

$K_H^{4,2} = 0.25 \pm 0.09$ at 22°) two values of K_H^0 at 22° can be calculated from the usual thermodynamic equations and the assumptions that (a) the activity coefficients of NaHSe and Na_2Se in these solutions are the same as those of NaOH and Na_2SO_4 , respectively, at the ionic strength of the solutions, and (b) Latimer's estimates of the entropies of HSe^- and Se^{2-} , namely, 22 and 0 e.u., respectively,¹⁰ are correct. These calculations give, from the measurements at 0.5° , $K_2^0 = 10^{-14.5 \pm 0.4}$ at 22° , where the limits of error come from the limits of error of the original measurement and my estimate of the reliability of the above assumptions. The measurement at 22° gives $K_2^0 = 10^{-15.9 \pm 0.8}$. If both measurements are taken into account with their estimated limits of error, the best value is probably $K = 10^{-15.0 \pm 0.6}$.

TABLE V

Compound	ACID CONSTANTS OF H_2A			Ref.
	pK_1	pK_2	$pK_2 - pK_1$	
H_2O	15.7			
H_2S	7.0	12.9	5.9	11, 12
H_2Se	3.6	15	11.4	6, 7
H_2Te	2.6	11	8.4	7, 3

(10) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1953.

(11) H. Kubli, *Helv. Chim. Acta*, **29**, 1962 (1946).

(12) N. Konopick and O. Leberl, *Monatsh. Chem.*, **80**, 781 (1949).

Table V gives the pK 's (where $pK = -\log K$) of several of the acids analogous to H_2Se .

Assuming a simple electrostatic model, one obtains the equations

$$pK_1 = \frac{Cz_1z_2}{r} = \frac{C}{r}$$

$$pK_2 = \frac{Cz_1z_2}{r} = \frac{2C}{r} \text{ and } pK_2 - pK_1 = \frac{C}{r}$$

where C is a constant, z_1 and z_2 are the charges on the ions, and r is the bond length of the atoms. On the basis of this model one would expect that pK_1 , pK_2 and $pK_2 - pK_1$ would increase from the heavier members of the series to the lighter members. This does not occur. The discrepancy is shown most distinctly by $pK_2 - pK_1$, where the value is lower for H_2S than for either H_2Te or H_2Se . Therefore, on the basis of this model, one would conclude that the value of K_2 for H_2S is anomalous. The assignment of partially covalent character to the bonds does nothing to help resolve this anomaly.

Acknowledgment.—I wish to express my appreciation to Professor Richard E. Powell and to Professor Robert E. Connick for their many helpful suggestions in connection with this work, which was performed under the auspices of the U. S. Atomic Energy Commission.

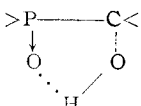
BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TEMPLE UNIVERSITY]

Phosphine Oxides. V. Intra- and Intermolecular Association¹

BY CAROLINE D. MILLER,^{2,3} ROBERT CLAY MILLER³ AND WILLIAM ROGERS, JR.

RECEIVED SEPTEMBER 27, 1957

An intramolecular hydrogen bond of the type  has been found in certain α -hydroxy phosphoryl compounds.

The strength of this bond has been related to the negativity of the phosphoryl oxygen. When the phosphoryl is extremely polarized, as in the phosphine oxides, an intermolecular association is also observed. This is probably a dipole-dipole interaction of these phosphoryl groups.

The spectra of a number of phosphoryl compounds have appeared recently in the literature, and various assignments have been made, both empirically and theoretically. The effect of electronegativity of the substituents on the phosphoryl stretching frequency has been shown,^{4,5} and the existence of hydrogen bonding phenomena involving the phosphoryl group has been demonstrated.^{6,7} Anal-

ogous relationships involving the carbonyl group have received somewhat more attention: and, with the exception of the steric differences of the tetrahedral phosphorus atom of the phosphoryl from the planar carbon atom of the carbonyl, there exists a notable similarity.

