Silver(I) Complexes of Vinyldiphenylphosphine

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Vinyldiphenylphosphine has been found to form 1:1 and 2:1 complexes with silver nitrate. In these complexes coordination occurs between Ag(I) and both the phosphorus atom and the vinyl double bond of the phosphine. Structures have been assigned for these complexes, based primarily on infrared and H^1 and P^{31} n.m.r. spectral data.

The ability of tertiary phosphines to form complex salts with metal derivatives, especially halides and carbonyls, is well known.[1,2] Complexes of unsaturated tertiary phosphines, however, have not been reported. Vinyldiphenylphosphine readily forms 1:1 and 2:1 complexes, respectively, with ethanolic silver nitrate upon mixing of the components in correct molar proportions. These complexes are white crystalline solids, stable to hydrolysis and light, and are essentially monomeric.

Table I

Some Characteristic Infrared Frequencies (cm.$^{-1}$) of Vinyldiphenylphosphine and Its Complexes[a]

$CH_2{=}CHPPh_2$	$CH_2{=}CHPPh_2 \cdot AgNO_3$	$(CH_2{=}CHPPh_2)_2 \cdot AgNO_3$	Assignment[b]
3077 (s)	3052 (m)	3050 (m)	CH stretching (CH_2)
1653 (w)	1566 (w)	1577 (w)	C=C stretching (vinyl)
1592 (s)	1592 (w)	1592 (m)	C=C stretching (phenyl)
1575 (w)	1581 (w)	. . .	C=C stretching (phenyl)
. . .	1370 (vs)	1370 (vs)	NO_3^- (assym., NO stretching)[c]
986 (s)	978 (s)	983 (s)	CH o.o.p. deformation
951 (s)	. . .	. . .	Unassigned
928 (s)	948 (s)	940 (m)	CH_2 o.o.p. deformation
. . .	833 (s)	835 (s)	NO_3^- o.o.p. deformation

[a] w = weak, m = medium, s = strong, v = very, o.o.p. = out-of-plane. [b] L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960. [c] See ref. 4 and 5.

A comparison of the infrared spectra of these Ag(I) complexes with the spectrum of the parent phosphine (Table I) reveals changes which may be attributed to coordination of the vinyl double bond with Ag(I). The vinyl CH stretching absorption at 3077 cm.$^{-1}$ is shifted to lower frequency by about 25 cm.$^{-1}$ and is accompanied by a slight decrease in intensity. Butadiene complexes[3] of Pt(II) and Pd(II) and the cyclobutadiene complex[4,5] of Ag(I) are reported to have a weak band at the 3050–3060-cm.$^{-1}$ region. The out-of-plane CH_2 deformation vibration at 928 cm.$^{-1}$ is weakened slightly and displaced to higher frequency by about 16 cm.$^{-1}$, whereas the out-of-plane CH deformation vibration at 986 cm.$^{-1}$ is shifted to lower frequency by about 5 cm.$^{-1}$ with no change in intensity. An unassigned band at 950 cm.$^{-1}$ either disappears or becomes masked by the band at 980 cm.$^{-1}$. Owing to overlapping of aromatic vibrations, the assignment of the vinyl C=C stretching frequency for the vinyl phosphine complexes cannot be made with certainty; however, the band at about 1570 cm.$^{-1}$ is probably due to this vibration which appears at 1653 cm.$^{-1}$ in the vinylphosphine. A decrease in the C=C stretching frequency in the 1600-cm.$^{-1}$ region has been reported for olefin–metal salt complexes[3-7] and aromatic metal carbonyl complexes,[8] the decrease being from 65 to as much as 143 cm.$^{-1}$. The strong bands at 718 and 830 cm.$^{-1}$ are indicative of the free, uncoordinated nitrate anion.

Furthermore, absorption of the vinyl region of the proton n.m.r. spectra of the complexes is shifted slightly downfield relative to the parent phosphine (Table II), and changes in the total line shape (line broadening and peak overlap) are observed (Figure 1). These results are quite consistent with the infrared spectra in that the nature of the C–C bond in these complexes is that of a double bond perturbed by Ag(I). Although both silver isotopes do have a magnetic moment with spin of 0.5, no attempt was made to determine the Ag–H^1 coupling constant. However, it is believed that the observed line width and peak shifts are a result of the silver atom and may be discernible with nuclear spin–spin decoupling experiments. Slight downfield proton chemical shifts have been observed with complexes of simple olefins and Ag(I)[4,5] or Pt(II).[9] As shown in Table II, small downfield shifts also occur

Table II

Proton and Phosphorus N.m.r. Chemical Shifts[a]

Compd.	δ (vinyl protons)[b]	δ (phenyl protons)[b]	δ (phosphorus)
$CH_2{=}CHPPh_2$	6.04	7.28	+13.8
$(CH_2{=}CHPPh_2)_2 \cdot AgNO_3$	6.21	7.34	+11.0
$CH_2{=}CHPPh_2 \cdot AgNO_3$	6.24	7.39	. . .

