**5-Fluoro-2-methoxycarbonylbiphenyl.**—Prepared from methyl 2-bromo-4-fluorobenzoate (103 g.), iodobenzene (91 g.), and copper powder (82 g.), **5-fluoro-2-methoxycarbonylbiphenyl** was collected at 110–118° (0.2 mm.), and redistilled (53 g., 52%), b.p. 108–110° (0.1 mm.), $n^{25}\text{D}$ 1.5662. Vapor phase chromatography analysis showed only one peak.

*Anal.* Calcd. for $C_{14}H_{11}FO_2$: C, 73.0; H, 4.79. Found: C, 73.1; H, 5.10.

**2-Amino-6-nitrobiphenyl.**—2,6-Dinitrobiphenyl[13] (24 g.) in ethanol (350 ml.) was boiled under reflux for 3 hr. during the addition of a solution of sodium sulfide (28 g.) and sulfur (6.9 g.) in water (85 ml.). The ethanol was mostly removed by distillation and the product poured into water and isolated with dichloromethane. Three recrystallizations from dilute ethanol gave **2-amino-6-nitrobiphenyl** as yellow needles (7.5 g., 35.5%), m.p. 74–75°.

*Anal.* Calcd. for $C_{12}H_{10}N_2O_2$: C, 67.3; H, 4.67. Found: C, 67.5; H, 4.99.

**2-Fluoro-6-nitrobiphenyl.**—2-Amino-6-fluorobiphenyl (6 g.) in concentrated hydrochloric acid (30 ml.) and water (30 ml.) was diazotized at 0.5°. Fluoboric acid (60 ml.) was added and the diazonium fluoborate filtered, washed with cold methanol and ether, and dried overnight in a vacuum desiccator. The solid was decomposed by heat and the residue extracted with petroleum ether (b.p. 30–35°, six 50-ml. portions). Evaporation of this ether gave an oil which solidified on scratching. Recrystallization from petroleum ether (b.p. 30–35°) gave pure **2-fluoro-6-nitrobiphenyl** as very pale yellow needles (3.5 g., 60%), m.p. 67–68°.

*Anal.* Calcd. for $C_{12}H_8FNO_2$: C, 66.5; H, 3.69; N, 6.45. Found: C, 66.7; H, 3.99; N, 6.82.

**2-Carboxy-5-fluorobiphenyl.**—A mixture of the methyl ester of 5-fluorobiphenylcarboxylic acid (2.1 g.), sodium hydroxide (10 ml. of 1 *N*), and ethanol (20 ml.) was kept overnight at 40° and then acidified. The **2-carboxy-5-fluorobiphenyl** was isolated with ether and then crystallized from petroleum ether (b.p. 60–68°) in white needles (1.5 g., 76%), m.p. 110°.

*Anal.* Calcd. for $C_{13}H_9FO_2$: C, 72.2; H, 4.17. Found: C, 72.0; H, 4.47.

**3-Fluorofluorenone.**—2-Carboxy-5-fluorobiphenyl (0.5 g.) was allowed to stand in concentrated sulfuric acid (10 ml.) at room temperature for 1 hr. The solution turned deep violet. Pouring into water gave an almost theoretical yield of **3-fluorofluorenone** which crystallized from petroleum ether (b.p. 90–100°)-benzene in yellow needles, m.p. 129–130°.

*Anal.* Calcd. for $C_{13}H_7FO$: C, 78.8; H, 3.54. Found: C, 79.0; H, 4.00.

**5-Hydrazinobiphenyl-2-carboxylic Acid Hydrazide.**—2-Carboxy-5-fluorobiphenyl (1 g.) and hydrazine (1 g.) were treated under reflux overnight. Addition of ethanol gave an almost theoretical yield of the **hydrazide** which crystallized from ethanol in cream-colored plates, m.p. 140°.

*Anal.* Calcd. for $C_{13}H_{14}N_4O$: C, 64.5; H, 5.78; N, 23.2. Found: C, 64.6; H, 6.18; N, 22.9.

