

taric acid. After five crystallizations from acetone the product melted at 116–117°;  $[\alpha]^{25}_D - 57.3^\circ$  (*c* 1.5, methanol).<sup>5</sup>

Anal. Calcd. for  $C_{12}H_{17}NO \cdot C_{18}H_{14}O_8$ : C, 65.56; H, 5.69; N, 2.55. Found: C, 65.48; H, 5.73; N, 2.41.

(-)- $\beta$ -Dimethylamino- $\alpha$ -methylpropioiphenone Hydrochloride. —(-)- $\beta$ -Dimethylamino- $\alpha$ -methylpropioiphenone acid dibenzoyl(-)-tartrate (156.5 g., 0.285 mole) was treated with 56 ml. of 28% ammonia in 340 ml. of water. The liberated (-)- $\beta$ -dimethylamino- $\alpha$ -methylpropioiphenone was extracted with 1400 ml. of ether, washed with water (85 ml.), and dried with anhydrous magnesium sulfate. The dry ether solution was just acidified with anhydrous hydrogen chloride. The precipitated hydrochloride was filtered, washed with ether, and dried to yield 61.2 g. (94%) of product;  $[\alpha]^{25}_D - 42^\circ$  (*c* 1, water). The crude (-)- $\beta$ -dimethylamino- $\alpha$ -methylpropioiphenone hydrochloride was recrystallized from ethyl acetate-methanol solution to yield 52.9 g of purified hydrochloride which melted at 157–159°;  $[\alpha]^{25}_D - 49^\circ$  (*c* 1, water).<sup>6</sup>

(+)- $\alpha$ -Methyl- $\beta$ -dimethylaminopropioiphenone Hydrochloride. —This hydrochloride, prepared from (+)- $\beta$ -dimethylamino- $\alpha$ -methylpropioiphenone acid dibenzoyl(+)-tartrate using the same procedure described for the (-)-isomer, melted at 153–155°;  $[\alpha]^{25}_D + 47^\circ$  (*c* 1, water).<sup>7</sup>

$\alpha$ -(+)-4-Dimethylamino-1,2-diphenyl-3-methyl-2-butanol Hydrochloride. —A solution containing 5.93 kg. (31 moles) of (-)- $\beta$ -dimethylamino- $\alpha$ -methylpropioiphenone in 50 l. of ether was added to a stirred solution of benzylmagnesium chloride prepared from 7.9 kg. (62 moles) of benzyl chloride, 1.9 kg. (78 g.-atoms) of magnesium, and 100 l. of ether. After complete addition the reaction mixture was stirred for 3 hr. and then decomposed by addition of 20 l. of saturated aqueous ammonium chloride solution. The ether solution was decanted from the inorganic material and dried over anhydrous sodium sulfate. The hydrochloride salt was prepared in the usual manner; and after two recrystallizations from methanol-ethyl acetate solution, the product melted at 231–233°; 6.05 kg. (61%). An authentic sample of the product melted at 234–235°;  $[\alpha]^{25}_D + 52^\circ$  (*c* 1, water). The mixture melting point with an authentic sample<sup>1</sup> was not depressed.

$\alpha$ -(-)-4-Dimethylamino-1,2-diphenyl-3-methyl-2-butanol Hydrochloride. —This compound was prepared from 5.8 g. (0.03 mole) of (+)- $\beta$ -dimethylamino- $\alpha$ -methylpropioiphenone, 7.9 g. (0.062 mole) of benzyl chloride, 1.9 g. (0.078 g.-atom) of magnesium, and 150 ml. of ether following the procedure for the  $\alpha$ -(+)-isomer. The product was recrystallized twice from methanol-ethyl acetate solution and melted at 234–235°;  $[\alpha]^{25}_D - 53.4^\circ$  (*c* 1, water); 8.0 g. (69%). The mixture melting point with an authentic sample<sup>1</sup> was not depressed.

(5) S. Ose, Hakamatsu, and Y. Minaki, Japan Patent 4417 (1958) [*Chem. Abstr.*, **53**, 12310<sup>b</sup> (1958)], report this compound to melt at 122–125°.

(6) Ref. 2 reports the ketone from degradation studies to melt at 153–154°;  $[\alpha]^{25}_D - 47^\circ$  (*c* 1, water).

(7) This compound is not isolated in ref 5. Instead a dilute hydrochloric acid solution of the ketone is reduced to the (-)-aminocarbinal.

## The Diphenylhydroxyborane Ester of *o*-Aminophenol<sup>1</sup>

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The synthesis of borimidazolines and related substances from aryl dihydroxyboranes and various *o*-arylene diamines is now well known,<sup>2–5</sup> and a new

(1) The support of this work by the U. S. Army Research Office (Durham) is gratefully acknowledged.

(2) M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3076 (1958).

