example, was prepared in 77–90% yield from *n*-dodecyl alcohol, thiourea and 48% hydrobromic acid after seven hours of reaction; use of hydrochloric acid gave only 24% yield after twenty-eight hours.

The best procedure was as follows: In a 1-liter, three-necked round-bottomed flask fitted with a stirrer and a reflux condenser were placed 0.50 mole of the appropriate alcohol, 0.50 mole of thiourea and 1.50 moles of hydrogen bromide as 48% hydrobromic acid (double these amounts of thiourea and hydrobromic acid were used for making hexamethylene and decamethylene dithiols). The mixture was refluxed for nine hours with stirring. A solution of 60 g. (1.5 moles) of sodium hydroxide in 600 ml. of water was then added; a stream of nitrogen was passed over the surface of the liquid; and the mixture was refluxed without stirring for two hours. The layers were separated, and the acidified aqueous layer was extracted with three 50-ml. portions of ether. The ethereal extracts and original organic layer were combined, dried over calcium sulfate (Drierite), and fractionally distilled through a 12-inch helix-packed column.

The yields of several mercaptans obtained by this means are as follows: *n*-butyl, 91%; isobutyl, 56%; *n*-hexyl, 71%; *n*-octyl, 73%; *n*-dodecyl, 77%[5]; cetyl, 64%[5]; benzyl, 72%; β-phenylethyl, 70%; hexamethylene, 63%; decamethylene, 48%; *s*-butyl, 64%; cyclohexyl, 19%; 2-octyl, 59%. The purity of the products was established by comparison of the boiling points and refractive indices with the best data given in the literature.

Yields of mercaptans from alcohols by this method are as good as those from the alkyl bromides, so that the intermediate step of converting the alcohol to the bromide can advantageously be eliminated.

As is also found in the reaction between alkyl halides and thiourea, the yields are best for primary and poorest for tertiary mercaptans due to the tendency toward olefin formation in the latter types. The experiments of Sprague and Johnson[4] have shown that for mercaptans such as cyclohexyl or *t*-butyl the best procedure would be to use hydrochloric acid instead of hydrobromic and resort to long reaction periods. The reaction failed in attempts to prepare allyl mercaptan, *t*-butyl mercaptan, triphenylmethyl mercaptan, and *p*-nitrothiophenol, using hydrobromic acid.

It is reasonable to suppose that the course of the reaction to form the isothiouronium salts (I–II) involves the intermediate formation of an alkyl halide. On the other hand, it is possible that the hydroxyl group of the alcohol (I) may be directly replaced by the S-isothiouronium group. The available evidence indicates that both mechanisms may obtain. For example, the difference in reaction rates using hydrochloric and hydrobromic acids favors the former; one would not expect such a difference if these act only in their capacity as acids rather than as reagents to replace the alcoholic hydroxyl group by halogen. A further experiment, however, shows that the intermediate halide is not absolutely necessary: *n*-octyl mercaptan was obtained by refluxing with stirring 65 g. (0.50 mole) of *n*-octyl alcohol, 38 g. (0.50 mole) of thiourea, and 77 g. (0.75 mole) of concentrated sulfuric acid for nine hours. The mixture was then worked up with alkali in the same manner as described above. The yield of *n*-octyl mercaptan, not obtained completely free from *n*-octyl alcohol, was judged by refractive indices to be 5.1%. It was identified through its addition product with benzalacetophenone, m. p. 46.5–47°; mixed m. p. with an authentic sample of β-*n*-octylmercapto-β-phenylpropiophenone, 46.5–47.2°. The authentic sample was prepared by refluxing 1.0 g. (0.048 mole) of benzalacetophenone and 0.7 g. (0.048 mole) of *n*-octyl mercaptan in 3.0 ml. of 95% ethanol for one-half hour. The product separated on cooling; one recrystallization from 95% ethanol gave white needles, m. p. 47.5–48°.

(5) In the preparation of higher mercaptans such as dodecyl and cetyl, oxidation of some product to the disulfide is unavoidable; in these two cases were also obtained yields of 22 and 35% of the respective disulfides.

