the hydroxyl in the α-hydroxyphosphine oxides cannot be explained geometrically, since the longer phosphoryl bond in these compounds would lead, all other things being equal, to a longer O . . . . . . O distance and hence a smaller $\Delta\nu_{OH}$. It seems reasonable to postulate that the more polarized P→O is sufficiently attracted to the hydroxyl to induce a small angular deformation of the O–P–C and/or the P–C–O valence angles and thus reduce the O . . . . . . O distance. Calorimetric[6] and spectroscopic[7] studies of the interaction of various phosphoryl compounds with proton-donating solvents indicate the greater tendency of the phosphine oxide to coördinate.

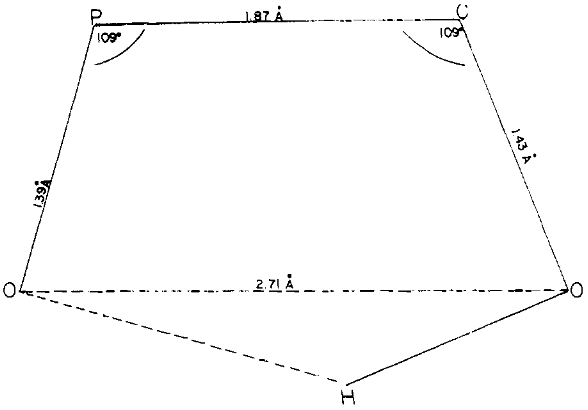

Fig. 2.—Intramolecular hydrogen bonding in α-hydroxyphosphoryl compounds.

TABLE IV

DIETHYL α-HYDROXYALKANEPHOSPHONATES, ArCH(OH)P-(O)$(OC_2H_5)_2$

Ar	M.p., °C. uncor.	Yield, %	P, %		N, %	
			Calcd.	Found	Calcd.	Found
2-$O_2NC_6H_4$	122.5–123.1	79.5	10.7	10.8	4.8	4.8
3-$O_2NC_6H_4$	91.5– 92.1	84.4	10.7	10.8	4.8	4.8
4-$O_2NC_6H_4$	90.2– 91.0	79.5	10.7	10.8	4.8	4.8
2-ClC_6H_4	80.0– 80.6	70.5	11.1	11.0	12.7[a]	12.5[a]

[a] Chlorine, %.

Experimental

The spectra described here were obtained with a Perkin-Elmer Model 112 double-pass spectrometer equipped with rock salt optics after a preliminary scan of the entire rock salt region of the spectrum, using a Perkin-Elmer Model 21 double beam instrument. Long term reproducibility at 3000 cm.$^{-1}$ was about 10 cm.$^{-1}$ and at 1200 cm.$^{-1}$, 3 cm.$^{-1}$. The superimposed water vapor spectrum served as an internal calibration.

Liquid samples were scanned as capillary films and in carbon disulfide solutions in amalgam sealed cells of suitable thickness. Crystalline samples were mulled in mineral oil and, when their solubilities permitted, were dissolved in carbon disulfide.

The synthesis and analysis of the compounds whose spectra were studied have been, for the most part, described in earlier papers in this series. Experimental procedures and physical constants for previously unreported compounds are given below.

Preparation of Diethyl α-Hydroxyalkanephosphonates.—According to the method of Abramov,[14] several new α-hydroxyalkanephosphonate esters were prepared as listed in Table IV. An equimolar mixture of 0.05 mole of diethyl phosphonate and the appropriate substituted benzaldehyde was treated slowly with a few drops of a solution of sodium in ethanol. The mixture was cooled during the exothermic reaction. On standing overnight at 0°, a 70–85% yield of the desired product was obtained. The products were recrystallized from *n*-hexane:benzene mixtures.

