our interest in potential antimetabolites of pyridoxine. 3-*O*-*p*-Toluenesulfonylpyridoxol was found by Dr. Charles A. Nichol to be devoid of any vitamin or antivitamin activity in *Saccharomyces carlsbergensis*.

Experimental

α^4,α^5-*O*-Isopropylidenepyridoxol.—(a). Pyridoxol hydrochloride (12.0 g., dried) was suspended in acetone (300 ml., freshly distilled). A fine stream of dry hydrogen chloride gas was passed into the suspension, the reaction mixture being kept in an ice bath. After 25 min., 13.0 g. of hydrogen chloride was taken up. The reaction mixture was shaken on a wrist action shaker for 1 hr. and was kept at −10 to −20° overnight. Filtration and washing with dry ether yielded 10.0 g. of crystalline material, which was shown by thin-layer chromatography on silica gel "G" (chloroform–methanol, 1:1) to consist of starting material and α^4,α^5-*O*-isopropylidenepyridoxol hydrochloride in about equal proportions. The mixture of the hydrochlorides was suspended in potassium carbonate solution (100 ml.), and was kept at 5° for several hours. The crude isopropylidenepyridoxol (5.4 g., 44%) had a m.p. of 165–170°, which was raised to 184–185° after crystallization from aqueous methanol.

Anal. Calcd. for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.05, H, 7.36; N, 6.60.

(b). Pyridoxol hydrochloride (12.0 g.) was suspended in acetone (250 ml.) and cooled in ice. Hydrogen chloride gas (11.0 g.) was passed into the suspension in the course of 5 min. Further processing was carried out as described in (a). The yield was 9.1 g. (74%) of crude material of m.p. 170–175; the infrared spectrum of which was essentially the same as that of authentic α^4-α^5-*O*-isopropylidenepyridoxol.

Hydrolysis of α^4,α^5-*O*-isopropylidenepyridoxol.—The ketal (0.245 g.) was dissolved in 1 *N* hydrochloric acid and was heated at 85–90° for 40 min. Water was removed on a flash evaporator, and the residue was dried. The material (0.225 g.) had a m.p. of 210–212° dec., and its infrared spectrum was indistinguishable from that of authentic pyridoxol hydrochloride.

3-*O*-Benzoyl-α^4,α^5-*O*-isopropylidenepyridoxol.—The ketal (2.415 g.) was dissolved in dry pyridine (50 ml.), cooled to 0°; and treated with benzoyl chloride (2.5 ml.). After standing for 2 hr., water (50 ml.) was added. The benzoate (3.23 g.) crystallized on standing in a refrigerator, and had a m.p. of 104–106°. Crystallization from aqueous ethanol raised the m.p. to 107–109°.

Anal. Calcd. for $C_{18}H_{19}NO_4$: C, 69.00; H, 6.10; N, 4.47. Found: C, 68.86; H, 6.43; N, 4.34.

3-*O*-*p*-Toluenesulfonyl-α^4-α^5-*O*-isopropylidenepyridoxol.—The ketal (1.05 g.) was dissolved in pyridine (50 ml.) and treated with *p*-toluenesulfonyl chloride (2.23 g.) at room temperature for 16 hr. Addition of water gave an oily product which crystallized on prolonged standing. Crystallization from ethanol yielded the pure tosylate (1.45 g.), m.p. 145–146°.

Anal. Calcd. for $C_{18}H_{21}NO_6S$: C, 59.49; H, 5.83; S, 8.80. Found: C, 59.76; H, 6.00; S, 8.96.

3-*O*-Methanesulfonyl-α^4,α^5-*O*-isopropylidenepyridoxol was similarly obtained. The mesylate had a m.p. of 72–73° after crystallization from ether–petroleum ether.

Anal. Calcd. for $C_{12}H_{17}NO_6S$: C, 50.17; H, 5.97; S, 11.17. Found: C, 49.97; H, 6.05; S, 11.29.

