The yield of *tert.*-butylmagnesium *bromide* in one of the smaller-sized runs was 33.1%. Under corresponding conditions the yield of *tert.*-butylmagnesium *chloride* was 49.71%. Earlier results by Gilman and McCracken under different conditions showed *tert.*-butylmagnesium *bromide* to be formed in a 20.6% yield.

The maximum yield of *tert.*-butylmagnesium chloride obtained in the several experiments was 58%. In large-sized runs the yield is improved as is evidenced by a 62% yield of trimethylacetic acid from a two and one half mole run of *tert.*-butyl magnesium chloride and carbon dioxide in which fine commercial turnings were used, and by a 69–70% yield when 200 mesh magnesium powder was used.

The authors gratefully acknowledge a liberal supply of *tert.*-butyl alcohol from the Petroleum Chemical Corporation of New York.

Summary

As a result of a study of several factors in the preparation of *tert.*-butylmagnesium chloride it is now possible to obtain this Grignard reagent in quite satisfactory yields.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY NO. 564]

A FURTHER STUDY OF THE INTERACTION OF SULFUR AND PARA-TOLUIDINE IN THE PRESENCE OF LITHARGE: THIO-PARA-TOLUIDINE AND RELATED COMPOUNDS[1]

BY MARSTON TAYLOR BOGERT AND LEONARD SMIDTH[2]

RECEIVED AUGUST 2, 1927 PUBLISHED FEBRUARY 4, 1928

Introductory

Sulfur dissolves freely in molten *p*-toluidine to a perfectly clear, transparent, pale yellow solution, which can be heated to about 180° before there is evidence of any reaction, when a slow evolution of hydrogen sulfide begins, gradually increasing as the temperature rises and accompanied by a darkening of the solution, with the ultimate production of dehydrothio-*p*-toluidine (V), primulines (VI), and other substances.

In the presence of litharge, or other hydrogen sulfide absorbents, however, the reaction begins at much lower temperature (130–145°), as shown first by Merz and Weith,[3] with thio-*p*-toluidine (III) as the chief product.

This Merz and Weith process has been investigated by Bogert and Mandelbaum,[4] who found that the melt contained both thio- and dithio-

---

[1] Presented in abstract before the Division of Dye Chemistry at the Baltimore Meeting of the American Chemical Society, April 8, 1925.

[2] DuPont Fellow at Columbia University for the academic year 1923–1924.

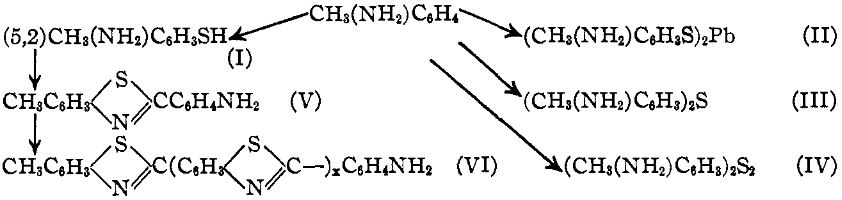
[3] Merz and Weith, *Ber.*, **4**, 393 (1871).

[4] Bogert and Mandelbaum, THIS JOURNAL, **45**, 3045 (1923).

p-toluidine (IV) and who proved that the sulfur in these products was *ortho* to the amino and *meta* to the methyl groups.

In examining this Merz and Weith fusion further in the experiments which follow, we used one equivalent of sulfur per mole of *p*-toluidine and, in addition to thio- and dithio-*p*-toluidine, succeeded in isolating from the melt small quantities (less than 1%) of dehydrothio-*p*-toluidine.

