[Contribution from the Noyes Chemical Laboratory, University of Illinois]

bis(*p*-NITROPHENYL) SULFIDE[1]

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A study of *bis*(*p*-nitrophenyl) sulfide was initiated in the hope of obtaining definite information as to the possibility of the existence of thiosulfoxides—a type of derivative which had been reported for this sulfide (1) and also postulated as intermediate in the Levinstein process (2, 3). While this work was in progress Price and Stacy (4) showed that the material which had been identified by the Russian workers as *bis*(*p*-nitrophenyl) thiosulfoxide was in reality a mixture of the sulfide with the corresponding linear disulfide. The present paper is a report of certain other observations on the behavior of *bis*(*p*-nitrophenyl) sulfide.

Perhaps the most interesting of these is the reaction with sodium disulfide, discovered in an early attempt to synthesize the supposititious thiosulfoxide by heating *bis*(*p*-nitrophenyl) sulfide with sodium disulfide. Although the desired sulfurization occurred, the resulting product was not a thiosulfoxide but the well-known, linear disulfide. This reaction, involving the formation of a disulfide from a monosulfide, appears to be new in type.

$$NO_2C_6H_4SC_6H_4NO_2 \xrightarrow{Na_2S_2} NO_2C_6H_4SSC_6H_4NO_2$$

Another product was *p*-nitrothiophenol, formed presumably by cleavage of the disulfide. This reaction had been carried out by Fromm and Wittmann (5) by use of alcoholic sodium hydroxide. The cleavage of disulfides by alkali has been shown to be a general reaction. Reduction of a nitro group occurred also, *p*-aminophenyl *p*-nitrophenyl sulfide being formed.

When *bis*(*p*-nitrophenyl) sulfide was treated with an excess of sodium disulfide, the disulfide was produced along with a mixture of amines. The amines were acetylated and the resulting acetyl derivatives were separated by fractional crystallization. Three amines were isolated, all containing sulfur. The first (m.p. 181–183°) was identified as *bis*(*p*-acetaminophenyl) disulfide (I) (6).

$$\underset{\text{I}}{CH_3CONHC_6H_4SSC_6H_4NHCOCH_3} \quad \underset{\text{II}}{CH_3CONHC_6H_4SC_6H_4NHCOCH_3}\cdot$$

$$\underset{\text{III}}{(CH_3CO)_2NC_6H_4SSC_6H_4NO_2}$$

The structure was established by synthesis. *bis*(*p*-Nitrophenyl) disulfide was reduced with tin and hydrochloric acid and the resulting amino thiol was oxidized with iodine in acid solution. Acetylation of the *bis*(*p*-aminophenyl) disulfide produced a compound (m.p. 181–184°) which did not depress the melting point of the amide (m.p. 181–183°) isolated from the mixture.

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The second amide (m.p. 208–210°) to be isolated from the mixture appeared to be *bis*(*p*-acetaminophenyl) sulfide (II). This compound, which had been made previously, had the melting point 209–210°. The third amide (m.p. 212–213°) was isolated only in very small amounts and was believed to be *p*-diacetaminophenyl *p*-nitrophenyl disulfide (III).

A word should be said about the melting point of *bis*(*p*-nitrophenyl) sulfide. Price and Stacy gave the melting point as 160–161°, and our purest samples melted slightly lower. All previous workers had reported the value of 154° (1, 5, 7, 8). Since this compound had been prepared by so many investigators and since its identity was so essential to the original problem, a systematic examination of its structure and purity was undertaken.

The reaction of *p*-nitrochlorobenzene and sodium sulfide in ethanol solution was found to give the sulfide, unchanged *p*-nitrochlorobenzene, and *p*-aminophenyl *p*-nitrophenyl sulfide. The use of ethylene glycol as a solvent materially improved the method and led to the isolation of essentially pure sulfide as the only product. The sulfide crystallized from glacial acetic acid, xylene, or absolute ethanol in long needles. The analysis of a pure sample gave the correct values for carbon, hydrogen, and nitrogen. Results of molecular weight determinations in benzophenone afforded satisfactory checks with the calculated value (276). A determination of the nitro groups, by use of stannous chloride and iodine as reagents, gave values for "nitro" nitrogen close to the calculated value.

