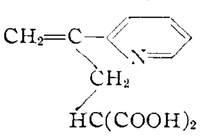
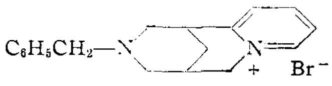
(dec.) (Found: C, 59.66; H, 5.13), secured by saponification of the diethyl ester which results from interaction of sodio malonic ester with 2-(α-pyridyl)-allyl acetate,[6] was condensed with benzylamine and formaldehyde; the Mannich reaction, accompanied by decarboxylation and cyclization, yielded N-benzyl-3-(α-pyridyl)-piperidine-5-carboxylic acid, which was converted without purification to the ethyl ester,[7] b.p. 183–184° (0.1 mm.) (Found: 3, 74.45; H, 7.84). Lithium aluminum hydride reduction afforded N-benzyl-3-(α-pyridyl)-5-methylolpiperidine (III),[7] b.p. 193–194° (0.1 mm.) (Found: C, 76.78; H, 8.24; N, 9.84). Refluxing III with hydrobromic acid led to the 5-bromomethylpiperidine, which, as the free base, was quaternized without isolation to the tricyclic pyridinium bromide IV, m.p. 170.5–171.5° (Found: C, 62.80; H, 6.29; N, 8.23). The salt, on oxidation with alkaline ferricyanide, gave rise to *dl*-N-benzylcytisine, m.p. 137.5–139° (Found: C, 77.16; H, 7.22), the infrared spectra (obtained in chloroform and carbon disulfide) of which were identical in every detail with the corresponding spectra of N-benzylcytisine, m.p. 140–142° (Found: C, 77.23; H, 7.39), obtained by monoalkylation of the alkaloid. Hydriodic acid cleavage[8] of *dl*-N-benzylcytisine afforded *dl*-cytisine, m.p. 145–146° (Found: C, 69.53; H, 7.46); the infrared spectra of the synthetic base and natural alkaloid were indistinguishable.

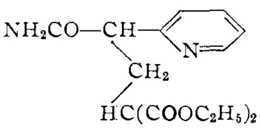


II



IV

The key intermediate III was also attained by an alternate series of steps. The addition of α-pyridylacetamide, m.p. 119–120° (Found: C, 62.06; H, 6.19), to methylenemalonic ester yielded the Michael product (V), m.p. 106° (Found: C, 58.15; H, 6.57), which was cyclized by means of sodium methoxide to 3-(α-pyridyl)-5-carboethoxyglutarimide, m.p. 136–138° (Found: C, 59.65; H, 5.81). Alkylation of the glutarimide, accomplished by heating the sodium salt with benzyl chloride, followed by lithium aluminum hydride reduction, gave rise to: (1) N,5-dibenzyl-3-(α-pyridyl)-5-methylolpiperidine, m.p. 146–147° (Found: C, 80.52; H, 7.51; N, 7.69), resulting from dialkylation, and (2) the desired alcohol III, identified by boiling point, infrared spectral comparison, and conversion to IV.



V

Since the alkaloids caulophylline (N-methylcytisine)[9] and rhombifoline (N-but-3-enylcytisine)[8] have been previously obtained by alkylation of cytisine,[8,10] the synthetic route described above thereby embraces these natural products as well.

Acknowledgment.—This work was supported by grants from the Research Committee of the Wisconsin Alumni Research Foundation and from the National Science Foundation. The authors wish to express their gratitude to Professors Marion and Galinovsky for gifts of cytisine.

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[6] F. Bohlmann, N. Ottawa and R. Keller, *Ann.*, **587**, 162 (1954).

[7] The ratio of *cis* and *trans* isomers was not determined.

[8] W. F. Cockburn and L. Marion, *Can. J. Chem.*, **30**, 92 (1952).

[9] J. U. Lloyd, *Proc. Am. Pharm. Assoc.*, **41**, 115 (1893); F. B. Power and A. H. Salway, *J. Chem. Soc.*, **103**, 191 (1913).

[10] A. Partheil, *Ber.*, **24**, 635 (1891).

