3-(1-Piperidino)-5-nitrothianaphthene-1-dioxide.—A 94% yield of this compound was obtained within thirty minutes by the reaction of 3-bromo-5-nitrothianaphthene-1-dioxide with a two molar excess of piperidine in refluxing ethanol solution. After crystallization from ethanol it melted at 197–198° (with dec.).

Anal. Calcd. for $C_{13}H_{14}O_4N_2S$: N, 9.53. Found: N, 9.29.

In a similar manner a 94% yield of **3-diethylamino-5-nitrothianaphthene-1-dioxide**, m. p. 210°, was obtained.

Anal. Calcd. for $C_{12}H_{14}O_4N_2S$: N, 9.92. Found: N, 9.74.

3-Bromo-5-aminothianaphthene-1-dioxide.—Reduction of 3-bromo-5-nitrothianaphthene-1-dioxide in ethanol solution was brought about in 81% yield using stannous chloride and concd. hydrochloric acid, according to the method of Fries, *et al.*[6] The product, m. p. 233°, was obtained as yellow needles by crystallization from ethanol.

Anal. Calcd. for $C_8H_6O_2NSBr$: N, 5.38. Found: N, 5.46.

3-Diethylamino-5-aminothianaphthene-1-dioxide.—By refluxing a mixture of 0.65 g. (0.0025 mole) of 3-bromo-5-aminothianaphthene-1-dioxide, 0.55 g. (0.0075 mole) of diethylamine and 10 ml. of ethanol for one hour, there was obtained 0.44 g. (70%) of a cream-colored solid, m. p. 180–184°. Purified four times by crystallization from ethanol, the material melted at 194°.

Anal. Calcd. for $C_{12}H_{16}O_2N_2S$: C, 57.11; H, 6.39. Found: C, 56.65; H, 6.43.

Summary

1. 3-Bromo-5-nitrothianaphthene was obtained in the bromination of 5-nitrothianaphthene. From the nitration of 5-nitrothianaphthene a dinitro- and trinitrothianaphthene were isolated, which are believed to be 3,5-dinitro- and 3,5,7-trinitrothianaphthene.

2. The electron attracting power of a nitro group in the 3-position of several thianaphthenes was found to be strong enough to prevent oxidation of the sulfur atom under the usual conditions.

3. 3-Diethylamino-5-aminothianaphthene-1-dioxide, which is a vinylog of N,N-diethyl sulfanilamide, and is closely related to bis-(4-aminophenyl)-sulfone has been prepared.

EVANSTON, ILLINOIS RECEIVED JANUARY 17, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

The Decomposition of Dibutylchloramine

BY GEORGE F WRIGHT

It has recently been found that aliphatic secondary amines can be nitrated in organic acid anhydrides when a chloride catalyst is present[1]; further, that the formation of the nitramine proceeds *via* the chloramine. Unsatisfactory yields of certain nitramines have been attributed to the instability of this intermediate.[2] It thus seemed worthwhile to re-investigate the stability of chloramines. Dibutylchloramine, which was chosen for this study, has been found to decompose to complex mixtures. Partial identification of these mixtures indicates that extensive intramolecular chlorination has taken place.

Chlorine, which has been reported as a product when chloramines are treated with excess hydrogen chloride,[3] was obtained in 68% yield from dibutylchloramine, I, in methanol. The expected dibutylammonium chloride, IV, was produced in 55% yield. It is not unreasonable to assume that this decomposition proceeds by formation from I of dibutylchloramine hydrochloride, II, which decomposes spontaneously in excess of hydrogen chloride to dibutylammonium chloride, IV.

The spontaneous decomposition of dibutylchloramine yielded dibutylammonium chloride released by reaction I → V. No chlorine was evolved. A liquid could be distilled out of the tar left when electropositive chlorine had disappeared, but this liquid showed a peculiar instability. Immediately after distillation a hydrochloride began to precipitate, but ceased after a certain amount had appeared. After redistillation the precipitation was resumed approximately to the same extent as before.

This distillate is considered to be a mixture of VI, VIII, X and XI which is formed by the action of chlorine released by initial decomposition of I. It is thought that the mixture loses hydrogen chloride until the basicity is reduced by hydrochloride formation, and that this loss is resumed after removal from the hydrochloride by distillation. The aldimine structure of the mixture has been confirmed by alkaline decomposition in presence of *p*-bromobenzenesulfonyl chloride to give the bromosulfonyl derivatives of monobutylamine.