Anal.[6] Calcd. for $C_{23}H_{30}OS$: C, 77.91; H, 8.53. Found: C, 77.80; H, 8.22.

Further experiments of interest in comparing the chlorine and bromine derivatives in this reaction are as follows: A mixture of 65 g. (0.50 mole) of *n*-octyl alcohol and 254 g. (1.50 moles) of 48% hydrobromic acid were refluxed in a 1-liter, round-bottomed flask for nine hours. It was then extracted with two 50-ml. portions of ether, dried over calcium sulfate (Drierite), and fractionally distilled through a 12-inch helix-packed column to give 79 g. (82%) of *n*-octyl bromide, b. p. 93° (20 mm.); $n^{20}D$ 1.4520. The same procedure, using 150 ml. (1.80 moles) of concentrated hydrochloric acid, resulted in the recovery of 62 g. (95%) of *n*-octyl alcohol, b. p. 96–97°; $n^{20}D$ 1.4290.

A similar procedure, using 48.5 g. (0.65 mole) of *n*-butyl alcohol, 49.5 g. (0.65 mole) of thiourea, 194 ml. (2.30 moles) of concentrated hydrochloric acid, and a nine-hour reaction period, followed by the addition of 92 g. (2.30 moles) of sodium hydroxide in 500 ml. of water and refluxing for three hours, gave a 41-g. (85%) recovery of *n*-butyl alcohol, b. p. 117°; $n^{20}D$ 1.3988. Inclusion of 313 g. (2.30 moles) of pulverized zinc chloride in this reaction mixture gave on distillation 30 g. (50%) of *n*-butyl chloride, b. p. 77°; $n^{20}D$ 1.4002. No *n*-butyl mercaptan was obtained.

Thus both the replacement of hydroxyl by halogen and of halogen by the S-isothiouronium group, assuming this reaction course, are influenced by the choice of halogen acid.

(6) Microanalysis carried out by Mr. Howard Clark.

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RECEIVED MAY 23, 1946

Some Heterocyclic Acetic Acids in Plant Hormone Tests

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In extension of studies on polynuclear hetero types, some acetic acid derivatives of dibenzofuran, dibenzothiophene, phenoxathiin and carbazole have been prepared for plant hormone tests.

Experimental

2-Dibenzofurylacetic Acid.—This compound has been prepared by three different procedures.[1,2]

1. Arndt–Eistert Reaction.—Five and one-half g. (0.026 mole) of 2-dibenzofurancarboxylic acid was refluxed for forty-five minutes with an excess of thionyl chloride. After removing the excess thionyl chloride by distillation, the residual acid chloride was crystallized from benzene as colorless needles, m. p. 103–104°; yield 5.6 g. (93%).

Anal. Calcd. for $C_{13}H_7O_2Cl$: Cl, 15.22. Found: Cl, 15.03.

To an ether solution of diazomethane obtained from 15 g. (0.146 mole) of nitrosomethylurea was added 5 g. (0.022 mole) of 2-dibenzofurancarboxylic acid chloride and the solution was allowed to stand overnight. After removal of the ether and recrystallization from benzene–ligroin there was obtained an 86% yield of yellow crystals of diazomethyl 2-dibenzofuryl ketone, m. p. 126–127°.

Anal. Calcd. for $C_{14}H_8O_2N_2$: N, 11.86. Found: N, 12.02.

To a stirred and refluxed solution of 2.5 g. (0.01 mole) of diazomethyl 2-dibenzofuryl ketone in 50 cc. of dioxane was added 13 cc. of concentrated ammonium hydroxide and then 3 cc. of a 10% solution of silver nitrate. After heating and stirring for one hour, the hot solution was filtered from the silver oxide and shaken with cold water. The precipitated crude 2-dibenzofurylacetamide was obtained

(1) Arndt and Eistert, *Ber.*, **68**, 200 (1935).