**Reductions of the Fluoronitrobiphenyls to the Corresponding Amines.**—The reductions of the fluoronitrobiphenyls to the corresponding amines were carried out using the method of Marler and Turner.[6] The amines were characterized as their acetyl derivatives. 2-Amino-6-fluorobiphenyl had been characterized previously only by its acetyl derivative. The yields, melting points, and analysis data are shown in Tables I and II.

**Synthesis of the Fluoro-10-methyl-10,9-borazarophenanthrenes.**—The method of Dewar, Kubba, and Pettit[4] was used to prepare the boron–nitrogen heterocycles. The 10-methyl group was introduced by the action of methylmagnesium iodide on the fluoro-10-chloro-10,9-borazarophenanthrenes. The crude methyl compounds were purified by chromatography on alumina (Merck) with petroleum ether (b.p. 30–35°) as eluent. Sublimation and one or more crystallizations from petroleum ether (b.p. 30–35°) gave the pure compounds. The yields in Table III refer to analytical samples.

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[13] J. Forrest, *J. Chem. Soc.*, 601 (1960).

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# The Reaction of Trimethyl Thioborate with Diazoalkanes[1]

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The interaction of trimethyl thioborate with several diazoalkanes has been studied. Trimethyl thioborate and diazomethane leads only to polymethylene; trimethyl thioborate reacts with phenyldiazomethane to give methyl benzyl sulfide and *trans*-stilbene; trimethyl thioborate reacts with ethyl diazoacetate to give ethyl S-methylmercaptoacetate and diethyl S-methylmercaptosuccinate; trimethyl thioborate reacts with phenylbenzoyldiazomethane to give methyl diphenylthioacetate. These several products are rationalized in terms of the alternate pathways illustrated in Fig. 1.

Numerous examples of the interaction of diazoalkanes, principally diazomethane, with inorganic compounds have been reported in the literature.[3] In some cases the inorganic compound undergoes methylenation with diazomethane as, for example, stannic chloride which reacts to form various chloromethyl derivatives; *e.g.*, $ClCH_2SnCl_3$.[4] In other cases the inorganic material acts as a polymerization catalyst as, for instance, the trialkylborons, the trialkyl borates, and the boron halides,[5] the main action on diazomethane being to form polymethylene.[6] The present work extends the list of boron compounds reactive toward diazo compounds to include trimethyl thioborate Although, in common with the boron compounds just mentioned, it induces polymerization of diazomethane, it reacts with substituted diazomethanes in several other ways, the nature of which depends upon the particular diazoalkane.

**Trimethyl Thioborate and Diazomethane.**—This reaction leads to the production of polymethylene, the catalytic action of trimethyl thioborate being rationalized in terms of pathway A–A₁ (see Fig. 1) according to a recent suggestion.[7] The tendency for the first-formed complex to react further with diazomethane rather than to undergo internal rearrangement must derive from the very great reactivity of the $-CH_2N_2^{\oplus}$ moiety. If groups hindering the intermolecular reaction with additional molecules of diazo compound are attached to the diazonium center, the reaction may then take

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[2] Postdoctoral research associate 1961–62 on leave of absence from School of Liberal Arts, Kyoto University, Kyoto, Japan.

[3] D. Seyferth, *Chem. Rev.*, **55**, 1155 (1955).

[4] A. Ya. Yakubovich, S. P. Makarov, and G. I. Gavrilov, *J. Gen. Chem. USSR*, **22**, 1788 (1952); *Chem. Abstr.*, **47**, 9257 (1953).

[5] H. Meerwein, *Angew. Chem.*, **60**, 78 (1948).

[6] Under special conditions, however, fluoromethylboron difluoride can be obtained from boron trifluoride and diazomethane [J. Goubeau and K. H. Rohwedder, *Ann.*, **604**, 168 (1957)].

