

flask and concentrated under diminished pressure at room temperature. The residual oil was dissolved in 30 ml. of 10% sulfuric acid, treated with Darco and added slowly to 100 ml. of 15% aqueous sodium bicarbonate. The pink precipitate was dissolved in 5% aqueous sodium hydroxide and treated with Norite. The solution was acidified with 10% sulfuric acid and added to a bicarbonate solution. The nearly white product, after drying *in vacuo* over phosphorus pentoxide, melted at 142–144°. No satisfactory solvent for recrystallization was found. About 0.5 g. of the solid was treated with ammoniacal silver nitrate,<sup>5</sup> and the diethylaniline formed was recovered by steam distillation and identified as the picrate and the chloroplatinate by melting points and mixed melting points.

(2) **Coupling Reaction.**—The diazonium salt solution prepared from 1.8 g. of *p*-aminobenzoic acid in 20 ml. of 3 *N* hydrochloric acid and 0.9 g. of sodium nitrite in 5 ml. of water was added slowly at 0° to 2.5 g. of the diethylaminobenzeneboronic acid in 10 ml. of 3 *N* hydrochloric acid. The resulting mixture was poured with stirring into 15 ml. of 6 *N* sodium hydroxide solution. The precipitate which formed in the deep violet solution was collected and dissolved in 50 ml. of glacial acetic acid. The filtered solution was diluted with 100 ml. of water and the red-brown solid which precipitated was recrystallized from 50% ethanol, yielding 2.9 g. (65%) of the pure substance, m. p. 248–250°.

*Anal.* Calcd. for  $C_{17}H_{20}BN_3O_4$ : C, 59.8; H, 5.9; B, 3.2. Found: C, 59.7; H, 5.7; B, 3.3.

**C. Conversion of Benzeneboronic Acid to Benzene by the Action of Cuprous Hydroxide.**—The reducing solution prepared from ammoniacal cupric sulfate<sup>7</sup> and hydroxylamine was mixed with benzeneboronic acid under the conditions of the diphenic acid preparation.<sup>7</sup> The odor of benzene was evident immediately. The hydrocarbon produced from 1 g. of the boronic acid was recovered by steam distillation and treated with nitric and sulfuric acids. The *m*-dinitrobenzene so formed, m. p. 87–89°, was identified by melting point and mixed melting point.

**D. Attempts to Use Mercuriphenyl Derivatives in the Boronic Acid Synthesis.**—No evidence of reaction was observed when a mixture of 8.5 g. of acetoxymercuribenzene and 23 g. of *n*-butyl borate was heated on the steam-bath for one hour. The mixture was heated at 140–150° for three hours and poured into excess 3 *N* hydrochloric acid. Evaporation of ether extracts of the aqueous solution yielded no benzeneboronic acid. Similar results were obtained in experiments in which benzene was used as solvent for the reagents.

A mixture of 8.2 g. of *o*-chloromercuriphenol, 16 g. of *n*-butyl borate and 50 ml. of benzene was heated under reflux for fourteen hours and then poured into excess 6 *N* hydrochloric acid. The organic liquid was removed by distillation and the hot aqueous solution was filtered and cooled. The recovery of *o*-chloromercuribenzene, m. p. 150°, was almost quantitative.

### Summary

Several azo dyes containing the boronic acid group have been prepared by the action of diazonium salts on *m*-hydroxybenzeneboronic and *m*-diethylaminobenzeneboronic acids. One such dye has been prepared by coupling diazotized *m*-aminobenzeneboronic acid with *m*-hydroxybenzeneboronic acid. There is no indication of the loss of the boronic acid function during these couplings.

The cuprous hydroxide solution prepared from ammoniacal cupric sulfate and hydroxylamine is an effective reagent for the removal of the boronic acid group from the benzene nucleus.

Attempts to effect reaction between *n*-butyl borate and *o*-chloromercuriphenol or acetoxymercuribenzene have been unsuccessful.

