[CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT, AMERICAN CYANAMID COMPANY, CALCO CHEMICAL DIVISION]

Benzotriazole Analogs of Certain Naphthalene Dye Intermediates[1]

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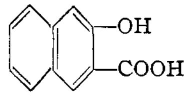
The 5-hydroxybenzotriazole-4- and 6-carboxylic acids have been prepared and their properties compared with those of the analogous 2-hydroxynaphthalene-1- and 3-carboxylic acids. Various arylides of these acids have been prepared for a study of their coupling reactions.

The close analogy between the chemical properties of naphthalene derivatives and the N-phenyl derivatives of benzotriazole has been extensively studied by Fries and co-workers.[2]

More recently, the analogy has been extended to benzotriazole derivatives unsubstituted in the triazole ring. For example, Fries and co-workers[3] have shown that 4-aminobenzotriazole and the isomeric 5-amino compound couple directly with diazo compounds to form azo dyes like the analogous α- and β-naphthylamines. They have also shown that 5-hydroxybenzotriazole on chlorination behaves much like β-naphthol. Fieser and Martin[4] have prepared 5-hydroxybenzotriazole by a different method and have coupled it with diazotized aniline, *p*- and *o*-toluidine to form azo dyes, which, unlike the analogous dyes from β-naphthol, were found to be alkali soluble.

No work has been done, however, on the hydroxybenzotriazolecarboxylic acids. In view of the fact that 3-hydroxy-2-naphthoic acid (I) and its anilide, Naphthol AS (II), are important coupling components for the production of azo dyes and pigments, it was considered desirable to prepare the analogous 5-hydroxybenzotriazole-6-carboxylic acid (III) and its anilide (IV) and to investigate their properties.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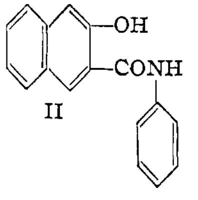
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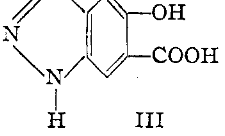
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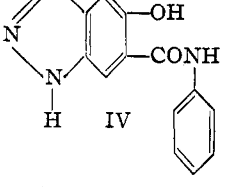
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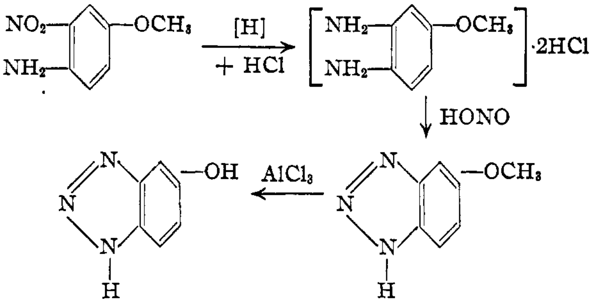
The first approach to the synthesis of the desired analog of Naphthol AS, namely, 5-hydroxybenzotriazole-6-carboxyanilide (IV), used as a starting material the commercially available 4-amino-3-nitroanisole. This was reduced catalytically to 3,4-diaminoanisole, isolated as the dihydrochloride in nearly quantitative yields.[5] This, on treatment with nitrous acid in aqueous solution, formed readily 5-methoxybenzotriazole, m.p. 126.8–127.2°,[6]



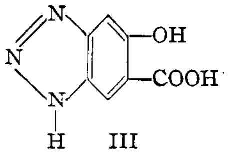
which was demethylated in chlorobenzene solution by the aid of aluminum chloride, in 69% yield. The product, 5-hydroxybenzotriazole, checked closely in melting point and other properties with the material reported by Fieser and Martin.[4]

A comparison of the colors obtained with three different diazo compounds and the two coupling compounds, 5-hydroxybenzotriazole and β-naphthol, is given in Table I.

