Authentic 1,1,4-4-Tetraphenylbutatriene Authentic tetraphenylbutatriene was synthesized from 1,1,4,4-tetraphenyl-2,3-dihydroxybutyne-2 by the method of Kuhn and Wallenfels,[13] m.p. 236–237° (lit.[13] m.p. 236.5–237°).

Reaction of 1,1-diphenyl-2-nitroethylene with dry potassium t-butoxide. Dry potassium *t*-butoxide was prepared by adding *t*-butyl alcohol to a refluxing mixture of potassium in dry toluene or xylene. After 2 hr. reflux, the mixture was filtered under nitrogen and the residue of potassium *t*-butoxide was washed thoroughly with dry ether. The best yields of triene were obtained when this material was used as soon after preparation as possible. In a typical run, 1,1-diphenyl-2-nitroethylene (2.0 g., 8.8 mmoles) was dissolved in 150 ml. of dry heptane. The system was flushed with dry nitrogen and heated to reflux. To the refluxing solution was added in small portions 2.0 g. (18 mmoles) of dry potassium *t*-butoxide. After each addition, a red color developed in the reaction mixture. The mixture was refluxed for 5 hr. after completion of the addition. It was then filtered, while hot, through a Buchner funnel. Upon cooling, the heptane filtrate deposited 0.12 g. (7.6%) of yellow crystals, m.p. 236–237°; admixture with authentic 1,1,4,4-tetraphenylbutatriene showed no melting point depression.

Anal. Calcd. for $C_{28}H_{20}$: C, 94.37; H, 5.63. Found: C, 94.12; H, 5.60.

The infrared spectrum was identical with that of authentic tetraphenylbutatriene.

Evaporation of the heptane filtrate almost to dryness afforded 0.34 g. (17%) of the starting material.

Both the residue from the above filtration of the hot reaction mixture and the filtrate (after evaporation to dryness) were analyzed for diphenylacetylene. This was effected by gas chromatography of samples of each (chloroform extract of the residue) employing a six-foot column of Tide at 198° and 15 p.s.i. internal pressure in a Perkin-Elmer model 154-B vapor fractometer. Neither sample showed any peak near 7.4 min., the retention time of authentic diphenylacetylene.

Quantitative determination of tetraphenylbutatriene and unchanged 1,1-diphenyl-2-nitroethylene. The concentration of the triene and unchanged starting material were determined quantitatively by utilizing the Beckman DK-2 Spectrophotometer. Absorptions at 420 mμ (triene) and 360 mμ (starting material) were employed. Both compounds obeyed Beer's Law and no absorption from products resulting from *beta*-addition to the nitroolefin appeared at these wave lengths. It was therefore possible to analyze the reaction products for triene and nitroolefin directly. A typical run is given below. The other results are summarized in Table I.

Reaction of 1,1-diphenyl-2-nitroethylene with a t-butyl alcohol solution of potassium t-butoxide in the presence of cyclohexene. 1,1-Diphenyl-2-nitroethylene (0.02 g., 8.8×10^{-5} moles) was dissolved in 8 ml. of dry heptane. To this solution was added 1 ml. (1×10^{-2} moles) of cyclohexene. The three-necked flask was flushed well with dry nitrogen and 1.0 ml. of a *t*-butyl alcohol solution of potassium *t*-butoxide (8.0×10^{-4} moles) was added dropwise by means of a syringe. The solution was refluxed, with constant agitation, for 30 min. at which time the hot mixture was poured into 30 ml. of boiling chloroform. The solution was washed twice with 50-ml. portions of saturated salt solution and dried over anhydrous magnesium sulfate. The solution was made up to volume with chloroform in a 50-ml. volumetric flask followed by dilution with chloroform of 1:10. The amount of triene and starting material were then calculated directly from the ultraviolet spectrum to be 2.3% and 14%, respectively.

A blank, differing from the above reaction only in that 9 ml. of heptane was used as the solvent rather than 8 ml. of heptane and 1 ml. of cyclohexene also gave a 2.3% yield of triene.

GAINESVILLE, FLA.

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[13] R. Kuhn and K. Wallenfels, *Ber.*, **71**, 783 (1938).