URBANA, ILLINOIS

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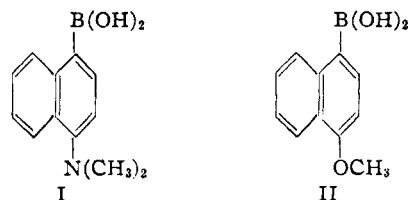
## Synthesis and Reactions of Some Substituted Naphthaleneboronic Acids

BY H. R. SNYDER AND F. W. WYMAN<sup>1</sup>

It has been shown<sup>2</sup> that azoboronic acids can be obtained by coupling of diazonium compounds with *m*-hydroxybenzeneboronic acid and with *m*-diethylaminobenzeneboronic acid. There is no indication of displacement of the boronic acid function in such coupling reactions. In connection with a projected synthesis of boron-containing azo dyes of possible use in physiological studies, it became desirable to determine whether the boronic acid group attached to an aminonaphthyl or alkoxynaphthyl radical might be expected to withstand the conditions of the coupling reaction and other substitutions. It would appear that the most drastic tests of the stability of the boronic acid group in such substances could be made on compounds having the 1,4-orientation. Accordingly, 4-dimethylamino-1-naphthaleneboronic acid (I) and 4-methoxy-1-naphthaleneboronic acid (II) have been prepared for study.

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(2) Snyder and Weaver, *THIS JOURNAL*, **69**, 232 (1947).



The boronic acids (I and II) were prepared by the usual method from the Grignard reagents and butyl borate. Each substance melted with decomposition over a range which varied with the rate of heating and with the previous history of the sample. This behavior is characteristic of boronic acids and is to be ascribed to the dehydration of the substances (and their hydrates) to the boron oxides. Satisfactory combustion analyses of the compounds I and II were not attained, because of the varying degree of hydration of the analytical samples and the entrapment of particles of carbon in the glass-like residue of boric oxide

formed in the combustion. However, both substances were alkali-soluble, showing the presence of the boronic acid group, and satisfactory neutralization equivalents were obtained on samples of both. The aminoboronic acid (I) was titrated with standard acid, with the aid of a pH meter, and the methoxyboronic acid was titrated with standard alkali in the presence of mannitol with phenolphthalein as the indicator.

The single recorded attempt to prepare *o*-dimethylaminobenzeneboronic acid apparently failed because of the extraordinary ease of hydrolysis of the substance, the only product isolated having been dimethylaniline.<sup>3</sup> This observation, together with that of detectable hydrolysis of 1-naphthaleneboronic acid during recrystallization from water,<sup>4</sup> leads to the prediction that 4-dimethylamino-1-naphthaleneboronic acid should be extremely labile. The properties of the substance are in accord with this prediction. Treatment of the aminoboronic acid, dissolved in cold glacial acetic acid, with dilute (1:1) nitric acid caused the displacement of the boronic acid group and the formation of 2,4-dinitro-1-dimethylaminonaphthalene. It is likely that the first step was the replacement of the boronic acid group, for under the identical conditions 1-dimethylaminonaphthalene was not nitrated. Enhancement of the reactivity of the boronic acid group by the amine group is indicated by the fact that  $\alpha$ -naphthaleneboronic acid was only slightly attacked under the conditions mentioned, although it was converted to 1,3-dinitronaphthalene when the test was made with concentrated nitric acid and with a much longer time of reaction. A similar ejection of the boronic acid group from the benzene nucleus has been observed<sup>5</sup> in the nitration of benzeneboronic and *p*-methoxybenzeneboronic acids, but under unspecified conditions which may have been relatively more drastic than those employed here.

Both the boronic acid group and the dimethylamino group were replaced when the aminoboronic acid was treated with nitrous acid in strong acetic acid solution. Evidently 4-nitroso-1-dimethylaminonaphthalene first formed, but was hydrolyzed in the reaction mixture to the nitrosonaphthol. When the aminoboronic acid was heated with aqueous sodium bisulfite or with alcoholic picric acid the boronic acid group was replaced by hydrogen. The cleavage with picric acid, discovered in an attempt to prepare the picrate of the aminoboronic acid, occurred with surprising facility. In contrast, the boronic acid group was quite stable to hydrolysis by alkali in the absence of air; cleavage to 1-dimethylaminonaphthalene did occur, but part of the unchanged aminoboronic acid was recovered after four hours of boiling with 10% sodium hydroxide. More complicated reactions with aqueous alkali occurred in the pres-

ence of air; dimethylamine was evolved and a high-melting insoluble organic product containing neither boron nor nitrogen was formed.