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NUCLEAR MAGNETIC RESONANCE SPECTRA OF THE CONDENSED PHOSPHATES

Sir:

As part of a general study of the chemical shifts in the nuclear magnetic resonance spectra[1] of phosphorus compounds, some observations were made which give fundamental support to the idea previously developed,[2,3] that in the phosphates there is a difference between isolated, end, middle, and branching-point PO_4 groups. These four kinds of PO_4 groups each give a separate resonance peak in the nuclear magnetic resonance spectrum. When the chemical shift is measured in parts per million of the applied magnetic field (7140 gauss) and phosphorus tribromide is used as the reference standard, the positions given in Table I are found for the resonance peaks of various types of PO_4 groups.

TABLE I

Type of PO_4 group	Chemical shift[a] p.p.m.
Orthophosphate ions (isolated groups)	
trisubstituted (normal) salts	233
1 to 3 hydrogens/P atom	238
End groups	
doubly substituted (no H^+ ions)	244
1 to 2 hydrogens/P atom	247
Middle groups	
short chains	256
long chains	259
Branching points	
alkali metal ultraphosphates	268
azeotropic phosphoric acid[6]	272

[a] The chemical shifts of the various phosphates are measured to *ca.* ± 2 p.p.m. with respect to each other. The actual measurements were made relative to 85% orthophosphoric acid; however, the values reported are referred to phosphorus tribromide as the zero reference and were obtained by adding the value of the phosphorus tribromide shift, relative to orthophosphoric acid, to each result.

Examination of the spectrum of sodium tripolyphosphate solutions shows two peaks, one for the end groups and one for the middle groups.

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[1] E. M. Purcell, *Science*, **118**, 431–436 (1953); F. Bloch, *Science*, **118**, 425–430 (1953); Varian Associates, Palto Alto, Calif., "*Radiofrequency Spectroscopy*," **1**, No. 1 (1953), No. 2 (1954) and No. 3 (1955).

[2] J. R. Van Wazer and K. A. Holst, THIS JOURNAL, **72**, 639 (1950); J. R. Van Wazer, *ibid.*, **72**, 647 (1950); *ibid.*, paper X in press; and "Encyclopedia of Chemical Technology" (Kirk and Othmer, editors), Interscience, New York, 1953, Vol. X, pp. 403–429, 469–472.

[3] J. R. Van Wazer, THIS JOURNAL, **72**, 644 (1950).

The area of the peak corresponding to the end group is exactly twice as large as the middle-group peak in a pure sample of $Na_5P_3O_{10}$. As expected, pyrophosphate solutions show only the end-group peak. Spectra of solutions of the various phosphate glasses exhibit end- and middle-group peaks of the heights to be expected from the average chain length.[2,3] For glasses having chain lengths greater than *ca.* 75, the end-group peak is so small we have not been able to detect it because of signal-to-noise limitations.[4] The trimeta- and tetrametaphosphate rings show only one peak in solution—the peak corresponding to middle groups.

Because of rapid hydrolysis[5] at branching points, the peak corresponding to this type of PO_4 group could not be determined for aqueous solutions but was measured on solid ultraphosphates heated to their softening temperatures. Azeotropic phosphoric acid[6] and several sodium ultraphosphates—all of which should have shown middle-group as well as branching-point peaks—exhibited only one peak, which we have tentatively ascribed to branching points in Table I. This peak is very broad and, for the azeotropic phosphoric acid, disappeared immediately upon dissolution. The fresh solution of the azeotropic acid showed only end- and middle-group peaks, with the ratio of these peaks being of the expected magnitude.

A second-order effect is observed when weakly acidic hydrogens are substituted for alkali metal ions in phosphate solutions. Hydrogen covalently bonded to isolated or end groups leads to a positive shift of approximately 4 p.p.m. This effect is in accord with the fact that the electronegativity of hydrogen and phosphorus are equal—a fact which is very important in phosphate chemistry, as we have previously pointed out.[3] These results and some other interesting findings (such as fine structure in the tripolyphosphate spectrum) will be discussed in more detail in a forthcoming paper.

(4) Measurements were made on the high resolution spectrometer (Model V 43000 B) manufactured by Varian Associates, Palo Alto, Calif., equipped with a 12.3 mc. probe. By going to a 17.2 mc. probe on the same instrument, the resolution will increase by a factor of 1.4 and the signal-to-noise ratio will be improved by an approximate factor of 2.