[CONTRIBUTION NO. 31 FROM THE EXPLORATORY RESEARCH LABORATORY, DOW CHEMICAL OF CANADA, LIMITED]

Aryldiazonium Tetrachloroborates and Tetrabromoborates

G. A. OLAH AND W. S. TOLGYESI

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Aryldiazonium tetrachloroborates and tetrabromoborates were prepared from (1) the corresponding aryldiazonium halides and boron trihalides, (2) primary aromatic amines and nitrosonium tetrachloroborate, (3) the reaction of $N_2O_3 \cdot BCl_3$ and $N_2O_3 \cdot BBr_3$ with primary aromatic amines.

The first reference to diazonium tetrafluoroborates is that of Bart[1] in 1913 who prepared them by treating aromatic diazo compounds with complex fluoroboric acids and their salts. Owing to the great stability and practical application of the diazonium tetrafluoroborates, considerable research has since been carried out on these compounds.[2] As intermediates in the Schiemann reaction, aryldiazonium tetrafluoroborates are prepared either by diazotizing aromatic primary amines and then treating the prepared diazonium compounds with fluoroboric acid or fluoborates or by carrying out the diazotization directly in aqueous fluoboric acid.[3] Wannagat and Hohlstein[4] in an improved method prepared aryldiazonium tetrafluoroborates from primary aromatic amines and nitrosonium tetrafluoroborates. No aryldiazonium tetrachloroborates or tetrabromoborates, however, have been reported previously.

Tetrachloroborate and tetrabromoborate complexes are considerably less well known than the corresponding tetrafluoroborates. Muetterties[5] ob-

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[1] H. Bart, Ger. Patent **281,055** (Oct. 7, 1913) [*Chem. Abstr.*, **9**, 1830 (1915)].

[2] H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," Wiley, New York, 1949.

[3] G. Balz and G. Schiemann, *Ber.*, **60B**, 1186 (1927); E. Wilke-Dorfurt and G. Balz, *Ber.*, **60**, 115 (1927); A. Roe, *Org. Reactions*, 193–228 (1949).

[4] U. Wannagat and G. Hohlstein, *Chem. Ber.*, **88**, 1839 (1955).

[5] E. L. Muetterties, *J. Am. Chem. Soc.*, **79**, 6563 (1957).

tained potassium, rubidium, and cesium tetrachloroborates by the interaction of boron trichloride with alkali metal chlorides under pressure and high temperatures. Lappert[6] prepared pyridinium tetrachloroborates and tetrabromoborates from the corresponding pyridinium halides and boron trihalides. Gerard and Mooney[7] have observed that the reaction of boron trichloride with certain primary amines proceeds *via* disproportionation to give the tetrachloroborates $RNH_3 \cdot BCl_4$ and an aminoboron dichloride, $RNHBCl_2$, instead of giving the expected adduct, $RNH_2 \cdot BCl_3$. Herbert[8] studied the halogen exchange between boron trichloride and a number of chloride salts using Cl^{36} as a radiotracer. Both tetramethylammonium chloride and tetraethylammonium chloride exchange chloride rapidly with liquid boron trichloride. These results can be interpreted only on the basis of a mechanism which involves the formation of the tetrachloroborate anion. Alkylammonium tetrachloroborates and trifluorochloroborates[9] were prepared from the corresponding alkylammonium halides and boron trihalides in liquid hydrogen chloride. The electron acceptor properties of boron trichloride have been reviewed and findings suggesting the presence of the tetrachloroborate ion in some complexes are discussed. Infrared bands at 690 and 660 cm.$^{-1}$ were assigned to this ion.[10] The asymmetric stretching vibration of the BBr_4^- ion was observed at 593 cm.$^{-1}$.[11] Recently a comprehensive report on infrared investigation of tetrachloroborate complexes was published.[12] Tetrachloroborate complexes generally show a very broad strong band in the 630–750 cm.$^{-1}$ region.

To enable further investigation of the properties of organic tetrahaloborate complexes, aryldiazonium tetrachloro and tetrabromoborates were prepared. It was not possible to use the simple methods previously reported for the preparation of the aryldiazonium tetrafluoroborates. No aqueous chloro- or bromoboric acid exists, neither are their salts stable in aqueous solutions. Therefore, the preparation of the diazonium salts could not be effected through simple diazotization of the corresponding amines, with subsequent addition of the complex haloboric acid or its salts.