3-*O*-*p*-Toluenesulfonylpyridoxol was obtained by hydrolysis of *p*-toluenesulfonyl-α^4,α^5-*O*-isopropylidenepyridoxol (0.90 g.) with 10% formic acid (100 ml.) containing 20 ml. of ethanol. After heating for 30 min. on a steam bath, the solvents were removed on a flash evaporator, and the oil was crystallized from ethanol. The monotosylate (0.63 g.) had a m.p. of 184–186°, which was raised to 186–187 by two crystallizations from a mixture of chloroform and methanol.

Anal. Calcd. for $C_{15}H_{17}NO_5S$: C, 55.72; H, 5.30; S, 9.90. Found: C, 55.87; H, 5.56; S, 10.22.

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The Ultraviolet Light-Catalyzed Decomposition of N-Chlorodi-*n*-butylamine

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The effect of ultraviolet light on N-chlorodi-*n*-butylamine in carbon tetrachloride and benzene was studied in order to secure more information on the function of the sulfuric acid in the Hofmann–Löffler reaction.[1,2] The irradiation caused the precipitation of di-*n*-butylamine hydrochloride in amounts which varied with the temperature and time used. The results obtained are given in Table I.

TABLE I

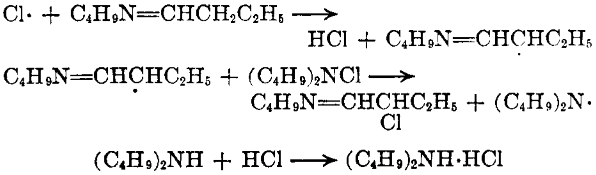
YIELDS OF DI-*n*-BUTYLAMINE HYDROCHLORIDE FORMED IN THE IRRADIATION OF N-CHLORODI-*n*-BUTYLAMINE

Temp. °C.	Time, hr.	Per cent yield[b]
25	24[a]	1.3
25	24	12.4
25	1140	47.3
6	24	11.7
77	96	55.7
25[c]	24	14.0

[a] Absence of light. [b] Basis of N-chloroamine present. [c] In benzene, the remaining runs were in carbon tetrachloride.

The carbon tetrachloride filtrate from the 1140-hour run gave after treatment with alkali only one identifiable product, *n*-butylamine, which was isolated and identified as *n*-butylbisbenzenesulfonimide.

The products obtained parallel those obtained by Wright[3] in the thermal decomposition of N-chlorodi-*n*-butylamine and are formed by the following free radical mechanism



$$(C_4H_9)_2NCl \xrightarrow{h\nu} (C_4H_9)_2N\cdot + Cl\cdot$$

$$2(C_4H_9)_2N\cdot \longrightarrow (C_4H_9)_2NH + C_4H_9N{=}CHCH_2C_2H_5$$

$$Cl\cdot + C_4H_9N{=}CHCH_2C_2H_5 \longrightarrow HCl + C_4H_9N{=}CH\underset{\cdot}{C}HC_2H_5$$

$$C_4H_9N{=}CH\underset{\cdot}{C}HC_2H_5 + (C_4H_9)_2NCl \longrightarrow C_4H_9N{=}CH\underset{Cl}{C}HC_2H_5 + (C_4H_9)_2N\cdot$$

$$(C_4H_9)_2NH + HCl \longrightarrow (C_4H_9)_2NH\cdot HCl$$

Further chlorination of the Schiff's base of α-chlorbutyraldehyde is possible to the dichloro derivative. Products derived from the chlorinated butyraldehydes were not found in this investigation but have been reported by Wright.[3]

The results indicate that di-*n*-butylamine free radicals in carbon tetrachloride undergo mainly a bimolecular disproportionation reaction. In the Hofmann–Löffler reaction the radical is protonated and is prevented from undergoing this disproportionation by the repulsion of the positive charges.

