m.p. 178–180°). Mixed melting point with the biosynthetic preparation[9] was 176–178° (corr.).

Anal. Calcd. for $C_{16}H_{17}O_7N \cdot H_2O$: C, 54.40; H, 5.39; N, 3.96. Found: C, 55.06; H, 5.60; N, 3.62.

Paper chromatography in 1-butanol–1-propanol–water; 2/1/1, gave R_f = 0.15; mixed chromatogram with biosynthetic compound gave one fluorescent spot R_f = 0.19. When large amounts were chromatographed, an additional slower moving fluorescent spot was observed. This could be decreased but not removed by repeated recrystallizations. Paper electrophoresis on Whatman 3 MM, *p*H 9.2, 0.05*M* borate, 500 volts, for 3.5 hr. gave one major fluorescent spot which moved 7 cm. toward the anode. The biosynthetic preparation had the same mobility. The minor component moved 1 cm. toward the cathode.

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(9) The author is indebted to Dr. Mortimer Levitz for a sample of this preparation.

Products of the Oxidation of Nitrolutidine and Nitrocollidine

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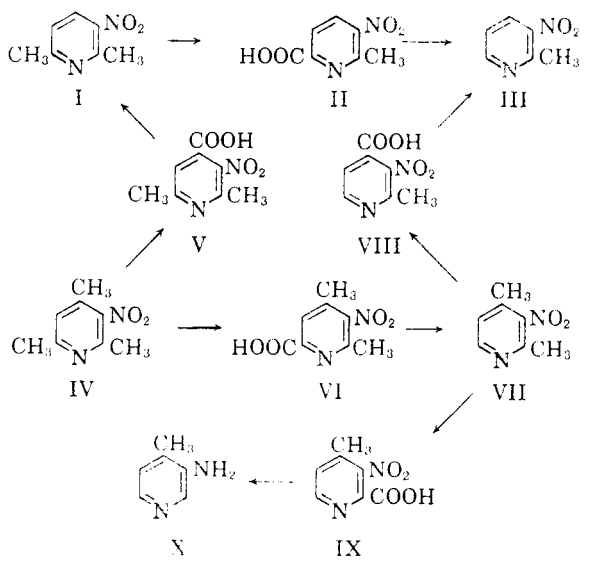
The nitration of 2,6-lutidine using the method of Plazek[2] gave an 80% yield of 3-nitro-2,6-lutidine (I). Upon treating this product with an amount of potassium permanganate calculated to oxidize one methyl group, an acid (II) was obtained in 17% yield which was then decarboxylated in 97% yield to 3-nitro-2-methylpyridine (III). Again, oxidation of this material gave 17% of a nitropyridinecarboxylic acid which was shown to be 3-nitro-2-pyridinecarboxylic acid[3a] by comparison with the corresponding amino compound of known structure prepared by Sucharda.[3b] Kogl and co-workers[4] oxidized 3-nitro-2,4,6-collidine (IV) to a mixture of three acids; the main product melted at 136°, which they assumed to be 3-nitro-2,4-dimethylpyridine-6-carboxylic acid (VI). We oxidized the nitrocollidine and obtained two acids. The third acid, if present, was in an amount not detected by our method. The acid melting at 138° was the main product and was decarboxylated to a



nitrolutidine (VII) which on further oxidation gave two products both nitromethylpyridinecarboxylic acids. The lower melting (IX) of these two acids was then decarboxylated and the product proved to be 3-nitro-4-methylpyridine by reduction to 3-amino-4-methylpyridine (X) and comparison with a known sample. The higher melting acid (VIII) was decarboxylated and the product identified as 3-nitro-2-methylpyridine (III). Thus it is definitely established that the original main oxidation product of nitrocollidine is 3-nitro-2,4-dimethylpyridine-carboxylic acid (VI) as it is the only one that could produce the obtained result. The second acid melted at 238° which was an indication that it might be a 4-carboxylic acid, namely, 3-nitro-2,6-dimethylpyridine-4-carboxylic acid (V). This was confirmed when the product of decarboxylation was shown to be 3-nitro-2,6-lutidine (I).

