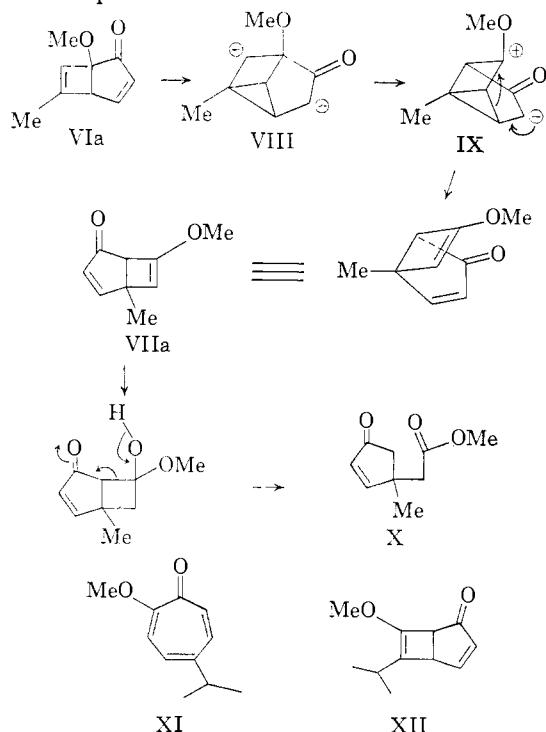


meric structure (III or VI).<sup>5</sup> In these latter structures the ultraviolet maximum is at a somewhat longer wave length than expected for a simple cyclopentenone. This bathochromic shift may be attributed to interaction between the non-conjugated double bond in the four-membered ring and the cyclopentenone chromophore,<sup>5</sup> as indicated by excited state VIII. Light induced migration of the carbonyl carbon gives rise to excited state IX which can collapse to ground state VIIa. Hydrolysis of VIIa via the hemiketal leads directly to ester X. In accord with prediction based upon this mechanistic picture, irradiation of  $\gamma$ -thujaplicin methyl ether (XI) in methanol gave XII (other unidentified products are formed).

Satisfactory analyses have been obtained for all new compounds.



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(5) O. L. Chapman and D. J. Pasto, *J. Am. Chem. Soc.*, **82**, 3642 (1960).

(6) National Science Foundation Cooperative Predoctoral Fellow, 1959-1961.

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### HCP, A UNIQUE PHOSPHORUS COMPOUND

Sir:

We wish to report the first<sup>1</sup> successful synthesis of a trivalent phosphorus compound that unquestionably contains a multiple P-C bond.<sup>2</sup>

Methinophosphide (HCP) has been prepared by passing phosphine through a low intensity (50-100 amperes, 25 volts) rotating arc struck between graphite electrodes contained in a water-cooled copper reactor.<sup>3</sup> The average operating pressure was 40 mm. and the gaseous products were quenched in traps maintained at  $-196^{\circ}$ . In a typical arc experiment, 20 g. of  $\text{PH}_3$  was treated in about one hour.<sup>4</sup> The condensable volatile products, HCP and acetylene in 1:4 molar ratio with traces of phosphine and ethylene, were separated on a gas-chromatographic column (helium carrier gas, ethyl N,N-dimethyl oxalamate partition fluid, silica gel support). A large excess and fast throughput of helium were necessary to minimize loss of HCP through polymerization.

HCP is a very reactive colorless gas, stable to storage in the pure state only at temperatures below its triple point of  $-124 \pm 2^{\circ}$ . The vapor pressure at this temperature is approximately 30 mm. The monomer polymerizes slowly at  $-130^{\circ}$  and more rapidly at  $-78^{\circ}$  to a black solid. Both the monomer and the freshly formed polymer are extremely pyrophoric when exposed to air, even at low temperatures. However, on prolonged standing, the insoluble and infusible polymer becomes considerably less reactive.

*Anal.* Calcd. for  $(\text{HCP})_x$ : H, 2.27; C, 27.28; P, 70.45. Found: H, 2.95; C, 26.77; P, 71.07.

This establishes the empirical proportions of the monomer since no other products are formed in the polymerization.