[7] A. G. Davies, D. G. Hare, O. R. Khan, and J. Sikora, *Proc. Chem. Soc.*, 172 (1961).

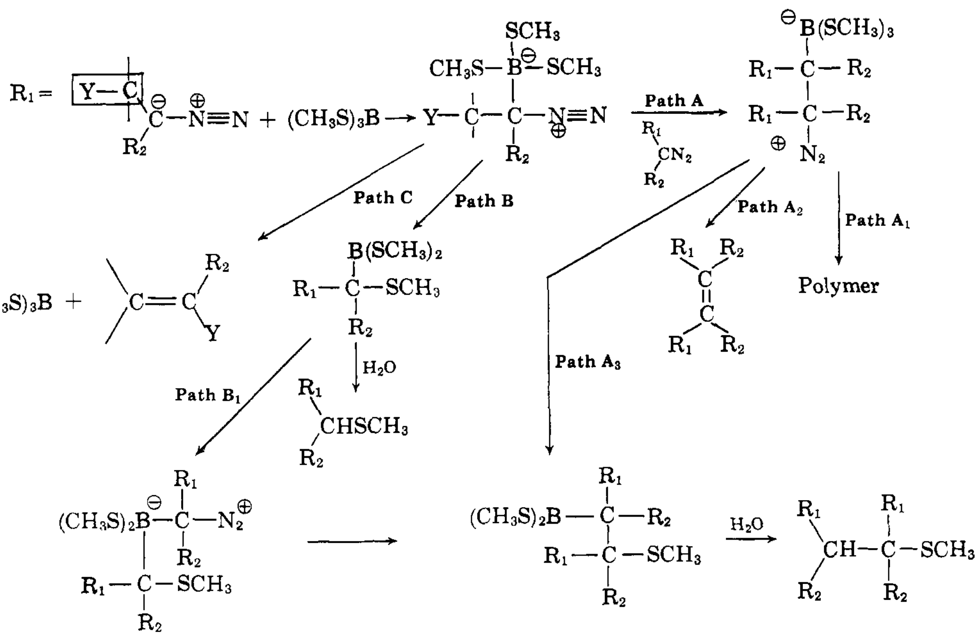


Fig. 1.—Reaction pathways for trimethyl thioborate and diazoalkanes.

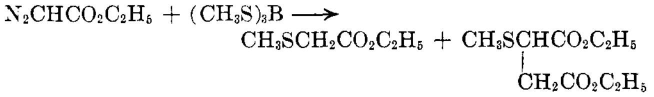
alternative courses as illustrated by the following examples.

**Trimethyl Thioborate and Phenyldiazomethane.**—The major product from this reaction is methyl benzyl sulfide (I), isolated in *ca.* 40% yield, and its formation is rationalized by pathway B (see Fig. 1). A second product, isolated in smaller amount, has been identified

$$C_6H_5CHN_2 + (CH_3S)_3B \longrightarrow \underset{\text{I}}{CH_3SCH_2C_6H_5} + \underset{\text{II}}{C_6H_5CH{=}CHC_6H_5}$$

as *trans*-stilbene. Phenyldiazomethane alone is known to produce stilbene, and it is, therefore, uncertain in the present case whether or not the trimethyl thioborate is involved in its formation. A reasonable mechanism implicating the boron compound is illustrated by pathway A–A₂ in which the first-formed complex reacts intermolecularly with a second mole of phenyldiazomethane (path A—similar to the second step in the diazomethane polymerization) to give an intermediate which then achieves stabilization along an intramolecular pathway (path A₂).

