have assigned also the cyclic oxyphosphorane structure.[4] These assignments are, therefore, mutually strengthened by the results summarized in this communication.

Diketol Cyclic Phosphate (IIA).—M.p. 106–112° (slow crystallization from ether or benzene–hexane). *Anal.* Calcd. for $C_9H_{15}O_6P$: C, 43.2; H, 6.0; P, 12.4; mol. wt., 250. Found: C, 43.2; H, 6.0; P, 12.4; mol. wt., 250 (alkaline titration at pH 7.0). Infrared in CCl_4 (μ): split CO at 5.77, 5.81 (s); PO at 7.68 (s); CH_3OP at 9.52 (vs); no OH. H^1 n.m.r. in $CDCl_3$ *vs.* TMS (fresh solution) (τ): CH_3OP at 6.07, $J_{HP} = 12$ c.p.s.;

CH_3CO at 7.65; $CH_3\overset{|}{C}$— at 8.42. IIA is sensitive to

moisture. Complete hydrolysis of IIA (benzene, excess water, reflux) gave 3,4-dimethyl-3,4-dihydroxy-2,5-hexanedione,[2] m.p. 95–96°.

Hemiketal Cyclic-Phosphate (III).—M.p. 114–115° (CH_2Cl_2-hexane). *Anal.* Calcd. for $C_{11}H_{19}O_7P$: C, 42.6; H, 6.8; P, 11.0. Found: C, 42.6; H, 7.1; P, 11.0. Infrared in $CHCl_3$ (μ): OH at 2.83 (broad); PO at 7.70 (s); $POCH_3$ at 9.50 (vs); no CO. H^1 n.m.r. (freshly prepared $CDCl_3$ solution *vs.* TMS) (τ): OH at

5.77; CH_3OP at 6.15, $J_{HP} = 12$ c.p.s.; CH_3O—$\overset{|}{C}$—

(hemiketal): 6.65; $CH_3\overset{|}{C}$— at 8.50, 8.55 (double

intensity) and 8.58 (three of the four high-field methyl lines were resolvable). Under certain conditions, III can be reconverted into IIA by removal of methanol.

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(4) (a) F. Ramirez, N. B. Desai and N. Ramanathan, *Tetrahedron Letters*, **No. 5**, 323 (1963); (b) F. Ramirez and N. Ramanathan, *J. Org. Chem.*, **26**, 3041 (1961); (c) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, **82**, 2652 (1960).

(5) Alfred P. Sloan Fellow, 1961–1963

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Equalization of Electronegativity[1]

Sir:

Recently, Hinze, Whitehead and Jaffé[2] have made real progress toward the derivation of an electronegativity scale for groups and radicals, based on an extension of the definition of electronegativity for atomic orbitals originally given by Pritchard and Sumner.[3] However, Hinze, Whitehead and Jaffé neglect the effect of overlap between bonding orbitals, and are then led logically to the principle of equalization of the
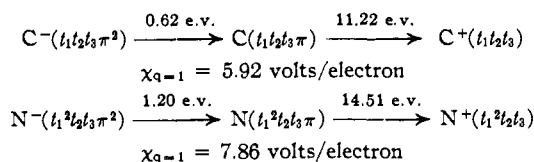
(1) Based on a lecture given at the Gordon Research Conference on Inorganic Chemistry at New Hampton, N. H., August 6–10, 1962.

(2) J. Hinze, M. A. Whitehead and H. H. Jaffé, *J. Am. Chem. Soc.*, **85**, 148 (1963).

(3) H. O. Pritchard and F. H. Sumner, *Proc. Roy. Soc.* (London), **A235**, 136 (1956).

electronegativities of the orbitals forming the bond. In neglecting the overlap, they are in effect making a classical prediction of the electron distribution in the bond from the known (albeit quantum) properties of the constituent atoms, and the result must be in error to some extent. The order of magnitude of this error can be seen from the following calculation.

Consider an isolated π-bond between a carbon atom and a nitrogen atom in an extended organic system. (There is no difference in principle between π-bonds and σ-bonds.) This $>C=N-$ bond can be treated by the self consistent electronegativity molecular orbital approximation of Pritchard and Sumner[3] in which the coulomb integral α_q for each atom is identified with the electronegativity χ_q of its π-orbital, where q is the occupation number of that orbital. The relevant valence state ionization energies for carbon and nitrogen are taken as[4]

$$C^-(t_1t_2t_3\pi^2) \xrightarrow{0.62 \text{ e.v.}} C(t_1t_2t_3\pi) \xrightarrow{11.22 \text{ e.v.}} C^+(t_1t_2t_3)$$
$$\chi_{q=1} = 5.92 \text{ volts/electron}$$

$$N^-(t_1^2t_2t_3\pi^2) \xrightarrow{1.20 \text{ e.v.}} N(t_1^2t_2t_3\pi) \xrightarrow{14.51 \text{ e.v.}} N^+(t_1^2t_2t_3)$$
$$\chi_{q=1} = 7.86 \text{ volts/electron}$$

In each cycle of the calculation the overlap integral and the values of α_q for the two atoms are adjusted according to the values of q obtained in the previous cycle, until a self consistent set of charge densities is obtained. The results for the $C=N$ system, with $r_{CN} = 1.34$ Å., are[5]

Atom	Charge	Electronegativity
C	0.946 electron	6.50 volts/electron
N	1.054 electron	7.13 volts/electron

Clearly the difference in electronegativity is considerably reduced in bond formation, but the electronegativities are not equalized. This would have required us to get $q_N = 1.082$, $q_C = 0.918$ and thus $\chi_q = 6.775$ volts/electron for both atoms.

This calculation suggests, therefore, that in general, the bond electronegativities of each atom will differ from the equalization value by something in excess of 10% of the original difference in electronegativity between the two constituent orbitals. This is quite a serious error and must be taken into account before a satisfactory electronegativity scale for radicals and groups can be finally established by the method of Hinze, Whitehead and Jaffé.

(4) G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962).

(5) D. G. Rush, M. S. Thesis, Manchester, 1962. Apparently there was an error in the effective Z used for the overlap integrals for pyridine in ref. 3: the self consistent charge densities should be N atom 1.057, *ortho* C atoms 0.976, *meta* C atoms 0.997, *para* C atoms, 0.996; this is compatible with the strong preference of OH⁻ and NH₂⁻ for attack in the ortho position.

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Mechanism of the Low-Temperature Scavenging of Methyl-d_3 Radicals by Nitric Oxide

Sir:

The detailed mechanism by which nitric oxide scavenges free radicals has been a matter of considerable discussion since the discovery[1] of its inhibitory effect on free radical chain processes. Although it is generally agreed that the first step is one of direct addition to form a nitroso compound, *viz.*

$$R\cdot + NO \,(+M) \longrightarrow RNO \,(+M) \qquad (1)$$
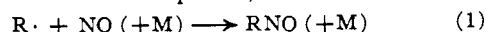
(1) L. A. K. Stavely and C. N. Hinshelwood, *Proc. Roy. Soc.* (London), **A154**, 335 (1936).