There are two possible monomeric structures,  $\text{H}-\text{C}\equiv\text{P}$  and  $\text{H}-\text{P}\equiv\text{C}$ , and numerous polymeric structures that can be assigned. Analysis of the mass spectrum of this compound out to 204 m./e. units lends strong support to a monomeric formulation, since no peaks at 88 (dimer) or 132 (trimer) were detectable. The data, however, do not distinguish between HCP and HPC structures because rearrangement, *i.e.*, hydrogen migration, is common in mass spectral analyses of unsaturated

m./e.	Rel. intensity	Assignment
45	1.3 (theor. 1.29) <sup>5</sup>	$\text{HC}_{12}\text{P}^+$
44	100	$\text{HC}_{12}\text{P}^+$ , $\text{C}_{13}\text{P}^+$
43	16.7	$\text{C}_{12}\text{P}^+$
32	1.4	$\text{HP}^+$
31	12.1	$\text{P}^+$
22	4.0	$\text{HC}_{12}\text{P}^{++}$ , $\text{C}_{13}\text{P}^{++}$
$15^{1/2}$	0.5	$\text{P}^{++}$
13	3.1	$\text{HC}_{12}^+$ , $\text{C}_{13}^+$
12	3.7	$\text{C}_{12}$

(1) The literature contains relatively few references to the carbon-phosphorus triple bond. W. B. Shober and F. W. Spanutius [*J. Am. Chem. Soc.*, **16**, 229-232 (1894)] claim a synthesis of NaCP, without analytical data, but their work could not be confirmed in this laboratory. H. Albers [*Angew. Chem.*, **62**, 443-467 (1950)] discusses the existence of HCP and HCAs.

(2) In ylides,  $\text{R}_2\text{PCR}_2$ , the P-C bond certainly has multiple bond character but the ionic form is probably the major contributor to the ground state.

(3) The hollow cathode was positioned coaxially with a cup-shaped anode so that a conical arc curtain was maintained.

(4) Long operating times were precluded in our arc apparatus because of plugs of red and yellow phosphorus from thermal decomposition of  $\text{PH}_3$ . This disproportionation accounted for the major portion of phosphorus values introduced into the reactor and resulted in very low yields of condensable off-gases (0.5-1.0 g.).

(5) This value is based on intensity of 44 peak for  $\text{HC}_{12}\text{P}^+$  and  $\text{C}_{13}\text{P}^+$ .

compounds and, in fact, m./e. peaks assignable to both  $\text{HC}^+$  and  $\text{HP}^+$  were observed.

The infrared spectrum of solid HCP monomer at  $-196^\circ$  is wholly consistent with the HCP structure. The fundamentals are given below and compared with those found for solid HCN at the same temperature. There is also a band in

	$\nu$ (cm. <sup>-1</sup> )	Assignment	$K$ (dynes/cm. 10 <sup>9</sup> )
HCP	3180	C-H str.	5.4
HCN	3120	C-H str.	5.4
HCP	1265	C-P str.	8.7
HCN	2120	C-N str.	16.2
HCP	671	C-H bend	
HCN	830 <sup>6</sup>	C-H bend	

the HCP spectrum at  $1354 \text{ cm.}^{-1}$  which appears to be the first overtone of the C-H bending vibration and a weak broad band at  $812 \text{ cm.}^{-1}$  that could be a combination band of the C-H bending with a lattice vibration. There is no absorption in the  $2350\text{--}2440 \text{ cm.}^{-1}$  region characteristic of P-H stretch.

Further support for the  $\text{HC}\equiv\text{P}$  structure was obtained from the reaction of the monomer with excess anhydrous  $\text{HCl}$  at  $-110^\circ$ . Under these conditions,  $\text{CH}_3\text{PCl}_2$  was the sole product.

(6) The value for  $\text{HCN(g)}$  is  $712 \text{ cm.}^{-1}$ . The marked shift to higher wave numbers suggests strong hydrogen bonding in solid HCN.

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### THIABENZENE. I. 1,2,4,6-TETRAPHENYLTHIABENZENE, A NEW CONJUGATED RING SYSTEM

Sir:

2,4,6-Triphenylthiopyrylium perchlorate<sup>1</sup> (I, 2.5 g.) suspended in 100 ml. of ether under an atmosphere of nitrogen was treated with 3.5 equivalents of phenyllithium in ether. Solid I disappeared rapidly giving a deep red-violet solution. After 5 min., aqueous ammonium chloride was added, the ethereal layer then was washed with water and dried over potassium carbonate. After adding 50–75 ml. of purified petroleum ether (b.p.  $30\text{--}60^\circ$ ) and chilling in Dry Ice-acetone, the violet solution was decanted from ca. 0.2 g. of light-colored solid and evaporated to dryness *in vacuo*. The residual violet resin was redissolved in 30 ml. of ether and poured into 250 ml. of petroleum ether cooled in a Dry Ice-acetone bath. The finely divided amorphous violet thiabenzene (II), m.p. ca.  $45\text{--}48^\circ$ , weighed 0.7 g.