It is our belief that the first product of the action of sulfur upon *p*-toluidine in these fusions is the mercaptan(I), and that this is the progenitor of most of the other products formed, as shown in the following diagram



Ziegler[5] argued many years ago, in discussing the production of dehydrothio-*p*-toluidine from *p*-toluidine and sulfur, that since sulfur possesses many properties which recall those of the halogens, it might be expected to substitute either nuclear or side-chain hydrogen depending upon conditions, that high temperature favored side-chain substitution and that the first phase of the reaction, therefore, probably consisted in the formation of *p*-aminobenzylmercaptan, which condensed with a second mole of *p*-toluidine to *p*-aminobenzyl-*p*-toluidine, $H_2NC_6H_4CH_2NHC_6H_4CH_3$, and this latter was then transformed into dehydrothio-*p*-toluidine by the further action of the molten sulfur. The Farbwerke Hoechst[6] subsequently patented the manufacture of dehydrothio-*p*-toluidine from *p*-aminobenzyl-*p*-toluidine, but no one has yet reported the finding of any *p*-aminobenzyl-*p*-toluidine in the dehydrothio-*p*-toluidine melt, and the experiments of Bogert and Snell[7] demonstrated quite conclusively that the dehydrothio-*p*-toluidine obtained in following out these patent specifications owed its origin to unchanged *p*-toluidine remaining in the initial material used. In fact, when toluene itself is heated with sulfur for some time, stilbene is formed in very small amount,[4,8] but no benzyl mercaptan.

Bogert and Mandelbaum[4] separated the products of these Merz and Weith fusions by taking advantage of their different basicities and extracting them successively from a benzene solution of the melt with a series of acids each stronger than its predecessor, *p*-toluidine thus being removed first, then thio-*p*-toluidine and finally dithio-*p*-toluidine.

---

[5] Ziegler, *Ber.*, **23**, 2475 (1890).

[6] Farbwerke Hoechst, Ger. pat. 104,230 (May 8, 1899); *Friedländer*, **5**, 83 (1901).

[7] Bogert and Snell, *Color Trade J.*, **14**, 109 (1924).

[8] Aronstein and van Nierop, *Rec. trav. chim.*, **21**, 450 (1902).

We have now found that the opposite procedure is preferable, namely, the extraction of the melt with excess of mineral acid and the fractional precipitation of the bases by gradual neutralization of this acid solution with ammonia, whereby they are separated in the reverse order, dithio-*p*-toluidine being thrown down first and *p*-toluidine last.

A perusal of the experimental details of the two processes will make it manifest that the former (fractional extraction with acids) was better adapted to the recovery of the thio-*p*-toluidine than of the dithio compound, because of the accumulation of tars in the final extracts. For similar reasons, the ammonia precipitation method favored the recovery of the dithio derivative, and incidentally disclosed the fact that the amount of dithio formed was much greater than previously suspected. The two methods thus supplement each other in a very helpful manner and indicate that, based upon the amount of *p*-toluidine actually consumed in the reaction, the yield of thio-*p*-toluidine is about 25–30%, and of dithio 15–20%.

In the presence of hydrochloric acid, *p*-toluidine and sulfur interacted to give mainly tar, with but very small amounts of impure dithio-*p*-toluidine, although it has been stated by Hodgson[9] that the latter can be obtained in this way.

Efforts to convert thio-*p*-toluidine into the 3,9-dimethylphenothiazine,[10] by the action of soda lime, zinc chloride or concd. hydrochloric acid all failed.

Although, as is well known, thio-*p*-toluidine can be easily diazotized and combined with suitable couplers to form azo dyes, our experiments show that it does not itself function as a coupler for diazotized aromatic bases.

Like Truhlar,[11] we, too, experienced considerable difficulty in getting pure compounds by the application of the diazo reaction to thio-*p*-toluidine, the products being mostly tars from which we were unable to isolate any crystalline material; but when these tars were oxidized with a mixture of nitric and sulfuric acids, crystalline sulfones were isolated in approximate purity.

In the experiments to obtain a chlorine derivative, the action of concd. hydrochloric acid upon the diazonium chloride gave rise to what appeared to be a mixed ether, whose percentage composition corresponded to the formula $(CH_3C_6H_3ClSC_6H_3CH_3)_2O$, and which may be identical with a product obtained by Truhlar in a similar reaction, described by him as an easily frozen oil containing chlorine and which he was unable to identify.

Attempts to substitute the amino groups by bromine resulted in the

---

[9] Hodgson, Brit. pat. 15,466, July 3, 1911; *C. A.* **7,** 264 (1913).