Monobutylamine as its hydrochloride also was formed when the hydrochloride of the mixture was treated with methanol. The aldehydic fraction remaining after precipitation of the salt with ether was unstable, so it was treated with phenylhydrazine hydrochloride in ethanol. A distinctive blood-red color appeared which faded when the hydrochloride of ethylglyoxal precipitated. The color change is remindful of that which occurs when dichloroacetaldehyde is converted to glyoxal osazone.[4] Since the color change does not occur when ethylglyoxal is treated with phenylhydrazine, this hydrochloride, which is convertible to the known osazone,[5] is probably formed from

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[1] Wright, *et al.*, *Can. J. Res.*, **26B**, 89, 257 (1948).

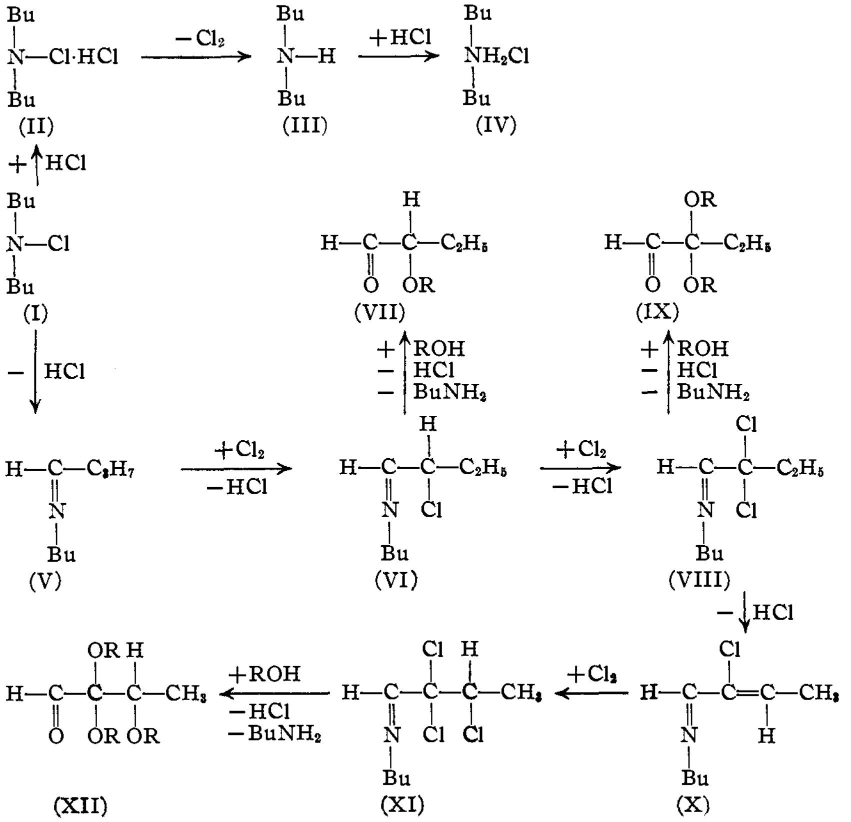
[2] K. K. Carroll and G. F Wright, *ibid.*, **26B**, 271 (1948).

[3] Houben, "Die Methoden der organischen Chemie," 3rd ed., Vol. 4, Georg Thieme, Leipzig, 1941, p. 569.

[4] G. Oddo and G. Cusmano, *Gazz. chim. ital.*, **41**, [II], 246 (1911).

[5] L. Wolff, *Ann.*, **288**, 20 (1895); E. Kolshorn, *Ber.*, **37**, 2476 (1904).

2,2-dichlorobutanal. On this basis the mixture must consist largely of VIII, and its analysis approximated that expected for VIII.



This analysis must, however, have been fortuitous, because in hot ethanol–hydrochloric acid a complex mixture of dinitrophenylhydrazones precipitated after a reproducible and characteristic induction period, presumed to involve alcoholysis. The least soluble compound in the complex mixture from dinitrophenylhydrazine treatment was, according to its analysis, the dinitrophenylosazone of ethoxyethylglyoxal, XII (R = Et, shown as its diethyl ketal). Substantiation for the constitution of XII was obtained when methanolic dinitrophenylhydrazine produced the homologous methyl ether (R = Me). Out of the remaining mixture only the most soluble compound could be identified by analysis; it was the 2,4-dinitrophenylhydrazone of 2-ethoxybutanal, VII. Thus evidence is at hand for three compounds in the postulated mixture, VI, VIII, X and XI.