Recent work at this Laboratory has resulted in the synthesis of several new classes of organophosphorus compounds, whose spectra have also been recorded, from which certain information concerning their structure and properties may be deduced. Chronologically the first, and structurally the simplest, of these are the disubstituted phosphine oxides, $\text{R}_2\text{P}(\text{O})\text{H}$. Prior to their general synthesis,⁸ such compounds were tentatively classed as trivalent phosphinous acids, $\text{R}_2\text{P}-\text{OH}^9$. However, the presence of strong P-H absorption at 2335 cm^{-1}

(1) Presented at the Meeting of the American Chemical Society at New York, N. Y., September 1957. For the fourth paper in this series, see R. C. Miller, C. D. Miller, W. Rogers and L. A. Hamilton, *THIS JOURNAL*, **79**, 424 (1957).

(2) Abstracted in part from the dissertation submitted by C. D. M. to the Temple University Graduate Council in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Experimental Station, E. I. du Pont de Nemours Co., Wilmington, Delaware.

(4) L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

(5) J. V. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, *THIS JOURNAL*, **76**, 5185 (1954).

(6) G. M. Kosolapoff and J. F. McCullough, *ibid.*, **73**, 5392 (1951).

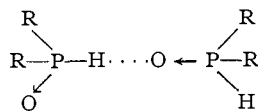
(7) E. Halpern, J. Bouck, H. Finegold and J. Goldenson, *ibid.*, **77**, 4472 (1955).

(8) R. H. Williams and L. A. Hamilton, *ibid.*, **74**, 5418 (1952).

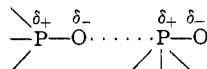
(9) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950.

and a P→O absorption at 1190 cm.⁻¹, together with the absence of any absorption which could reasonably be assigned to an O-H stretching mode (except, perhaps, for a slight shoulder near 2700 cm.⁻¹) is strong evidence that these compounds exist as the tetravalent form, predominantly if not exclusively.

An interesting detail of the spectra of these compounds is the unmistakable shift of the phosphoryl absorption from 1150–1155 cm.⁻¹ in the solid state to 1190 cm.⁻¹ in carbon disulfide solution. An intermolecular association is strongly indicated; it is not, however, the most obvious, since the P-H



frequency decreases, rather than increases, upon solution (2335 cm.⁻¹ in solid state; 2283 cm.⁻¹ in carbon disulfide solution). Similar evidence for intermolecular association of the phosphoryl group of trialkyl phosphine oxides is observed. Solution of tri-*n*-octylphosphine oxide in carbon disulfide produces an increase in frequency from 1142 to 1170 cm.⁻¹. This almost certainly can be attributed to dipole-dipole association of the phosphoryl groups.



The association of the disubstituted phosphine oxides is probably similar, and the shift of the P-H stretching frequency can be interpreted as reflecting the change of electron affinity of the phosphorus atom in the associated and non-associated states.

While the number of compounds containing P-H groups which we have examined is too limited to draw any firm conclusions, it seems to be generally true that the P-H frequency varies with the nature of the other substituents upon the phosphorus in the same sense as does the phosphoryl. The rather wide (for an X-H type vibration) range of P-H absorption from compound to compound has been noted by Bellamy¹⁰ without any explanation. Available data from this Laboratory and from the literature for the P-H frequency in tetravalent species are listed in Table I. Plotting these frequencies against the sum of the phosphoryl shift constants⁹ of the other two substituents, excluding the oxygen, gives a smooth curve, as shown in Fig. 1. Trivalent species would not be expected to obey this relationship.

TABLE I
P-H FREQUENCIES IN VARIOUS TETRAVALENT PHOSPHORUS COMPOUNDS

Compound	ν P-H (cm. ⁻¹)
(C ₂ H ₅ O) ₂ P(O)H	2433
C ₆ H ₅ (C ₂ H ₅ O)P(O)H	2350 ⁴
C ₆ H ₅ P(O)(H)OH	2381 ⁴
(<i>n</i> -C ₈ H ₁₇) ₂ P(O)H	2335
(<i>n</i> -C ₁₈ H ₃₇)P(O)(H)OH	2375

(10) C. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 263.