When the aminoboronic acid was treated with diazotized *p*-aminobenzoic acid, the boronic acid group was replaced by the azobenzoic acid residue. The dye obtained was identical with that produced by the coupling with 1-dimethylaminonaphthalene and its conversion to 1,4-naphthoquinone established with certainty the 1,4-orientation of the amino and azo groups. 1-Naphthaleneboronic acid was stable to the diazonium salt under the conditions employed with I. Dyes obtained by coupling I with diazotized *m*-aminobenzoic acid, diazotized anthranilic acid and tetrazotized benzidine did not give qualitative tests for boron and were not further investigated.

4-Methoxy-1-naphthaleneboronic acid (II) was more stable to the various reagents. It was recovered from the treatment with dilute nitric acid in glacial acetic acid at temperatures near 0°, but was converted to 2,4-dinitro-1-naphthol when the reaction was carried out at room temperature. Similarly, it was unattacked by nitrous acid in strong acetic acid at about 0°, but at room temperature it was hydrolyzed to 1-methoxynaphthalene. Boiling 50% acetic acid converted it to the same product. When a solution of the boronic acid (II) in aqueous sodium hydroxide was boiled in an open beaker hydrolysis occurred slowly and 1-methoxynaphthalene was formed. The methoxyboronic acid (II) coupled with diazotized *p*-aminobenzoic acid, but the dye formed did not contain boron and it was not further investigated.

### Experimental

**4-(*N,N*-Dimethylamino)-1-bromonaphthalene.**—*N*-Acetyl-1-naphthylamine was brominated according to the method of Meldola,<sup>6</sup> but with chloroform rather than acetic acid as the solvent. The bromoamide was hydrolyzed with ethanolic hydrochloric acid,<sup>6</sup> and the bromoamine was methylated by use of the procedure described by Gilman and Banner<sup>7</sup> for *N,N*-dimethyl-*o*-toluidine, except that a greatly increased quantity of water (2 liters for a run with 0.5 mole of amine) was employed in making up the reaction mixture. In most preparations the crude material was converted to the picrate by addition to a boiling 8% solution of picric acid (87.5% of the theoretical amount based on the amine methylated) in 95% ethanol. The crude picrate (m. p. 150–154°) which separated when the solution was cold was washed twice with cold ethanol, suspended in water, and treated with aqueous ammonia. The regenerated amine was collected in ether, dried over potassium carbonate and distilled; b. p. 137–139° (2 mm.); yield 55%. It was found possible to distil the crude amine, without the preliminary purification through the picrate, provided the pressure did not exceed 1 mm. nor the bath temperature 160°.

The amine was prepared also by direct bromination of dimethyl-1-naphthylamine, a procedure employed previously by Friedländer and Welms,<sup>8</sup> who did not purify the product. In the present work an insufficient quantity

(5) Meldola, *Ber.*, **11**, 1906 (1878).

(6) Johnson and Sandborn, "Org. Syn.," 2nd ed., Coll. Vol. I, 111 (1941).

(7) Gilman and Banner, *THIS JOURNAL*, **62**, 344 (1940).

(8) Friedländer and Welms, *Ber.*, **21**, 3127 (1888).

(3) König and Scharnbeck, *J. prakt. Chem.*, [2] **128**, 153 (1930).

(4) Branch, Yabroff and Bettmann, *THIS JOURNAL*, **58**, 1850 (1934).

(95%) of bromine, as a 40% solution in carbon tetrachloride, was added during one and one-half hours to a cooled and stirred 1 *M* solution of the tertiary amine in the same solvent. The precipitated hydrobromide was collected, washed with the solvent and suspended in water. The free amine, regenerated by the addition of 10% sodium hydroxide solution, was collected in ether, dried and distilled at 1 mm.; b. p. 115–130° (1 mm.). Although this product contained some dimethyl-1-naphthylamine it could be used for the preparation of the Grignard reagent. It could be purified through the picrate, as described above, and the picrate was identical with that of the material made by methylation of the bromoamine; the melting point of either sample of picrate, after two recrystallizations from 95% ethanol, was 154–156°. The trinitrobenzene derivatives, m. p. 94–95°, also were identical; the trinitrobenzene derivative of a sample from the direct bromination was analyzed.

*Anal.* Calcd. for  $C_{18}H_{15}O_6N_4Br$ : C, 46.66; H, 3.24. Found: C, 46.80; H, 3.34.

To establish the 1,4-orientation of the product from the bromination a sample was converted to 4-dimethylamino-1-naphthoic acid by treatment of the Grignard reagent with carbon dioxide; the amino acid melted at 162–163° (lit.,<sup>8</sup> 163–165°).

