubts frequently arise regarding the quality of the parent starch, the possibility of hydrolytic degradation during fractionation, and the purity of the final fractions. The present investigations were initiated primarily to isolate the linear and branched components of various common starches by optimum fractionation techniques, and to establish precise standards of purity and degree of degradation on the basis of iodine affinity and intrinsic viscosity. As this work progressed, the substantial differences between the linear fractions from the various starches required further elucidation from a molecular standpoint. This led to the development of a technique for separating the total linear material into a graded series of subfractions by partial precipitation methods. Various reducing value determinations for aldehydic end-groups have been investigated as a means for comparing the relative molecular size of the linear fractions and subfractions. These physical and chemical criteria have likewise had application in estimating the degree of hydrolysis of various modified starches and in elucidating the mechanism of β -amylase action on the starch fractions. Through the kindness of A. L. Potter and W. Z. Hassid, osmotic molecular weights and non-aldehydic end-group assays (by periodate oxidation) have been reported on many of the identical fractions here described.¹

In the present paper, the linear and branched

starch components are designated as the A-fraction and the B-fraction, respectively, in conformance with previously established definitions.²

Source of Starches.—Various samples of commercial corn starch were selected over a period of four years, choosing those lots which possessed the highest "hot paste viscosity." The wheat starch was an experimental batch produced at the Northern Regional Research Laboratory by sulfur dioxide steeping. Tapioca starches included samples from Brazil (kindly supplied by Mr. George Caesar of Stein, Hall and Company) and from the Dominican Republic, in each case selected by reason of high paste viscosity. Limited data are likewise available on the A-fraction from pre-war Javanese tapioca. Potato starches were of Maine and Idaho origin, from the New England Starch Company and Idaho Potato Starch Company, respectively. Data are also included on the B-fraction from pre-war German potato starch. Since commercial sago starch is frequently bleached with oxidizing agents, a sample of virgin unmodified sago flour was secured through the courtesy of Dr. C. G. Caldwell of the National Starch Company. This was suspended in methanol and screened through silk bolting cloth, then repeatedly sedimented in methanol and finally in distilled water. This treatment served to remove all foreign material and most of the pigment. Easter lily starch was furnished by Dr. R. M. Hixon of Iowa State College. The corn, wheat, sago and lily starches were defatted by five two-hour digestions under reflux with boiling 85% methanol, filtering and washing with 85% methanol after each digestion. In later studies, raw corn starch (non-defatted) was fractionated directly.

Fractionation Methods.—In all cases, primary separation was effected by selective precipitation with Pentasol (commercial mixture of amyl alcohols marketed by Sharples Solvents). Where the starch was dissolved by autoclaving, defatted starch was employed and the system was buffered at pH 6.2–6.3 prior to autoclaving by the addition of 40 ml. of 20% phosphate solution (16.4% with respect

(1) Potter and Hassid, *This Journal*, **70**, 3488, 3774 (1948).

(2) Schoch in "Advances in Carbohydrate Chemistry," edited by Pigman and Wolfrem, Vol. I, Academic Press, New York, N. Y., 1945, pp. 247–277.