*Anal.* Calcd. for  $\text{C}_{29}\text{H}_{22}\text{S}$ : C, 86.51; H, 5.52; S, 7.96; mol. wt., 402. Calcd. for  $\text{C}_{29}\text{H}_{22}\text{S}\cdot\frac{1}{2}\text{Et}_2\text{O}$ : C, 84.70; H, 6.19; S, 7.29. Found: C, 85.26, 84.94; H, 5.80, 5.70; S, 7.06; mol. wt., 380 (cryos., benzene).

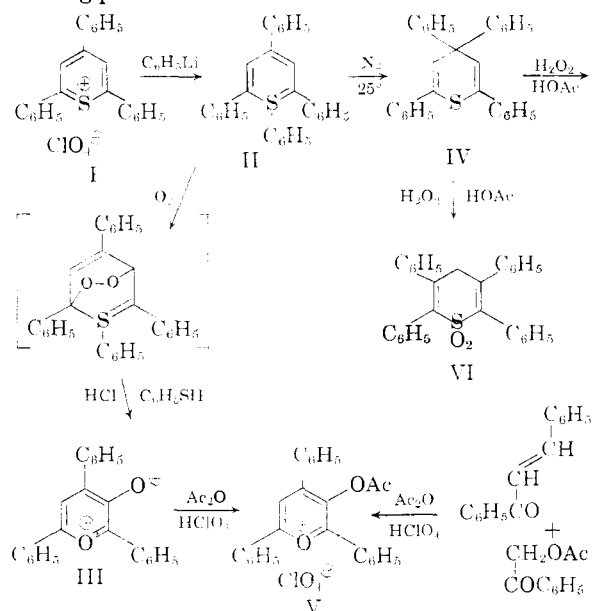
Analysis indicated the retention of some ether. Purification was obstructed by the chemical reactivity and the non-crystalline character of the product. The principal ultraviolet maxima occurred at 244 and  $524 \text{ m}\mu$  (ethanol), the major in-

frared bands at 6.28, 6.70, 6.95, 7.05, 8.05 and  $14.40 \mu$ .

An ethereal solution of II, prepared from 10 g. of I, after washing with aqueous ammonium chloride and water, was treated with oxygen for 30 min. The violet color faded to orange-yellow. On bubbling dry hydrogen chloride into the solution, the odor of thiophenol immediately became evident<sup>2</sup> and a deep orange precipitate settled from solution. The solid was dissolved in acetone, precipitated by water and recrystallized as dark red needles (III) from acetone, 4.45 g. (60%), m.p.  $193.5\text{--}195^\circ$ .

*Anal.* Calcd. for  $\text{C}_{23}\text{H}_{16}\text{O}_2$ : C, 85.20; H, 4.96. Found: C, 85.19; H, 5.09. From the mother liquors, small amounts of two colorless compounds  $\text{C}_{23}\text{H}_{16}\text{O}_3$ , m.p.  $181^\circ$  (0.7 g.) and  $280^\circ$  (0.25 g.) and 0.4 g. of 2,4,4,6-tetraphenylthiapyran (IV) m.p.  $156\text{--}157^\circ$ , were obtained.

The red compound III (0.4 g.) was dissolved in 15 ml. of acetic anhydride containing 6 drops of sulfuric acid and refluxed for 4 hr. After cooling, the reaction mixture was poured into 150 ml. of ice-cold 20% perchloric acid. The microcrystalline yellow product was recrystallized from glacial acetic acid as canary-yellow platelets of 3-acetoxy-2,4,6-triphenylpyrylium perchlorate (V), 0.3 g. (60%), m.p.  $230\text{--}231.5^\circ$ . *Anal.* Calcd. for  $\text{C}_{25}\text{H}_{18}\text{ClO}_7$ : C, 64.31; H, 4.10; Cl, 7.60. Found: C, 64.09; H, 4.16; Cl, 7.83. The same product was obtained by the reaction of benzalacetophenone with phenacyl acetate in acetic anhydride containing perchloric acid. The infrared spectra were identical and there was no depression of mixture melting point.



II lost its violet color slowly on standing under nitrogen, in bulk or in solution. When 200 mg. was sealed under nitrogen and kept for 20 days, a pale yellow resin resulted. Recrystallization from methanol gave 50 mg. of IV, m.p.  $155\text{--}156^\circ$ .

(2) The thiophenol was characterized further by conversion to 2,4-dinitrodiphenyl sulfide, m.p.  $119\text{--}120^\circ$  (R. W. Bost, J. O. Turner and R. D. Norton, *J. Am. Chem. Soc.*, **54**, 1985 (1932)).

(1) R. Wizinger and P. Ulrich, *Helv. chim. acta*, **39**, 207 (1956).