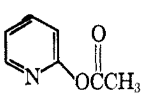
of a ketene acetal intermediate, followed by a hydrolysis sequence.

Ethoxyacetylene very slowly combined with 4-pyridone to give a crude liquid, which was fractionated by distillation. The first cut solidified on cooling and was characterized as the known 4-acetoxypyridine (III).[19] This particular compound is very unstable and upon exposure to moisture quickly reverts to 4-pyridone. The second product darkened on exposure to light, but sufficient spectral information was gathered to permit the red liquid to be described as N-(1-ethoxyvinyl)-4-pyridone (IV). In the infrared spectrum, peaks were observed at 1640 (conjugated ketone) and 1290 cm^{-1} (vinyl ether), while the ultraviolet contained a maximum at 277 mμ, somewhat displaced from the band at 256 mμ in 4-pyridone. Again the nuclear magnetic resonance spectrum held the expected signals at δ 1.38 (methyl), 4.04 (aliphatic methylene), 4.17 and 4.45 (vinyl methylene), 6.36 (two ring hydrogens near oxygen), and 8.05 (two ring hydrogens near nitrogen). In conclusion, 2- and 4-pyridone add to ethoxyacetylene to afford both O and N substitution, but do not react in a Diels-Alder fashion under the conditions described here.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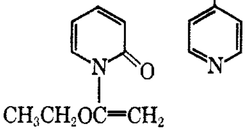
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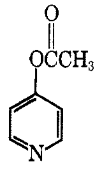
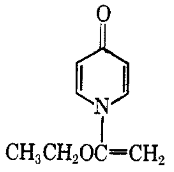

III


IV

Experimental Section[20]

2-Acetoxypyridine (I) and N-(1-Ethoxyvinyl)-2-pyridone (II).—A solution of 2-pyridone (18.0 g, 0.189 mole) and ethoxyacetylene (33 ml, furnished as a 62% hexane azeotrope from the Humphrey Chemical Company) in chloroform (100 ml) under anhydrous conditions was refluxed for 20 days, at which time there was added additional ethoxyacetylene (20 ml). By 27 days the 2-pyridone had disappeared from the reaction liquid as judged by thin layer chromatographic screening. The chloroform was removed under reduced pressure and the residual black oil was distilled to yield 2-acetoxypyridine [17.4 g, 67%; clear liquid; bp 74-76° (0.95 mm) (lit.[8] 110-112° (10 mm)); n^{21}_{D} 1.5032; the ultraviolet spectrum gave λ_{max} 227 (ϵ 1760), 258 (2640), 264 sh (2100), and 303 broad mμ (786); the infrared spectrum gave 3080 w (aromatic CH), 3015 w, 2935 w (acetoxy CH), 1768 s (C=O), 1628 m (C=C), 1595 s, 1573 m, 1471 s (CH_3), 1435 s (C=N), 1371 s (CH_3), 1195 vs (C-O-C), 1146 m, 1045 m, 1012 m, 995 m, 915 m, 841 m, (CH), 770 m, and 740 m cm^{-1}; the nmr spectrum showed peaks at δ 2.27 (methyl, singlet, area 3), 7.21 (ring hydrogen 3, doublet, area 1, J = 8 and 1 cps), 7.23 (ring hydrogen 5, pair of doublets with fine structure, area 1, J = 8, 5, and 1 cps), 7.82 (ring hydrogen 4, doublet of triplets, area 1, J = 8, 8, and 2 cps), 8.48 (ring hydrogen 6, pair of doublets, area 1, J = 5 and 2 cps)] and N-(1-ethoxyvinyl)2-pyridone [10.2 g, 33%; yellow oil; bp 108-110° (1.2 mm); n^{21}_{D} 1.5421; the ultraviolet spectrum λ_{max} gave 227 (ϵ 6100) and 303 broad mμ (4530); the infrared spectrum gave 3120 w (aliphatic CH), 3080 w, 3010 w, 2975 m, 2930 w, 2895 w, 2880 w, 1670 s (C=O), 1598 s, 1533 s, 1385 m, 1286 s, 1210 m, 1141 m, 1090 s, 1045 m, 977 m, 856 m (=CH_2), and 762 m cm^{-1}; the nmr spectrum showed peaks at δ 1.32 (methyl, triplet, area 3, J = 7 cps), 4.00 (aliphatic methylene, quartet, area 2, J = 7 cps), 4.47 and 4.40 (vinyl methylene, AB pattern, area 2, J = 3 cps), 6.27 (ring hydrogen 5, triplet, area 1, J = 1 cps), 6.55 (ring hydrogen 3, doublet, area 1, J = 10 cps), 7.50 (ring hydrogen 4, pair of doublets, area 1, J = 10 and 7 cps), and 7.55 (ring hydrogen 6, doublet, area 1, J = 7 cps).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.15; H, 6.62; N, 8.30.