**4-Dimethylamino-1-naphthaleneboronic Acid.**—The Grignard reagent was prepared by refluxing for two hours a mixture of 25 g. of the bromo compound, 2.4 g. of magnesium, a crystal of iodine and 250 ml. of dry ether. The resulting solution, cooled to room temperature, was added over a period of about one-half hour to a vigorously stirred solution of 50 g. of *n*-butyl borate in 500 ml. of dry ether, the temperature of which was maintained at –15°. The mixture was allowed to stand overnight in the cooling bath before it was hydrolyzed by the addition of 100 ml. of water. The ether layer was washed several times with 50-ml. portions of cold water and then extracted with six 25-ml. portions of 5% hydrochloric acid. The combined acid extracts were evaporated at room temperature to give 12.2 g. (48%) of crude hydrochloride of the aminoboronic acid (I). The material was stored in this form, and the free aminoboronic acid was generated as needed by the dropwise addition of 10% sodium hydroxide solution to an aqueous solution of the hydrochloride until no further precipitation occurred. After two similar reprecipitations from dilute acid and drying *in vacuo* at room temperature the 4-dimethylamino-1-naphthaleneboronic acid (I) melted at 82–85°. Its neutralization equivalent, as determined by titration with 0.05 *N* hydrochloric acid with the aid of a Hellige pH meter, was within the limits of 212–215 (calcd. 214.9).

**Reactions of 4-Dimethylamino-1-naphthaleneboronic Acid.** (a) **With Nitric Acid.**—To a stirred solution of 1 g. of the aminoboronic acid in 10 ml. of glacial acetic acid, cooled in an ice-bath, was added dropwise 1 ml. of a cold solution of equal volumes of water and concentrated nitric acid. After ten minutes the mixture was diluted with 75 ml. of cold water, and the yellow solid which formed was collected. This solid melted at 81–85°; after three recrystallizations from 95% ethanol it melted at 88–89°, alone or mixed with authentic<sup>9</sup> 2,4-dinitro-1-dimethylaminonaphthalene.

1-Naphthaleneboronic acid was recovered from similar experiments in which it was substituted for the aminoboronic acid. Even when the reaction mixture was allowed to stand overnight before dilution, the 1-naphthaleneboronic acid recovered was only slightly contaminated (m. p. 180–188°) and was readily purified [to a m. p. of 198–200° (lit.<sup>3</sup> not above 202°)] by a single reprecipitation from alkaline solution and one recrystallization from ethanol. When concentrated nitric acid was substituted for the diluted nitric acid and the reaction mixture was allowed to stand overnight, the only product isolated was 1,3-dinitronaphthalene, m. p. 143–144°, identified by a mixed melting point with an authentic specimen.

(b) **With Nitrous Acid.**—To a solution of 1 g. of the aminoboronic acid in 10 ml. of glacial acetic acid, vigorously stirred in an ice-bath, was added dropwise 1.5 ml. of 20% aqueous sodium nitrite solution. After fifteen minutes the mixture was diluted with 50 ml. of cold water and filtered. The solid was dissolved in dilute sodium hydroxide solution and reprecipitated with dilute hydrochloric acid. After recrystallization from aqueous ethanol it decomposed at 193–195° (lit.<sup>10</sup> for 4-nitroso-1-naphthol, 194°). It contained no boron.

*Anal.* Calcd. for  $C_{10}H_7NO_2$ : C, 69.36; H, 4.08. Found: C, 69.48; H, 4.09.

(c) **With Aqueous Sodium Bisulfite.**—A mixture of 2 g. of the aminoboronic acid and about 20 ml. of 20% aqueous sodium bisulfite solution was refluxed for four hours. Careful neutralization and reacidification of a portion of the cooled solution did not cause the separation of any solid; the addition of alkali caused the separation of an oily base. The oil was collected in ether, dried, recovered from the solvent and added to alcoholic picric acid. The picrate melted at 145–146° (lit.,<sup>11</sup> 145°) alone or mixed with the picrate of 1-dimethylaminonaphthalene.

(d) **With Picric Acid.**—To a boiling solution of 1 g. of picric acid in 25 ml. of 95% ethanol was added a solution of 1.2 g. of the aminoboronic acid in 10 ml. of ethanol. The mixture was refluxed for about fifteen minutes, after which it was cooled and the solid which separated was recrystallized from 95% ethanol. The picrate melted at 142–144°, and a mixture with the picrate of 1-dimethylaminonaphthalene melted at 143–144°.