The reactions I → IX seem to occur in one operation when dibutylchloramine is decomposed during fourteen hours in boiling ethanol. From the solution could be isolated (on the mole for mole basis) a 23% yield of monobutylamine, a 48% yield of dibutylamine, a 9% yield tentatively identified as *n*-butyl-N-butyramide; and finally ethylglyoxal was identified as its osazone. The ethylglyoxal must have been present as such or as its diethylketal, IX, since the red color was not observed during osazone formation.

The decomposition of dibutylchloramine in acetic acid was very slow at 25° but could be accelerated to completion (negative test for electropositive chlorine) in one hour by reaction at 90°. A 39% yield of dibutylammonium chloride was formed, as well as two distillable fractions. Neither of these was N-*n*-butylpyrrolidine.[6] The lower boiling of the two fractions was undoubtedly dibutylacetamide. The other fraction does not undergo the characteristic delayed precipitation with ethanolic dinitrophenylhydrazine.

The decomposition of dibutylchloramine in acetic anhydride was even more extensive than in the solvents recorded above. Reaction in this anhydrous medium was much more rapid than in acetic acid or ethanol, and was violent at 65°. A low yield of dibutylammonium chloride was produced when one or two equivalents of the anhydride were employed, but none was found when three equivalents were used. The distillate from the residue was unstable. Partial separation provided a 21% yield of butyl butyramide,[2] at least 20% of dibutylacetamide, and two aldehydic fractions from which phenylhydrazine derivatives of ethylglyoxal were obtained.

Aid from the Canadian National Research Council is gratefully acknowledged.

Experimental[7a]

Dibutylchloramine with Hydrogen Chloride.—Five grams (0.0316 mole) of dibutylchloramine in 12 cc. of methanol was cooled to 0° while hydrogen chloride was passed through until saturation. The chlorine which was evolved amounted to 0.023 mole (68%). The residual salts remaining after evaporation of the solvent weighed 3.8 g. and after neutralization with alkali were identified by distillation as 0.02 g. of butylamine, 2.30 g. (55%) of dibutylamine and 0.04 g. of an oil which contained combined chlorine. Aldehydic material was lost during the evaporations, but a remaining trace gave a derivative with dinitrophenylhydrazine melting at 234°. According to its mixed melting point this was identical with the ethoxyethylglyoxal dinitrophenylosazone which is discussed later.

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[6] G. H. Coleman and G. E. Goheen, THIS JOURNAL, **60**, 730 (1938).

[7a] All melting points have been corrected against known standards.

Dibutylchloramine with Sulfuric Acid-Water.—When 42.3 g. (0.26 mole) of dibutylchloramine was added to a mixture of 80 cc. (1.5 mole) *concd.* sulfuric acid and 30 cc. (1.67 mole) of water it was necessary to cool the mixture slightly. It was heated one day at 90° with strong evolution of chlorine, but at the end of this time, the electropositive chlorine test was negative. The whole was poured into ice and extracted with ether to remove a little oil which was discarded. The cooled aqueous layer was made basic with 135 g. of sodium hydroxide and was then extracted with ether and this solution dried with sodium hydroxide. Distillation yielded 20.3 g., b. p. 42–51° (11 mm.), $n^{25}\text{D}$ 1.4327, of N-butylpyrrolidine in 61% of the theoretical yield. This was redistilled at 155–157° (754 mm.) to free it from contamination with an impurity which contained chlorine. The distillate, which had the same refractive index, was identified by precipitation of N-butylpyrrolidine picrate from hydrochloric acid solution with saturated picric acid, m. p. 123–124.5°, after crystallization from 95% ethanol.[7]

Dibutylchloramine in Ethanol.—A solution of 16.3 g. (0.1 mole) of dibutylchloramine in 50 cc. of absolute ethanol became very dark after boiling for fourteen hours until a negative electropositive chlorine test was obtained. The ethanol was removed under 150 mm. pressure, the residue taken up in 2% hydrochloric acid and extracted three times with ether. This ether solution, dried with magnesium sulfate, was distilled to yield 1.79 g. boiling at 35–42° (0.25 mm.); $n^{25}\text{D}$ 1.4484. This was redistilled to remove a small first fraction, then a second fraction at 74–76° (10 mm.). When this main distillate was treated with phenylhydrazine and a little acetic acid in ethanol and then diluted with water, a precipitate (m. p. *ca* 110°) appeared. This melted at 115° after crystallization from petroleum ether (b. p. 60–70°) and was the osazone of ethylglyoxal.[5]

Anal. Calcd. for $C_{16}H_{18}N_4$: C, 72.2; H, 6.84; N, 21.0. Found: C, 71.8; H, 7.04; N, 20.7.