[a] δ in p.p.m. [b] Measured from the approximate center of the line shape relative to internal tetramethylsilane.

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(1) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 25–26.

(2) G. Booth, *Advan. Inorg. Chem. Radiochem.*, **6**, 1 (1964).

(3) P. J. Hendra and D. B. Powell, *Spectrochim. Acta*, **18**, 1195 (1962).

(4) H. P. Fritz, J. F. W. McOmie, and N. Sheppard, *Tetrahedron Letters*, **No. 26**, 35 (1960).

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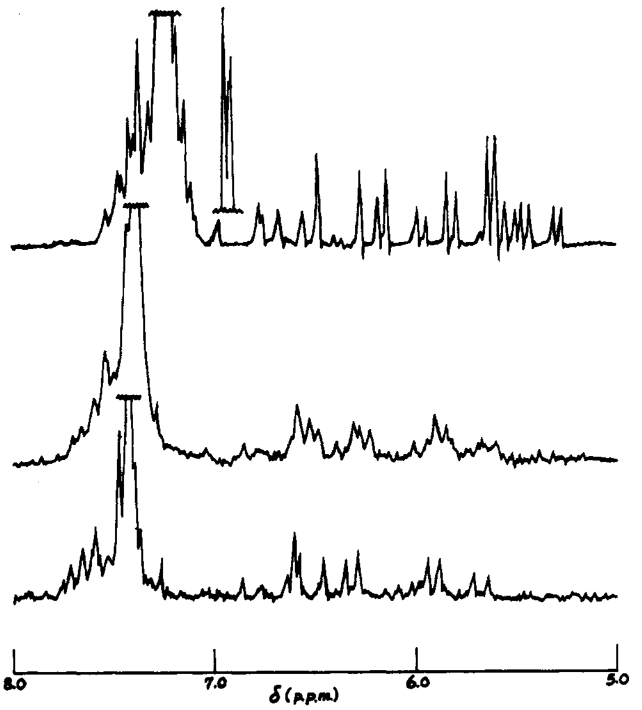
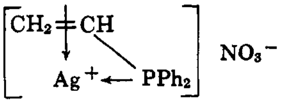


Figure 1.—The H^1 n.m.r. spectra of vinyldiphenylphosphine and its complexes (20 wt. % solutions in deuteriochloroform): top, $CH_2{=}CHPPh_2$; middle, $CH_2{=}CHPPh_2 \cdot AgNO_3$; bottom, $(CH_2{=}CHPPh_2)_2 \cdot AgNO_3$.

in the phenyl region, the cause of which is not understood fully. It might be interpreted as a deshielding effect due to the inductive effect of the phosphorus atom on the phenyl protons, brought about by the approach of Ag(I) to the phosphorus nucleus. The small upfield P^{31} chemical shifts (Table II) indicate no formal valence change in the phosphorus atom of the complexes. They could, however, be explained as due to a shielding effect exerted on the phosphorus nucleus by the approach of the relatively large Ag(I). This would mask any deshielding of the phosphorus nucleus due to the P–Ag electronic attraction. Thus, both proton and phosphorus n.m.r. data appear to indicate that the vinyl portion of the molecule is the major site of interaction with Ag(I).

Available data are insufficient to assign definite structures to these Ag(I) complexes; however, tentative structures 1 and 2 may be given to the 1:1 and 2:1 complexes, respectively. Structure 1 is analogous to the chelate structure suggested for the phenylacetylene–silver nitrate complex,[7] whereas structure 2 is similar to the chelate structure established for the complexes of the type (phosphine–arsine)$_2$Ag(I).[10] It is known that unsaturated molecules can form three types of complexes with Ag(I) (*viz.* 1:1, 1:2, and 2:1),[11] whereas tertiary phosphines can form four types of complexes with Ag(I) (*viz.* 1:1, 2:1, 3:1, and 4:1).[12] Many of these complexes are quite unstable.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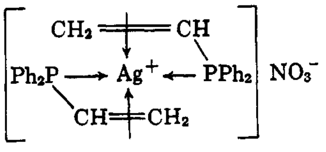
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The vinylphosphine–silver nitrate complexes could be homopolymerized by cationic catalysts or copolymerized by free-radical catalysts, the polymerization behavior being essentially identical with that of the parent vinylphosphine.[13,14] However, the polymers of the complexes were grayish, and turned black when exposed to heat or ultraviolet radiation. Thus, it appears that the Ag(I) complexes lose their stability upon polymerization and that reduction of Ag(I) to Ag(0) occurs even in the dark under the polymerization conditions. Presumably the reduction reaction is catalyzed by free radicals. The unusual stability of the vinylphosphine–silver nitrate complexes and the subsequent loss of stability upon polymerization must be attributed to the stabilizing effect of chelation involving both the phosphorus atom and the vinyl double bond.