The reduction of *bis*(*p*-nitrophenyl) sulfide with tin and hydrochloric acid produced the diamino sulfide; m.p. 105–107° (7). The diacetyl derivative was prepared also; m.p. 214–215° (cor.). The preparation of *p*,*p*′-*bis*(4-nitrophenylthio)azobenzene was undertaken according to the directions of Zincke, since its melting point of 164° was so close to that found for the sulfide (8). The azo compound was isolated (m.p. 159–162°) and proved to be different from the sulfide.

Hodgson and Wilson report that the action of fused sodium sulfide on *p*-nitrochlorobenzene leads to the formation of *bis*(*p*-nitrophenyl) sulfide as the only product (9). We were unable to confirm these results; instead we isolated 4,4′-dichloroazobenzene (m.p. 179°) and 4,4′-dichloroazoxybenzene (m.p. 154°) from the reaction mixture. The azo compound was converted to the azoxy derivative by the action of perhydrol in glacial acetic acid. Both compounds upon treatment with fuming nitric acid gave a trinitroazoxy derivative (m.p. 186–187.5°) in which the orientation of the nitro groups was not determined. A similar result was obtained by Werigo, who oxidized the corresponding bromoazobenzene and obtained a trinitroazoxy derivative; m.p. 174° (10). Willgerodt observed the formation of 4,4′-dichloroazobenzene from *p*-nitrochlorobenzene and potassium ethoxide at 150–200° in a sealed tube (11). The reaction of *p*-dinitrobenzene and sodium sulfide was observed by Blanksma to give 4,4′-dinitroazobenzene (12). The work of Hodgson and Wilson was not supported by any experimental details, and we believe that they were in error on this point.

The reaction between sodium disulfide and 2,4-dinitrochlorobenzene proceeded readily to give a compound which had the composition calculated for *bis*(2,4-dinitrophenyl) disulfide. Oxidation of this compound gave a 5% yield of *bis*(2,4-dinitrophenyl) sulfone (13). Similar results were obtained with 2-nitro-4-carbomethoxychlorobenzene. The *bis*(2-nitro-4-carbethoxyphenyl) disulfide melted at 149–150° and when oxidized gave an 8% yield of *bis*(2-nitro-4-carbethoxyphenyl) sulfone (m.p. 205–206°) and an equivalent amount of sulfuric acid determined as barium sulfate. These results may be explained readily by reference to the equilibrium, $Na_2S_2 \rightleftharpoons Na_2S + S$, which probably exists under the conditions employed.

EXPERIMENTAL

Reaction of bis(p-nitrophenyl) sulfide and sodium disulfide. A solution of sodium disulfide, prepared by dissolving 0.64 g. of sulfur in a solution of 4.8 g. of sodium sulfide ($Na_2S \cdot 9H_2O$) in 25 ml. of hot ethylene glycol, was added to 5.52 g. of *bis*(*p*-nitrophenyl) sulfide dissolved in 250 ml. of hot absolute ethanol. The mixture was heated under reflux for 24 hours and cooled. The solid which precipitated was washed well with ethanol, and dissolved in water. Addition of lead acetate to the aqueous solution produced a white precipitate of lead hydroxide, which dissolved upon the addition of alkali. The addition of sulfuric acid (10%) to the original solution caused the precipitation of sulfur and the evolution of sulfur dioxide. No hydrogen sulfide or sulfide ion could be detected.