[10] Kehrmann, *Ber.*, **39,** 915 (1906).

[11] Truhlar, *Ber.*, **20,** 664 (1887).

replacement of one amino by bromine and the other by hydrogen, as proved by the formation of a monobromo sulfone on oxidation. The di-iodo sulfone, however, was obtained from thio-*p*-toluidine in good yield. All efforts to get a dicyano derivative through the diazo reaction were unavailing.

Experimental Part

Fusion of *p*-Toluidine, Sulfur and Litharge.—These fusions were carried out as described by Bogert and Mandelbaum,[4] except that we found that a slightly lower temperature (130–140°, instead of 140–145°) gave rather better results.

To determine what effect, if any, the litharge had upon *p*-toluidine in the presence of steam, litharge and the toluidine were added to boiling water and the mixture boiled for some time under a reflux condenser. No change whatever occurred and the *p*-toluidine crystallized from the colorless aqueous solution as the latter cooled.

A suspension of litharge and sulfur (excess) in boiling water rapidly blackened with formation of lead sulfide and evolution of traces of sulfur dioxide.

The fusion conditions were varied as follows:

(1) When an intimate mixture of sulfur (1, 1.5 and 3 equivalents) with excess of litharge was added slowly *to* molten *p*-toluidine (one mole), there was some improvement in the yield of thio-*p*-toluidine, but more *p*-toluidine remained unchanged and was recovered.

(2) A mixture of *p*-toluidine (one mole) and excess of litharge was added to molten sulfur (1.5 or 5 equivalents), but the yields of thio-*p*-toluidine were not thereby improved and more tar was formed.

Working up of the Melt.—The cold pulverized melt obtained from 535 g. (5 moles) of *p*-toluidine, 160 g. (5 equivalents) of sulfur and 800 g. (2.8 moles) of litharge, was extracted repeatedly with 800 cc. portions of 10% hydrochloric acid (or sulfuric) with which it was boiled vigorously for five minutes and the extract filtered hot. The use of stronger acid caused such a copious effervescence of hydrogen sulfide that it was difficult to keep the solution from boiling over.

Each hot filtered 800 cc. acid extract was poured into 1000 cc. of cold water, which precipitated weakly basic resins. The filtrate from these resins was then warmed and treated carefully with ammonium hydroxide solution until the odor of *p*-toluidine was detected. This precipitated the mono- and dithiotoluidines. Neutralization (with ammonia) of the filtrate from these thiotoluidines caused the separation of practically pure *p*-toluidine.

To recover as much as possible of the mono- and dithiotoluidines present, the thiotoluidine precipitates from the four acid extracts were combined, redissolved in 1800 g. of 10% hydrochloric acid and ammonium hydroxide solution added cautiously to this solution, whose temperature was maintained sufficiently high (30–50°) to cause the precipitated dithio compound to separate in a viscous and not a solid form. The color of this viscous precipitate changed as the addition of ammonia proceeded, being yellow at first, then pink and finally red. It was removed mechanically as it accumulated. When all of the crude dithio compound had been precipitated, further addition of ammonia caused the separation of the solid monothio-*p*-toluidine and the precipitate became crystalline. The first portions of this crystalline precipitate were contaminated with some of the dithio derivative and were removed and worked up separately. Further addition of ammonium hydroxide to the filtrate precipitated thio-*p*-toluidine as a pale yellow solid. The neutralization with ammonia was continued until the odor of *p*-toluidine was noted or, in the absence of unchanged *p*-toluidine, until neutrality was reached.

The crude products were purified by a repetition of the process described. In the case of the crude disulfide, its hot dilute acid solution was first poured into sufficient cold water to separate small amounts of basic resins. The filtrate was then precipitated carefully by ammonia as before, any thio-*p*-toluidine obtained being worked up with the crude thio-*p*-toluidine fraction. With a little experience the end-points in this separation are easily and quickly noted.