Deuterium Exchange in α-Hydroxyphosphoryl Compounds.—A sample of the desired α-hydroxyphosphoryl compound was dissolved in *p*-dioxane (Eastman Chemical—twice fractionated over sodium) and treated with a ten-fold quantity of 99.6% deuterium oxide. After the cloudy solution had stood at room temperature for 18 hours under nitrogen, the solvent was evaporated, and the product was recrystallized from *n*-hexane. 3.72 g. of $(n\text{-}C_8H_{17})_2P(O)\text{-}C(OH)CH_2CH_2CH_2CH_2CH_2$, melting at 67.5–68.1°, yielded 3.53 g. of product, melting at 67.5–68.2°, which showed a strong O–D band. Likewise, 1.97 g. of $(C_2H_5O)_2\text{-}P(O)C(OH)CH_2CH_2CH_2CH_2CH_2$,[15] melting at 73.0–73.8°, yielded 1.12 g. of product, melting at 73.0–74.2°, whose infrared spectrum indicated considerable deuteration.

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(14) V. S. Abramov, *Doklady Akad. Nauk S.S.S.R.*, **73**, 487 (1950); *C. A.*, **45**, 2855 (1951).

(15) V. S. Abramov, *Zhur. Obshchei Khim.*, **22**, 647 (1952); *C. A.*, **47**, 5351 (1953).

PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KENTUCKY]

The Polarography of Quinoxaline. II.[1] 6-Substituted Derivatives[2]

BY MURRAY P. STRIER AND J. C. CAVAGNOL[3]

RECEIVED AUGUST 16, 1957

The reduction of 6-aminoquinoxaline, 6-bromoquinoxaline, 6-chloroquinoxaline, 6-ethoxyquinoxaline and 6-methoxyquinoxaline at the dropping mercury electrode is similar to that for quinoxaline. Studies were conducted in aqueous buffered media at *p*H's 2, 4, 6, 8 and 10. Two major waves are found at *p*H's 2, 4 and 6 whereas only the first major wave occurs at *p*H's 8 and 10. The first major wave represents reduction to the 1,4-*dihydro* stage. At *p*H 2 the differentiated nature of this wave is indicative of a bimolecular reduction in two successive one-electron steps. At higher *p*H's reduction is directly to the dihydroquinoxaline. For 6-aminoquinoxaline, the latter occurs at all *p*H's. The second major wave is due to the evolution of hydrogen catalyzed by the 1,4-dihydroquinoxalinium ion. Though the true criterion for polarographic reversibility is not established, Hammett's equation is found applicable to the first major wave throughout the *p*H range studied. Relative heights of the second major wave can be explained qualitatively on the basis of the electronic influences of the substituents.

Introduction.—In two comprehensive investigations of the polarographic behavior of quinoxaline (I) in buffered aqueous media it was postulated that reduction stopped at the 1,4-*dihydro* stage.[1,4] At *p*H's 1 and 2 the differentiated nature of the wave

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(1) This paper is an extension of the work described in the article by M. P. Strier and J. C. Cavagnol, THIS JOURNAL, **79**, 4331 (1957).

(2) Abstracted from a dissertation submitted to the Graduate School by Murray P. Strier in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Jan., 1952.

(3) Research Center, General Foods Corporation, Tarrytown, N. Y.

(4) G. Sartori and C. Furlani, *Ann. chim.* (*Rome*), **45**, 251 (1955); *C. A.*, **49**, 15557f (1955).