The original alcohol filtrate was evaporated *in vacuo*, water was added to the residual glycol solution, and the precipitated solid (3.5 g.) was extracted with 200 ml. of hot 10% hydrochloric acid. The residue (0.6 g.), fractionated from glacial acetic acid, gave two products. The first, *bis*(*p*-nitrophenyl) disulfide, m.p. 178–180°, was purified by recrystallization from xylene. The second product melted at 135–137° after recrystallization from ethanol, and at 135–140° when mixed with a sample of the eutectic mixture of mono- and disulfides (m.p. 135–145°) (6).

The hydrochloric acid extract was made alkaline with sodium hydroxide and the amine (1.5 g.) precipitated; m.p. 137–140°. It proved to be *p*-aminophenyl *p*-nitrophenyl sulfide and was recrystallized from a mixture of benzene and petroleum ether (b.p. 60–90°).

When the aqueous-alcohol filtrate, after removal of these products, was made acidic with hydrochloric acid, a yellow solid precipitated. It was dissolved in benzene, and a small amount of insoluble material was removed. The benzene solution was extracted with 5% sodium hydroxide, and the aqueous solution treated with powdered iodine. A small yield of *bis*(*p*-nitrophenyl) disulfide was obtained, which served to identify the original material as *p*-nitrothiophenol.

Reaction of bis(p-nitrophenyl) sulfide and excess sodium disulfide. A mixture of 0.06 mole of sodium disulfide in 50 ml. of ethylene glycol and 0.02 mole of nitrophenyl sulfide in 200 ml. of absolute ethanol was heated for 20 hours, cooled, and filtered. The precipitate was completely soluble in water and proved to be sodium thiosulfate.

The filtrate was concentrated *in vacuo*, and the organic material was precipitated with water as in the previous experiment. The material (3.5 g.) was an oil and was isolated by ether extraction. The aqueous layer was acidified and extracted with ether. The product isolated was *bis*(*p*-nitrophenyl) disulfide, resulting from the air oxidation of the thiophenol.

The oil mentioned above, which was almost entirely soluble in hydrochloric acid, was purified by repeated extraction from alkaline solutions. It was treated with 10 ml. of acetic anhydride, and the mixture was warmed for 15 minutes. The product was isolated in the usual manner and was fractionated into three compounds by recrystallization from alcohol-water mixtures. The first (m.p. 181–183°) proved to be *bis*(*p*-acetaminophenyl) disulfide, identical with a sample prepared from *bis*(*p*-nitrophenyl) disulfide. The second (m.p. 208–210°) showed no depression in melting point when mixed with a sample of *bis*(*p*-acetaminophenyl) sulfide. The third (m.p. 212–213°) was apparently a *p*-diacetaminophenyl *p*-nitrophenyl disulfide.

Anal. Calc'd for $C_{16}H_{16}N_2O_2S_2$ (m.p. 181–183°): C, 57.8; H, 4.82; N, 8.43.
Found: C, 58.40; H, 5.10; N, 8.34.

Anal. Calc'd for $C_{16}H_{16}N_2O_2S$ (m.p. 208–210°): C, 64.00; H, 5.34; N, 9.32.
Found: C, 62.83; H, 5.28; N, 9.06.

Anal. Calc'd for $C_{16}H_{14}N_2O_4S_2$ (m.p. 212–213°): C, 53.1; H, 3.87; N, 7.74.
Found: C, 52.42; H, 4.66; N, 7.40.

Preparation of bis(p-acetaminophenyl) disulfide (m.p. 182°). To a hot solution of *bis*(*p*-nitrophenyl) disulfide in glacial acetic acid was added 5 ml. of concentrated hydrochloric acid and several pieces of tin. Reduction was effected by heating and by the addition from time to time of portions of acid and pieces of tin. The process was continued until all the original disulfide was dissolved, about 30 ml. of acid being required. The hot solution was filtered, and an aqueous solution of iodine and potassium iodide was added slowly until a red color persisted. The solution was cooled, and alkali was added until the precipitate of stannic hydroxide completely dissolved. The amine, extracted with ether and isolated in the usual manner, weighed 1.5 g.; it was treated with 10 ml. of acetic anhydride, and the mixture was warmed for 15 minutes. The amide was recrystallized from an acetic acid-water mixture; yield 1.2 g.; m.p. 181–184° (8). Repeated recrystallizations of the substance from ethanol-water mixtures did not change its melting point.