The yields of crude products from one of these fusions were as follows: weakly basic resins (precipitated from acid solution by dilution), 70 g.; dithio-*p*-toluidine, 80 g., or 17%; monothio, 121 g. or 26%; *p*-toluidine recovered, 167 g. The yields of mono- and dithiotoluidine are calculated on the basis of the net amount of *p*-toluidine consumed in the operation.

From one of these fusions, conducted at 140–145°, 20 g. of the resinous products precipitated by dilution of the acid solution was extracted repeatedly with large volumes of boiling water and yielded a total of 0.96 g. of impure dehydrothio-*p*-toluidine (m. p. 186°), or less than 1% of that calculated from the initial materials. When the fusion temperatures were below 140°, only traces of this compound could be found in the melts. No trithio-*p*-toluidine was isolated from the melt, nor any compounds other than those already mentioned.

The Interaction of *p*-Toluidine and Sulfur in the Presence of Concentrated Hydrochloric Acid.—Hodgson[12] reports a nearly theoretical yield of trithio-*o*-toluidine when he heated together *o*-toluidine, hydrochloric acid and sulfur for two to three hours at 185–190°, and similar results in the case of aniline.[13] We repeated this work with *o*-toluidine and obtained excellent yields of the trithio-*o*-toluidine, melting at 225° (uncorr.). Hodgson gives the melting-point of the pure product as 226–227° (uncorr.).

In his original patent,[9] Hodgson states that *p*-toluidine, under similar conditions, gives a dithio derivative, and hence we carried out various experiments with *p*-toluidine, hydrochloric acid and sulfur, following the Hodgson process, but succeeded in obtaining only very small amounts of impure dithio-*p*-toluidine, together with some unchanged *p*-toluidine and a large amount of tar. The difference in the behavior of the two toluidines when treated in exactly the same way was striking.

Thio-*p*-toluidine, as prepared by the process described, was usually colorless and melted above 100°. Its further purification was accomplished by crystallization from diluted alcohol; or the solution in hot 10% hydrochloric acid, after precipitation of any disulfide (unless the disulfide is precipitated first by ammonia, the addition of concd. hydrochloric acid tends to throw down its hydrochloride as well as that of the monosufide), was treated with concd. hydrochloric acid until precipitation began, when the solution was allowed to cool and the hydrochloride separated in colorless, feathery

---

[12] Hodgson, *J. Chem. Soc.*, **101**, 1693 (1912).

[13] Hodgson and Dix, *ibid.*, **105**, 952 (1914).

needles, which were dissolved in boiling water and the free base precipitated by neutralization with ammonia. A single crystallization from diluted alcohol than gave colorless leaves, m. p. 103–104°, in agreement with the literature.

Heated above its melting-point, it was unchanged at 150°; at 180–190°, small amounts of ammonia were given off; at 200°, ammonia and hydrogen sulfide; at 205–210°, ammonia, hydrogen sulfide and *p*-toluidine (identified by its odor, its melting point and the melting point of its aceto derivative). The residue was brown and amorphous, and its benzene solution was strongly fluorescent.

No change was detected when thio-*p*-toluidine and concd. hydrochloric (or 25% sulfuric) acid were heated together for six hours at 200°, except the formation of some *p*-toluidine. When fused for several hours with sulfur, thio-*p*-toluidine was not decomposed, nor could any dehydrothio-*p*-toluidine be isolated from the melt.

A mixture of 71 g. of thio-*p*-toluidine (m. p. 103–104°) and 19 g. of sulfur was heated at 140–150° and 65 g. of litharge added gradually during eight hours. By extracting the cooled and pulverized melt with hydrochloric acid, 60 g. of crude thio-*p*-toluidine (that is, 84.5% of the original amount) was recovered, together with a small quantity of acid-soluble tars. The thio-*p*-toluidine formed in the *p*-toluidine-sulfur fusion, therefore, is not very rapidly or extensively decomposed by the litharge and sulfur added.

In acid solution, thio-*p*-toluidine refused to couple with diazotized sulfanilic acid. On the other hand, azo dyes are readily produced by uniting diazotized thiotoluidine with suitable couplers, and were patented long ago by Dahl & Co.[14] We verified this by coupling the diazotized thiotoluidine with H-acid in sodium carbonate solution and obtained an azo dye which gave deep purple shades on wool, fast to light, acids, alkali or soap.