EXPERIMENTAL

3-Nitro-2,6-lutidine. 2,6-Lutidine (174 g.) was nitrated by the method of Plazek[2] to give 200 g. (81%) of 3-nitro-2,6-lutidine (I), boiling at 105° (10 mm) and melting at 38°.

3-Nitro-2-methylpyridine-6-carboxylic acid (II). One hundred grams of 3-nitro-2,6-lutidine in 1.5 l. of water was heated to 90° and treated with 200 g. of solid potassium permanganate in small portions over a period of 1.5 hr. After removal of the manganese dioxide, the filtrate was extracted with ether to recover 50 g. of unchanged nitro compound. The aqueous solution was evaporated to low volume and acidified. Ten grams of acid was recovered melting at 126°.

Anal.[5] Calcd. for $C_7H_6O_4N_2$: C, 46.16; H, 3.32. Neut. equiv., 182. Found: C, 45.96; H, 3.37. Neut. equiv., 185.

3-Nitro-2-methylpyridine. 3-Nitro-2-methylpyridine-6-carboxylic acid (14.2 g.) was decarboxylated by heating under nitrogen (bath temp. 205°) under 320 mm. pressure. There was obtained 10.5 g. (97.6%) of 3-nitro-2-methylpyridine[3a] (III) boiling at 104° (15 mm) and melting at 28.5°. The

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picrate melted at 122.3°, the hydrochloride at 157–158°, and the chloroferrate[6] at 82.5°.

3-Aminopyridine-2-carboxylic acid. 3-Nitro-2-methylpyridine (III) (25 g.) was oxidized by 57 g. of potassium permanganate as previously described. There was obtained 3 g. of acid which was recrystallized from alcohol-water and melted at 122–123°. The yield of purified product was 12% based on starting material not recovered.

This acid (2 g.) was reduced by heating in a mixture of powdered iron, hydrochloric acid, and alcohol for 2 hrs. The amino acid was purified thru the copper salt and there was obtained 1 g. (62%) melting at 217°. Mixed melting point with a sample of this acid prepared by the method of Sucharda[3b] showed no depression.

3-Nitro-2,4,6-collidine. 2,4,6-Collidine (180 g.) was nitrated according to Plazek.[2] There was obtained 226 g. (93%) boiling at 120° (19 mm.) and melting at 38°.

Acid mixture by oxidation of 3-nitro-2,4,6-collidine. 3-Nitrocollidine (IV) (200 g.) was oxidized with 400 g. of solid potassium permanganate as previously described. The crude acid obtained was recrystallized from alcohol-water (1:1) to give 25 g. (13% based on starting material unrecovered) of 3-nitro-2,4-dimethylpyridine-6-carboxylic acid (IV) melting at 138°.

Anal. Calcd. for $C_8O_2N_2$: C, 48.98; H, 4.11. Found: C, 49.20; H, 3.89.

On standing the filtrate gradually deposited 0.5 g. of 3-nitro-2,6-dimethylpyridine-4-carboxylic acid (V) melting at 238°.

Neut. equiv. Calcd. for $C_8H_8O_2N_2$: 196. Found: 194.

3-Nitro-2,4-dimethylpyridine. 3-Nitro-2,4-dimethylpyridine-6-carboxylic acid (VI) (30 g.) was decarboxylated at a bath temperature of 180–220° in a nitrogen atmosphere at 260 mm. There was obtained 20 g. (86%) of 3-nitro-2,4-dimethylpyridine (VII) boiling at 113° (20 mm.). The material had a freezing point of 9.5°, formed a picrate melting at 151°, and a hydrochloride melting at 144°.

Anal. Calcd. for $C_7H_8O_2N_2$; C, 55.26; H, 5.30. Found: C, 54.93; H, 5.36.