4-Acetoxypyridine (III) and N-(1-Ethoxyvinyl)-4-pyrdone (IV).—A solution of 4-pyridone (18.0 g, 0.189 mole) and ethoxyacetylene (33 ml) in chloroform (200 ml) under anhydrous conditions was refluxed for 5 days, at which time there was added additional ethoxyacetylene (15 ml). By 12 days the 4-pyridone had disappeared from the reaction liquid as judged by thin layer chromatographic screening. The chloroform was removed under reduced pressure and the residual black oil was distilled to yield 4-acetoxypyridine [10.6 g, 41%; bp 120-125° (2.1 mm); white needles, unstable to air; mp 130-133° (sealed capillary) and 135-145° (open capillary) (lit.[19] mp 140-150°); in the latter case, the recovered sample possessed an infrared spectrum consistent with a mixture of both 4-pyridone and 4-acetoxypyridine; the ultraviolet spectrum gave λ_{max} 256 mμ (ϵ 15,100); the infrared spectrum gave 3080 w, 3065 w (aromatic CH), 2920 w (acetoxy CH), 1727 s (C=O), 1662 s (C=C), 1635 s (C=C), 1601 s, 1555 m, 1578 w (CH_3), 1400 m (C=N), 1372 s (CH_3), 1339 m, 1255 s, 1191 s (C-O-C), 1075 s, and 850 s cm^{-1} (CH)] and N-(1-ethoxyvinyl)-4-pyridone [5.4 g, 17%; red oil; bp 140-148° (0.75 mm); n^{20}_{D} 1.5784; the ultraviolet spectrum gave λ_{max} 277 mμ (ϵ 5630); the infrared spectrum gave 2980 w (CH), 1640 s (C=O), 1590 s (C=C), 1470 m (CH_3), 1407 m, 1368 m, 1341 m (CH_3), 1290 s, 1186 s, 1130 w, 1111 w, 1095 m, 1042 s, 978 m, and 848 s (CH) cm^{-1}; the nmr spectrum showed peaks at δ 1.38 (methyl, triplet, area 3, J = 7 cps), 4.04 (aliphatic methylene, quartet, area 2, J = 7 cps), 4.17 and 4.45 (vinyl methylene, AB pattern, area 2, J = 4 cps), 6.36 (ring hydrogens 3 and 5, doublet, area 2, J = 8 cps), and 8.05 (ring hydrogens 2 and 6, doublet, area 2, J = 8 cps).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 64.84; H, 6.68; N, 8.27.

Registry No.—I, 3847-19-6; II, 14210-19-6; III, 14210-20-9; IV, 14210-21-0; ethoxyacetylene, 927-80-0; 2-pyridone, 142-08-5; 4-pyridone, 108-96-3.

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[20] The boiling and melting points are uncorrected. The infrared spectra were determined as neat films or in pressed potassium bromide disks with a Perkin-Elmer Model 421 spectrophotometer, ultraviolet spectra were measured in 95% ethanol on a Cary Model 14 spectrophotometer, and nuclear magnetic resonance spectra were obtained on a Varian A-60 spectrometer. Thin layer chromatography utilized silica gel G as the support, chloroform-methanol (1:1) for elution, and iodine vapor for development. Microanalyses were provided by the Microanalytical Laboratory, Department of Chemistry, Stanford University.