TABLE I

Coupling component	Amine diazotized: 2,5-Dichloroaniline	*p*-Nitraniline	Dianisidine
β-Naphthol	Scarlet	Red	Blue
5-Hydroxybenzotriazole	Orange	Orange	Purple

The 5-hydroxybenzotriazole was then subjected to the Kolbe reaction in order to introduce a carboxyl group. The method given by Schmelzer, *et al.*,[7] for the production of 2-hydroxycarbazole-3-carboxylic acid was followed. Theoretically this reaction could give rise to two acids: 5-hydroxybenzotriazole-6-carboxylic acid (III) or 5-hydroxybenzotriazole-4-carboxylic acid (V). By analogy with β-naphthol,[8] V should form at lower temperatures (below 130°), and III at higher temperatures (above 250°).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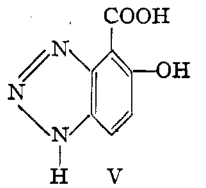
V

That the acid formed by the Kolbe reaction is actually 5-hydroxybenzotriazole-4-carboxylic acid (V) and not the isomeric 6-carboxylic acid (III)

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(1) Presented before the Organic Chemistry Section, XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September, 1951.

(2) K. Fries and E. Roth, *Ann.*, **389**, 318 (1912); K. Fries, *et al.*, *ibid.*, **454**, 121 (1927).

(3) K. Fries, *et al.*, *ibid.*, **511**, 213 (1934).

(4) L. F. Fieser and E. L. Martin, THIS JOURNAL, **57**, 1835 (1935).

(5) R. W. Bost and E. E. Towell, *ibid.*, **70**, 903 (1948).

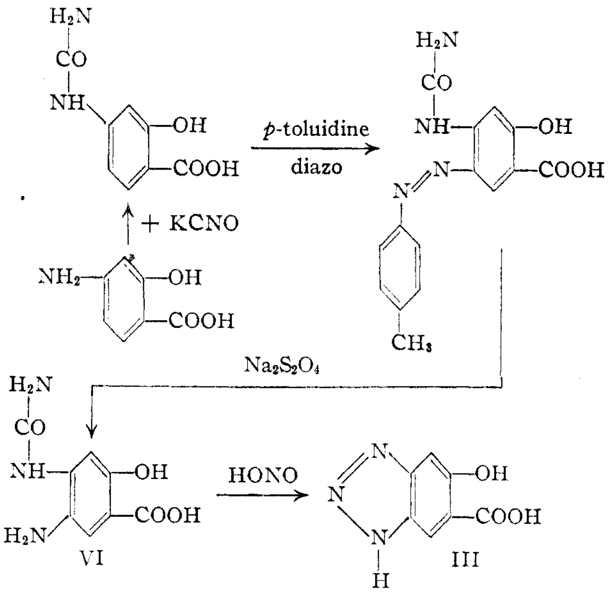
(6) Feldman and Usovskaya, *J. Gen. Chem.*, **18**, 1699 (1948); *C. A.*, **43**, 2618^f (1949).

(7) U. S. Patent 1,819,127, General Aniline, 1931.

(8) R. Schmitt and E. Burkard, *Ber.*, **20**, 2701 (1887); German Patent 50,341, *Friedländer*, **2**, 133 (1889).

was proved by an unambiguous synthesis of the latter, starting from 4-aminosalicylic acid. The compound thus obtained differed from the Kolbe product in melting point and chemical behavior

The first step in the synthesis of III was the reaction of 4-aminosalicylic acid with aqueous potassium cyanate to give 4-ureidosalicylic acid.[9] *p*-Toluidine was then diazotized and the diazo compound coupled in alkaline medium with 4-ureidosalicylic acid to form an azo dye. Reduction of this dye by alkaline sodium hydrosulfite solution gave 5-amino-4-ureidosalicylic acid (VI) which on treatment with nitrous acid was cyclized to form the desired 5-hydroxybenzotriazole-6-carboxylic acid (III). The fact that the free amino group in VI is in the 5-position and not in the 3-position was easily proved by a simple reaction, *viz.*, the formation of an indophenol by the oxidation of a *p*-aminophenol in the presence of dilute acid and an equivalent amount of *o*-toluidine by the oxidizing action of sodium dichromate.[10] 5-Amino-4-ureidosalicylic acid showed the typical blue indophenol reaction under these conditions.



A comparison of some of the properties of the 5-hydroxybenzotriazole-4-carboxylic acid (V) obtained from the Kolbe reaction, and the isomeric 6-carboxylic acid (III) obtained from 4-aminosalicylic acid, is given in Table II.