Preparation of bis(p-nitrophenyl) sulfide. Method I. A solution of 24 g. of sodium sulfide ($Na_2S \cdot 9H_2O$) in 150 ml. of water was added carefully, in portions, to a solution of 32 g. of *p*-nitrochlorobenzene in 100 ml. of hot absolute ethanol according to the directions of Nietzki and Bothof (9). After the initial, vigorous reaction had subsided, the mixture was heated under reflux for 6 hours. A solid and an oil separated during this period. The aqueous layer and the oil were decanted, and the residual solid was washed with alcohol and water. When recrystallized from glacial acetic acid, it formed yellow needles; m.p. 159–160°. The oil yielded the amino nitro sulfide (m.p. 143°), more of the sulfide, and some starting material. The melting point recorded by Nietzki and Bothof for the sulfide was 154° (7).

Anal. Calc'd for $C_{12}H_8N_2O_4S$: C, 52.2; H, 2.90; N, 10.1.
Found: C, 52.21; H, 2.70; N, 9.98 (separate sample).

Method II. A solution of 7.5 g. of sodium sulfide ($Na_2S \cdot 9H_2O$) in 50 ml. of ethylene glycol was added to a solution of 10 g. of *p*-nitrochlorobenzene in 25 ml. of absolute ethanol. The mixture darkened characteristically, but the reaction proceeded smoothly. The reaction mixture was heated on a steam-bath for 3 hours during which the color changed from dark red to orange, and crystals began to appear. The mixture was cooled and filtered, and the product was recrystallized from absolute ethanol. It formed beautiful, long, flat, yellow needles (m.p. 159°) identical with the substance obtained by Method I.

Determination of nitro groups in bis(p-nitrophenyl) sulfide. The reagents used were 0.1062 *N* aqueous iodine and stannous chloride solution, 35 g. in 70 g. of 25% hydrochloric acid. A sample of sulfide (0.2 g.) and 15 ml. of stannous chloride reagent were placed in a sealed tube (Pyrex) and heated in an oven at 120°, with intermittent shaking until clear. This required about 2 hours. The material was then washed into a 100-ml. volumetric flask and a 10-ml. aliquot portion was titrated with iodine to an end point, starch being used as an indicator. A blank was similarly carried through the procedure. The calculations were made on the basis of 1 ml. of $0.1\ N\ I_2 \approx 0.0002335$ g. of N_2 present in the nitro group. The results were as follows: Calc'd for $NO_2C_6H_4SC_6H_4NO_2$: N, 10.1 Found: (Sample I) N, 9.84; (Sample II) N, 10.36.

Reduction of bis(p-nitrophenyl) sulfide (9). A 2-g. sample of the sulfide was dissolved in a mixture of glacial acetic and hydrochloric acids. Small pieces of tin were added and the mixture warmed until all the material was in solution. The mixture was filtered and the amine isolated in the usual manner. The amine was recrystallized from a mixture of benzene and petroleum ether and had the melting point 105–107°. The melting point of *bis*(*p*-aminophenyl) sulfide is 108°.

Attempts to prepare a sulfonium salt of bis(p-nitrophenyl) sulfide. A solution of 0.5 g. of sulfide in chloroform was treated with 0.23 g. of methyl sulfate under reflux for one-half hour. Only the original sulfide was obtained.