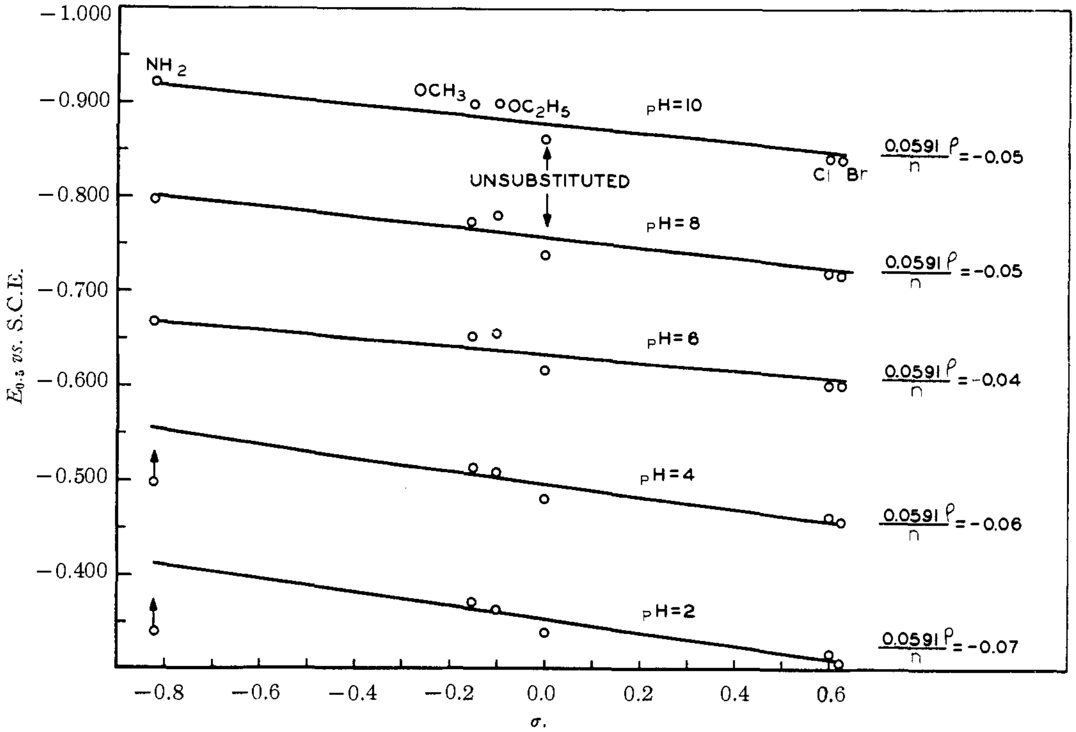
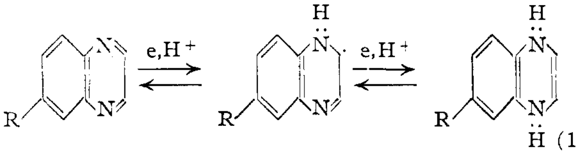


Fig. 1.—Half-wave potentials of the first major wave for 4.5 × 10^{-4} M solutions of quinoxalines *vs.* σ-values at various *p*H levels.

was indicative of a process wherein dihydroquinoxaline is formed by two consecutive single electron steps according to the scheme



(1)

I II III

where R = H. At *p*H's ≥ 4 a simultaneous 2-electron process was proffered for the conversion of I to III, and at *p*H 3 it was observed that reduction could proceed by either process.

Catalytic hydrogen evolution was evident at *p*H's < 7 regardless of buffer concentration and was found at *p*H 7 at high buffer concentration. The catalytic wave was believed to be caused by the monobasic 1,4-dihydroquinoxalinium ion. Reference to the first and second acidic dissociation constants for tetrahydroquinoxaline precluded ascribing any catalytic activity to the dibasic dihydroquinoxalinium ion.

In the current investigation it was of interest to know how the reduction process was affected by the electronic influences of substituents in the 6-position. The substituents were $-NH_2$, $-Br$, $-Cl$, $-OC_2H_5$ and $-OCH_3$. The *p*H levels explored were 2, 4, 6, 8 and 10. Ultimately, it was hoped to learn whether any of the 1,2,3,4-tetrahydroquinoxalines could be obtained electrochemically from the corresponding quinoxaline. If this were possible then the suitable experimental conditions could be used for obtaining tetrahydroquinoxalines from the appropriate quinoxalines by controlled electrolytic reduction procedures.

Experimental

Materials.—The quinoxalines used in this investigation were prepared by the method of Cavagnol and Wiselogle[5] and purified by two to five sublimations. The compounds had the melting points

6-Aminoquinoxaline	156–157°
6-Bromoquinoxaline	49.3–50.2°
6-Chloroquinoxaline	62.5–62.8°
6-Ethoxyquinoxaline	79.5–80.0°
6-Methoxyquinoxaline	60.0–60.3°

and were used as 0.010 M aqueous stock solutions stored under nitrogen in the dark.

Buffers.—A system of buffers was used which had been found previously[1] to give well-defined waves for quinoxaline. They were the "High" buffers at *p*H's 2, 4, 6, 8 and 10 with ionic strengths in the neighborhood of 0.6 M.

Apparatus and Procedure.—The apparatus and details of the experimental procedure have been given elsewhere.[1] The capillary used for these derivatives delivered 2.14 mg. sec.$^{-1}$ of mercury into distilled water.