The aqueous liquor from which were obtained the acid insoluble fractions described above, was made basic to release an amine fraction. Upon distillation, this yielded 1.7 g. of monobutylamine $n^{25}\text{D}$ 1.3643, b. p. 78–80° (754 mm.), (23% of theoretical), and then 6.3 g. of authentic dibutylamine, b. p. 32° (0.25 mm.), $n^{25}\text{D}$ 1.4156 (48% of theoretical) and 1.3 g. of material, b. p. 70–78° (0.01 mm.), $n^{25}\text{D}$ 1.4413, m. p. −10°. According to boiling point and refractive index this fraction may be N-butylbutyramide. It would not react with dinitrophenylhydrazine in dilute ethanolic hydrochloric acid but on treatment of 0.2 g. overnight with 1 g. of *p*-bromobenzenesulfonyl chloride in 7 cc. of 10% alkali, it yielded 0.1 g. of *n*-butyl bis-*p*-bromobenzenesulfonimide, m. p. 107–114°. After crystallization from ethanol, this melted without depression at 115° when mixed with the authentic material.[8]

Thermal Decomposition of Dibutylchloramine.—It required six weeks at 38° before 4.5 g. (0.028 mole) of dibutylchloramine no longer gave an electropositive chlorine test. The brown residue was suspended in ether and filtered to remove 2.25 g. of dibutylammonium chloride (49% of theoretical) which was identified as its styphnate, m. p. 91.4–91.9°. The ether filtrate was distilled, finally at 0.01 mm. to yield 0.93 g., b. p. 40–47°, $n^{25}\text{D}$ 1.4534. This distillate precipitated a small amount of salt. It was redistilled *in toto* at 50° (0.006 mm.) $n^{25}\text{D}$ 1.4539.

Anal. Calcd. for $C_8H_{15}NCl_2$: C, 49.2; H, 7.75; N, 7.19. Found: C, 49.8; H, 8.05; N, 7.76.

When 0.489 g. (0.0025 mole) of this material was treated with 1.53 g. (0.006 mole) of *p*-bromobenzenesulfonyl chloride and 19.2 cc. (0.012 mole) of 5% aqueous sodium hydroxide at 0° and then shaken two hours at 25° a solid formed which was filtered off after neutralization of the alkali. It weighed 0.16 g. and melted at about 60°. Several crystallizations from hot ethanol raised this to 115.3°. The identical material could be prepared from the salt remaining after the N-butyldichlorobutaldimine was distilled under reduced pressure. This is evidently identical with the *n*-butyl-*bis*-bromobenzenesulfonimide reported with melting point of 116°.[8]

Anal. Calcd. for $C_{16}H_{17}NO_4S_2Br_2$: C, 37.6; H, 3.36; N, 2.74. Found: C, 37.9; H, 3.64; N, 3.26.

The compound designated above as N-butyldichlorobutanaldimine (5.72 g. 0.029 mole) was dissolved in 25 cc. of dry ether and treated with hydrogen chloride. No chlorine was evolved. After evaporation of the ether, the residue weighed 6.8 g. (quantitative yield). No satisfactory melting point of this material could be obtained. When it was dissolved in 17 cc. of methanol to which 250 cc. of dry ether was added a new precipitate appeared in smaller quantity (2.98 g.). It melted at 213–213.5° and according to analysis was butylammonium chloride in 97% yield.

Anal. Calcd. for $C_4H_{12}NCl$: C, 43.8; H, 11.03. Found: C, 43.4; H, 10.80.