TABLE II

Test	5,4-Acid (V)	5,6-Acid (III)
Melting p., °C.	208.5–209	272–280 dec.
Ferric chloride	Deep red-violet	Deep red-violet
Dye with diazotized *p*-nitraniline in acid solution	Bright reddish-orange	Yellowish-orange
Same dye in alkaline solution	Reddish-violet	Deep bluish-violet

An interesting analogy to the naphthalene series is found in the fact that 5-hydroxybenzotriazole-4-carboxylic acid is decarboxylated on boiling in water, a behavior parallel to that of 2-hydroxy-1-naphthoic acid.[11] The decarboxylation product was found to be identical in melting point and chemical reaction to the 5-hydroxybenzotriazole previously obtained by demethylation of 5-methoxybenzotriazole. The 5-hydroxybenzotriazole-6-carboxylic acid, on the other hand, like the analogous 3-hydroxy-2-naphthoic acid, does not decarboxylate under the same conditions. An attempt to prepare III by the Kolbe reaction from 5-hydroxybenzotriazole at higher temperature was not successful.

The arylides of 5-hydroxybenzotriazole-4- and 6-carboxylic acids were prepared by the reaction of the acid, phosphorus trichloride and the desired aromatic amine in dry chlorobenzene solution, according to the general method for preparation of arylides of 3-hydroxy-2-naphthoic acid.[12]

The close analogy between 5-hydroxybenzotriazole-4-carboxylic acid (V) and the corresponding naphthalene compound 2-hydroxy-1-naphthoic acid is also clearly demonstrated in the coupling reaction of these compounds with diazotized aromatic amines. In each case the formation of dye is accompanied by the evolution of carbon dioxide, the coupling occurring in the position previously occupied by the carboxyl group. This coupling reaction, as well as those of the isomeric acid and of the corresponding arylides, are still under investigation and they will be reported at a later date.

Experimental

3,4-Diaminoanisole Dihydrochloride.—This compound was prepared by a modification of the procedure of Bost and Towell.[5]

5-Methoxybenzotriazole.—Eighteen and six-tenths grams of 3,4-diaminoanisole dihydrochloride (0.088 mole), dissolved in 200 ml. of water, and 50 ml. of 5 *N* hydrochloric acid, was iced internally to -2° and treated at -2 to 0°, with 90 ml. of *N* sodium nitrite solution during about 20 minutes. The mixture was stirred for half an hour, clarified and neutralized to a negative test on congo red paper with 5 *N* sodium hydroxide; yield 6.3 g., or 48%, m.p. 124.1–124.8°.

An additional 2.1 g. (16%) of product was obtained from the filtrate by extracting with butanol and evaporating the extract; m.p. 122–122.5°, total yield 8.4 g., 64%.

Recrystallized from water, pale tan crystals, m.p. 126.8–127.2°. Feldman and Usovskaya[6] report m.p. 124–126°.

5-Hydroxybenzotriazole.—To a mixture of 50 ml. of chlorobenzene and 5 g. (0.0335 mole) of 5-methoxybenzotriazole was added with stirring at room temperature 7.5 g. of anhydrous aluminum chloride (0.056 mole), and the mixture was refluxed with stirring for 1.5 hours. The crude hydroxy compound was isolated by dilution with 100 ml. of water and filtration; yield 3.6 g. or 79.4%, m.p. 223–227.3°.

This was purified by recrystallization from 14 parts of boiling water, with Nuchar; recovered 2.2 g. of colorless crystals, m.p. 235.5–236.5°.

Further recrystallization from water did not change the m.p. Fries, *et al.*,[3] obtained a yellowish product m.p. 228°; Fieser and Martin,[4] report m.p. 234–235° for colorless micro-needles.

5-Hydroxybenzotriazole-4-carboxylic Acid.—A one-liter nickel-lined steel autoclave was charged with an intimate mixture of 20 g. of 5-hydroxybenzotriazole (0.148 mole), 95.5 g. of anhydrous potassium carbonate (0.955 mole) and 115 g. of solid glass beads. The mixture was heated in the autoclave with open vent for 6 hours at 160–165° and then under 600 lb. of carbon dioxide pressure for 16 hours at 180–190°. The contents of the autoclave were dissolved in 600 ml. of water, decanted from the glass beads, heated at 50°

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[9] R. Harrt and A. Hurn, *Helv. Chim. Acta*, **32**, 384 (1949).