Nitrosonium tetrachloroborate ($NO^+BCl_4^-$), as such, has not been reported in the literature. Partington and Whynes[13] investigated the nitrosyl chloride–boron trichloride addition compounds and reported that a 1:1 compound $NOCl.BCl_3$ could be obtained. When formed from equimolar quantities of the starting materials, it is a lemon-yellow solid, melting in a sealed tube at 26–27° forming two liquid layers; the upper clear, reddish, the lower, orange or opaque. On heating to 65°, the lower layer disappears. This behavior corresponds with the phase diagram described by Roozeboom.[14] On the melting point curve, the maximum corresponding to compound formation, is not reached since a completely closed curve (probably similar to that of the nicotine-water system) cuts the apex and the compound does not melt without decomposition. No effort was made to clarify the structures of the 1:1 addition compound.

In our investigation of the nitrosyl chloride–boron trichloride system, it was found that it is possible to prepare a slightly yellow colored addition compound by treating difluorodichloromethane (Freon 12) solutions of the components at −50°. On evaporation of the solvent and any excess reagents at low temperatures in a vacuum system, the complex was obtained as a colorless, crystalline compound with a decomposition point of 24–25° (a considerable vapor pressure showing already at 20°). Analytical determinations are in accordance with a 1:1 composition $NOCl \cdot BCl_3$. The compound is insoluble in apolaric solvents but dissolves more readily in polaric solvents such as nitrobenzene. Decomposition at atmospheric pressure takes place quantitatively in the absence of moisture according to the equilibrium

$$NOCl \cdot BCl_3 \rightleftharpoons NOCl + BCl_3$$

By cooling, the addition complex is reformed, but needs further purification because it is yellow in color owing to absorbed nitrosyl chloride. Infrared investigation of the complex shows an absorption peak at 2123 cm.$^{-1}$ which could be assigned as the stretching frequency of the NO^+ ion. The absorption peak observed in the 1800 cm.$^{-1}$ region corresponds to NO in NOCl. From these data the solid complex was considered as nitrosonium tetrachloroborate ($NO^+BCl_4^-$) in equilibrium with its components and the oxygen coordinated polarized covalent complex

$$NOCl \cdot BCl_3 \rightleftharpoons NO^+BCl_4^-$$

Nitrosonium tetrachloroborate, upon reaction with primary aromatic amines at temperatures between −15 and −5°, gave the corresponding aryldiazonium tetrachloroborates

$$ArNH_2 + NO^+ BCl_4^- \longrightarrow ArN_2^+ BCl_4^- + H_2O$$

The aryldiazonium tetrachloroborates are considerably more sensitive to hydrolysis than the

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(6) M. F. Lappert, *Proc. Chem. Soc.*, 121 (1957).

(7) W. Gerard and E. F. Mooney, *Chem. and Ind.*, 1259 (1958).

(8) R. H. Herbert, *J. Am. Chem. Soc.*, 80, 5080 (1958).

(9) T. C. Waddington and F. Klanberg, *Naturwissenschaften*, 20, 578 (1959).

(10) W. Kynaston and H. S. Turner, *Proc. Chem. Soc.*, 304 (1958).

(11) T. C. Waddington and J. A. White, *Proc. Chem. Soc.*, 1960, 85.

(12) W. Kynaston, B. E. Larcombe, and H. S. Turner, *J. Chem. Soc.*, 1960, 1772.

(13) J. R. Partington and A. S. Whynes, *J. Chem. Soc.*, 1949, 3135.

(14) H. W. B. Roozeboom, "Die heterogenen Gleichgewichte vom Standpunkt der Phasenlehre," Verlag Friedr. Vieweg, Braunschweig, 1919, 2, 175.