Results and Discussions

As had been obtained for quinoxaline, two major waves whose half-wave potentials are *p*H-dependent exist for each system at *p*H 2, 4 and 6 whereas only the first major wave is present at *p*H 8 and 10. At *p*H 2, with one exception, the first major wave is partially differentiated into equal segments. This is indicative of a bimolecular reduction wherein one electron and one proton are added in each of two successive steps. The wave obtained for 6-aminoquinoxaline does not show any differentiation at *p*H 2. The second major wave for 6-aminoquinoxaline is preceded by a small wave that appears to be an adsorption wave. The half-wave potentials of the first major wave for 4.5 × 10^{-4} M solutions of each reductant are given in Fig. 1.

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(5) J. C. Cavagnol and F. Y. Wiselogle, This Journal, **69**, 795 (1947).

Variations in reductant concentration from 2.3×10^{-4} *M* to 6.8×10^{-4} *M* do not affect the half-wave potentials or diffusion current constants significantly for the first major waves. The largest variations were noted in the half-wave potentials for 6-ethoxyquinoxaline and for 6-methoxyquinoxaline at *p*H 6. There, increases of −0.010 v. and −0.011 v., respectively, occur in half-wave potentials as the reductant concentration is increased by 2.3×10^{-4} *M*. These trends do not necessarily apply to 6-chloroquinoxaline whose concentration was not varied in this study. As the concentration of reductant is increased in the case of the bromo, ethoxy and methoxy derivatives, the diffusion current portion of the second major wave becomes less distinct. This is due to merging with the decomposition wave of the supporting electrolyte. For the second major waves, half-wave potentials become increasingly more negative with increasing reductant concentration; also, diffusion current constants vary inversely with reductant concentration. These results are in accord essentially with those noted previously for quinoxaline.[1]

The average of the diffusion current constants of the first major waves for 4.5×10^{-4} *M* solutions of quinoxaline at these *p*H's is 3.30. For the 6-substituted derivatives the average is 3.28. Hence, the first major wave of the 6-substituted derivatives involves two electrons. Plots of half-wave potentials of this wave *versus* *p*H for each reductant are characterized by "breaks" at *p*H 6. The slope of the lines up to *p*H 6 is −0.07 for each system except for 6-aminoquinoxaline for which the slope is −0.08. At higher *p*H's the slope is −0.06 for each system. Hence, *n* electrons and *n* protons are involved in the electrode process. Wave analyses of the first major waves give values of *n* that vary from 0.6 to 1.5, mainly, up to and including *p*H 6. Exceptions exist at *p*H 6 for quinoxaline and 6-aminoquinoxaline where the values are 1.7 and 2.0, respectively. Above *p*H 6 the values of *n* vary from 1.4 to 1.8. These results indicate that less reversible electrode processes may exist at *p*H's below 6 than at higher *p*H's.

The plot of half-wave potentials *versus* *p*H of the second major wave for 4.5×10^{-4} *M* solutions of quinoxaline was linear with the slope being −0.055. Essentially, similar behavior is noted for the 6-substituted quinoxalines. Evidently, these substituents in the 6-position do not alter the course of reduction to the 1,4-*dihydro* stage. As indicated previously,[1] failure to obtain tetrahydroquinoxalines from quinoxalines by polarographic means in aqueous media at *p*H's > 7 where kinetic waves are absent is due to an isolated double bond formed in the 2,3-position. The ethylenic bond is not reduced under such conditions.

Application of Hammett's Rule to the First Major Wave.—During the past several years, references have appeared on the relationship of Hammett's sigma values with polarographic half-wave potentials.[6] Application of Hammett's σ-values to reversible polarographic half-wave potentials is justified as follows. The relationship between the standard e.m.f., E^0, and the equilibrium constant, *K*, for a reversible electrolytic reduction involving *n* electrons where reactants and products are at unit activity and the temperature of the reaction is 25° is

$$E^0 = \frac{0.0591}{n} \log K \qquad (2)$$

The Hammett equation[7] is

$$\log K - \log K_0 = \rho\sigma \qquad (3)$$

where the *K*'s represent either equilibrium or rate constants. K_0 is the constant for the unsubstituted or reference member and *K* is the corresponding constant for a *meta-* or *para*-substituted compound of the same family. Rho is the slope of the plot for a particular reaction and sigma is the substituent constant independent of the reaction. From the relationship between $E_{0.5}$ and E^0 given by Kolthoff and Lingane for a reversible reduction dependent on *p*H, this equality exists