[10] German Patent 139,204, *Friedländer*, **7**, 73 (1903).

[11] Kauffmann, *Ber.*, **15**, 807 (1882).

[12] U. S. Patent 1,101,111, Griesheim Elektron, 1914.

with 5 g. of Nuchar and 5 g. of Filter-Cel and filtered. The filtrate was acidified. The impure product was purified by solution in sodium hydroxide and fractional acidification. After acidification to *p*H 6, a brown impurity was filtered off and the filtrate again decolorized with Nuchar at room temperature. Acidification of the orange solution to *p*H 3 and filtration at 2° yielded 12.9 g. (48.7%) of a white product, m.p. 203–203.5°. By recrystallization from water, colorless, hair-like needles were obtained, m.p. 209–209.5°.

Anal. Calcd. for $C_7H_5N_3O_3$: C, 46.9; H, 2.80; N, 23.5. Found: C, 46.6; H, 2.85; N, 23.8.

Attempted Preparation of 5-Hydroxybenzotriazole-6-carboxylic Acid by the Kolbe Reaction at High Temperature.—The reaction was carried out as above, using 40.5 g. of 5-hydroxy-1,2,3-benzotriazole (0.30 mole), 194 g. of potassium carbonate and 230 g. of glass beads. This mixture was heated with open vent at 160° for 4 hours and then at 250° for 16 hours under 600 lb. carbon dioxide pressure. A black, alkali-insoluble product, 43.4 g., was isolated. The filtrate on acidification yielded 3.8 g. of a product which did not melt or decompose up to 300°.

Anilide of 5-Hydroxybenzotriazole-4-carboxylic Acid.—A solution of 100 ml. of chlorobenzene and 2.55 g. (0.0142 mole) of 5-hydroxybenzotriazole-4-carboxylic acid was dried by distilling out 5 ml. of the solvent, 1.89 g. of aniline (0.0203 mole) was added, and the mixture was cooled to 70°. There was then added dropwise, with stirring at 68 to 70°, during one hour, a solution of 0.85 g. of phosphorus trichloride (0.0062 mole) in 45 ml. of dry chlorobenzene. The mixture was then heated up to 134° in one hour, and refluxed for two hours and 40 minutes. At the end of this time the evolution of hydrogen chloride gas had ceased. The reaction mixture was allowed to cool to room temperature, the small residue was removed by filtration, and the filtrate was extracted with aqueous sodium hydroxide. Acidification of the aqueous extract gave a cream-colored, sticky precipitate, which became hard on standing; yield 1.9 g., or 52.5%, m.p. 184–185.5°.

Crystallization from alcohol gave colorless crystals, very sparingly soluble in water and giving no color with ferric chloride, m.p. 187–187.5°.

Anal. Calcd. for $C_{13}H_{10}N_4O_2$: C, 61.4; H, 3.94; N, 22.05. Found: C, 61.6; H, 3.96; N, 21.9.

***o*-Anisidide of 5-Hydroxybenzotriazole-4-carboxylic Acid.**—This compound was prepared from 3.0 g. of 5-hydroxybenzotriazole-4-carboxylic acid (0.01675 mole) and 3.0 g. of *o*-anisidine in the same manner as the anilide; yield of crude product 3.8 g., 80.0%, m.p. 198–199°.

Purified by repeated crystallization from alcohol until a constant m.p. of 212° was obtained.

Anal. Calcd. for $C_{14}H_{12}N_4O_3$: C, 59.1; H, 4.22; N, 19.7. Found: C, 58.5; H, 4.2; N, 19.0.

α-Naphthylamide of 5-Hydroxybenzotriazole-4-carboxylic Acid.—This compound was prepared from 4.48 g. of 5-hydroxybenzotriazole-4-carboxylic acid (0.025 mole) and 5.2 g. of α-naphthylamine (0.0364 mole) by the method used for the anilide. Refluxing for 6.5 hours was necessary, and the crude product had to be washed with dilute hydrochloric acid to rid it of traces of α-naphthylamine; crude yield 4.4 g., or 57.8%, m.p. 192–193°.

This was recrystallized twice from alcohol, m.p. 213–214°.

Anal. Calcd. for $C_{17}H_{12}N_4O_2$: C, 67.1; H, 3.95; N, 18.45. Found: C, 67.2; H, 3.90; N, 18.4.