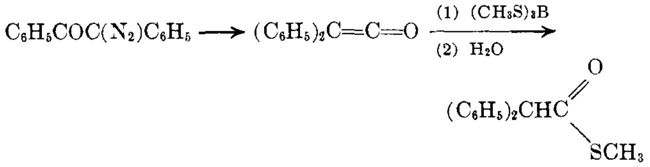
**Trimethyl Thioborate and Ethyl Diazoacetate.**—The major product from the reaction of trimethyl thioborate with ethyl diazoacetate is ethyl S-methylmercaptoacetate (III), and its formation can be rationalized, as in the previous example, by pathway B (see Fig. 1). The second product, however, is not diethyl fumarate



$$N_2CHCO_2C_2H_5 + (CH_3S)_3B \longrightarrow \underset{\text{III}}{CH_3SCH_2CO_2C_2H_5} + \underset{\text{IV}}{CH_3S\underset{|}{C}HCO_2C_2H_5}\atop \qquad CH_2CO_2C_2H_5$$

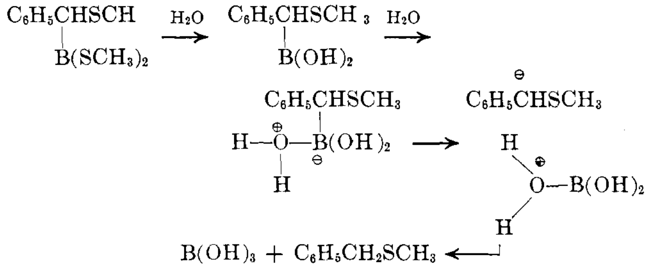
(pathway A–A₂) but diethyl S-methylmercaptosuccinate (IV), the formation of which is rationalized by pathway B–B₁ (a possible alternative is pathway A–A₃).

**Trimethyl Thioborate and Phenylbenzoyldiazomethane.**—In this case still another possibility arises, *viz.*, rearrangement of the diazo compound itself, and it is this course that appears to be preferred. Thus, from trimethyl thioborate and phenylbenzoyldiazomethane the major product isolated is methyl diphenylthioacetate (V). That it probably forms *via* diphenylketene as an intermediate [*via* path C (see Fig. 1)] was demonstrated by treating diphenylketene with trimethyl thioborate and isolating V as the major product.



V

The reaction pathway presented in Fig. 1 indicates the last step in the sequences to be a hydrolysis in which a C–B bond undergoes cleavage. This is a conversion which ordinarily requires fairly strenuous conditions as, for example, benzylboronic acid which undergoes C–B cleavage with hot 5% sodium hydroxide solution.[8] The conditions of hydrolysis in the present instances are much milder, and if Fig. 1 is a correct portrayal of the reaction course it must be accepted that the hydrolysis proceeds with unexpected facility in these cases. The hydrolysis of the intermediate from phenyldiazomethane and trimethyl thioborate, to take a specific example, may progress in the following fashion.



According to this mechanism the ease of cleavage of the C–B bond can be related to the ability of the carbon atom of this bond to support a negative charge. That divalent sulfur has the capability of stabilizing an adjacent carbanionic center has been demonstrated in

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[8] J. R. Johnson, M. G. Van Campen, and O. Grummitt, *J. Am. Chem. Soc.*, **60**, 111 (1938).

several instances,[9] and it may be this factor that is responsible for the facile cleavage in these cases.

## Experimental[10]

Trimethyl thioborate was prepared by the reaction of lead methyl mercaptide and boron tribromide[11] and was obtained as a colorless oil with b.p. 205–208° (750 mm.), 101–103° (20 mm.) (reported m.p. 205–208°[9], 101.1° (17.7 mm.)[12]).

**Trimethyl Thioborate and Diazomethane.**—A solution of 9.4 g. (0.22 mole) of diazomethane [prepared by base-catalyzed decomposition of N,N′-dinitroso-N,N′-dimethylterephthalamide (Du Pont EXR-101), redistilled, and dried over potassium hydroxide and sodium] in 200 ml. of dry ether was added, over a period of 2 hr., to a stirred and cooled (−45 to −55°) solution containing 11.0 g. (0.072 mole) of trimethyl thioborate in 100 ml. of dry ether. The reaction mixture was allowed to warm to room temperature and to stand overnight. Filtration yielded 2.6 g. (84% based on diazomethane) on a nonvolatile, ether-insoluble white powder assumed to be polymethylene, and evaporation of the ether solution and distillation of the residue yielded unchanged trimethyl thioborate.