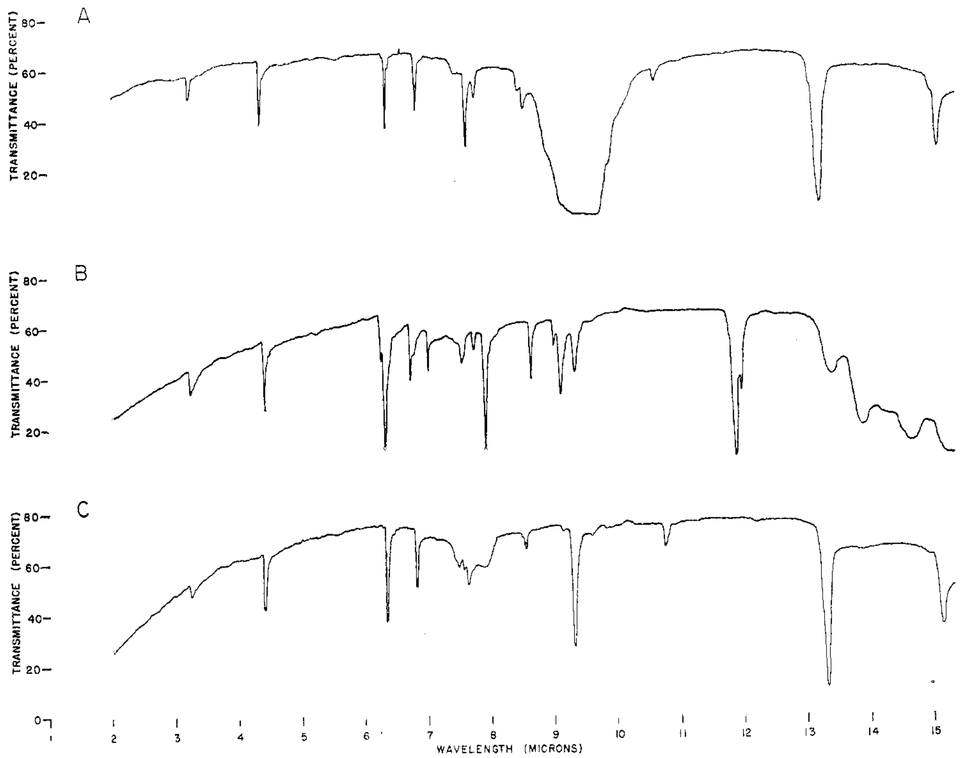
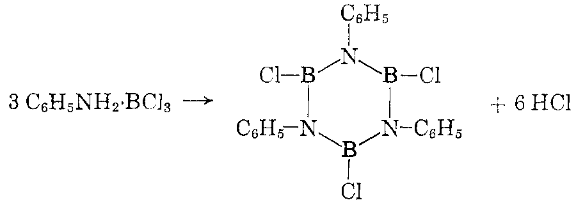


Fig. 1. (A) Phenyldiazonium tetrafluoroborate $C_6H_5N_2^+BF_4^-$, (B) phenyldiazonium tetrachloroborate $C_6H_5N_2^+BCl_4^-$, (C) phenyldiazonium tetrabromoborate $C_6H_5N_2^+BBr_4^-$

corresponding tetrafluoroborates. The equimolar amount of water, formed in the diazotization reaction, consequently tends to decompose the complexes. Therefore, it is necessary to control the temperature carefully and to remove the diazonium salts as quickly as possible from the reaction mixture. Another reason for the need of carefully regulating the temperature and not allowing it to rise above −5° is related to the thermal decomposition of the nitrosonium tetrachloroborate to nitrosyl chloride and boron trichloride. The released boron trichloride reacts with aniline to form a 1:1 addition compound, which, on thermal decomposition, yields triphenyl trichloroborazole.[15]



An alternate way of preparation of aryldiazonium tetrachloroborates was found by treating primary aromatic amines with the 1:1 complex of nitrogen trioxide with boron trichloride. This complex, which is a crystalline white solid is easily formed by mixing at low temperatures dichlorodifluoromethane (Freon 12) solutions of nitrogen trioxide and boron trichloride. Its structure in analogy with the $N_2O_3{\cdot}BF_3$ complex isolated and investigated by Backman[16] is suggested to be

$$BCl_3 + ON \vdots :NO_2 \longrightarrow (Cl_3B \longleftarrow NO_2)^-NO^+$$

and acts as a powerful nitrosating agent. The corresponding aryldiazonium tetrachloroborates are formed in high yields, but are difficult to obtain in pure form, because that equimolar amount of water formed in the diazotation reaction tends to hydrolyze the complexes and the products are consequently contaminated with boric acid. Boric acid contamination is also due to the fact that the $N_2O_3{\cdot}BCl_3$ complex is fairly unstable, decomposes slowly at room temperature to nitrosyl chloride and boron trioxide.