Hydrogenolysis by Hydrogen Transfer. Role of Palladium-Charcoal on Halogenated Benzo-Pyridine System

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In a systematic investigation on the synthesis of isoquinoline derivatives,[1-3] it has been observed that when 5-chloro-3-methyl-3,4-dihydroisoquinoline (IIIa) was subjected to dehydrogenation with palladium-charcoal (Pd-C) in tetralin or diphenyl ether in a carbon dioxide atmosphere, not only dehydrogenation but also dehalogenation occurs, yielding 3-methylisoquinoline (IVe)[4] in place of the expected 5-chloro-3-

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[1] T. N. Ghosh and B. Bhattacharya, *J. Indian Chem. Soc.*, **37**, 111 (1960).

[2] T. N. Ghosh, B. K. Ghosh, and B. Bhattacharya, *J. Sci. Ind. Res., India*, **21B**, 133 (1962).

[3] B. Bhattacharya, *Indian J. Chem.*, **2**, 25 (1964); B. Bhattacharya, *ibid.*, in press.

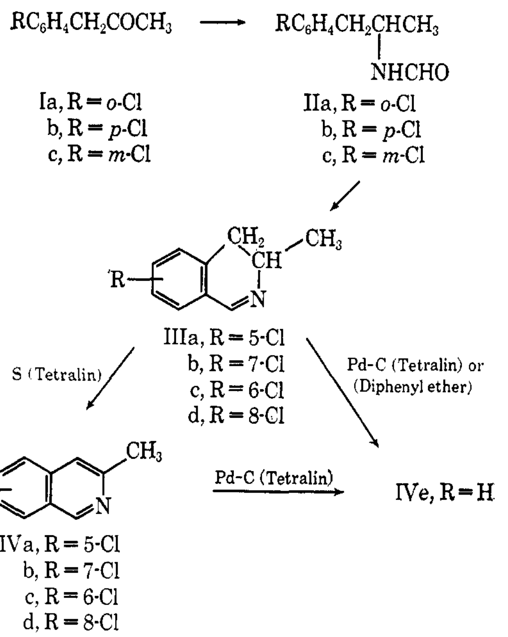
[4] S. Gabriel and A. Neumann, *Ber.*, **25**, 3563 (1892).

methylisoquinoline (IVa). Similar behavior was observed with the 6-, 7-, and 8-chloro derivatives (IIIb–d). Removal of chlorine atoms of 4,7-dichloroquinoline[5] with Pd–C in tetralin suggests that a chlorine atom occupying any position of the benzene ring of the benzo-pyridine system can be eliminated by this technique.

Metal-catalyzed hydrogen transfer in organic compounds between a substance acting as donor and a wide range of acceptors has been studied.[6,7] Ghosh, *et al.*,[8] have also observed such a type of hydrogen transfer in the isoquinoline series. It appears that chlorine has been eliminated in the form of palladous chloride and not as hydrogen chloride since no hydrochloride of the base can be detected either in the solvent or in the palladium–charcoal. The aqueous extract does not furnish any isoquinoline on basification; on the contrary it gives a positive test for chloride and palladium ions and also yields palladium sulfide with hydrogen sulfide.[9] The poor yield of palladous chloride may be due to its decomposition at 250° in the carbon dioxide atmosphere.[9] The reaction appears to involve the formation of palladium hydride[10,11] which takes up a chlorine atom, itself being converted to palladous chloride. The formation of palladium hydride is also supported by the fact that the compounds IVa–d remain unaffected in diphenyl ether which is incapable of donating hydrogen. Conversion of IVa–d to IVe with Pd–C in tetralin only and that of IIIa–d to IVe in tetralin as well as diphenyl ether prove conclusively that hydrogenolysis is caused by hydrogen transfer from either tetralin or the 3,4 positions of the pyridine nucleus of the benzo–pyridine system.

6-, 7-, and 8-chloro-3-methyl-3,4-dihydroisoquinolines (IIIb–d) were synthesised in the usual way. The mixture of IIId and IIIc was separated by chromatography over alumina. The assignment of 6-chloro and 8-chloro derivatives is based on infrared and nmr spectra. The infrared spectrum of IIId has a sharp band at 778 cm^{-1} [12,13] which is due to 1,2,3 substitution; this band is absent in IIIc which shows instead two other significant bands at 897[14] and 820 cm^{-1} [15] evidently due to 1,2,4 substitution in the aromatic ring.