$$E_{0.5} - E^0_{0.5} = E - E^0_0 \qquad (4)$$

where $E^0_{0.5}$ is the half-wave potential for the unsubstituted reductant and E^0_0 is the standard e.m.f. for the reaction involving the reductant. Now, the Hammett equation can be expressed in terms of half-wave potentials, *i.e.*

$$E_{0.5} - E^0_{0.5} = \frac{0.0591}{n} \rho\sigma \qquad (5)$$

Thus, a plot of half-wave potentials *versus* Hammett's σ-values should be linear with a slope of $0.0591\ \rho/n$ if the Hammett relation is applicable. Though the Hammett equation is for a thermodynamically reversible system, it has been found applicable to irreversible polarographic systems. Apparently, the kinetics of the irreversible step are the same for each member of the series.[8] Hence, the criterion of reversibility is not necessary to justify the use of the Hammett equation in polarographic systems.

Cavagnol and Wilson[9] found in their study of the thermodynamic acidity constants of 1,2,3,4-tetrahydroquinoxaline and its 6-methyl and 6-methoxy derivatives that it is feasible to consider the 6-position as "*meta*" to N^4 and "*para*" to N^1 in weighing electronic influences due to a substituent at that position. If 1,4-addition occurs, as shown in equation 1, then N^1 and N^4 are involved equally in the reduction process and a substituent in the 6-position exerts a combined "*meta*" and "*para*" influence in this reaction. Hence, the σ-values for each substituent in the application of equation 3 to the first major wave of quinoxalines must be the sum of its *meta* and *para* values. In Fig. 1 are plotted half-wave potentials *vs.* the sum of *meta* and *para* σ-values for each substituent at the different *p*H levels studied. Half-wave potentials become less negative as the electron-withdrawing influence of the substituent increases. Discounting the behavior manifested by the amino derivative at *p*H 2

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[6] R. W. Brockman and D. E. Pearson, THIS JOURNAL, **74**, 4128 (1952); P. Zuman, *Chem. Listy*, **47**, 1234 (1953); Z. R. Grabowski, *Roczniki Chem.*, **28**, 513 (1954); E. L. Colichman and S. K. Liu, THIS JOURNAL, **76**, 913 (1954).

[7] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, Chapter VII.

[8] S. Wawzonek, *Anal. Chem.*, **28**, 638 (1956).

[9] J. C. Cavagnol and G. Wilson, Jr., THIS JOURNAL, **72**, 3752 (1950).

and 4, where the amino function partakes in salt formation, essentially linear behavior is obtained over the whole *p*H range. The lines have slopes varying from -0.04 to -0.07. Though Hammett's equation is applicable for the polarographic reduction of quinoxalines to the *dihydro* stage, the influence of substituents is relatively weak. For example, Brockman and Pearson[6] obtained slopes of -0.25 in their study of the polarographic reduction of benzophenones.

The variations in heights of the second major wave with *p*H are influenced by the electronic nature of the substituents. The electron-acceptor substituents, bromo and chloro, cause the heights to decrease with increasing *p*H whereas electron-donor substituents, ethoxy and methoxy, cause the heights to increase with increasing *p*H up to and including *p*H 6. These trends can be explained qualitatively on the basis that catalytic activity increases with increasing dissociation of the 1,4-dihydroquinoxalinium ion. Electron-acceptor substituents cause the pK_a's to be lower than for the electron-donor containing systems. In each instance the proton removed from the monobasic 1,4-dihydroquinoxalinium ion comes from N^1, the "*para*" nitrogen.

Acknowledgment.—M.P.S. wishes to express his appreciation to N. J. Klein for preparing the 6-amino-, 6-chloro- and 6-methoxyquinoxaline, to J. C. W. Chien for the 6-bromoquinoxaline and to C. H. Hibbitts for the 6-ethoxyquinoxaline.