One gram of sulfide was dissolved in 10 ml. of methyl sulfate and heated at 100°, under a reflux condenser protected by a calcium chloride tube, for 96 hours. The mixture was diluted with water and filtered; the residue was unchanged sulfide. The filtrate was treated with mercuric chloride solution, shaken well, and allowed to stand overnight. A small amount of tan precipitate formed; it was recrystallized and proved to be the original sulfide; m.p. 158–160°.

Reaction of p-nitrothiophenol and p-nitrochlorobenzene. The *p*-nitrothiophenol was prepared from 32 g. of *p*-nitrochlorobenzene according to the directions of Bennett and Berry (14). The solution of the sodium salt in 150 ml. of water was added to a solution of 15 g. of *p*-nitrochlorobenzene in 100 ml. of alcohol, and the mixture was heated under reflux until the red color lightened. The reaction product was a difficultly separable mixture from which were isolated *p*-aminophenyl *p*-nitrophenyl sulfide, *p*-nitrochlorobenzene, and a small amount of *bis*(*p*-nitrophenyl) sulfide.

Preparation of p,p'-bis(4-nitrophenylthio)azobenzene (10). A mixture of 10 g. of *bis*(*p*-nitrophenyl) disulfide, m.p. 181°, dissolved in 150 ml. of alcohol and a solution of 6 g. of sodium hydroxide, dissolved in 30 ml. of water was heated for 20 minutes. The mixture was cooled, diluted with 1500 ml. of water, and filtered. The precipitate was extracted with hot hydrochloric acid. The residue, after recrystallization from glacial acetic acid, melted at 159–163°. A mixture of this compound and *bis*(*p*-nitrophenyl) sulfide melted at 135–140°. Repeated recrystallizations from benzene and acetic acid gave well-formed crystals; m.p. 159–162°. The melting point of the azobenzene is given as 164° (7, 10).

Preparation of p,p'-dichloroazoxybenzene. Six grams of *p*-nitrochlorobenzene was added to 20 g. of sodium sulfide ($Na_2S \cdot 9H_2O$) which had been heated at 110° for one hour, and the mixture was heated at 100° for 20 hours. The deep red mass was treated with 50 ml. of absolute ethanol and filtered. The precipitate was washed well with water and recrystallized from a small amount of glacial acetic acid. After several recrystallizations about 0.5 g. of *p,p'*-dichloroazoxybenzene was obtained; m.p. 154°.

Anal. Calc'd for $C_{12}H_8Cl_2N_2O$: C, 54.00; H, 3.00.
Found: C, 54.03; H, 2.81.

Preparation of p,p'-dichloroazobenzene. Two hundred grams of powdered sodium sulfide ($Na_2S \cdot 9H_2O$) was heated in an oil-bath at 110° for several hours while being agitated mechanically. To the solution was added 60 g. of *p*-nitrochlorobenzene, and the mixture was stirred and heated at 100° for 20 hours. The contents of the flask were cooled, diluted with 500 ml. of water, and filtered. The precipitate was extracted with hot 10% hydrochloric acid, and the residue was recrystallized several times from glacial acetic acid. The product was obtained as orange-yellow plates; m.p. 177–179°. The melting point of *p,p'*-dichloroazobenzene as recorded in the literature is 183° (15). An elementary analysis gave positive tests for nitrogen and chlorine, negative results for the sulfur.

Anal. Calc'd for $C_{12}H_8Cl_2N_2$: C, 57.40; H, 3.18.
Found: C, 56.77; H, 3.05.

Nitration of p,p'-dichloroazobenzene. About 0.5 g. of the azo compound was treated carefully with 3 ml. of nitric acid (sp. gr. 1.5), and the mixture was heated on a steam-bath for one hour. A yellow precipitate, obtained by dilution of the mixture with water, was recrystallized from glacial acetic acid; m.p. 186–187°. After a second treatment with 3 ml. of nitric acid, the product melted at 186–187.5°.

Anal. Calc'd for $C_{12}H_5Cl_2N_6O_7$: C, 35.70; H, 1.24; N, 17.4.
Found: C, 36.28; H, 1.59; N, 16.59.