The nmr spectrum of IIId contains a doublet around δ 8.05 due to H-1 which is split by H-3 by *meta*-coupling. This proton is more deshielded by the chlorine atom at position 8 than is H-1 in IIIb and the doublet is shifted to a higher field around δ 7.6. The splitting around 6.5 in IIId is due to three vicinal nonequivalent protons, characteristic of an ABC system. In IIIc this splitting is for three aromatic protons which form an AB$_2$ pattern.



Experimental Section

Melting points and boiling points are uncorrected. Melting points were determined in a "Büchi" melting point apparatus. The ultraviolet spectra (wavelengths expressed in mμ, extinction coefficients as ϵ) were determined with a Hilger spectrophotometer, Model H 700, in ethanol using quartz cells. Infrared spectra were determined with a Perkin-Elmer Model 137 on NaCl prism. Nmr spectra were determined with a Varian A-60 spectrometer at 60 Mc on solution in deuteriochloroform. Nmr absorptions are reported in parts per million (ppm) on the δ scale relative to tetramethylsilane (Me$_4$Si) as an internal standard. Sarabhai-Merck alumina was used for thin layer and column chromatography. The petroleum ether used was of bp 40–60°. The methanol was pure and dried over magnesium metal. The refractive index was determined with a Hilger refractometer.

Preparation of 1-*o*-Chlorophenyl-2-formamidopropane (IIa).—Ammonium carbonate (66 g) was dissolved in 66 g of formic acid (98–100%) and water was distilled out until the internal temperature recorded 165°. It was cooled to 100° and 30 g of *o*-chlorobenzyl methyl ketone[16] was added. Water was again distilled off slowly until the temperature reached 180°; it was maintained at 180–185° for 8 hr, then poured into ice water and extracted with ether. Removal of ether left a thick liquid (23 g), bp 208–210° (15 mm), n^{20}D 1.5439.

Anal. Calcd for $C_{10}H_{12}ClNO$: C, 60.76; H, 6.08; N, 7.09. Found: C, 60.91; H, 6.12; N, 7.18.

1-*p*-Chlorophenyl-2-formamidopropane (IIb).—It was similarly prepared from 1-*p*-chlorobenzyl methyl ketone:[17] thick liquid, bp 197–198° (3 mm); n^{20}D 1.5430.

Anal. Calcd for $C_{10}H_{12}ClNO$: C, 60.76; H, 6.08; N, 7.09. Found: C, 60.81; H, 6.17; N, 7.13.

***m*-Chlorobenzyl Methyl Ketone (Ic). *m*-Chlorophenylacetoacetonitrile.**—To boiling alcoholic sodium ethoxide (105.6 g of sodium dissolved in 1335 ml of dry ethanol) was added a mixture of 542 g of *m*-chlorobenzyl cyanide and 467.6 g of ethyl acetate during 1 hr and the mixture was refluxed for 8 hr. The reaction product was poured into ice water, washed with ether, and acidified with glacial acetic acid (blue litmus). The solid (440 g) was crystallized from benzene as colorless microcrystals, mp 102–103°.

Anal. Calcd for $C_{10}H_8ClNO$: C, 62.02; H, 4.13; N, 7.24. Found: C, 62.13; H, 4.27; N, 7.08.

A mixture of 440 g of *m*-chlorophenylacetoacetonitrile, 902 ml of glacial acetic acid, and 1959 ml of commercial hydrochloric acid was refluxed for 24 hr. The reaction mixture, after cooling, was diluted with twice its volume of water and the ketone Ic was isolated with benzene. The benzene solution, after washing with

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(16) I. B. Johns and J. M. Burch, *J. Am. Chem. Soc.*, **60**, 919 (1938).

(17) T. M. Patrick, Jr., E. T. McBee, and H. B. Hass, *ibid.*, **68**, 1134 (1946).

10% sodium hydroxide, was concentrated to afford 285 g of Ic, a straw-colored liquid, bp 84–85° (1 mm), $n^{20}\mathrm{D}$ 1.5322.

Anal. Calcd for C_9H_9ClO: C, 64.09; H, 5.34. Found: C, 64.22; H, 5.39.

The semicarbazone crystallized from ethanol–water as colorless flakes, mp 151–152°.

Anal. Calcd for $C_{10}H_{12}ClN_3O$: C, 5.32; H, 5.32; N, 18.62. Found: C, 53.41; H, 5.43; N, 18.73.