This was identified by treatment of 1 g. (0.0092 mole) of salt with 3 g. (0.012 mole) of bromobenzenesulfonyl chloride and 40 cc. (0.05 mole) of 5% aqueous sodium hydroxide in the cold. This yielded 2.56 g. (97%) of N-butyl-*p*-bromobenzenesulfonamide, m. p. 56–57°, and was contaminated with the 116° compound described above. This was washed with carbon tetrachloride and crystallized twice from 1:4 benzene–petroleum ether (b. p. 60–70°) to melt at 54–54.5°. Since this is lower than that previously reported[7] (58°), the compound was identified by analysis.

Anal. Calcd. for $C_{10}H_{14}NSO_2Br$: C, 41.2; H, 4.84. Found: C, 41.5; H, 4.89.

When the methanol–ether solution, from which the butylammonium chloride was isolated, was evaporated to a small volume and diluted with water, a water-insoluble phase separated. Its ether solution, dried and distilled, yielded 0.37 g., b. p. 43–45° (12 mm.), $n^{25}\text{D}$ 1.4515. When this substance was treated with phenylhydrazine hydrochloride in ethanol, the suspension first turned yellow, then after five minutes was blood-red. This color disappeared by the next day to leave yellow crystals melting at 162°. This crop was crystallized from ethanol and then ground in dioxane to melt at 169–170.6°. It was slightly soluble in dilute hydrochloric acid. The compound was evidently a hydrochloride.

Anal. Calcd. for $C_{16}H_{19}N_4Cl$: C, 63.6; H, 6.36; N, 18.5. Found: C, 63.7; H, 6.57; N, 18.5.

When this compound was dissolved in ethanol and treated with aqueous sodium hydroxide and water, the precipitate melted at 110°. Crystallization from petroleum–ether (b. p. 60–70°) raised this to 114–115°. A mixed melting point with the osazone of ethylglyoxal was not lowered.

Crude "N-Butyl Dichlorobutaldimine" with Dinitrophenylhydrazine.—A suspension of 1.45 g. (0.0073 mole) of 2,4-dinitrophenylhydrazine in 150 cc. of ethanol and 3 cc. of concentrated hydrochloric acid was boiled with 1.18 g. (0.006 mole) of crude N-butyldichlorobutanaldimine. After one minute the clear solution became cloudy and a yellow precipitate began to appear. After fifteen minutes, this had become red. The suspension was filtered hot to remove 0.88 g. of orange-red precipitate, m. p. 232–234°. This was crystallized from dioxane (80 cc. per g.) as dark red prisms which melted at 241.1–241.6°. It contained no chlorine and is thought to be the osazone of 3-ethoxyethylglyoxal.

Anal. Calcd. for $C_{18}H_{20}N_8O_9$: C, 44.3: H, 3.69; N, 22.8. Found: C, 44.4; H, 3.67; N, 22.4.

When the ethanol solution (from which this osazone was filtered) was cooled, an orange precipitate weighing 0.25 g., m. p. *ca.* 200°, was obtained. This obvious mixture was crystallized thrice from dioxane (20 cc. per g.) to melt at 227.5–228°. The precipitate contained

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(7) L. C. Craig and R. M. Hixon, This Journal, **53**, 187 (1931).

(8) Ssolonina, *J. Russ. Phys.-Chem. Soc.*, **31**, 640 (1899).

chlorine. The analysis conformed most closely with that expected for 3-chlorobutanal 2,4-dinitrophenylhydrazone.

Anal. Calcd. for $C_{10}H_{11}N_4O_4Cl$: C, 42.0; H, 3.85; N, 19.5. Found: C, 42.7; H, 3.70; N, 18.9.

The ethanolic filtrate from which this compound was isolated when diluted with water, precipitated 0.17 g. of yellow material, m. p. *ca.* 85°, which was dissolved in hot ethanol to give a first crop, m. p. 185–187°, not further investigated. Further cooling yielded 0.05 g., m. p. 92.8°. This melting point was not raised by further crystallization from ethanol. The compound contained no chlorine.

Anal. Calcd. for $C_{12}H_{16}N_4O_5$: C, 48.6; H, 5.45; N, 18.9. Found: C, 48.1; H, 5.46; N, 19.1.

When this process with dinitrophenylhydrazine was carried out in methanol instead of ethanol, the hot methanol-insoluble precipitate melted at 234°. It was crystallized from boiling nitromethane (40 cc./g.), then extracted with boiling chloroform and finally recrystallized from nitromethane to melt at 242–244°. A mixed melting point of this dinitrophenyl osazone of 3-methoxyethylglyoxal with the ethoxy analog melted at 227°.