DIACETO DERIVATIVE.—This was prepared as recorded by Bogert and Mandelbaum[4] and corresponded in appearance and melting point with their description. It was subjected to some further tests, with the following results.

To attempted bromination, nitration or sulfonation, it proved very resistant, decomposition generally occurring before the desired substitution could be realized. At laboratory temperature, a mixture of concd. nitric and sulfuric acids (75:30) oxidized it to the corresponding diaceto sulfone; this proved to be a convenient way of preparing the latter compound, instead of the permanganate method employed by Bogert and Mandelbaum.

Bis(2-Acetamino-5-methylphenyl) Sulfoxide, $(CH_3CONHC_6H_3(CH_3))_2SO$.—Attempts to oxidize thio-*p*-toluidine in acetone solution with hydrogen dioxide, by the method of Gazdar and Smiles,[15] resulted in tar and unchanged initial material, but no appreciable yield of sulfoxide. Hinsberg,[16] however, has found that aceto derivatives often can be used advantageously for such oxidations and we followed this lead successfully.

To a well cooled solution of 5 g. of thio-*p*-toluidine in 6 cc. of acetic anhydride, there were added 20 cc. of glacial acetic acid and 2 cc. of 30% hydrogen dioxide ("Superoxole"). After standing for twelve hours at room temperature, the solution was poured into a large volume of water and the acid neutralized with ammonia. The precipitate crystallized from alcohol in colorless hexagonal plates, m. p. 212° (corr.); yield, 2 g. or 28%.

Anal. Calcd. for $C_{18}H_{20}O_3N_2S$: C, 62.75; H, 5.87. Found: C, 62.79; H, 5.89.

---

[14] Dahl & Co., Ger. pat. 34,299; *Friedlander*, **1**, 534 (1885); Brit. pat. 14,232 of 1885.

[15] Gazdar and Smiles, *J. Chem. Soc.*, **93**, 1833 (1908).

[16] Hinsberg, *Ber.*, **41**, 2836 (1908).

Bis(2-Chloro-5-methylphenyl) Sulfone.—A solution of 5 g. of thio-*p*-toluidine in 80 cc. of water and 12 cc. of concd. hydrochloric acid was diazotized at 0° with an aqueous solution of 3.3 g. of sodium nitrite and 6 g. of copper powder was added. After standing for an hour, the mixture was heated at 100° until the evolution of gas ceased. The tarry precipitate was oxidized as described beyond for the analogous iodo derivative. The product was a pale brown, amorphous solid which decomposed slowly above 95°; yield, 2.1 g., or 33%. It was readily soluble in chloroform or acetone, less readily in benzene and practically insoluble in alcohol.

Anal. Calcd. for $C_{14}H_{12}O_2Cl_2S$: C, 53.32; H, 3.84. Found: C, 53.91; H, 3.46.

Bis(2-Chloro-5,5'-dimethylphenylsulfide)-2,2'-Oxide, $(CH_3C_6H_3ClSC_6H_3CH_3)_2O$.—A solution of 24.5 g. of thio-*p*-toluidine in 100 cc. of concd. hydrochloric acid and 150 cc. of water was diazotized at 0° (some of the thiotoluidine hydrochloride tends to separate as the temperature of the solution falls) by a solution of 15 g. of sodium nitrite in 75 cc. of water. After standing for thirty minutes at 0°, the solution was poured into 450 cc. of concd. hydrochloric acid and the mixture left overnight at room temperature. Gas was evolved slowly. The solution was heated gradually to boiling. A black oil soon separated and the reaction appeared to be at an end. The oil was removed, washed with strong aqueous caustic alkali, then with water, after which it was distilled at 80 mm. pressure and a fraction collected at 265° which formed a colorless oil that darkened gradually on standing; yield, 15 g. or 59%.

Anal. Calcd. for $C_{28}H_{24}OCl_2S_2$: C, 65.75; H, 4.69; S, 12.52; Cl, 13.90. Found: C, 65.66; H, 5.07; S, 12.81; Cl, 14.42.