**Trimethyl Thioborate and Phenyldiazomethane.**—A solution containing 9 g. (0.076 mole) of phenyldiazomethane (prepared from phenylbenzoyldiazomethane by the method of Yates and Shapiro[13]) in 100 ml. of anhydrous ether was added, over a period of 100 min., to a solution of 5.2 g. (0.034 mole) of trimehyl thioborate in 50 ml. of anhydrous ether cooled to −30°. The ether was then removed by evaporation, the residue was treated with 200 ml. of 5% sodium hydroxide solution, and the mixture was refluxed for 30 min. Extraction with ether, removal of the ether by evaporation, and distillation of the residue yielded 3.9 g. (36% based on phenyldiazomethane) of material with b.p. 89–92° (15 mm.), identified as methyl benzyl sulfide by comparison with an authentic sample prepared from benzyl chloride and lead methyl mercaptide. The still residue was recrystallized from ethanol to yield 1.0 g. (7%) of pale yellow crystals, m.p. 121.5–124° (124–125° after a second recrystallization), identified as *trans*-stilbene by comparison with an authentic sample, m.p. 124–125°.

**Trimethyl Thioborate and Ethyl Diazoacetate.**—A solution of 19.2 g. (0.17 mole) of ethyl diazoacetate in 50 ml. of petroleum ether (b.p. 33–36°, dried over sodium) was added, over a period of 20 min., to a stirred solution containing 10.2 g. (0.0067 mole) of trimethyl thioborate in 50 ml. of dry petroleum ether, the reaction being carried out at room temperature. During the addition, the solvent refluxed rather vigorously from the heat of the reaction. The mixture was then cooled to room temperature, treated with 50 ml. of saturated sodium chloride solution, and extracted with ether. After washing with 10% sodium carbonate solution and drying over anhydrous magnesium sulfate, the ether was removed and the residue was distilled to give 6.1 g. (28% based on ethyl diazoacetate) of ethyl S-methylmercaptoacetate with b.p. 62.5–64° (13 mm.), 0.7 g. of a middle fraction with b.p. 65–136° (13 mm.), and 1.5 g. (8%) of diethyl S-methylmercaptosuccinate with b.p. 137° (13 mm.). The lower boiling fraction was identified by an infrared spectral comparison with an authentic sample and by a melting point comparison of its *p*-toluidide, m.p. 102–103°, with an authentic sample, m.p. 102–103° (neat and admixed). The higher boiling fraction was identified by its analysis, by an infrared comparison with a sample synthesized by an alternate route, and by its hydrolysis to the known S-methylmercaptosuccinic acid.

*Anal.* Calcd. for $C_9H_{16}O_4S$: C, 49.09; H, 7.27. Found: C, 48.96; H, 7.08.

This was effected by treatment of a 0.55-g. sample of the ester with alcoholic potassium hydroxide for 6 hr.[14] The crude product was recrystallized from benzene–acetone to yield 0.20 g. (45%) of S-methylmercaptosuccinic acid, m.p. 131–134°. Further recrystallization of the latter provided material with m.p. 134–136° (reported[15] m.p. 136.8°). An alternate synthesis of diethyl S-methylmercaptosuccinate was achieved by treating 33.0 g. (0.33 mole) of maleic anhydride dissolved in 30 ml. of water containing 3.0 g. of potassium hydroxide and heated to 96–98° with methyl mercaptan bubbled in over a period of 3 hr.[16] The resulting product (*ca.* 27 g.) was refluxed for 1 hr. with 40 g. (0.33 mole) of thionyl chloride. After removal of the excess reagent, the residue was treated with 100 ml. of ice-cold ethyl alcohol. Distillation of the resulting product yielded 13.5 g. (19%) of a colorless liquid, b.p. 82–84° (0.2 mm.). An infrared spectral comparison showed this to be identical with the higher boiling fraction described previously. By hydrolysis of the ester with cold alcoholic potassium hydroxide S-methylmercaptosuccinic acid, m.p. 134–136°, was obtained.