The 2,4-dinitrophenylhydrazone was obtained from ethanol–ethyl acetate as yellowish red microcrystals, mp 124–125°.

Anal. Calcd for $C_{15}H_{13}ClN_4O_4$: C, 51.7; H, 3.73; N, 16.07. Found: C, 52.01; H, 4.01; N, 16.14.

Nelson, *et al.*,[18] reported the characteristics of the ketone to be bp 82–86° (1 mm); $n^{20}\mathrm{D}$ 1.5351; 2,4-dinitrophenylhydrazone mp 104.5–106.5°; and semicarbazone mp 142–144°.

1-*m*-Chlorophenyl-2-formamidopropane (IIc) was prepared in the same manner as was IIa. A colorless heavy liquid with bp 184–185° (3 mm), $n^{20}\mathrm{D}$ 1.5442, was obtained.

Anal. Calcd for $C_{10}H_{12}ClNO$: C, 60.76; H, 6.08; N, 7.09. Found: C, 60.89; H, 6.14; N, 7.15.

5-Chloro-3-methyl-3,4-dihydroisoquinoline (IIIa).—Phosphorous pentoxide (111 g) was dissolved in 72 ml of orthophosphoric acid (85%) under stirring in a dry atmosphere and heated at 98–100° for 2 hr. To the syrupy mass was added 17.5 g of IIa at 70° followed by 22.5 ml of phosphorus oxychloride. The temperature was raised slowly to 130–140° under vigorous stirring and maintained for 8 hr; then it was poured into ice water, washed with ether, and basified with sodium hydroxide. The liberated base IIIa was isolated with ether. This was purified by the HCl–NaOH method. Removal of ether left a colorless liquid (5 g): bp 95–96° (0.1 mm); $n^{20}\mathrm{D}$ 1.5638; λ_{max} 256 mμ (ϵ 8134).

Anal. Calcd for $C_{10}H_{10}ClN$: C, 66.85; H, 5.57; N, 7.80. Found: C, 67.05; H, 5.71; N, 7.95.

The picrate crystallized from ethanol as yellow needles, mp 163–164°.

Anal. Calcd for $C_{10}H_{10}ClN$, $C_6H_3N_3O_7$: N, 13.71. Found: N, 13.91.

7-Chloro-3-methyl-3,4-dihydroisoquinoline (IIIb).—This isoquinoline was pepared from IIb in the same manner as described in case of IIIa. The colorless base IIIb, bp 96–98° (1 mm), solidified on standing and crystallized from petroleum ether (bp 60–80°): mp 59–60°; λ_{max} 256 mμ (ϵ 8939).

Anal. Calcd for $C_{10}H_{10}ClN$: C, 66.85; H, 5.57; N, 7.80. Found: C, 66.97; H, 5.68; N, 8.07.

The picrate was obtained from ethanol as yellow shining plates, mp 150–151°.

Anal. Calcd for $C_{10}H_{10}ClN$, $C_6H_3N_3O_7$: N, 13.71; Found: N, 13.83.

Modified Method of Preparation of 3-Methylisoquinoline (IVe).—Cyclization of 27.5 g of 1-phenyl-2-formamidopropane[19] was carried out exactly in the same manner as described in case of IIIa and the 3-methyl-3,4-dihydroisoquinoline was obtained as colorless liquid (14 g): bp 79–80° (0.01 mm); $n^{20}\mathrm{D}$ 1.5434; λ_{max} 256 mμ (ϵ 8347).

Anal. Calcd for $C_{10}H_{11}N$: C, 82.76; H, 7.59; N, 9.66. Found: C, 83.84; H, 7.78; N, 9.87.

The picrate crystallized from ethanol as yellow needles, mp 140–141° (lit.[19] mp 140–141°).

The above 3-methyl-3,4-dihydroisoquinoline was dehydrogenated and the base, bp 98–99° (0.3 mm), solidified on standing and crystallized from petroleum ether (bp 60–80°) as colorless plates: mp 66–67°; λ_{max} 222, 268, 314 mμ (ϵ 32,450, 3348, 1498).

Anal. Calcd for $C_{10}H_9N$: C, 83.92; H, 6.20; N, 9.79. Found: C, 83.88; H, 6.37; N, 9.95.