To overcome the difficulty of the decomposing action of the water formed in direct diazotation a simple method was found for the preparation of diazonium tetrachloroborates. When primary aromatic amines react with nitrosyl chlorides, diazonium chlorides are formed.[17] The diazonium chlorides can be isolated as relatively stable solids and handled without difficulty under nonaqueous inert solvents such as hydrocarbons. When aryldiazonium chlorides were treated in a suspension of

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[15] R. C. Jones and C. R. Kinney, *J. Am. Chem. Soc.*, **61**, 1378 (1939).

[16] G. B. Bachman and T. Hokama, *J. Am. Chem. Soc.*, **79**, 4370 (1957).

[17] Pabst and Girard, *Ber.*, **12**, 365 (1879); Ger. Patent **6034**; Brit. Patent **2811** (1878).

TABLE I

ARYLDIAZONIUM TETRACHLOROBORATES $ArN_2^+BCl_4^-$

Ar	Yield, %	Dec. Point	Cl %		N % (as N_2 in Diazonium Salt)	
			Calcd.	Found	Calcd.	Found
Phenyl	96	85–87	55.1	54.6	10.9	10.8
o-Tolyl	92	35–37	52.2	51.4	10.3	10.5
p-Tolyl	89	87	52.2	51.9	10.3	10.1
o-Nitrophenyl	91	90–92	46.9	45.8	9.2	9.8
m-Nitrophenyl	83	109	46.9	45.8	9.2	9.6
p-Nitrophenyl	89	101	46.9	46.0	9.2	9.3
m-Bromophenyl	78	33–35	42.1	41.3	8.3	8.5
p-Fluorophenyl	84	106	51.4	50.8	10.2	9.9

carbon tetrachloride and petroleum ether at −15 to −10° with boron trichloride, the corresponding aryldiazonium tetrachloroborates were formed with an almost quantitative yield.

$$ArN_2^+Cl^- + BCl_3 \longrightarrow ArN_2^+ BCl_4^-$$

Properties and yields of the preparation aryldiazonium tetrachloroborates are summarized in Table I. The infrared spectra of the diazonium tetrachloroborates resemble those of the aryldiazonium tetrafluoroborates having a characteristic N=N stretching vibration at 2260 cm.$^{-1}$ and a broad band corresponding to the BCl_4^- between 630 and 750 cm.$^{-1}$

Lappert first proved the existence of the tetra bromoborate ion in pyridinium tetrabromoborate.[6] Alkylammonium tetrabromoborates were prepared[18] from alkylammonium bromide and boron tribromide in liquid hydrogen bromide. Consequently, an attempt was made by us to extend investigations on the preparation of aryldiazonium tetrabromoborates. Attempts to prepare nitrosonium tetrabromoborate from nitrosyl bromide and boron tribromide were unsuccessful. Although there is proof of complex formation upon mixing the components in Freon 12 solution, no uniform stable compound could be isolated. It was, therefore, not possible to try the reaction of primary aromatic amines with the nitrosonium salt.

Aryldiazonium tetrabromoborates were first successfully obtained when we reacted primary aromatic amines with the 1:1 complex of dinitrogen trioxide with boron tribromide. The complex, a crystalline solid, somewhat brownish in color due to possible bromine or nitrosyl bromide contamination, is formed in a very exothermic reaction when equimolar quantities of nitrogen trioxide and boron tribromide are treated in Freon 12 (CCl_2F_2) solution at low temperature. The complex decomposes slowly at room temperature to nitrosyl bromide and boric oxide. The obtained aryldiazonium tetrabromoborates were however not pure and contained always boric oxide as contamination, formed by hydrolysis through the water formed in the diazotation reaction or decomposition of the $N_2O_3 \cdot BBr_3$ complex.

To obtain aryldiazonium tetrabromoborates in pure form, an analogous way to the one applied for the preparation of aryldiazonium tetrachloroborates was found suitable.