*Anal.* Calcd. for  $C_{18}H_{15}O_7N_4$ : C, 54.00; H, 4.00. Found: C, 53.79; H, 4.05.

(e) **With Aqueous Sodium Hydroxide.**—A solution of 2 g. of the aminoboronic acid in 40 ml. of deoxygenated 10% aqueous sodium hydroxide was refluxed for four hours under an atmosphere of illuminating gas. Extraction of the cooled solution with ether and removal of the solvent gave a drop of an oil; this oil gave a picrate which melted at 145–146°, alone or mixed with the picrate of 1-dimethylaminonaphthalene. Acidification of the alkaline aqueous solution caused the separation of a solid which redissolved in excess acid. After two reprecipitations from dilute acid by the dropwise addition of dilute alkali the solid melted at 80–83°, and the melting point was not lowered by admixture of the aminoboronic acid (I).

In a similar experiment in which the alkaline solution was boiled in an open beaker for eight hours (with occasional addition of water to maintain an approximately constant volume) none of the aminoboronic acid was recovered. The only product isolated was a dark, neutral solid, containing neither nitrogen nor boron, for which no recrystallization solvent was found.

(f) **With Diazonium Salts.**—1. Diazotized *p*-aminobenzoic acid: To the cold diazonium chloride solution prepared from 1.3 g. of *p*-aminobenzoic acid were added a solution of 2 g. of the aminoboronic acid in 20 ml. of cold 10% hydrochloric acid and a solution of 14 g. of sodium acetate in 25 ml. of cold water. The mixture was stirred for six hours at 0–5° and then allowed to stand overnight at the same temperature. The red solid was separated, dried and recrystallized from absolute ethanol. The substance did not contain boron; it melted at 204–206° (dec.), and the melting point was unaffected by admixture of the dye [m. p. 204–206° (dec.)] obtained by coupling 1-dimethylaminonaphthalene with the same diazonium salt.

*Anal.* Calcd. for  $C_{19}H_{17}O_2N_2$ : C, 71.48; H, 5.36. Found: C, 71.86; H, 5.53.

(10) Shriner and Fuson, "Identification of Organic Compounds," 2nd ed., John Wiley and Sons, New York, N. Y., 1940, p. 229.

(11) "Organic Reagents for Organic Analysis," by the staff of Hopkins and Williams, Ltd., Chemical Publishing Co., Brooklyn, 1946, p. 138.

(9) Ullmann and Bruck, *Ber.*, **41**, 3935 (1908).

Reduction<sup>12</sup> of the dye and oxidation<sup>13</sup> of the diamine so formed gave 1,4-naphthoquinone, identified by melting point and mixed melting point.

2. Other diazonium salts: Coupling under the same conditions with diazonium salts from *m*-aminobenzoic acid, anthranilic acid and benzidine gave dyes which were found not to contain boron and were not investigated further.

**4-Methoxy-1-naphthaleneboronic Acid.**—To the Grignard solution (concentration about 0.8 *M*) from 4-methoxy-1-bromonaphthalene<sup>14</sup> was added dropwise an equimolar amount of *n*-butyl borate as an ether solution of concentration about 1.1 *M* while the temperature was maintained at  $-60^{\circ}$ . The reaction mixture was allowed to remain in the cooling bath overnight. It was treated with water, and the product was recovered by several extractions of the ether solution with 2% aqueous sodium hydroxide. The crude boronic acid was obtained in 53% yield by acidification of the alkaline extracts. It was purified by reprecipitation from dilute alkali by acidification, followed by precipitation from ethanol by dilution with water. Samples dried *in vacuo* at room temperature underwent visible decomposition at about  $150$ – $155^{\circ}$ , in an ordinary melting point determination, but the decomposition product (presumably the anhydride) did not melt completely at temperatures up to  $250^{\circ}$ . A reproducible melting point of  $195^{\circ}$  could be determined by the instant immersion method.<sup>15</sup> The boronic acid was titrated in 20% ethanol solution containing mannitol with 0.05 *N* sodium hydroxide solution to a phenolphthalein end-point; the neutralization equivalent was found to be within the limits of 199–203 (calcd. 201.8).