Nitration of p,p'-dichloroazoxybenzene. A 0.5-g. sample of the azoxy compound was oxidized with nitric acid (sp. gr. 1.5) according to the procedure for the related azo compound. The product was yellow; m.p. 186–187°. A mixture with the nitration product of *p,p'*-dichloroazobenzene had the melting point 186–187°.

Perhydrol oxidation of 4,4'-dichloroazobenzene. A small sample of the azo compound was dissolved in glacial acetic acid and 10 ml. of perhydrol (30%) was added over a period of 5 hours to the hot solution (16). The solution changed from an orange color to a light yellow. The heating was continued for 8 hours, and the mixture was cooled and diluted with water. The solid, when collected and recrystallized from an aqueous-ethanol mixture, formed crystals (m.p. 154–156°) identical with the 4,4′-dichloroazoxybenzene isolated previously.

Preparation of p-aminophenyl p-nitrophenyl sulfide (9). A solution of 32 g. of *p*-nitrochlorobenzene in 100 ml. of absolute ethanol was placed in a 500-ml., round-bottomed flask equipped with a long, efficient condenser, and the solution was heated almost to boiling on a steam-bath. To this hot solution was added, in small portions through the condenser, a solution of 24.0 g. of sodium sulfide ($Na_2S \cdot 9H_2O$) in 150 ml. of water. After the mixture had been heated for one hour, a solution of 8 g. of sodium sulfide in 30 ml. of water was added, and the mixture heated under reflux for 10 hours.

When the reaction was complete there were present an aqueous-alcohol layer, an oil, and a solid. The products of two similar experiments were combined. The hot solvent and the oil were decanted from the solid, and the solid was washed with alcohol and recrystallized from glacial acetic acid; m.p. 158–159°. This compound was identical with an authentic sample of *bis*(*p*-nitrophenyl) sulfide. The remainder of the reaction mixture was cooled well, and the solid was collected by filtration, the filtrate being discarded.

The solid material was placed in a flask together with 50 ml. of concentrated hydrochloric acid and 300 ml. of water, and the mixture subjected to steam distillation until 1200 ml. of distillate had been collected. When cooled, the distillate yielded 3 g. of *p*-nitrochlorobenzene. The mixture in the flask was filtered while hot, the filtrate being a clear yellow liquid. The residual solid was a mixture, difficult to separate, and consisting mostly of the sulfide mentioned above.

The filtrate was cooled and neutralized with sodium hydroxide. The amine was removed by filtration and recrystallized from a mixture of benzene and petroleum ether (b.p. 60–90°); m.p. 138–142°; yield 4 g.

Preparation of bis(2,4-dinitrophenyl) disulfide. The directions of Blanksma (12) were followed, 13.3 g. of 2,4-dinitrochlorobenzene, 8 g. of sodium sulfide ($Na_2S \cdot 9H_2O$), and 1.0 g. of sulfur being used. The crude product (12 g.) was washed well with water and alcohol.

Anal. Calc'd for $C_{12}H_6N_4O_8S_2$: C, 36.2; H, 1.51.
Found: C, 36.45; H, 1.47.

Oxidation of the bis(2,4-dinitrophenyl) disulfide mixture. A 4-g. sample of the crude mixture obtained in the preceding experiment was oxidized with 15 ml. of nitric acid (sp. gr. 1.5) in the usual manner. The reaction mixture was diluted with 60 ml. of water, and the precipitated solid collected and dried; yield, 0.245 g. Several recrystallizations from glacial acetic acid gave white needles (m.p. 240–241°), corresponding to the literature value (240°) for *bis*-2,4-dinitrophenyl sulfone (17). The filtrate after removal of the sulfone was evaporated *in vacuo*. The residue solidified and was easily soluble in water. Neutralization of the aqueous solution with potassium carbonate gave yellow crystals of the potassium salt of 2,4-dinitrophenylsulfonic acid. The crystals exploded with a purple flame on ignition.