This compound was insoluble in strong caustic alkali solutions. A distinctive and striking property was the deep blue color it gave when treated with concd. sulfuric acid. Oxidation with acid permanganate failed to yield a crystalline sulfone, while strong oxidation with nitric acid broke down the molecule to unidentified products soluble in the diluted acid.

2-Bromo-5,5'-dimethylphenyl Sulfone, $CH_3BrC_6H_3SO_2C_6H_4CH_3$.—Ice was added to 17 g. of concd. sulfuric acid until the temperature was reduced to 0°, when 5 g. of thio-*p*-toluidine was stirred in and the solution diazotized with an aqueous solution of 3 g. of sodium nitrite. To this diazo solution, there were added 30 g. of potassium bromide and 10 g. of copper powder, and the rest of the process followed that described for the analogous chloro and iodo derivatives. The product was a brownish, amorphous solid which decomposed slowly at about 69–72°; yield, 1.6 g. or 24%. It dissolved easily in chloroform, acetone or benzene, less freely in ether, only slightly in carbon tetrachloride and was practically insoluble in alcohol.

Anal. Calcd. for $C_{14}H_{13}O_2BrS$: C, 51.69; H, 4.00. Found: C, 52.16; H, 3.64.

These figures indicate that one only of the two original amino groups of thio-*p*-toluidine was replaced by bromine, while the other was substituted by hydrogen, but not enough pure material was left to check this by determining also the percentage of bromine present.

Bis(2-Iodo-5-methylphenyl) Sulfone.—To a diazo solution prepared from 5 g. of thio-*p*-toluidine and the requisite amounts of hydrochloric acid and sodium nitrite, there was run in slowly a cold saturated aqueous solution of 12 g. of potassium iodide. When the first rapid evolution of nitrogen subsided, the mixture was warmed at 100° until no more gas was given off. The black, viscous precipitate was collected, washed with water, dissolved in glacial acetic acid and sufficient potassium acid sulfite added to convert any free iodine into potassium iodide. When this solution was poured into water, a yellow, gummy precipitate separated. This was added in small quantities to a mixture of concd. nitric (15 cc.) and sulfuric (6 cc.) acids and the mixture warmed until a copious evolution of nitrogen oxides occurred. The oxidation was completed very quickly. The acid liquid was poured into water, the precipitate removed, warmed with strong caustic soda solution, the undissolved material dissolved in boiling glacial acetic acid, the solution decolorized and poured into water. The precipitate was collected, washed with hot alcohol and subjected to further purification by re-solution in glacial acetic acid, decolorization and reprecipitation by dilution. This precipitate, when washed with water and alcohol and dried, appeared as a pale brownish, amorphous solid which began to decompose in the neighborhood of 82°; yield, 4.3 g. or 42%. It dissolved freely in chloroform, acetone or carbon disulfide, less readily in benzene, but slightly in ether and was practically insoluble in alcohol or carbon tetrachloride.

Anal. Calcd. for $C_{14}H_{12}O_2I_2S$: C, 33.73; H, 2.43; S, 6.44; I, 50.96. Found: C, 33.14; H, 2.25; S, 6.30; I, 50.25.

Dithio-*p*-toluidine.—The crude product obtained in the process described was purified further by dissolving it in hot alcohol, adding water or, better, ammonium hydroxide solution, to incipient clouding and allowing the solution to cool. The yellow, lustrous leaflets obtained, melted at 88–89°, in accord with the literature.

Hodgson[17] reports that when dithio-aniline (10 g.) is boiled for eight hours with dry aniline (20.4 g.), the yield of monothio-aniline is practically equal to that calculated, but that the presence of water retards this reaction and may inhibit it entirely. From this latter statement, it would seem unlikely that much thio-aniline could be formed from the dithio during an aniline-sulfur-litharge fusion, for steam is given off continuously during this reaction due to the gradual addition of the litharge. Yet, K. A. Hofmann[18] states that he obtained thio-aniline by heating an aniline solution of dithio-aniline for one and one-half hours at 170–180°, with the gradual addition of somewhat more than one mole of litharge, and Hodgson,[19] who repeated Hofmann's experiments, isolated both *o,o'*- and *o,p'*-monothio-anilines from the melt.