Reduction in a Parr low pressure hydrogenation apparatus using palladum on charcoal gave a quantitative yield of amine melting at 74–75°.

Decarboxylation of 3-nitro-2,6-dimethylpyridine-4-carboxylic acid (V). One gram of this acid was decarboxylated in the above manner to give 3-nitro-2,6-dimethylpyridine (I) melting at 38°. The picrate melted at 141° and a mixed melting point with authentic material showed no depression.

Acid mixture from the oxidation of 3-nitro-2,4-dimethylpyridine. Ten grams of nitro compound (VII) was oxidized by 20 g. of potassium permanganate as previously described. The crude acid mixture so obtained was recrystallized from alcohol-water (1:1). The first crop obtained by cooling a short time was 0.5 g. of 3-nitro-4-methylpyridine-2-carboxylic acid (IX) melting at 138°.

Anal. Calcd. for $C_7H_6O_4N_2.H_2O$: C, 42.03; H, 4.03. Found: C, 41.56; H, 3.73.

On standing overnight the mother liquor from the above product precipitated 1.5 g. of 3-nitro-2-methylpyridine-4-carboxylic acid (VIII) melting at 250–252° (sealed tube).

Anal. Calcd. for $C_7H_6O_4N_2$: C, 46.16; H, 3.32. Neut. equiv., 182. Found: C, 46.44; H, 3.45. Neut. equiv., 185.

3-Amino-4-methylpyridine. 3-Nitro-4-methylpyridine-2-carboxylic (IX) acid (0.5 g.) was decarboxylated with a bath temperature of 145°. The decarboxylated material was then reduced by refluxing for 1 hr. in a mixture of ethyl alcohol, iron powder, and hydrochloric acid. After making the mixture basic, extracting with ether and evaporating, there was obtained white crystals of 3-amino-4-methylpyridine (X) melting at 105° and giving no melting point depression with an authentic sample.[3a,7]

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3-Nitro-2-methylpyridine. 3-Nitro-2-methylpyridine-4-carboxylic (VIII) acid (1.5 g.) was decarboxylated at a bath temperature of 280° to yield 0.8 g. of 3-nitro-2-methylpyridine[3a] (III) melting at 28.5°. The picrate melted 122–123° and the hydrochloride 157–158°.

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Dichlorophosphination

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Although the reaction of aromatic compounds with phosphorus trichloride and anhydrous aluminum chloride, dichlorophosphination, has long been known[1] and improved upon[2,3] the orientation of the entering group has generally been assumed and has been determined in only a few cases. For example, Kosolapoff[4,5] used an extended fractional crystallization of the mixed tolylphosphonic acids to determine the isomer distribution. He found an *ortho:meta:para* ratio of 1.0 : 2.7 : 6.3 for the tolylphosphonic acids with an approximate 15% loss of the acids during the crystallizations. Ethylbenzene yielded mainly the *para* isomer with a small amount of an ethylphenylphosphonic acid which was thought to be the *meta* isomer (*meta:para* = *ca.* 1.0 : 8.8). Other workers have generally assumed that dichlorophosphination gives only the *para* isomer[2b,6–8] or a mixture of *ortho* and *para* isomers.[4]

We have examined the dichlorophosphination of ethylbenzene, *p*-xylene, and chlorobenzene, utilizing a combination of infrared and vapor phase chromatographic techniques to establish the isomer distribution. Ethylbenzene formed only the *meta* and *para* isomers in a ratio of 1.00/1.63,[9] and *p*-xylene yielded only the 1,2,4- isomer. On the other

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(9) A small quantity of phenyldichlorophosphine was identified presumably arising from a dealkylation of ethylbenzene. A similar phenomenon has been observed during the dichlorophosphination of *sec*-amylbenzene.[2] We thank Dr. D. R. Stern for helpful discussions concerning alkyl group migration reactions. See D. R. Stern, Ph.D. thesis, University of Southern California, 1951