(2) Fieser and Kilmer, THIS JOURNAL, **62**, 1354 (1940).

in a 70% yield, and crystallization from ethanol gave the pure amide, m. p. 209–210°.

Anal. Calcd. for $C_{14}H_{11}O_2N$: N, 6.22. Found: N, 6.31.

The 2-dibenzofurylacetic acid was obtained by refluxing the amide with thirty parts of a 15% ethanolic solution of potassium hydroxide for four hours and then crystallizing the precipitated acid from ethanol as colorless needles, m. p. 162–163°; yield 87%.

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.33; H, 4.47. Found: C, 74.24; H, 4.61.

2. Willgerodt Reaction.—A mixture of 2 g. (0.01 mole) of 2-acetyldibenzofuran, 8 cc. of purified dioxane, and 1 g. of sulfur in 10 cc. of a solution of ammonium sulfide was heated in a sealed tube at 160° for ten hours. The yellow crystals which deposited on cooling were crystallized from ethanol to give 1.5 g. (70%) of 2-dibenzofurylacetamide, m. p. 209–210°. There was no depression in a mixed melting point determination with the amide obtained from the Arndt–Eistert reaction.

3. From 2-Dibenzofurylmethyl Chloride.—A solution of 1 g. (0.005 mole) of 2-dibenzofurylmethyl chloride[3] and 0.33 g. (0.006 mole) of potassium cyanide in 10 cc. of ethanol was refluxed for three hours, and then evaporated almost to dryness under reduced pressure. Addition of water precipitated the 2-dibenzofurylmethyl cyanide which, after crystallization from ethanol, melted at 100–102°; yield 0.52 g. (55%).

Anal. Calcd. for $C_{14}H_9ON$: N, 6.76. Found: N, 7.01.

A solution of 0.4 g. (0.002 mole) of 2-dibenzofurylmethyl cyanide in a mixture of 5 cc. of 50% sulfuric acid and 5 cc. of glacial acetic acid was refluxed for one hour, cooled, and diluted with water. Crystallization from ethanol gave the acid melting at 162–163°, which was shown to be identical with the acid prepared by hydrolysis of the acid amide.

4-Dibenzothienylacetic Acid.—First, 5 g. (0.021 mole) of 4-dibenzothiophenecarboxylic acid[4] was converted by thionyl chloride to 4-dibenzothiophenecarboxylic acid chloride which after crystallization from benzene was obtained as colorless needles, m. p. 159–160°; yield 4.9 g. (92%).

Anal. Calcd. for $C_{13}H_7OClS$: Cl, 14.38. Found: Cl, 14.47.

Second, from 4 g. (0.016 mole) of 4-dibenzothiophenecarboxylic acid chloride and diazomethane was obtained an 86% yield of diazomethyl 4-dibenzothienyl ketone as yellow crystals, m. p. 161–162° after crystallization from ethanol.

Anal. Calcd. for $C_{14}H_8ON_2S$: N, 11.11. Found: N, 11.39.

Third, in accordance with the Arndt–Eistert procedure described for 2-dibenzofurylacetic acid, 2.5 g. (0.01 mole) of diazomethyl 4-dibenzothienyl ketone was converted in a 61% yield to 4-dibenzothienylacetamide, m. p. 205–206° after crystallization from ethanol.

Anal. Calcd. for $C_{14}H_{11}ONS$: N, 5.80. Found: N, 5.97.

Fourth, the amide on hydrolysis by refluxing for three hours with a 15% ethanolic potassium hydroxide solution gave, subsequent to acidification and crystallization from ethanol, an 89% yield of 4-dibenzothienylacetic acid, m. p. 161.5–162.5°.

Anal. Calcd. for $C_{14}H_{10}O_2S$: S, 13.22. Found: S, 13.35.

2-Phenoxathiinacetic Acid.—In accordance with the Willgerodt reaction described for 2-dibenzofurylacetic acid, there was obtained from 2 g. (0.008 mole) of 2-acetylphenoxathiin[5] 1.4 g. (68%) of yellow crystals of 4-phenoxathiinacetamide, m. p. 202–203° after crystallization from ethanol.