Some complexes of the vinylphosphine with Hg(II) chloride have also been prepared, and their structures are being investigated. Attempts to prepare complexes with Zn(II) or Mg(II) chloride resulted in resinous complexes which no longer contained the vinyl group. These chlorides are apparently sufficiently acidic to initiate cationic polymerization of the vinylphosphine.

Experimental

All melting points and boiling points are uncorrected. Microanalyses and molecular weight determinations were by Galbraith Laboratories, Knoxville, Tenn. The infrared spectra of complexes (4% KBr) were recorded on a Baird-Atomic spectrophotometer, the H^1 n.m.r. spectra on a Varian A-60 spectrometer, and the P^{31} n.m.r. spectra in concentrated chloroform solutions on a Varian DP-60 spectrometer at 19.3 Mc./sec., using 85% H_3PO_4 as an external standard.

Vinyldiphenylphosphine.—The vinylphosphine was prepared from diphenylchlorophosphine and vinylmagnesium chloride[15,16] in 80% yield, b.p. 123–124° (0.3 mm.), $n^{30}\text{D}$ 1.6247.

$CH_2{=}CHPPh_2 \cdot AgNO_3$.—The vinylphosphine (2.12 g., 10 mmoles) was added to a solution of silver nitrate (1.7 g., 10 mmoles) in boiling ethanol (80 ml.). The solution was evaporated and the residue was recrystallized from isopropyl alcohol giving 2.9 g. (76% yield) of white needles, m.p. 123.5–124.5°.

Anal. Calcd. for $C_{14}H_{13}AgNO_3P$: C, 45.19; H, 3.52; N, 3.76; P, 8.33; mol. wt., 382. Found: C, 44.36; H, 3.51; N, 3.55; P, 8.13; mol. wt., 441, 445, and 460 (0.0114, 0.0196, and 0.0215 *M* in benzene)

$(CH_2{=}CHPPh_2)_2 \cdot AgNO_3$.—The above procedure was repeated with 20 mmoles of the phosphine. The product (4.7 g., 70% yield) recrystallized from isopropyl alcohol as a white solid, m.p. 108–109°.

Anal. Calcd. for $C_{28}H_{26}AgNO_3P_2$: C, 56.58; H, 4.41; N, 2.36; P, 10.43; mol. wt., 594. Found: C, 56.61; H, 4.51; N, 2.39; P, 10.55; mol. wt., 570 (0.0245 *M* in benzene).

The 2:1 complex was also prepared in low yield by shaking the vinylphosphine with an aqueous solution containing 1 equiv. of silver nitrate.

Properties of the Complexes.—Both the 1:1 and 2:1 complexes were soluble in alcohols, acetone, chloroform, aromatic

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[12] A. Turco, C. Panattoni, and E. Frasson, *Ricerca Sci. Suppl.*, **29**, 544 (1959); *Chem. Abstr.*, **54**, 148 (1960); R. C. Cass, G. E. Coates, and R. G. Hayter, *J. Chem. Soc.*, 4007 (1955); F. A. Cotton and D. M. L. Goodgame, *ibid.*, 5267 (1960); C. A. Streuli, Proceedings of the Symposium on Titrimetric Methods, Cornwall, Ont., Can., 1961, p. 97; *Chem. Abstr.*, **57**, 6865 (1962).

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solvents, and hot water. They were not hydrolyzed in hydrochloric acid, and unchanged after a 2-hr. exposure in air at 45–50° to ultraviolet light from a 100-w. Hanovia mercury arc lamp (Model 608A36) at a distance of 4 in.

Homopolymerization of the complexes with boron trifluoride etherate gave a dark brown oligomer; copolymerizations with styrene and ethyl acrylate using a free-radical catalyst were sluggish, and gave gray copolymers which turned black by heat or light.