The picrate was obtained from ethanol as yellow needles, mp 197–198° (lit.[19] mp 197–198°).

Gibson[19] synthesised 3-methylisoquinoline by cyclizing 1-phenyl-2-formamidopropane with phosphorous pentoxide in tetralin and subsequent dehydrogenation and established the base as picrate in both cases. No details regarding their yield and characteristics of the bases were mentioned. By changing the condensing agent and cyclizing medium, the yield of the base has been greatly improved.

Action of Palladium–Charcoal on IIIa–d. Formation of 3-Methylisoquinoline (IVe).—A mixture of 4 g of (IIIa–d), 100 ml of tetralin, and 1.3 g of palladium–charcoal (10%) was heated under reflux at 240–245° (bath temperature) for 4 hr during which a current of dry carbon dioxide was passed. Palladium–charcoal containing palladous chloride was filtered off, after cooling, in a dry system and washed thoroughly with dry ether. The base was extracted out from the filtrate with two 50-ml portions of 10% hydrochloric acid. The acid solution was washed with ether, filtered through Norit, and basified with 10% sodium hydroxide. The liberated base IVe was isolated with ether and the ether was removed when a solid crystallized from petroleum ether (bp 60–80°): mp 66–67°; λ_{max} 222, 268, 314 mμ (ϵ 32450, 3348, 1498). The mixture melting point upon admixture with an authentic sample of IVe[4] showed no depression.

The same reaction of dehydrogenation and dehalogenation was realized when the reaction was carried out in diphenyl ether in place of tetralin.

The palladium–charcoal containing palladous chloride was triturated with chloride-free water and tested for palladium and chlorine. The mother liquor gave a positive test for chloride ion when treated with silver nitrate in the presence of concentrated HNO_3 and the precipitate of palladium sulfide with hydrogen sulfide.[9]

Cyclization of IIc. Formation of IIIc and IIId.—Cyclization of IIc and isolation of the corresponding isoquinolines IIIc and d were carried out according to the method mentioned in the case of IIIa. The mixture was a colorless mobile liquid: bp 105–106° (0.5 mm); a 82% yield was obtained; $n^{20}\mathrm{D}$ 1.5748.

The mixture was subjected to thin layer chromatography on alumina. The developing solvent was petroleum ether (bp 40–60°) plus dry methanol (39:1, v/v). A spray of Dragendorff's reagent made the chromatogram spots visible. The R_f value of IIId was found to be 0.74 and that of IIIc was 0.44.

Separation of A (IIId) and B (IIIc).—In column chromatographic separation, the mixture (10 g) in petroleum–methanol (39:1) was passed over 250 g of alumina when the first moving A (2.86 g) and the rest B (7.14 g) were obtained. Removal of the solvent was done under reduced pressure at 40°. The fraction A (IIId) was colorless: bp 107–108 (0.8 mm); $n^{20}\mathrm{D}$ 1.5741; λ_{max} 218, 260 mμ (ϵ 21,540, 9417). The infrared spectra exhibited bands at 1613 (>C=N) and 778 cm^{-1} (1,2,3 substitution). The nmr signals at δ 8.05 are due to deshielding by the chlorine atom of the 8 position and splitting at 6.5 is due to three vicinal nonequivalent protons.

Anal. Calcd for $C_{10}H_{10}ClN$: C, 66.85; H, 5.57; N, 7.80. Found: C, 66.92; H, 5.71; N, 7.68.

The picrate crystallized from ethanol as yellow needles, mp 214–215° dec.

Anal. Calcd for $C_{10}H_{10}ClN$, $C_6H_3N_3O_7$: N, 13.78. Found: N, 13.91.

Removal of the solvent of B left a colorless liquid: bp 106–107° (1 mm); $n^{20}\mathrm{D}$ 1.5749; λ_{max} 216, 262 mμ (ϵ 22,290, 14,010). The band at 1613 in the infrared spectra is for (>C=N) and the peaks at 820 and 897 cm^{-1} are due to 1,2,4 substitution. A doublet in nmr spectra around δ 7.6 is for chlorine at the 6 position and signals around 6.5 are for three aromatic protons.