Anal. Calcd. for $C_{14}H_{11}O_2NS$: N, 5.44. Found: N, 5.61.

Hydrolysis of the acid amide by refluxing with ethanolic potassium hydroxide gave an 85% yield of colorless needles of 2-phenoxathiinacetic acid, m. p. 136–137° after crystallization from benzene.

Anal. Calcd. for $C_{14}H_{10}O_3S$: S, 12.40. Found: S, 12.53.

2-Carbazolylacetic Acid.—First, the modified Willgerodt reaction with 2 g. (0.01 mole) of 2-acetylcarbazole[6] gave 1.3 g. (58%) of 2-carbazolylacetamide, obtained as yellow crystals, m. p. 236–237° after crystallization from ethanol.

Anal. Calcd. for $C_{14}H_{12}ON_2$: N, 12.50. Found: N, 12.39.

Then, hydrolysis of the acid amide by refluxing with ethanolic potassium hydroxide gave an 87% yield of the acid as colorless leaflets, m. p. 270–271° after crystallization from ethanol.

Anal. Calcd. for $C_{14}H_{11}O_2N$: N, 6.22. Found: N, 6.48.

3-Carbazolylacetic Acid.—A mixture of 2.1 g. (0.01 mole) of 3-acetylcarbazole, 1 g. of sulfur, 10 g. of ammonium sulfide and 10 cc. of purified dioxane was heated in a sealed tube for twelve hours at 160°. Recrystallization of the resulting yellow product from dioxane gave 1.9 g. (85%) of 3-carbazolylacetamide, m. p. 295–296°.

Anal. Calcd. for $C_{14}H_{12}ON_2$: N, 12.50. Found: N, 12.48.

Hyodrolysis of the amide by ethanolic potassium hydroxide gave 1.7 g. (90%) of 3-carbazolylacetic acid, m. p. 260–261° after crystallization from ethanol.

Anal. Calcd. for $C_{14}H_{11}O_2N$: N, 6.22. Found: N, 6.37.

2,8-Dibenzofuryldiacetic Acid.—A mixture of 2.5 g. (0.01 mole) of 2,8-diacetyldibenzofuran, 2 g. of sulfur, 20 g. of ammonium sulfide and 20 cc. of dioxane was heated at 160° for twelve hours. The resulting mixture was suspended in 100 cc. of 15% ethanolic potassium hydroxide, refluxed for three hours, filtered, and the filtrate acidified with hydrochloric acid. Recrystallization from acetic acid gave 1.5 g. (53%) of 2,8-dibenzofuryldiacetic acid, m. p. 230–231°.

Anal. Calcd. for $C_{16}H_{12}O_5$: C, 67.60; H, 4.22. Found: C, 67.69; H, 4.34.

Assays and Acknowledgment.—The authors are grateful to Dr. George S. Avery, Jr., of Connecticut College[7] for growth tests on some of the compounds. 2-Carbazolylacetamide, 2-carbazolylacetic acid and 2,8-dibenzofuryldiacetic acid were physiologically inactive in the Avena curved growth test (deseeded method), and in the tomato test (Hitchcock and Zimmerman). In connection with a study of other types, it was observed that triethylleadacetic acid at 1.4 mg./liter gave a suggestion of activity in the Avena straight growth test (Scheer).

(3) Prepared in accordance with directions provided by Paul T. Parker.

(4) Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938).

(5) Suter, McKenzie and Maxwell, THIS JOURNAL, **58**, 717 (1936).

(6) Meitzner, *ibid.*, **57**, 2327 (1935); Plant and Williams, *J. Chem. Soc.*, 1142 (1934).

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RECEIVED MAY 10, 1946

A Convenient Synthesis of 5-Methyltryptophan

BY MARY E. JACKMAN AND S. ARCHER

In connection with another problem the need arose for a sizeable quantity of 5-methyltryptophan. Robson[1] described a method for preparing

(1) Robson, *J. Biol. Chem.*, **62**, 495 (1924–1925).