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The Photochemical Conversion of Fumaronitrile and Acetone to Oxetanes

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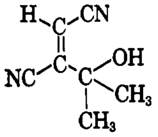
The light-catalyzed reaction of fumaronitrile and acetone provides a mixture of *cis*- and *trans*-oxetanedinitriles. The structures of the oxetanes are established and some of their acidic hydrolysis products described.

The light-catalyzed reaction of carbonyl compounds with olefins to form oxetanes[1] was ignored until Büchi's[2] investigation of the reaction 10 years ago. Since then a considerable effort has been expended in studying the scope and mechanism of the reaction.[3] Recently some older literature work came to our attention that suggested it contained one of the earliest examples of oxetane formation, although this had not been recognized.

Stoermer[4] had observed that fumaronitrile in ethanol isomerized under ultraviolet radiation to give a low yield of maleonitrile. In addition, a considerable amount of ethoxysuccinic acid was formed. In an attempt to improve the yield of the isomerization, Jennen[5] used acetone as the solvent.[6] While he did obtain some isomerization to maleonitrile, the principal product of the reaction was a material, $C_7H_8N_2O$, to which he assigned structure A,[7] since acid hydrolysis yielded a lactone acid which he regarded as oxyisoterebinic acid lactone (B).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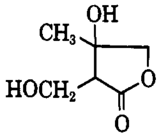
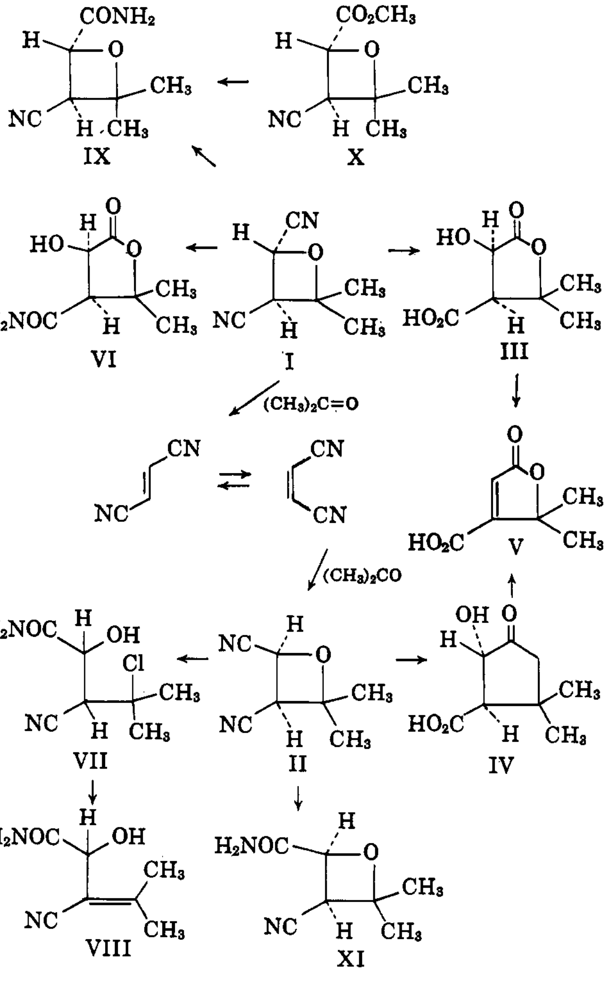

B

Since these structures appeared unlikely, we have repeated the reaction and followed the course of product formation by means of gas–liquid chromatography (g.l.c.). The first product observed was maleonitrile closely followed by the oxetane I (Scheme I). Finally oxetane II was noticed. After most of the starting material had been converted, the oxetanes were isolated and purified. The infrared spectra of both oxetanes showed a nitrile band but no hydroxyl or olefin absorption. The n.m.r. spectrum of I showed singlets for two methyl groups and a coupling of 6 c.p.s. for the remaining two protons. The corresponding coupling constant for the isomer II appeared to be 8.5 c.p.s. while the presence of the methyl groups was again indicated by two singlets.

SCHEME I



The reaction of acetone and fumaronitrile with ultraviolet light filtered out by Pyrex below 290 mμ led to the same product mixture but at a considerably slower reaction rate. Maleonitrile and acetone are converted to a mixture of the same compounds but with a higher proportion of II. However, in methanol, fumaronitrile is not isomerized to maleonitrile by ultraviolet light above 290 mμ. Apparently at this wave length

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[5] J. Jennen, *Bull. soc. chim. Belges*, **46**, 258 (1937).

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[7] Griffin[6] incorrectly quotes this structure as the dihydro compound.