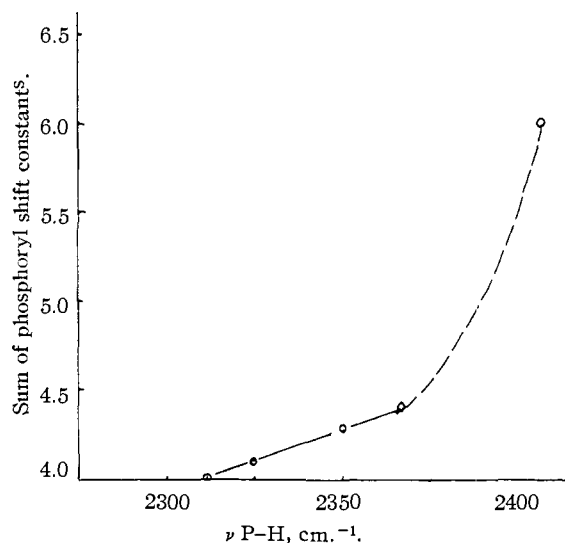
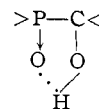
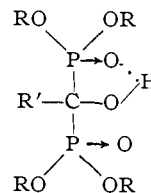


Fig. 1.—Variation of P-H stretching frequency.

From simple, symmetrical trisubstituted phosphine oxides, consideration was next directed to the dialkyl α -hydroxyalkylphosphine oxides, whose synthesis recently was reported.¹ Absorption data for these compounds are given in Table II. These compounds showed a strong phosphoryl absorption at 1100–1140 cm.⁻¹ in the crystalline state which increased to 1160–1165 cm.⁻¹ in carbon disulfide solution. In addition, these compounds exhibit a characteristic, strong, well-defined absorption near 3050–3100 cm.⁻¹ which shifted only slightly (3090–3150 cm.⁻¹) upon dissolving in carbon disulfide and whose frequency was thereafter independent of concentration at successive dilutions to 0.01 *M*. The assignment of this as a hydroxyl stretching frequency was confirmed by deuteration of several examples by recrystallization from D₂O-dioxane solution. Exchange was incomplete, but O-D absorption was observed as expected at 2340 cm.⁻¹. By coincidence, this is very nearly the frequency of the P-H in the parent disubstituted phosphine oxide. There was no evidence, either chemical or spectroscopic, of decomposition during deuteration. Moreover, decomposition in this medium might be expected to yield P-D rather than P-H groups. These data indicate that the hydrogen bonding of the hydroxyl is primarily intramolecular as



Recently an intramolecular hydrogen bond has been suggested by McConnell and Coover¹¹ in com-



(11) R. L. McConnell and H. W. Coover, THIS JOURNAL, **78**, 4450 (1956).

TABLE II
 PHOSPHORYL AND HYDROXYL FREQUENCIES IN VARIOUS α -HYDROXY PHOSPHINE OXIDES

Compound	$\nu_{P \rightarrow O}$ (crystalline), cm. ⁻¹	$\nu_{P \rightarrow O}$ (soln.), cm. ⁻¹	ν_{OH} (crystalline), cm. ⁻¹	ν_{OH} (soln.), cm. ⁻¹	ν_{OD} (crystalline), cm. ⁻¹
(<i>n</i> -C ₈ H ₁₇) ₂ P(O)C(OH)(CH ₂) ₂	1101	1165	3067	3105	..
(<i>n</i> -C ₈ H ₁₇) ₂ P(O)C(OH)(CH ₂) ₄ CH ₂	1117	1160	3110	3155	2347
(<i>n</i> -C ₈ H ₁₇) ₂ P(O)CH(OH)C ₆ H ₅	1124	1139	3095	3110	2337
(<i>n</i> -C ₈ H ₁₇) ₂ P(O)CH(OH)C ₆ H ₄ -2-NO ₂	1129	..	3030
(<i>n</i> -C ₈ H ₁₇) ₂ P(O)CH(OH)C ₆ H ₄ -2-Cl	1136	1160	3045	3090	..
(C ₆ H ₅ CH ₂) ₂ P(O)C(OH)(CH ₃) ₂	1102	..	3077
(C ₆ H ₅ CH ₂) ₂ P(O)CH(OH)(<i>n</i> -C ₃ H ₇)	1100	..	3075
	1147	} two bands	
(C ₆ H ₅ CH ₂) ₂ P(O)CH(OH)CH(CH ₃) ₂	1105	..	3077
(C ₆ H ₅ CH ₂) ₂ P(O)C(OH)(CH ₃)(C ₂ H ₅)	1097	..	3106
(C ₆ H ₅ CH ₂) ₂ P(O)CH(OH)C ₆ H ₄ -2-Cl	1111	..	3125