MADISON, NEW JERSEY

[CONTRIBUTION ISSUED AS NRC NO. 4643, FROM THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL]

Mass Spectra of Propyne and Propyne-d_3, and the Appearance Potentials of $C_3H_4^+$, $C_3H_3^+$ and Equivalent Deuterated Ions

BY J. COLLIN[1] AND F. P. LOSSING

RECEIVED OCTOBER 21, 1957

A comparison of the mass spectra of CH_3CCH and CD_3CCH shows that extensive migration of hydrogen atoms occurs in the propyne ion, the loss of H and D atoms occurring on a statistical basis. The appearance potentials of the $C_3D_3^+$ and $C_3D_2H^+$ ions from CD_3CCH do not show the difference in the energy of formation which would be expected if these ions were CD_3CC^+ and $^+CD_2CCH$, respectively. It is concluded that the $C_3D_3^+$ and $C_3D_2H^+$ ions are both propargyl ions, and that their formation involves an extensive rearrangement of hydrogen atoms. From a consideration of the value of D(H–C_3H_3) derived from these appearance potentials it is concluded that the excess energy available for the rearrangement is appreciably less than 9 kcal./mole, and is possibly almost zero. The ionization potentials of C_3D_3H and C_3H_4 are found to be the same within the experimental error.

Introduction

From a study of the appearance potentials of the $C_3H_3^+$ ion produced from allene, propyne, butyne and 1,2- and 1,3-butadienes by electron impact[2] it was concluded that this ion had the propargyl ($\overset{+}{C}H_2—C\equiv CH$) structure. It might therefore be expected that the formation of the $C_3H_3^+$ ion from propyne would be a simple process in which a H atom is split off from the methyl group, without any rearrangement of hydrogen atoms being involved. On the other hand, some preliminary experiments on the mass spectrum of $CD_3—C\equiv CH$ showed that, at least with 50 volt electrons, the loss of H and D was in the ratio 1:3, suggesting that in the $C_3H_4^+$ ion all the hydrogens were equivalent.[3] Furthermore, the ionic heats of formation indicated that the formation of the $C_3H_3^+$ ion from 1,3-butadiene and 2-butyne, for which a migration of a hydrogen atom is necessary, proceeds with little or no activation energy. In view of this, it is of interest to find whether the apparently straight-forward process for formation of the $C_3H_3^+$ ion from propyne itself also involves a migration and, if so, whether the required activation energy is sufficient to invalidate the determination of $D(C_3H_3\text{–}H)$ in propyne.[2] Consequently the abundance of C_3 ions and C_2 ions in the spectrum of propyne and of propyne-d_3 have been compared at lower electron energies, and the appearance potentials of $C_3D_3^+$ and $C_3D_2H^+$ ions have been measured and compared with the corresponding ion in propyne itself.

Experimental

The propyne was obtained from Farchan Research Laboratories. The sample of propyne-d_3, prepared by Merck and Company (Canada) was found to be 97.7–98.0% $CD_3—C\equiv CH$, the remainder being mainly $C_3D_2H_2$. Corrections were made to the mass spectra to remove the small contributions from this impurity. The mass spectrometer was a 90° Nier-type, and the method of measuring the appearance potentials was the same as that used previously.[2]

Results and Discussion

The relative intensities of C_3 and C_2 peaks in the mass spectrum of propyne at different electron accelerating potentials are given in Table I. In Table IIa are shown the corresponding peak intensities for propyne-d_3. In both cases the peaks have been corrected for contributions from carbon-13, and the propyne-d_3 spectrum has been corrected for contributions from the propyne-d_2 impurity. In Table IIb the spectrum of propyne-d_3 has been simplified by combining peaks of similar composition to facilitate comparison with the propyne spectrum. It can be seen that the intensities are quite similar for C_3 peaks but less so for C_2 peaks.

The most interesting feature of the spectrum in Table IIa is the ratio of the $C_3D_3^+$ and $C_3D_2H^+$

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[1] National Research Council of Canada Postdoctorate Fellow 1956–1957. Institut de Chimie Générale, Université de Liège, 1B Quai Roosevelt, Liège, Belgium.

[2] J. Collin and F. P. Lossing, THIS JOURNAL, **79**, 5848 (1957).

[3] J. B. Farmer and F. P. Lossing, *Can. J. Chem.*, **33**, 861 (1955).