(3) R. L. Letsinger and S. B. Hamilton, *J. Am. Chem. Soc.*, **80**, 5411 (1958).

synthesis for some of them, which is useful for certain characterizations and analytical applications, has been pointed out recently.<sup>6</sup> At about the time this class of substances was discovered, it was reported that the corresponding ester amide of *o*-aminophenol, although melting at 99–101° and boiling at 140–145° (2 mm.), was unstable.<sup>7</sup> Thus, the borimidazolines have remained a relatively unknown class of compounds, and their potential utility has not been realized. The present note reports the preparation of a closely related material which appears to be moderately stable.

Because of extensive experience of the stabilizing effect produced by N–B coordination in the boroxazolines,<sup>8</sup> it seemed likely that the same principle might be found to operate to permit the preparation of a stable borinic ester of *o*-aminophenol.

The compound obtained did, in fact, appear to be stable over a period of five to ten weeks. However, after several months on the shelf, it was noted that the material had discolored markedly. Nevertheless, the pure substance could be readily recovered from the discolored material merely by repeating the recrystallization. Thus, although the presumed N–B coordination does have the predicted stabilizing effect, its protective influence is distinctly weaker than that observed in any other boroxazolidine or boroxazolines analog that has yet been studied. This may be a result either of the sharply reduced basicity of the amino group substituent to an aromatic nucleus<sup>9</sup> or of a residual photosensitivity in the aromatic structure.

The question of the strength of the N–B coordination is not yet resolved. Whereas titration of *o*-aminophenol in 9:1 acetone–water gives a very sharp end point, covering eight pH units centering at pH 8.5, the acidic titration of the diphenylhydroxyborane ester in the same solvent gave a flat curve lying at lower pH values than the acidic branch of the curve for *o*-aminophenol itself. This result could be interpreted conveniently to signify an N–B coordination relatively very inert to hydrolysis. However, it might be also a result of extensive buffering action between the basic nitrogen atom and the acidic boron atom subsequent to a facile N–B cleavage, leaving the system to reflect only the acidic property of the phenol function. Available evidence does not now permit a choice between the two alternatives. Our laboratory intends no further work on this problem.

## Experimental

Diphenylhydroxyborane ester of *o*-aminophenol was prepared by placing diphenylhydroxyborane from the hydrolysis<sup>10</sup> of 2.0 g. of B,B-diphenylboroxazolidine in 100 ml. of toluene together with 1.2 g. of *o*-aminophenol (Eastman, freshly recrystallized from benzene). The mixture was refluxed through a Dean–Stark trap until no further water could be removed. After distillation

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(5) R. J. Brotherton and H. Steinberg, *J. Org. Chem.*, **26**, 4632 (1961).

(6) R. Neu, *Tetrahedron Letters*, No. **20**, 917 (1962).

(7) J. M. Sugihara and C. M. Bowman, *J. Am. Chem. Soc.*, **80**, 2443 (1958).

(8) (a) H. K. Zimmerman and H. Weidmann, *Ann.*, **628**, 37 (1959);

(b) T. G. Psarras, H. K. Zimmerman, Y. Rasiel, and H. Weidmann, *ibid.*, **655**, 48 (1962); (c) H. K. Zimmerman, D. W. Mueller, and W. F. Semmelrogge, *ibid.*, **655**, 54 (1962); (d) R. K. Stump, H. K. Zimmerman, A. A. Schlepfnik, and C. D. Gutsche, *ibid.*, in press.

(9) G. N. Chremos, H. K. Zimmerman, W. Cantrell, R. B. Meyer, and E. H. Zaetsch, *Z. Physik. Chem. (Frankfurt)*, **35**, 129 (1962).

(10) G. N. Chremos, H. Weidmann, and H. K. Zimmerman, *J. Org. Chem.*, **26**, 1683 (1961).

to about 20 ml., cooling gave a solid product which, after washing with petroleum ether (30–60°), gave 2.0 g., m.p. 161–162° dec. (after two recrystallizations from benzene, 174–174.5° dec.), of light cream colored crystals which were soluble in diethyl ether and chloroform and insoluble in petroleum ether and carbon tetrachloride.

Anal. Calcd. for C<sub>18</sub>H<sub>16</sub>NBO (273.1): C, 79.14; H, 5.90; N, 5.53. Found: C, 78.50; H, 5.64; N, 5.50.