Nitrosyl bromide makes it possible to prepare and isolate diazonium bromides in a manner similar to that used with nitrosyl chloride. Aryldiazonium bromides are formed when primary aromatic amines react with nitrosyl bromide.

$$ArNH_2 + NOBr \longrightarrow ArN_2^+Br^- + H_2O$$

The diazonium bromides can be isolated as relatively stable solids and handled without difficulty under an inert solvent such as a carbon tetrachloride–petroleum ether mixture. When aryldiazonium bromides reacted with boron tribromide in a suspension of carbon tetrachloride-petroleum ether mixture, the corresponding aryldiazonium tetrabromoborates were formed.

$$ArN_2^+Br^- + BBr_3 \longrightarrow ArN_2 BBr_4^-$$

Properties and yields of the aryldiazonium tetrabromoborates prepared are shown in Table II. The infrared spectra of the aryldiazonium tetrabromoborates resemble those of the diazonium tetrafluoroborates and tetrachloroborates. The characteristic N=N stretching vibration is at 2257 cm.$^{-1}$ Using sodium chloride optics, no characteristic band of the BBr_4^- anion was observed. The asymmetric stretching vibration of the anion is to be expected in the 590 cm.$^{-1}$ [11] region.

EXPERIMENTAL

All operations were carried out with the usual precautions to exclude moisture.

Nitrosonium tetrachloroborate. A solution of 6.5 g. (0.1 mole) nitrosyl chloride in 100 ml. of dichlorodifluoromethane (Freon 12) was added to a solution of 11.7 g. (0.1 mole) boron trichloride in 100 ml. Freon 12 over a period of 10 min. with constant stirring at −50°. An orange colored precipitate was formed. The solvent was evaporated and the product vacuum dried at −20° to remove any excess of the reagents. The yield was 16.2 g. (89%) of colorless, crystalline complex. Thermal decomposition of the material took place at 24–25° resulting in gaseous nitrosyl chloride and boron trichloride.

Anal. Calcd. for $NOBCl_4$ (182.7): Cl, 77.6; N, 7.7. Found: Cl, 76.9; N, 7 6.

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[18] T. C. Waddington and J. A. White, *Proc. Chem. Soc.*, 85 (1960).

TABLE II

Ar	Yield, %	Dec. Point	Br % Calcd.	Br % Found	N % (as N_2 in diazonium salt) Calcd.	N % (as N_2 in diazonium salt) Found
Phenyl	91	82	73.4	72.8	6.4	6.2
p-Tolyl	87	90–91	72.2	71.3	6.2	6.1
o-Nitrophenyl	83	100	66.5	65.8	5.8	5.5
p-Fluorophenyl	92	128–134	70.7	69.8	6.2	6.0

Phenyldiazonium tetrachloroborate from aniline and nitrosonium tetrachloroborate. To a stirred suspension of 20 g. (0.11 mole) of nitrosonium tetrachloroborate and 150 ml. of toluene maintained at −10° was added a solution of 9.3 g. (0.1 mole) of aniline in 100 ml. of toluene over a period of 20 min. Stirring was continued at −10° for 40 min. The pale yellow precipitate was filtered, washed with cold (0°) toluene and petroleum ether successively and dried in vacuum at 25° to remove solvents and any unchanged nitrosonium tetrachloroborate. The yield was 91%. Thermal decomposition point: 84–85°.

Anal. Calcd. for $C_6H_5N_2BCl_4$(257.8): Cl, 55.1; N, 10.9. Found: Cl, 54.4; N, 10.3.

$N_2O_3 \cdot BX_3$ (X = Cl, Br). A solution of 0.1 mole of boron trihalide in 100 ml. of difluorodichloromethane (Freon 12) was added dropwise to a continuously agitated solution of 7.6 g. (0.1 mole) of nitrogen trioxide in 100 ml. Freon 12 at −78°. Immediately an off yellow colored precipitate is formed in the strongly exothermic reaction. The solvent was then pumped off under slightly reduced pressure. A practically colorless crystalline complex remained, which based on gravimetric determination of the halogen content after hydrolysis is a 1:1 N_2O_3:BX_3 complex.