4-Ureidosalicylic Acid.—Thirty-two grams of pure pharmaceutical grade 4-aminosalicylic acid (0.209 mole) was dissolved in a mixture of 100 ml. of water and 40 ml. of 5 *N* sodium hydroxide. To this solution (alkaline to phenolphthalein) was added 16.2 g. of potassium cyanate (0.2 mole) and the mixture was stirred until solution was complete. The solution was cooled to 8° and carefully acidified at 8–15° with 50 ml. of 5 *N* hydrochloric acid. A thick white precipitate was formed. The mixture was heated to boiling to redissolve the precipitate, treated with charcoal and filtered. The filtrate was cooled to room temperature and treated with 35 ml. more 5 *N* hydrochloric acid to make strongly acid to congo red paper. The thick white precipitate which was formed was cooled and then filtered with suction, washed thoroughly with water and dried at 50°; yield 29.4 g., or 75.1%, m.p. 213°.

This was purified by recrystallization from 100 parts of water; m.p. 214.5°. Harrt and Hurn[9] give no melting point or method of preparation.

Anal. Calcd. for $C_8H_8N_2O_4$: C, 49.0; H, 4.08; N, 14.3. Found: C, 48.8; H, 4.03; N, 13.9.

5-(*p*-Tolylazo)-4-ureidosalicylic Acid.—A solution of 5.3 g. of *p*-toluidine (0.05 mole), 30 ml. of 5 *N* hydrochloric acid and 100 ml. of water was diazotized at 2–5° by the addition of 10 ml. of 5 *N* sodium nitrite solution. This diazo solution was added with stirring to a solution of 9.8 g. of 4-ureidosalicylic acid (0.05 mole) in 200 ml. of water and 40 ml. of 5 *N* sodium hydroxide. Coupling was rapid with the formation of a dark brownish-red solution of dye. The mixture was alkaline to phenolphthalein throughout, and at no time was there a positive test for free diazo. The dyestuff was precipitated by acidification with 30 ml. of 5 *N* hydrochloric acid, heated to 95° and filtered with suction, but not dried.

5-Amino-4-ureidosalicylic Acid.—The damp paste of 5-(*p*-tolylazo)-4-ureidosalicylic acid from the preceding preparation (equivalent to 0.05 mole) was dissolved in 500 ml. of water and 50 ml. of 5 *N* sodium hydroxide. The mixture was heated with stirring to 80° and to it was added with stirring at 78–88° during eight minutes, 25 g. of sodium hydrosulfite (0.119 mole). The decolorized solution was filtered hot to remove a small amount of black insoluble impurity, cooled externally to room temperature and made strongly alkaline to phenolphthalein by the addition of 10 ml. of 5 *N* sodium hydroxide. This solution was then extracted with seven 50-ml. portions of toluene to remove all of the *p*-toluidine. The solution was then cooled externally to 14° and acidified to approximately *p*H 5 by the gradual addition of 53 ml. of 5 *N* hydrochloric acid. The very light tan microcrystalline precipitate which was formed was filtered with suction, and dried at 50°; yield 7.6 g. or 72%, m.p. 244–247° with decomposition after gradual darkening.

The product is slightly soluble in water but readily soluble in either dilute acid or dilute alkali. A drop of ferric chloride added to its aqueous solution gives a dirty brown color followed by a brown precipitate. *p*-Nitraniline diazo added to its alkaline solution gives a deep brown solution, which on acidification gives a dull reddish-brown flocculent precipitate. The presence of the amino group in the 5-position, para to the hydroxyl group, was demonstrated by the following test: One-tenth of a gram of 5-amino-4-ureidosalicylic acid, two drops of *o*-toluidine and five drops of 5 *N* sulfuric acid were dissolved in 25 ml. of water in a test-tube. To this was added 1 ml. of saturated aqueous sodium dichromate solution. An immediate deep blue color developed. The same test was repeated with *p*-aminophenol and with 5-amino-2-hydroxybenzoic acid; in each case a deep blue color developed immediately. When the test was applied to *o*-aminophenol and its derivative 3-amino-4-hydroxybenzene sulfonamide a deep chocolate-brown color was obtained in each case.