Anal. Calcd for $C_{10}H_{10}ClN$: C, 66.85; H, 5.57; N, 7.80. Found: C, 66.87; H, 5.72; N, 7.93.

The picrate was obtained from ethanol as yellow needles, mp 175–176°.

Anal. Calcd for $C_{10}H_{10}ClN$, $C_6H_3N_3O_7$: N, 13.78. Found: N, 13.89.

Formation of Quinoline.—A mixture of 4 g of 4,7-dichloroquinoline, 250 ml of tetraline, and 2.5 g of palladium–charcoal (10%) was heated at 240–245° for 6 hr in a CO_2 atmosphere and the base was isolated, in the manner as described in the case of IVe, as a colorless liquid: bp 239°; picrate, mp 203.5–204.5°.

The formation of quinoline was identified by elemental analyses and superimposable ultraviolet absorption spectra of authentic sample.[20]

Dehydrogenation of IIIa–d.—The reaction was carried out in a similar manner as in the case of IVe using 1 g of flowers of sulfur in place of 0.5 g of palladium–charcoal. The base IVa is colorless: bp 109–110° (0.3 mm); $n^{20}\mathrm{D}$ 1.6092; λ_{max} 222, 276, 334 mμ (ϵ 50,910, 4587, 3656).

Anal. Calcd for $C_{10}H_8ClN$: C, 67.61; H, 4.51; N, 7.89. Found: C, 67.27; H, 4.67; N, 8.01.

The picrate was obtained from ethanol as fine yellow needles, mp 220–221°.

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Anal. Calcd for $C_{10}H_8ClN$, $C_6H_3N_3O_7$: N, 13.78. Found: N, 13.73.

The base IVb was crystallized from petroleum ether (bp 60–80°) as cream-colored microcrystals: mp 112–113°; λ_{max} 222, 260, 336 mμ (ε 51,840, 5944, 3045).

Anal. Calcd for $C_{10}H_8ClN$: C, 67.61; H, 4.51; N, 7.89. Found: C, 67.87; H, 4.66; N, 7.92.

The picrate was recrystallized from ethanol as yellow needles, mp 204–205°.

Anal. Calcd for $C_{10}H_8ClN$, $C_6H_3N_3O_7$: N, 13.78. Found: N, 13.71.

The base IVc was obtained from benzene as light cream crystals: mp 156–157°; λ_{max} 222, 256, 320 mμ (ε 39,780, 24,690, 8754).

Anal. Calcd for $C_{10}H_8ClN$: C, 67.61; H, 4.51; N, 7.89. Found: C, 67.87; H, 4.66; N, 8.04.

The picrate was recrystallized from ethanol as yellow flakes, mp 237–238°.

Anal. Calcd for $C_{10}H_8ClN$, $C_6H_3N_3O_7$: N, 13.78. Found: N, 13.92.

The base IVd was a tarry mass and was identified as the picrate, which was crystallized from ethanol as yellow flakes, mp 245–246° dec.

Anal. Calcd for $C_{10}H_8ClN$, $C_6H_3N_3O_7$: C, 47.23; H, 2.71; N, 13.78. Found: C, 47.41; H, 2.92; N, 13.50.

Registry No.—Ic, 14123-60-5; semicarbazone of Ic, 14123-61-6; 2,4-dinitrophenylhydrazone of Ic, 14154-01-9; IIa, 14123-62-7; IIb, 14123-63-8; IIc, 14123-64-9; IIIa, 14123-65-0; picrate of IIIa, 14123-66-1; IIIb, 14123-67-2; picrate of IIIb, 14123-68-3; IIIc, 14123-69-4; picrate of IIIc, 14172-87-3; IIId, 14123-70-7; picrate of IIId, 14123-71-8; IVa, 14123-72-9; picrate of IVa, 14123-73-0; IVb, 14123-74-1; picrate of IVb, 14123-75-2; IVc, 14123-76-3; picrate of IVc, 14172-88-4; picrate of IVd, 14123-77-4; IVe, 1125-80-0; 3-methyl-3, 4-dihydroisoquinoline, 14123-78-5; *m*-chlorophenylacetoacetonitrile, 14123-79-6.