Phenyldiazonium tetrachloro- and tetrabromoborate from aniline and $N_2O_3 \cdot BX_3$. To a stirred suspension of 0.12 mole of $N_2O_3 \cdot BX_3$ complex and 150 ml. of Freon 12 maintained at −30° was added a solution of 9.3 g. (0.1 mole) of aniline in 100 ml. of Freon 12 over a period of 15 min. Stirring was continued for another half hour. The pale yellow precipitate was then filtered, washed with Freon 12 and dried in vacuum. No attempt was made to purify the obtained diazonium salts from boric acid impurity. N% for $C_6H_5N_2BCl_4$, calculated 10.9, found 10.2, for $C_6H_5N_2BBr_4$, calculated 6.4, found 5.8.

Anal. Calcd. for $C_6H_6N_2BCl_4$:N, 10.9. Found: 10.2. Calcd. for $C_6H_5N_2BBr_4$: N, 6.4. Found: 5.8.

Aryldiazonium chlorides. A solution of 9.3 g. (0.1 mole) of the corresponding aminobenzene in 50 ml. of chloroform was added with stirring to a solution of 9.8 g. (0.15 mole) of nitrosyl chloride in 100 ml. of chloroform and 100 ml. of petroleum ether at −15 to −18° over a period of 30 min. The resulting suspension was filtered, the solid diazonium salt washed successively with cold chloroform (−15 to −18°) and petroleum ether, yielding a white amorphous material. Aryldiazonium chloride dissolved in the filtrate was precipitated by the evaporation of excess nitrosyl chloride, in vacuum, below 0° and was added to the previously obtained material after filtering and washing. The salts could be handled and stored safely in an inert organic solvent such as petroleum ether below 0°. Yields, calculated on the amounts of amino benzene used, were 72–89%.

Aryldiazonium tetrachloroborates from aryldiazonium chlorides and boron trichloride. Boron trichloride (25.3 g., 0.22 mole) was introduced over a period of 30 min. into a stirred suspension of 0.1 mole of the corresponding aryldiazonium chloride, 100 ml. of chloroform and 100 ml. of petroleum ether maintained at −10 to −18°. Stirring was continued for 1 hr. while the temperature of the mixture was allowed to rise to 20°. The off-white product was filtered, washed with petroleum ether, and dried in vacuum. Data on the aryldiazonium tetrachloroborates obtained are given in Table I.

Nitrosyl bromide. A rapid stream of nitric oxide was introduced into 40 g. (0.25 mole) bromine at −7 to −18° for a period of 1 hr., resulting in a weight increase of 6.8 g. (0.23 mole). A fraction of the product boiling between −5 and + 10° was removed by distillation and refractionated giving a product b.p. −4–2°, which was found by infrared spectroscopy to be pure nitrosyl bromide. Yield, calculated on the amount of bromine used, was 14.3%.

Aryldiazonium bromides. A solution of 9.3 g. (0.1 mole) of the corresponding aniline in 50 ml. of chloroform was added to a solution of 16.5 g. of nitrosyl bromide in the mixture of 100 ml. chloroform and 100 ml. of petroleum ether at −15 to −18° during a period of 30 min. Excess nitrosyl bromide was evaporated from the solution in vacuum at −5° to 0° and the precipitate was removed by filtration and washed with cold (−18°) petroleum ether. Yields of the obtained diazonium bromides were 72–86%.

Aryldiazonium tetrabromoborates. A 30-g. (0.12 mole) sample of boron tribromide was added over a period of 30 min. to a stirred suspension of 0.1 mole aryldiazonium bromide, 100 ml. of chloroform and 100 ml. of petroleum ether at −18° to −10°. Stirring was continued for 1 hr. while the temperature was allowed to rise to 20°. The pale pink product was filtered, washed with petroleum ether and dried in vacuum. Data on the obtained aryldiazonium tetrabromoborates are given in Table II.

The infrared spectra were obtained on a Perkin-Elmer Model 221 Spectrometer, using sodium chloride optics, as Nujol Fuorolube mulls.

Acknowledgment. The authors are indebted to Dr. Denys Cook for obtaining and interpreting the infrared spectrum.

SARNIA, ONT., CANADA