**Trimethyl Thioborate and Phenylbenzoyldiazomethane.**—A solution of 6.12 g. (0.004 mole) of trimethyl thioborate in 100 ml. of absolute ether was mixed with a solution of 6.25 g. (0.0028 mole) of phenylbenzoyldiazomethane in 300 ml. of absolute ether. Little if any reaction took place at room temperature, and the mixture was refluxed for 20 hr. It was then cooled in an ice bath, treated with 300 ml. of 5% sodium hydroxide solution, and stirred for 10 min. Working up in the usual manner gave 6.37 g. of crude material as a semisolid which, upon crystallization from ethanol, yielded 2.00 g. (29.5% based on phenylbenzoyldiazomethane) of methyl diphenylthioacetate, m.p. 86–90°. Additional recrystallization from ethanol provided colorless plates, m.p. 90–92°.

*Anal.* Calcd. for $C_{15}H_{14}OS$: C, 74.38; H, 5.78. Found: C, 74.35; H, 5.93.

The methyl diphenylthioacetate was characterized by hydrolysis and by comparison with a sample prepared by an independent route. Base-catalyzed hydrolysis yielded diphenylacetic acid, identical by mixture melting point (146–148°) with an authentic sample, and methyl mercaptan. The latter was characterized as 1-methylmercapto-2,4-dinitrobenzene, m.p. 125–127° (reported[17] m.p. 128°) obtained by treatment with 1-chloro-2,4-dinitrobenzene. An independent synthesis of methyl diphenylthioacetate was achieved by treating diphenylacetyl chloride with methyl mercaptan. The resulting product was shown by mixture melting point (90–92°) to be identical with that isolated from the reaction mixture described previously.

**Trimethyl Thioborate and Diphenylketene.**—To a solution of 6.00 g. (0.031 mole) of diphenylketene in 200 ml. of dry ether was added a solution of 6.00 g. (0.039 mole) of trimethyl thioborate in 100 ml. of dry ether. The mixture was refluxed for 25 hr. in an atmosphere of nitrogen, cooled in ice, treated with 400 ml. of 5% sodium hydroxide solution, stirred for 10 min., and worked up. From the base-soluble fraction there was obtained 2.91 g. of crude material comprised mainly of diphenylacetic acid, m.p. 144–146° after recrystallization. The neutral fraction consisted of 4.12 g. of solid from which 2.26 g. (28.5%) of methyl diphenylthioacetate was obtained, m.p. 84–87°. Further recrystallization from ethanol raised the melting point to 89–91°.

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(9) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962, p. 55–60.

(10) All melting points are corrected; all boiling points are uncorrected. Microanalyses were performed by Dr. J. Szcek's laboratory in Vienna, Austria.

(11) J. Goubeau and H. W. Whittmeier, *Z. anorg. allgem. Chem.*, **270**, 16 (1952).

(12) L. L. Petterson, R. J. Brotherton, and J. L. Boone, *J. Org. Chem.*, **26**, 3030 (1961).

(13) P. Yates and B. L. Shapiro, *ibid.*, **23**, 759 (1958).

(14) V. C. Barry, L. O'Rourke and D. Twomey, *Proc. Roy. Irish Acad.*, **51**, 223 (1947); *Chem. Abstr.*, **42**, 4134a (1948).

(15) T. Kaneko and S. Mii, *J. Chem. Soc. Japan*, **59**, 1382 (1938).

(16) U. S. Patent 2,581,514 (1952); *Chem. Abstr.*, **47**, 4363 (1952).

(17) R. W. Bost, J. O. Turner, and R. D. Norton, *J. Am. Chem. Soc.*, **54**, 1896 (1932).