Anal. Calcd. for $C_{17}H_{16}N_8O_9$: C, 42.8; H, 3.28. Found: C, 43.1; H, 3.41.

When the thermal decomposition of dibutylchloramine was effected at higher temperatures the reaction was complete in ten days at 58° and in one day at 95°. The yield of dibutylammonium chloride was lower (40–37%) but the products were essentially the same.

Dibutylchloramine in Acetic Acid.—A solution of 70.6 g. (0.434 mole) of dibutylchloramine n^{25}D 1.4348 in 86 cc. of acetic acid showed no tendency toward salt formation in one day, but when heated to 90°, the electropositive chlorine was consumed in one hour. The solvent was removed under 15 mm. pressure and the residue made alkaline with cold 15% aqueous sodium hydroxide. The oil which separated was taken up in ether, dried with magnesium sulfate and distilled to yield 22 g. (39% of theoretical) of dibutylamine, b. p. 30–36° (0.35 mm.), n^{25}D 1.4162 (identified as the styphnate, m. p. 93°) and then 17 g., b. p. 88–92° (0.05 mm.), n^{25}D 1.4500.

This fraction contained no N-butylpyrrolidine, since its dilute hydrochloric acid extract gave no picrate. When it was shaken with saturated sodium bisulfite, dried under vacuum, and redistilled, it first yielded 4.58 g., b. p. 120–5° (12 mm.), n^{25}D 1.4480, which was evidently impure dibutylacetamide. The characterization of this compound was effected by one-day reflux with an equal weight of sodium methoxide in 5 volumes of methanol which yielded, on distillation, dibutylamine in 20% yield, b. p. 45–50° (12 mm.), n^{25}D 1.4150. This was converted to dibutyl *p*-bromobenzenesulfonamide, m. p. 58–59°, for complete identification by mixed melting point.[9] In addition to this amine, purified dibutylacetamide, n^{25}D 1.4436, b. p. 119–121° (12 mm.), was recovered.

The second and main fraction from this redistillation of the 17-g. portion boiled at 127–130° (12 mm.), n^{25}D 1.4513. The compound contains chlorine. The analysis could not be correlated with any reasonable structure.

Anal. Calcd. for $C_9H_{18}NCl$: C, 61.6; H, 10.3; N, 7.97. Found: C, 61.1; H, 10.1; N, 7.88.

This product did not react with 2,4-dinitrophenylhydrazine in boiling dilute ethanolic hydrochloric acid. Some early fractions after removal of the dibutylamine in the initial distillation did, however, give ethoxyethylglyoxal dinitrophenylosazone, m. p. 238–240°, when treated under the same conditions.

Dibutylchloramine with Acetic Anhydride.—When a mixture of 48.9 g. (0.3 mole) of dibutylchloramine and 91.8 g. (0.9 mole) of acetic anhydride had reacted together for four hours a solid began to appear. After seven days, no more electropositive chlorine could be detected. The whole was poured into 500 g. of ice and neutralized with 140 cc. of 50% aqueous potassium hydroxide and extracted with ether. This ether solution was extracted with 35 cc. of 12% hydrochloric acid, then with aqueous sodium chloride solution, and was dried with magnesium sulfate for distillation. The acid washing liquor was made basic to yield 2.50 g. of oil, b. p. 109° (7 mm.), n^{25}D 1.4439, but no dibutylamine.

The dried ether solution was distilled first at 7 mm. to yield 4 g. of chlorinated material, not identified, n^{25}D 1.1456, and then at 0.5 mm. The principal distillate boiled at 78–95° and weighed 40 g. Although it was contaminated with material which contained halogen, its density at 20° (0.9) and its refractive index, n^{25}D 1.4445, showed that it was essentially halogen-free. By contrast, final fractions of 4.4 g. (b. p. 95–98°) and 7.1 g. (b. p. 128°) were rich in halogen according to their refractive indices, n^{25}D 1.4564 and n^{25}D 1.4729, respectively.

The principal yield of 40 g. was refractionated with difficulty because of continual decomposition. From it was obtained 8.27 g., b. p. 73° (0.02 mm.), n^{25}D 1.4407 melting at −8 to −10°. A mixed melting point with N-butylbutyramide, m. p. −7 to −6° was not lowered. This yield, 21% of theoretical, represents a minimum of the compound which actually was present. The remainder of the 40 g. of product was not positively identified but its refractive index, n^{25}D 1.4437, indicated that it was dibutylacetamide.