Preparation of bis(2-nitro-4-carbethoxyphenyl) disulfide. The procedure of Blanksma for the preceding disulfide was followed, 10.8 g. of 2-nitro-4-carbomethoxychlorobenzene, 6 g. of sodium sulfide ($Na_2S \cdot 9H_2O$), and 0.8 g. of sulfur being allowed to react in absolute ethanol. The mixture was heated for 15 minutes, and the product recrystallized from ethanol. The solid had the composition of *bis*(2-nitro-4-carbethoxyphenyl) disulfide, m.p. 149–150°, transesterification evidently having occurred.

Anal. Calc'd for $C_{18}H_{16}N_2O_8S_2$: C, 47.80; H, 3.54.
Found: C, 47.76; H, 3.61.

Oxidation of the bis(2-nitro-4-carbethoxyphenyl) disulfide mixture. A 4-g. sample was oxidized in the usual way. The solid obtained on dilution weighed 0.35 g. and had a composition corresponding to that of *bis*(2-nitro-4-carbethoxyphenyl) sulfone; m.p. 205–206°.

Anal. Calc'd for $C_{18}H_{16}N_2O_{10}S$: C, 47.80; H, 3.54.
Found: C, 49.50; H, 3.70.

The filtrate, when treated with a solution of barium chloride, gave 0.23 g. of barium sulfate, which did not darken or burn on ignition.

SUMMARY

bis(*p*-Nitrophenyl) sulfide has been found to undergo sulfurization when heated with sodium disulfide, yielding *bis*(*p*-nitrophenyl) disulfide. This reaction, the formation of a disulfide by sulfurization of the corresponding monosulfide, appears to be new in type.

The disulfides prepared from 2,4-dinitrochlorobenzene and 2-nitro-4-carbomethoxychlorobenzene by the action of sodium disulfide appeared to be contaminated with the corresponding monosulfides. In each case oxidation gave small amounts of sulfone.

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REFERENCES

(1) VOROZHTZOV AND KOZLOV, *J. Gen. Chem., U.S.S.R.*, **2,** 939 (1932).
(2) GREEN, *J. Chem. Soc. Ind.*, **41,** 469 (1914).
(3) MACY, The Composition of Levinstein HS, Reports on File at Army Chemical Center. See also MACY, *Science*, **106,** 355 (1947).
(4) PRICE AND STACY, *J. Am. Chem. Soc.*, **68,** 498 (1946). See also HUGHES AND O'LEARY, *J. Roy. Soc. N. S. Wales*, **81,**, 36 (1947).
(5) FROMM AND WITTMANN, *Ber.*, **41,** 2264 (1908).
(6) HINSBERG, *Ber.*, **39,** 2427 (1906).
(7) NIETZKI AND BOTHOF, *Ber.*, **27,** 3261 (1894).
(8) ZINCKE, *Ann.*, **400,** 1 (1913).
(9) HODGSON AND WILSON, *J. Chem. Soc.*, **101,** 1693 (1912).
(10) WERIGO, *Ann.*, **165,** 191 (1873).
(11) WILLGERODT, *Ber.*, **14,** 2636 (1881).
(12) BLANKSMA, *Rec. trav. chim.*, (2) **19,** 111 (1900).
(13) ELGERSMA, *Rec. trav. chim.*, **48,** 752 (1929).
(14) BENNETT AND BERRY, *J. Chem. Soc.*, 1668 (1927).
(15) BURNS, MCCOMBIE, AND SCARBOROUGH, *J. Chem. Soc.*, 2928 (1928).
(16) HICKINBOTTOM, "Reactions of Organic Compounds," p. 359, Longmans, Green and Co., 1936.
(17) BEILSTEIN AND KURBATOW, *Ann.*, **197,** 75 (1879).