(5) See refs. 2 and 3 as well as U. P. Strauss, E. H. Smith and R. L. Wineman, THIS JOURNAL, **75**, 3935 (1953); U. P. Strauss and T. L. Treitler, *ibid.*, **77**, 1473 (1955); and R. Pfanstiel and R. K. Iler, *ibid.*, **74**, 6062 (1952).

(6) G. Tarbutton and M. E. Deming, THIS JOURNAL, **72**, 2086 (1950); E. H. Brown and C. D. Whitt, *Ind. Eng. Chem.*, **44**, 615 (1952).

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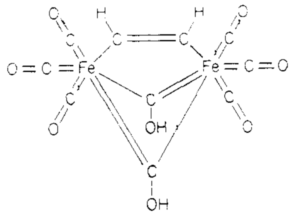
A BRIDGED IRON COMPLEX DERIVED FROM ACETYLENE AND IRON HYDROCARBONYL

Sir:

The recent discovery[1] of an organometallic compound derived from acetylene and dicobalt octacarbonyl led us to postulate the existence of a similar compound containing iron. A crystalline substance having the empirical formula $Fe_2C_{10}H_4O_8$ has been obtained by Reppe[2] from the reaction of acetylene at 20 atmospheres and 50° with an alkaline solution of iron hydrocarbonyl.

We have now synthesized this compound (I) in 70% yield by treating an alkaline solution of $NaHFe(CO)_4$ with acetylene at atmospheric pressure and room temperature. The compound crystallizes as the monohydrate.[2] Calculated for $Fe_2C_{10}H_4O_8 \cdot H_2O$: C, 31.45; H, 1.58; Fe, 29.25. Found: C, 31.40; H, 1.64; Fe, 29.06. We suggest structure A for the anhydrous compound based on the following evidence.



A

The infrared spectrum of $Fe_2C_{10}H_4O_8$ (I) in carbon disulfide shows two bands in the –OH region at 3565 cm.$^{-1}$ and 3463 cm.$^{-1}$, three bands in the C–O single bond region at 1271, 1174, and 1093 cm.$^{-1}$ and three bands in the C≡O triple bond region at 1998, 2033, and 2073 cm.$^{-1}$. These last three bands are similar to the three bands which appear in the spectrum of dicobalt octacarbonyl[3] and in that of the cobalt acetylene complex[1] where these bands have been attributed to C≡O stretching vibrations of the six terminal carbonyl groups. The *pKa* values[4] of the first and second hydrogen of I are 6.30 and 9.14. Evidence for the presence of phenolic type hydroxyl groups is the shift to longer wavelengths and increase in intensity of the ultraviolet spectrum when excess alkali is added to an aqueous solution of I. This change is similar to that accompanying the phenol → phenolate ion transformation. The presence of two hydroxyl groups was also demonstrated by the preparation of the dibenzoate. Addition of benzoyl chloride to a solution of I in dry pyridine and dilution of the reaction mixture with water gave the dibenzoate (II) in theoretical yield. Crystallized from ethanol–water, II forms yellow microcrystals which melt at 156° with decomposition. Calcd. for $Fe_2C_{24}H_{12}O_{10}$: C, 50.39; H, 2.11; Fe, 19.53. Found: C, 50.34; H, 2.13; Fe, 19.41.

The configuration of A may be assumed to be analogous to iron enneacarbonyl where all iron-carbon σ bonds are formed by d^2sp^3 hybrid orbitals. Another possible configuration is one in which the σ bonds from iron to the terminal carbons and to

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(1) H. W. Sternberg, H. Greenfield, R. A. Friedel, J. Wotiz, R. Markby, and I. Wender, THIS JOURNAL, **76**, 1457 (1954).

(2) W. Reppe and H. Vetter, *Ann.*, **582**, 133 (1953).

(3) H. W. Sternberg, I. Wender, R. A. Friedel and M. Orchin, THIS JOURNAL, **75**, 2717 (1953).

(4) Reppe and Vetter[2] observed only one acidic hydrogen, but their potentiometric titration gave an equivalent weight of 283 instead of that calculated for $Fe_2C_{10}H_4O_8$ which is 363. It is possible that these workers did not exclude oxygen during their titration; we have observed that unreliable results are obtained if the complex is titrated in the presence of oxygen.