5-Hydroxybenzotriazole-6-carboxylic Acid.—Four and two-tenths grams of crude dry 5-amino-4-ureidosalicylic acid (equivalent to 0.02 mole if pure) was dissolved in 100 ml. of water and 25 ml. of 5 *N* sodium hydroxide. The acid was then reprecipitated in finely divided form by the addition of 15 ml. of 5 *N* hydrochloric acid. The resulting slurry was cooled to 10° and to it was added, as fast as the nitrous acid was used up, 134 ml.of 0.1 *N* sodium nitrite solution. The nitrous acid was taken up rapidly at first, but very slowly toward the end. The mixture was stirred overnight at room temperature and the next day treated with 16 ml. additional of 0.1 *N* sodium nitrite to give a positive test on starch–iodide paper that lasted half an hour. The pale pink precipitate was filtered off and dried; yield 3.9 g.

The product was purified by boiling in 100 times its weight of water with an equal weight of Nuchar, filtering and adding sufficient dilute hydrochloric acid to the cooled filtrate to make acid to congo red paper. The precipitate, white needles, was dried at 50°. The product did not melt, but gradually turned black and decomposed between 272 and 280°.

Anal. Calcd. for $C_7H_5N_3O_3\cdot{}^1/_2H_2O$: C, 44.6; H, 3.19; N, 22.3. Found: C, 44.0; H, 3.36; N, 21.7.

Anilide of 5-Hydroxybenzotriazole-6-carboxylic Acid.—The procedure described above for the anilide of the isomeric 4-carboxylic acid was followed, using 440 ml. of dry chlorobenzene, 17.9 g. of 5-hydroxybenzotriazole-6-carboxylic acid and 13.5 g. of aniline. The refluxing period required was 11 hours. The yield of crude product, light chocolate brown, was 32.7 g., or 89.5%.

Attempts to recrystallize this product from water or alcohol were not successful. It was purified, to some extent, by dissolving in very dilute hot sodium hydroxide solution, stirring with Nuchar, filtering and acidifying the filtrate. The material thus purified was lighter brown in color, m.p. 250–253° with decomposition. Its aqueous solution gave a faint reddish-brown color with ferric chloride solution.

Anal. Calcd. for $C_{13}H_{10}N_4O_2$: C, 61.4; H, 3.94; N, 22.05; atomic ratio C/N, 3.250:1. Found: C, 56.35; H, 3.99; N, 18.8; C/N, 3.40:1.

Decarboxylation of 5-Hydroxybenzotriazole-4-carboxylic Acid.—One gram of 5-hydroxybenzotriazole-4-carboxylic acid (melting at 200–202°) was dissolved in 140 ml. of water and refluxed for 20 hours. The solution was then evaporated to 8 ml., cooled to room temperature and filtered. The grayish-white crystalline precipitate was filtered, washed, and dried at 100°; yield 0.57 g., m.p. 234–234.5°; it did not depress the m.p. of pure 5-hydroxybenzotriazole (235–235.5°). A 0.1% aqueous solution of the product gave a very pale ferric chloride test, characteristic of 5-hydroxybenzotriazole and sharply distinguishable from the intense coloration given by a 0.1% solution of the 4-carboxylic acid.

Attempted Decarboxylation of 5-Hydroxybenzotriazole-6-carboxylic Acid.—One gram of 5-hydroxybenzotriazole-6-carboxylic acid was boiled in 140 ml. of water and filtered to remove a trace of insoluble residue. The filtrate was refluxed overnight, and then evaporated to about 6.5 ml., and cooled to about 5°. There was obtained 0.18 g. of light brown precipitate, consisting of minute short needles.

A few mg. of this material dissolved in 10 ml. of water gave a deep violet color with ferric chloride, showing that it was still the carboxylic acid. The m.p. was also unchanged.