Decomposition occurred during all of these distillations and these decomposition products, caught in a trap chilled to −75°, weighed 8.8 g. Fractionation of the material was very unsatisfactory owing to a tendency toward separation into two phases when the liquid was warmed above 60°. The second phase disappeared when the distillation temperature reached 94°. The distillation yielded two main fractions boiling at 90–92° (750 mm.), wt. 2.2 g. and 1.13 g., b. p. 115–125° (750 mm.). The first of these fractions, n^{25}D 1.4580, could not be recognized by its analysis (32.1% carbon, 5.82% hydrogen) but it must have been largely ethylglyoxal since it gave a 60% yield of the monophenylhydrazone when it was treated with 1.1 equivalent of phenylhydrazine in ethanol. This compound, m. p. 133–136°, was purified by crystallization from ethanol and isopropyl ether to melt at 134.5–135.5°. It was then halogen-free.

Anal. Calcd. for $C_{10}H_{12}N_2O$: C, 68.3; H, 6.88; N, 15.9. Found: C, 68.6; H, 7.10; N, 15.9.

When 0.3 g. of this ethylglyoxal phenylhydrazone was treated in boiling ethanol solution with 0.3 g. of phenylhydrazine and then filtered, after treatment with Darco decolorizing charcoal, an oil appeared after dilution with water and acetic acid. When hydrochloric acid was added, this solidified to a crystal mass melting at 158–159°. Crystallization from hot ethanol–chloroform mixture yielded the phenylosazone hydrochloride of ethylglyoxal, m. p. 168°. This was identified by mixed melting point.

The aldehydic fraction boiling at 115–125° contained chlorine but no nitrogen, n^{25}D 1.3773, m. p. −8 to 0°. According to its analysis it might be 1-acetoxy-2-chloro-1,2-dihydroxybutane.

Anal. Calcd. for $C_6H_{11}O_4Cl$: C, 39.6; H, 6.1. Found: C, 39.4; H, 6.5.

When this material was treated with excess phenylhydrazine in ethanol plus a trace of acetic acid, it yielded the osazone of ethyglyoxal, m. p. 112–114°, authenticated by mixed melting point.

When 0.18 g. of this aldehydic distillate was treated with 0.18 g. of 2,4-dinitrophenylhydrazine in boiling ethanolic hydrochloric acid only a slight precipitate of ethoxyethylglyoxal 2,4-dinitrophenylosazone appeared. The main product, *ca.* 0.1 g., was precipitated by addition of water to melt at 155–175°. Repeated crystallization from boiling ethanol (30 cc./g.) raised this melting point to 194.5°. The compound contained chlorine, and is believed to be the hydrochloride of ethylglyoxal 2,4-dinitrophenylosazone.

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[9] J. W. Suggitt and G. F Wright, THIS JOURNAL, **69**, 2073 (1947).

Anal. Calcd. for $C_{16}H_{15}N_8O_8Cl$: C, 40.0; H, 3.14; N, 23.3. Found: C, 39.9; H, 3.16; N, 23.3.

Summary

1. The spontaneous decomposition of dibutylchloramine yields dibutylammonium chloride and a distillable fraction believed to be a mixture of N-*n*-butyl mono-, di- and trichlorobutanaldimines with the second of these compounds predominating. Other compounds seem to be present, but phenyl and dinitrophenylhydrazones and osazones of these three have been isolated.

2. Decomposition of dibutylchloramine in alcohols follows the same course, but hydrolysis of the aldimines occurs to give monobutylammonium chloride and ethylglyoxal.

3. Decomposition of dibutylchloramine in acetic acid or its anhydride gives also dibutylacetamide and, in the latter reagent, N-*n*-butylbutyramide.