 TABLE III
 PHOSPHORYL AND HYDROXYL FREQUENCIES IN VARIOUS α -HYDROXYALKANEPHOSPHONATE ESTERS

Compound	$\nu_{P \rightarrow O}$ (crystalline), cm. ⁻¹	$\nu_{P \rightarrow O}$ (soln.), cm. ⁻¹	ν_{OH} (crystalline), cm. ⁻¹	ν_{OH} (soln.), cm. ⁻¹	ν_{OD} (crystalline), cm. ⁻¹
(C ₂ H ₅ O) ₂ P(O)C(OH)(CH ₃) ₂ ^a	1188	1233	3250	3285	..
(C ₂ H ₅ O) ₂ P(O)C(OH)(CH ₂) ₄ CH ₂	1212	1231	3210	3210	2445
(C ₂ H ₅ O) ₂ P(O)CH(OH)C ₆ H ₅	1190	1230	3235	3280	..
(C ₂ H ₅ O) ₂ P(O)CH(OH)C ₆ H ₄ -2-NO ₂	1195	1232	3220	3260	..
(C ₂ H ₅ O) ₂ P(O)CH(OH)C ₆ H ₄ -3-NO ₂	1179	1230	3180	3180	..
(C ₂ H ₅ O) ₂ P(O)CH(OH)C ₆ H ₄ -4-NO ₂	1230	1230	3230	3230	..
	1193	} two bands	
(C ₂ H ₅ O) ₂ P(O)CH(OH)C ₆ H ₄ -2-Cl	1203	1232	3210	3280	..

^a Liquid sample.

pounds of the type on the basis of spectral evidence. In that case, the existence of such an intramolecular bond was reported to depend on the size of R'; a bulky group was claimed necessary to deform the carbon-phosphorus bond angle to make the chelate ring possible. In our own work, chelation occurred invariably, and the geometry of the chelate ring, as judged by the O-H stretching frequency, was only marginally affected by the nature of the substituents on the α -carbon atom as shown in Table II.

All of the association phenomena discussed above were strongly dependent on the nature of the substituents on the phosphorus atom. The spectra of the alkoxy analogs of these compounds (*i.e.*, phosphonate esters) were obtained, and in all cases similar phenomena were observed, modified, of course, by the less polar nature of the phosphoryl group in these compounds. This is reflected in the lesser ability of these groups to associate with themselves or with other groups, as indicated in the examples below.

In the dialkyl phosphonates, (RO)₂P(O)H, the P-H absorption occurs at 2430 cm.⁻¹ and is constant upon solution in carbon disulfide. The phosphoryl stretching frequency is 1253 cm.⁻¹, shifting to 1259 cm.⁻¹ in carbon disulfide solution. There is no spectroscopic evidence of association in these compounds.

The dialkyl α -hydroxyalkanephosphonates, (RO)₂P(O)C(OH)R'R'', show both inter- and intramolecular bonding, although to a lesser extent than the corresponding phosphine oxides. The phosphoryl frequency was observed in the region 1190-1220 cm.⁻¹ in the crystalline state, which

shifted to 1230 cm.⁻¹ in solution. The α -hydroxyl absorption occurred at 3180-3250 cm.⁻¹ in the crystalline state and 3180-3285 cm.⁻¹ in solution. Deuteration of a typical compound as described previously gave an O-D absorption at 2445 cm.⁻¹ for a crystalline sample. These data are summarized in Table III. The formation of an intramolecular hydrogen bond between a phosphoryl and an α -hydroxy substituent is probably a general phenomenon.