### Aqueous Chlorination of Dimethyl Sulfide

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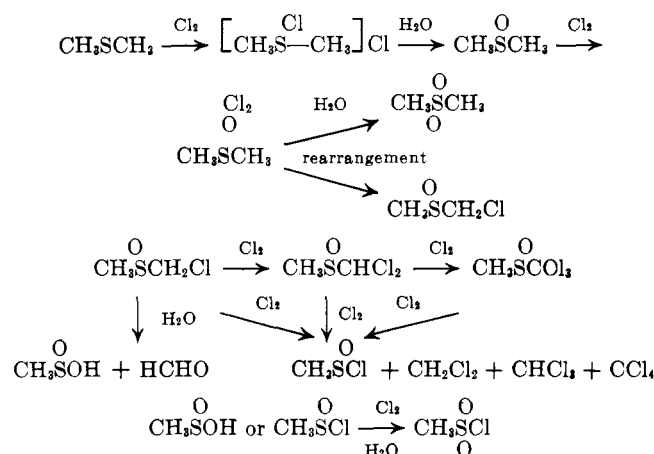
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The products resulting from the reaction of chlorine with dimethyl sulfide are determined by the choice of reaction conditions, particularly by the presence or absence of water. The pattern is similar to that observed with other bivalent sulfur compounds.<sup>1</sup>

Under anhydrous conditions chlorination proceeds stepwise with replacement of all the halogens on one carbon atom before any attack at the second one.<sup>2</sup> The chlorination using chlorine proceeds well until four chlorine atoms have been introduced while the main reaction beyond that point is cleavage to carbon tetrachloride and other products. The cleavage pattern here is analogous to that of the triphenylmethyl sulfides.<sup>3</sup>

Chlorinating dimethyl sulfide in the presence of water leads to products that are consistent with the following scheme.



The first reaction step is the very rapid formation of the dimethyl sulfide-chlorine adduct. The adduct, which rapidly rearranges to chloromethyl methyl sulfide in the absence of water,<sup>4</sup> is hydrolyzed by water to give dimethyl sulfoxide in 80% yield.

Introduction of a second chlorine at -10° initially produced an adduct as evidenced by a decreased heat

evolution and by the recovery of a 74% yield of dimethyl sulfide when a freshly prepared adduct solution in concentrated hydrochloric acid was reduced with methyl mercaptan at -10°.

When the dimethyl sulfoxide-chlorine adduct solution was allowed to warm to room temperature, it reacted partly to give dimethyl sulfone and partly by rearrangement and hydrolytic cleavage to give formaldehyde and acids. Although methanesulfinic acid was not positively identified its presence was indicated by the isolation of methyl methanethiosulfonate<sup>5</sup> from an experiment in which the temperature was allowed to rise to 45°. The presence of a large amount of water leads almost exclusively to sulfone formation. In common with dibutyl sulfone<sup>6</sup> and α-chlorobenzyl benzyl sulfone,<sup>1d</sup> dimethyl sulfone is inert to the chlorination conditions.

The cleaved carbon atom was isolated in different forms depending partly upon the extent of chlorination and the amount of water present as shown in Table I.

TABLE I

PRODUCTS FROM DIMETHYL SULFIDE (DMS) CHLORINATION IN HYDROCHLORIC ACID

Mole ratio Cl <sub>2</sub> /DMS	Mole ratio H <sub>2</sub> O/DMS	Mole yield per mole DMS
1	8.3	0.8 DMSO
2	16.7 <sup>a</sup>	0.7 DMSO <sub>2</sub>
2	8.3	0.2 to 0.4 DMSO <sub>2</sub> ; 0.3 HCHO
3	8.3	0.2 DMSO <sub>2</sub> ; 0.1 HCHO; 0.2 mesyl chloride
3	3.0	0.3 DMSO <sub>2</sub> ; 0.2 mesyl chloride; 0.05 CHCl <sub>3</sub>
4	8.3	0.2 DMSO <sub>2</sub> ; 0.14 mesyl chloride
5	2.5	0.1 DMSO <sub>2</sub> ; 0.47 mesyl chloride; 0.02 CH <sub>2</sub> Cl <sub>2</sub> ; 0.13 CHCl <sub>3</sub> ; 0.12 CCl <sub>4</sub>

<sup>a</sup> No hydrochloric acid present at start.

When the cleavage was accomplished by hydrolysis the carbon appeared as formaldehyde. Formic acid was found only in trace amounts. In chlorinations favorable for preparing mesyl chloride the carbon appeared as mixtures of methylene chloride, chloroform, and carbon tetrachloride. Methyl chloride was not found as a reaction product so the cleavage by chlorolysis occurred after the introduction of at least one α chlorine. In this respect the cleavage of the chlorinated sulfoxides is similar to that demonstrated for the benzyl, benzhydryl, and trityl sulfides by Schreiber and Fernandez.<sup>1d</sup>

The yield of mesyl chloride from chlorinating dimethyl sulfide in the presence of water is usually around 50% due largely to the formation of 15 to 30% of dimethyl sulfone. The yield can be increased to above 75% by chlorinating the sulfide to at least the monochloro level before introducing water. Hydrolysis of chloromethyl methyl sulfide to bis(methylthio)methane is not harmful since the latter gave an 83% yield of mesyl chloride under the reaction conditions.

Trichloromethyl chloromethyl sulfide is cleanly cleaved by excess chlorine at 20–30° in the presence of hydrochloric acid to give 83% of carbon tetrachloride and 81% of chloromethanesulfonyl chloride. The

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