Experimental[4]

Di-*n*-butylamine (11.6 g.) was chlorinated in pentane by the method of Coleman.[5] The yield of N-chlorodi-*n*-butylamine based on active halogen titration was 85%. This yield varied in other runs from 85–95%. The pentane was removed under reduced pressure at 0° and carbon tetrachloride (100 ml.) was added to the residue. The resulting solution was irradiated with an ultraviolet lamp for 1140 hr., after which time no more active halogen could be detected. The white solid (5.93 g.) obtained proved to be di-*n*-butylamine hydrochloride from its elemental analysis. The infrared spectra were identical with that of an authentic sample.

The filtrate was made alkaline and steam distilled. The distillate upon concentration to 100 ml. and treatment with sodium hydroxide and benzenesulfonyl chloride gave a sticky solid (2.8 g.) which melted at 80.5–81.5° after three recrystallizations from 80% ethanol. This product from its elemental analysis proved to be *n*-butylbisbenzenesulfonimide.

Anal. Calcd. for $C_{16}H_{19}NS_2O_4$: C, 54.39; H, 5.38. Found: C, 54.21; H, 5.37.

Since the literature[6] reports a melting point of 89–90°, an authentic sample was synthesized by treating *n*-butylamine with benzenesulfonyl chloride in alkali and found to melt at 81–82°. A mixture melting point and infrared spectra of the two samples were identical.

Acknowledgment.—The authors wish to express their appreciation to Smith, Kline and French Laboratories for a fellowship which made this investigation possible.

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The Reaction of 2- and 4-Triphenylmethylpyridine with Ethyl Iodide

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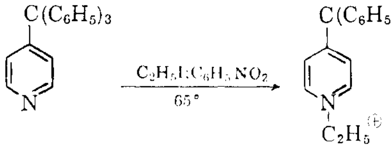
Several years ago we reported[1] that when the triphenylmethyl group is attached to an aromatic ring it functions as a neutral entity, *i.e.*, like hydrogen it is neither electron-supplying or -withdrawing. This conclusion was reached by a determination of its sigma constant, which was essentially zero.

Recently, in connection with another problem, we had occasion to measure the rates of reaction of 2- and 4-triphenylmethylpyridine with ethyl iodide. The results completely substantiate our earlier conclusion regarding the electrical effect of the triphenylmethyl group and provide graphic illustration of the steric bulk of this group.

The reaction of tertiary amines (like 2- and 4-triphenylmethylpyridine) with alkyl halides (Menschutkin reaction) has received considerable study.[2–4] For example, Professor Brown has used this reaction in a most effective way to demonstrate steric bulk in both the amine molecule as well as the alkyl halide.[5] Simple bimolecular kinetics are invariably observed in these reactions.



$$C_2H_5I:C_6H_5NO_2,\ 65° \longrightarrow C_2H_5^{\oplus}\ I^-$$

(I)

Table I lists representative rate data that were obtained for the reaction of 4-tritylpyridine with ethyl iodide (equation 1 above). The data for run I in this table are plotted in Fig. 1. *Significantly, 2-triphenylmethylpyridine did not react appreciably with ethyl iodide even after fifty hours under the same reaction conditions.*

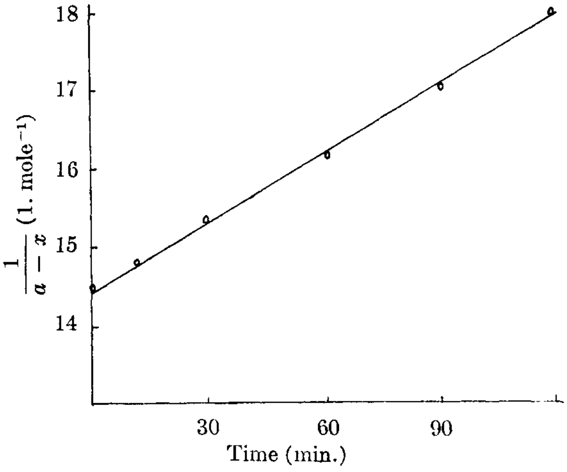


Fig. 1.—Rate data (run I) for the reaction of 4-triphenylmethylpyridine with ethyl iodide at 65°.

The data in Table I clearly substantiate our earlier conclusion[1] concerning the negligible electri-

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