Coupling Reactions. (1). **Preparation of 4-(*p*-Chlorophenylazo)-5-hydroxybenzotriazole.**—*p*-Chloroaniline (6.38 g., 0.05 mole) was dissolved in 100 ml. of 2.5 *N* hydrochloric acid and diazotized by the addition of 10 ml. of 5 *N* sodium nitrite solution at 10°. This solution was filtered and diluted to 200 ml. to make a 0.25 *M* solution. Eight ml. of this diazo solution (0.002 mole) was added with stirring to a solution of 0.286 g. of 5-hydroxybenzotriazole (0.00212 mole) dissolved in a mixture of 40 ml. of water, 4 ml. of *N* sodium hydroxide and 2 ml. of *M* sodium carbonate solution. A deep orange solution was formed immediately. After 15 minutes stirring, the solution was acidified to congo red paper by the addition of 1 ml. of 5 *N* hydrochloric acid. The reddish-orange precipitate formed was filtered, washed and dried at 100°; yield 0.47 g., m.p. 247–248.5° (decomposes slightly above m.p.). This was recrystallized from chlorobenzene without raising the m.p.

Anal. Calcd. for $C_{12}H_8ClN_5O$: C, 52.6; H, 2.92; Cl, 13.0; N, 25.6. Found: C, 52.8; H, 3.00; Cl, 13.2; N, 25.7.

(2). **Coupling of Diazotized *p*-Chloroaniline with 5-Hydroxybenzotriazole-4-carboxylic Acid.**—A 500-ml., three-necked flask was equipped with mercury seal, stirrer, dropping funnel, air inlet tube extending to a point near the bottom of the flask and an upper air exit tube leading to a bubbling tube containing barium hydroxide solution. A solution of 1.88 g. of 5-hydroxybenzotriazole-4-carboxylic acid (0.0105 mole) in 55 ml. of *N* sodium hydroxide and 100 ml. of water was poured into the flask, and a stream of carbon dioxide-free air was bubbled through the flask and thence through the barium hydroxide solution in a test-tube. There was then added with stirring through the dropping funnel 50 ml. of 0.20 *M* *p*-chloroaniline diazo solution (0.01 mole). An orange-brown precipitate of dye was formed together with considerable foam. After a few minutes stirring, the mixture was acidified strongly to congo red paper by the addition, through the dropping funnel, of 20 ml. of 5 *N* hydrochloric acid (a few drops of octyl alcohol was used to abate the foam). A copious white precipitate of barium carbonate was immediately formed in the bubbling tube.

The dye was filtered, washed and dried; yield 2.55 g. Repeated recrystallization from chlorobenzene gave an orange microcrystalline dye, m.p. 235–245° (dec.), mixed m.p. with 4-(*p*-chlorophenylazo)-5-hydroxybenzotriazole, 235–245° (dec.).

BOUND BROOK, NEW JERSEY

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Tetraalkoxygermanes[1]

BY OTTO H. JOHNSON AND H. E. FRITZ

RECEIVED JULY 25, 1952

The method of preparation, the yields and some of the common physical properties of six members of this series from tetramethoxygermane through tetrahexoxygermane and for tetracyclohexoxygermane are reported. Only one tetraalkoxygermane has been described previously.

Tetraethoxygermane was prepared by Tabern, Orndorff and Dennis[2] by the reaction between absolute ethanol and germanium tetrachloride in the presence of sodium metal. The melting point was reported as −81° and the boiling point as 185–187° at atmospheric pressure. Later Laubengayer and Brandt[3] also prepared tetraethoxygermane and reported a boiling point of 187°. The same year Sidgwick and Laubengayer[4] reported a density of 1.1278 at 30° for this compound.

The only other compound of this type reported in the literature is tetraphenoxygermane. This compound was prepared by Schwarz and Reinhardt[5] by the reaction between germanium tetrachloride and sodium phenolate. It is described as distilling at 210–220° (0.3 mm.) as a colorless, viscous oil.

This paper is a recapitulation of the values of a number of physical constants of the the first seven tetraalkoxygermanes as determined in this Laboratory.

Experimental

A two-necked 500-ml. flask was fitted with a reflux condenser and a dropping funnel both equipped with drying tubes. In the flask was placed 200 ml. of the appropriate anhydrous alcohol to which 8.8 g. (0.38 mole) of metallic sodium was added. In the case of methanol and ethanol the sodium was added in one-half gram portions while with the higher alcohols it was added in one portion followed by heating. The time required for the formation of the sodium alkoxide varied from 15 minutes for methanol to three hours for *n*-pentanol.

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(2) D. L. Tabern, W. R. Orndorff and L. M. Dennis, THIS JOURNAL, **47**, 2043 (1925).

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