A very tentative attempt was made to correlate the observed hydroxyl stretching frequencies with the calculated O O distances in these compounds. This must be considered approximate, since we have no certain knowledge of the phosphoryl bond length or the O-P-C bond angle in these compounds. Assuming tetrahedral angles and a P \rightarrow O distance of 1.39 Å,¹² an O O distance of 2.71 Å. is obtained, as shown in Fig. 2. From this, the predicted hydroxyl frequency shift may be calculated according to the equation of Pimentel and Sederholm¹³

$$\Delta\nu = 4.43 \times 10^3 (2.84 - R)$$

when R (the O O distance) is 2.71 Å., $\Delta\nu = 576$ cm.⁻¹. If the frequency of an unbonded hydroxyl is taken as 3700 cm.⁻¹, the observed $\Delta\nu$ for the phosphine oxides is ~ 580 cm.⁻¹ and for the phosphonates, ~ 450 cm.⁻¹. While both are within the ± 199 cm.⁻¹ variation found for various examples in the literature, the lower frequency of

(12) R. C. Gore, *Disc. Faraday Soc.*, 138 (1950).

(13) G. C. Pimentel and C. H. Sederholm, *J. Chem. Phys.*, **24**, 639 (1956).

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 \rightarrow 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. \ddagger Calorimetric⁶ and spectroscopic⁷ studies of the interaction of various phosphoryl compounds with proton-donating solvents indicate the greater tendency of the phosphine oxide to coordinate.

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 milled 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

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

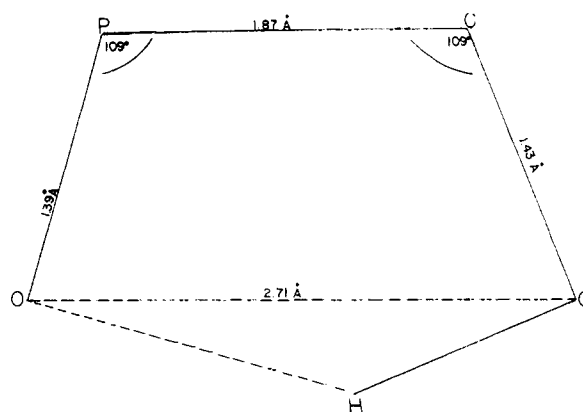


Fig. 2.—Intramolecular hydrogen bonding in α -hydroxyphosphoryl compounds.

TABLE IV

DIETHYL α -HYDROXYALKANEPHOSPHONATES, $\text{ArCH}(\text{OH})\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$

Ar	M.p., °C. uncor.	Yield, %	Calcd. P, %	Found P, %	Calcd. N, %	Found N, %
2-O ₂ NC ₆ H ₄	122.5–123.1	79.5	10.7	10.8	4.8	4.8
3-O ₂ NC ₆ H ₄	91.5–92.1	84.4	10.7	10.8	4.8	4.8
4-O ₂ NC ₆ H ₄	90.2–91.0	79.5	10.7	10.8	4.8	4.8
2-ClC ₆ H ₄	80.0–80.6	70.5	11.1	11.0	12.7 ^a	12.5 ^a

^a Chlorine, %.

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 $(n\text{-C}_8\text{H}_{17})_2\text{P}(\text{O})\text{C}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$, 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 $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{C}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$,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.

(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 Derivatives²

BY MURRAY P. STRIER AND J. C. CAVAGNOL³

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 pH's 2, 4, 6, 8 and 10. Two major waves are found at pH's 2, 4 and 6 whereas only the first major wave occurs at pH's 8 and 10. The first major wave represents reduction to the 1,4-dihydro stage. At pH 2 the differentiated nature of this wave is indicative of a bimolecular reduction in two successive one-electron steps. At higher pH's reduction is directly to the dihydroquinoxaline. For 6-aminoquinoxaline, the latter occurs at all pH'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 pH 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 investiga-

(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.

tions 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 pH's 1 and 2 the differentiated nature of the wave

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