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Tetrasodium Carbonyldiphosphonate. Synthesis, Reactions, and Spectral Properties

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In connection with a study of the metal ion chelating ability of phosphorus-containing ligands, it became of interest to synthesize a series of *gem*-diphosphonate salts. This note reports the synthesis of tetrasodium carbonyldiphosphonate,[2] a *gem*-diphosphonate with unique physical and chemical properties.

In 1958, Kabachnik and Rossiiskaya reported[3] the synthesis of tetramethyl carbonyldiphosphonate *via* a Michaelis–Arbusov rearrangement reaction of phosgene and 2 equiv of trimethyl phosphite. This claim was retracted shortly thereafter in a paper[4] in which the same authors showed that the reaction which actually takes place is a chlorination of the trialkyl phosphite, as shown in eq 1.

$$Cl_2C{=}O + P(OR)_3 \longrightarrow RCl + CO + ClPO_3R_2 \qquad (1)$$

The present synthesis of a carbonyldiphosphonate is outlined in Scheme I along with some further reactions of the compound.

The quantitative conversion of tetraisopropyl methylenediphosphonate (I) to tetraisopropyl dihalomethylenediphosphonate (II) has recently been realized.[5] Dihalomethylenediphosphonic acid (III) was prepared *via* the pyrolysis of II[6] and refluxed with enough aqueous sodium hydroxide so that the pH of the final solution was above 11. Yellow hydrated crystals of tetrasodium carbonyldiphosphonate (IV) were isolated by the addition of methanol.

The yellow solution obtained from dissolving IV in water was partially decolorized by titrating to pH 4.5 with HCl. This slightly yellow solution on standing deposited white crystals of disodium dihydroxymethylenediphosphonate (V). Dissolved V was reconverted into IV in solution by simply restoring the pH to about 11. Compound IV crystallizes from solution with a water content which corresponds closely with that calculated for the decahydrate. Most of this water is lost when IV is air dried and the yellow crystals crumble to a powder. Compound V is obtained in nearly anhydrous form.

The proof of structure of IV was accomplished by catalytic reduction and isolation of the product as disodium methanehydroxydiphosphonate (VIII) followed by the synthesis of VIII by two independent methods. These syntheses are outlined in Scheme II.

When I was allowed to react with an equimolar amount of hypohalite, it was partially converted to a mixture of mono- and dihalomethylenediphosphonates, VI and II. Hydrolysis of this mixture with refluxing HCl produced the acids VII and III which were separated by fractional crystallization of their aniline salts. When VII was refluxed with aqueous base (pH 11) and the resulting solution titrated with dilute HCl to pH 5, VIII was isolated by addition of methanol.

Another synthesis of VIII was achieved through the Nylén reaction of 3 equiv of sodium dialkyl phosphite with phosgene. The intermediate in this reaction is believed to be a phosphate–diphosphonate but has not been isolated and identified in a pure state.

Infrared and visible spectra of IV were obtained in an effort to verify the structural assignments. Compound IV exhibits its carbonyl stretching frequency at the unusually low value of 1612 cm^{-1}. It was necessary to prepare IV in D_2O using NaOD as the base in order to identify this band, as the yellow salt was not obtained in anhydrous form and the water of hydration tended to obscure this region.

The yellow color was found to be due to an absorption maximum at 413 mμ with a molar absorptivity of 11 l./mole cm. The visible spectrum was obtained in water solution.

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[2] An alternate name for this compound might be tetrasodium diphosphono ketone. By analogy with $O{=}C(COOH)_2$, one could name $O{=}C(PO_3H_2)_2$ carbonylmethylenediphosphonic acid, but we have preferred to shorten this to carbonyldiphosphonic acid.

[3] M. I. Kabachnik and P. A. Rossiiskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **48** (1957); *Chem. Abstr.*, **51**, 10366*h* (1957).

[4] M. I. Kabachnik and P. A. Rossiiskaya, *ibid.*, 1398 (1958); *Chem. Abstr.*, **53**, 6988*e* (1959).

[5] O. T. Quimby, J. B. Prentice, and J. D. Curry, submitted for publication.

[6] Such a pyrolysis route to phosphonic acids is known to be a general reaction of isopropyl esters. See, for example, A. E. Canavan, B. F. Dowden, and C. Eaborn, *J. Chem. Soc.*, 331 (1962).