**Reactions of 4-Methoxy-1-naphthaleneboronic Acid.**

(a) **With Nitric Acid.**—To a well-stirred suspension of one gram of the boronic acid in 10 ml. of glacial acetic acid at room temperature was added 1 ml. of a solution of equal volumes of concentrated nitric acid and water. Thirty minutes later the mixture was diluted with 50 ml. of cold water, and the solid which separated was recrystallized from 95% ethanol. The yellow solid melted at  $138$ – $139^{\circ}$ , and the melting point was not changed by the addition of authentic 2,4-dinitro-1-naphthol.

When the experiment was repeated with the temperature of the reaction mixture maintained at about  $2^{\circ}$  the 4-methoxy-1-naphthaleneboronic acid was recovered.

(b) **With Nitrous Acid.**—To a vigorously stirred suspension of 1 g. of the acid in 10 ml. of glacial acetic acid

at room temperature was added 1.5 ml. of 20% aqueous sodium nitrite solution. Thirty minutes later the mixture was filtered and the filtrate was diluted with 75 ml. of water. The diluted solution was extracted with ether and the oil which remained after evaporation of the ether was dissolved in ethanol, decolorized and treated with 1,3,5-trinitrobenzene. The crystals which formed melted at  $138$ – $139^{\circ}$  (lit.<sup>16</sup>  $138^{\circ}$ ) alone or mixed with the trinitrobenzene derivative of 1-methoxynaphthalene.

No reaction occurred when the experiment was carried out at  $0^{\circ}$ .

(c) **With Dilute Acetic Acid.**—A mixture of 1 g. of the boronic acid and 15 ml. of glacial acetic acid was refluxed for thirty minutes. Examination of the cooled solution revealed no evidence of reaction, so 10 ml. of water was added and the refluxing was continued for an additional half-hour. The cooled solution was diluted with 50 ml. of water and the oil which separated was extracted with ether. The ether extracts were washed with dilute alkali, dried and evaporated to give an oil which was identified as 1-methoxynaphthalene by conversion to the trinitrobenzene derivative as described in the preceding section.

(d) **With Aqueous Sodium Hydroxide.**—A solution of 1 g. of the boronic acid in 25 ml. of 10% aqueous sodium hydroxide was boiled gently for half an hour with occasional additions of water to keep the volume approximately constant. The cooled mixture was extracted with ether and the dried extracts were evaporated to give a small amount of an oil which was identified as 1-methoxynaphthalene by the melting point and mixed melting point of the trinitrobenzene derivative. Acidification of the alkaline solution caused the separation of 0.6 g. of the unchanged boronic acid (II).

### Summary

4-Dimethylamino-1-naphthaleneboronic acid and 4-methoxy-1-naphthaleneboronic acid have been prepared and subjected to the action of various reagents. The boronic acid group of either substance is removed readily by mild hydrolysis or by replacement under the influence of reagents such as dilute acids, dilute bases, nitric acid, nitrous acid and certain diazonium salts. The boronic acid group is more highly labilized by the 4-dimethylamino group than by the 4-methoxyl group.

(16) See p. 141 of the work cited in ref. 11.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## The Synthesis of $\beta$ -Carbolines. IV. 3-Aminoharman and Some of its Derivatives<sup>1</sup>

BY H. R. SNYDER, STANLEY M. PARMETER<sup>2</sup> AND HOWARD G. WALKER<sup>3</sup>

In the preceding paper the synthesis of 6-aminoharman by the reduction of the nitro compound was reported. It is to be expected that the isomeric 3-aminoharman may be prepared from harman-3-carboxylic acid by application of the

Hofmann<sup>4</sup> or Curtius<sup>5</sup> reaction. This paper reports the synthesis of 3-aminoharman from the acid azide and its conversion to the sulfanilyl derivative (III) and the 3-diethylaminopropyl derivative (IV), isolated as the dipicrate.

Preliminary tests indicated that the ester (I) could be converted to the hydrazide much more

(1) For the preceding paper see Snyder, Parmeter and Katz, *This Journal*, **69**, 222 (1947).

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(4) See Wallis and Lane, *The Hofmann Reaction*, "Organic Reactions," Vol. III, John Wiley and Sons, New York, N. Y., 1946, p. 267.

(5) See Smith, *The Curtius Reaction*, "Organic Reactions," Vol. III, John Wiley and Sons, New York, N. Y., 1946, p. 337.