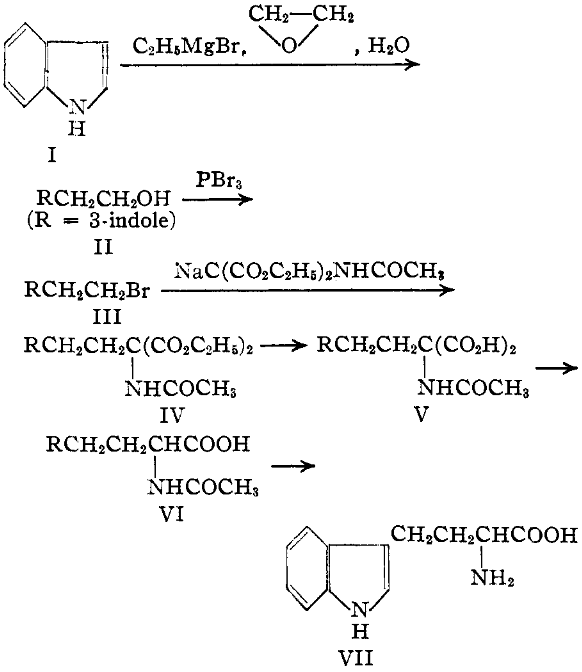
TORONTO, ONTARIO RECEIVED NOVEMBER 26, 1947

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

A Synthesis of *dl*-Homotryptophan

BY H. R. SNYDER AND FREDERICK J. PILGRIM

Homotryptophan [α-amino-γ-(3-indole)-butyric acid, VII] has been synthesized to permit physiological studies of the substance, particularly with reference to its possible action as an antimetabolite. The reactions employed in the synthesis are shown in the accompanying diagram.



Tryptophol (II) was prepared from indole (I) by the method of Oddo and Cambieri[1] which consists in the treatment of indole-magnesium bromide with ethylene oxide. Phosphorus tribromide was employed to convert tryptophol to the corresponding bromide (III) as described previously.[2] Alkylation of ethyl sodioacetylaminomalonate[3] by III was found to take place readily and in good yield (about 60%). The alkylation product, ethyl α-acetamino-α-carbethoxy-γ-(3-indole)-butyrate (IV), as obtained directly from the reaction mixture was of sufficient purity for conversion to V. Saponification of IV to the corresponding malonic acid, V, was effected by refluxing a mixture of IV with dilute sodium hydroxide solution; an almost quantitative yield of V was obtained.

Decarboxylation of the substituted malonic acid was brought about by refluxing an aqueous suspension of the material for several hours. *dl*-N-Acetylhomotryptophan (VI) was isolated from the mixture as the monohydrate. It was found convenient to purify the substance as the monohydrate; deacetylation of the pure monohydrate by hot dilute sodium hydroxide produced *dl*-homotryptophan (VII) in a state of high purity and in almost quantitative yield.

Experimental[4,5]

Ethyl α-Acetamino-α-carbethoxy-γ-(3-indole)-butyrate (IV).—To a solution prepared from 75 ml. of absolute ethanol and 0.58 g. of sodium were added 5.44 g. of ethyl acetaminomalonate and 5.50 g. of β-(3-indole)-ethyl bromide[2] (III). The reaction mixture was refluxed for fifteen hours with mechanical stirring. The hot mixture was filtered, the insoluble material on the filter was washed with 50 ml. of hot absolute ethanol, and the combined filtrate and washings were concentrated under reduced pressure to a small volume (about 20 ml.). The residue was cooled to 5° and filtered. The light yellow crystals on the filter were washed with 50 ml. of cold absolute ethanol to give a white product (IV), m. p. 161–163°; yield, 4.8 g. Concentration of the mother liquor to a few milliliters and addition of 30 ml. of anhydrous ether to the residue yielded a precipitate, mainly sodium bromide. Extraction of this precipitate with small portions of warm water left a residue of crude IV (0.3 g.), m. p. 153–156°. A dark oily residue was obtained when the mother liquor from the second crop of crude product was evaporated to dryness under reduced pressure. No additional product was isolated from the oily residue. The over-all yield of IV, sufficiently pure for conversion to V, was 5.1 g. (57.6%). A sample of pure IV, prepared for analysis by recrystallization from 95% ethanol, melted at 163–164°.

Anal. Calcd. for $C_{19}H_{24}O_5N_2$: N, 7.77. Found: N, 7.74.

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[1] Oddo and Cambieri, *Gazz. chim. ital.*, **69**, 19 (1939).

[2] Hoshino and Shimodaira, *Ann.*, **520**, 19 (1935).

[3] (a) Snyder, Shekleton and Lewis, THIS JOURNAL, **67**, 310 (1945): (b) Albertson and Archer, *ibid.*, **67**, 308 (1945).

[4] All melting points are corrected.

[5] Microanalyses by Miss Theta Spoor and Mr. Howard Clark.