It seemed desirable, therefore, to ascertain the behavior of dithio-*p*-toluidine under similar conditions, and the following experiments record the results.

A mixture of 6 g. of dithio-*p*-toluidine (carefully purified and free from the monothiotoluidine) and 20 g. of *p*-toluidine was heated for eight hours at 140–150°, while 10 g. of litharge was added gradually to the melt. From this melt there were recovered 5.1 g. of the original disulfide and 18 g. of *p*-toluidine, but no thio-*p*-toluidine. Increase in the fusion temperature to 165° did not alter this result materially, except that at the higher temperature some tar was formed.

To determine the effect of sulfur and litharge upon the disulfide, 9 g. of the latter was heated with 4 g. of sulfur for eight hours at 160–165°, while 10 g. of litharge was added gradually. Most of the initial disulfide was recovered from the melt unchanged, together with about 0.7 g. of acid-soluble resins.

Like the monosulfide, this disulfide may be used for the preparation of azo dyes.[9,20]

---

[17] Hodgson, *J. Chem. Soc.*, **125**, 1856 (1924).

[18] K. A. Hofmann, *Ber.*, **27**, 2810 (1894).

[19] Hodgson, *J. Soc. Dyers Colourists*, **40**, 333 (1924).

[20] British Dyestuffs Corp. Ltd. and H. H. Hodgson, Brit. pat. 235,334 of April 1, 1924.

Diazotized and coupled with H-acid in sodium carbonate solution, it gave a dye which produced purplish shades on wool, lighter in tone than the corresponding dye from the monosulfide, but resembling it in its fastness to light, acids, alkali and soap.

PICRATE.—Equal moles of the disulfide and picric acid were mixed in hot benzene solution and the picrate was crystallized as the solution cooled. Recrystallized from benzene it formed long, silky, yellow needles.

The DIACETO DERIVATIVE has been described by Bogert and Mandelbaum.[4] When it was oxidized either with nitric acid or with acid permanganate, the product appeared to be a sulfonic acid. We failed to obtain either a sulfoxide or a sulfone.

2-Amino-5-methylphenyl Mercaptan, $CH_3(NH_2)C_6H_3SH$.—Reduction of dithio-*p*-toluidine by zinc dust and acetic acid, or by tin and hydrochloric acid, gave the zinc or tin salts of the mercaptan, from which the mercaptan itself was liberated by the action of hydrogen sulfide.

In a typical experiment, 10 g. of the crude disulfide was dissolved in 200 cc. of boiling glacial acetic acid, 20 g. of zinc dust added gradually and the mixture refluxed for an hour. Longer boiling of the acetic acid solution proved detrimental to both yield and purity of the product. It was then filtered hot, the filtrate diluted with 2.5 volumes of water and allowed to stand for ten to fifteen minutes. On longer standing, impurities present in a crude initial disulfide are also likely to separate. The white, flocculent precipitate of zinc salt was collected, washed with water, then with a little ether and dried at 110°; yield, 5.6 g. or 45%.

Anal. 0.9824 g. ignited gave 0.2319 g. of ZnO, or 23.60%: calcd., 23.82%.

Liberated from its zinc or tin salts by hydrogen sulfide, the mercaptan gradually oxidized in the air to the disulfide.

Summary

1. A further study has been made of the Merz and Weith reaction for the production of thio-*p*-toluidine from *p*-toluidine, sulfur and litharge, and a new method of separating the products worked out which depends upon their fractional precipitation from acid solution by ammonia.
2. Various experiments are recorded which throw light upon the probable mechanism of the reaction, and indicate that the action of sulfur upon *p*-toluidine follows a somewhat different course from that of sulfur upon either aniline or *o*-toluidine.
3. Additional properties and reactions of both thio- and dithio-*p*-toluidine are described, including their conversion into various derivatives.

NEW YORK, N. Y.