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

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

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
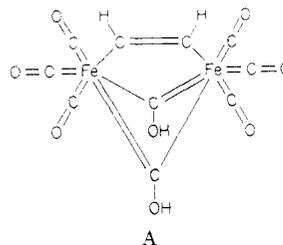
The infrared spectrum of $Fe_2C_{10}H_4O_8$ (I) in carbon disulfide shows two bands in the -OH region at 3565 cm.$^{-1}$ and 3463 cm.$^{-1}$, three bands in the C-O single bond region at 1271, 1174, and 1093 cm.$^{-1}$ and three bands in the C≡O triple bond region at 1998, 2033, and 2073 cm.$^{-1}$. 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

(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.

the bridge carbons are formed by dsp^3 hybrid orbitals and the bond from iron to the acetylenic carbon by an unhybridized d-orbital.

This complex is of interest for the following reasons: (1) It contains a novel resonating system

$$HO—C\underset{Fe}{\overset{Fe}{<\quad>}}C—OH$$
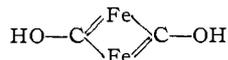
which is analogous to the cyclobutadiene system. (2) Although several metal hydrocarbonyls have been synthesized and studied, this is the first hydrocarbonyl in which the position of the hydrogen has been established. (3) Stable derivatives of a hydrocarbonyl are now available for study by physical methods. (4) This is the first evidence for the existence of an M=C-OH grouping, a type of linkage postulated[5] in surface intermediates in the Fischer-Tropsch reaction.

(5) H. H. Storch, N. Golumbic and R. B. Anderson, "The Fischer-Tropsch and Related Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 592.

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BOOK REVIEWS

Technique of Organic Chemistry. Volume I. Part III. Physical Methods of Organic Chemistry. Second Completely Revised and Augmented Edition. Editor ARNOLD WEISSBERGER, Research Laboratories, Eastman Kodak Co., Rochester, N. Y. . Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1954. xi + 2097-2530 pp. 16 × 23.5 cm. Price, $8.50.

The subjects covered in this, the third of three volumes comprising Volume I in a series on Technique of Organic Chemistry, will be of less general interest than those covered in earlier volumes. This is because the techniques under discussion, although potentially of wide applicability, are highly specialized and quite elaborate from an instrumental point of view. However, the standard of presentation continues to be of the highest and those who have occasion to seek authoritative information as to what can be done with these methods, and in a general way how it is done, will find this source invaluable.

The new chapters deal with Electron Microscopy (F. A. Hamm), Microspectroscopy (E. R. Blout), Determination of Streaming Birefringence (R. Signer), Measurement of Dielectric Constant and Loss (J. G. Powles and C. P. Smyth), Radio-frequency Spectroscopy (B. P. Dailey) and Neutron Diffraction (J. M. Hastings and L. Corliss). In addition there are short chapters supplementing previous chapters on viscosity of polymer solutions, crystal structure, electron diffraction, magnetic susceptibility and scintillation counting.

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Progress in Stereochemistry. Volume 1. By W. KLYNE, M.A., B.Sc., Ph.D. (Editor), Reader in Biochemistry, University of London (Postgraduate Medical School). Academic Press, Inc., Publishers, 125 East 23rd Street, New York 10, N. Y. 1954. x + 378 pp. 16 × 25 cm. Price, $8.00.

Stereochemistry, as discussed in this volume, transects the traditional disciplines of chemistry (although the strongest emphasis is in the organic field) and deals with electronic structure as well as with the orientation of groups and with reaction mechanisms as well as with stereo-isomerism. The book reflects the growing concern of chemists with physical methods and mechanisms of organic, inorganic and enzymatically catalyzed reactions and provides surprisingly up-to-date coverage of many important areas of chemical endeavor. As implied by the title the emphasis is on recent developments. There are, however, interesting similiarities between the present work and Freudenberg's classical volumes published some twenty-three years ago.

Volume One contains nine chapters and a brief appendix on bond lengths and valence angles. Each of these represents a noteworthy contribution and, in the opinion of the reviewer, Chapters 1, 2, 5, 7 and 9 are particularly outstanding. The chapters are as follows:

1. The Shapes of Simple Molecules (A. D. Walsh). This chapter contains a convenient tabulation of bond angles, bond lengths and shapes of di- to octatomic molecules. Generalizations are drawn from these data and are presented together with an excellent qualitative theoretical discussion.

2. The Conformation of Six-membered Ring Systems (W. Klyne). Dr. Klyne has provided us with an expert description of the results in this new field up to the end of 1954.

3. Stereochemical Factors in Reaction Mechanism and Kinetics (P. B. D. de la Mare). This section presents an interesting but limited and sketchy discussion of a very broad topic. Attention is paid chiefly to addition, elimination, nucleophilic substitution and certain 1,2-rearrangement reactions.

4. The Relationships Between the Stereochemistry and Spectroscopic Properties of Organic Compounds (E. A. Braude and E. S. Waight). Applications of both infrared and ultraviolet spectral methods are given, the latter with especially interesting sections on the correlation of absorption intensity with stereochemistry. The infrared section is rather limited.

5. The Correlation of Configurations (J. A. Mills and W. Klyne). This extraordinary section is one of the highlights of the book and is unsurpassed in excellence. The authors, who have themselves contributed brilliantly to the correlation of configurations, have written a stimulating and lucid review which is commensurate with their already demonstrated prowess in the field.

6. The Stereochemistry of the Hydrogen Bond (L. Hunter). Here is an interesting and well documented summary of data from both the organic and inorganic fields.

7. The Stereochemistry of Compounds of High Molecular Weight (E. J. Ambrose). This chapter contains a fine but brief discussion of general principles and methods, followed by a description of the stereochemistry of various long-chain hydrocarbons, proteins and polysaccharides.

8. Stereospecificity of Enzyme Reactions (V. P. Whittaker). The treatment of the subject matter in this chapter falls considerably below that which may be expected for such an important and dynamic field. It is occasionally too rudimentary, too discursive and too superficial and seldom incisive, current or exciting. Stereochemical, theoretical and even general discussion is surprisingly lacking.

9. The Stereochemistry of Complex Compounds (R. S. Nyholm). Professor Nyholm has written a clear and valuable introduction to the stereochemistry of complex compounds which will appeal to chemists of all fields. The