

compounds and, in fact, m./e. peaks assignable to both HC^+ and HP^+ were observed.

The infrared spectrum of solid HCP monomer at -196° 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

	ν (cm. ⁻¹)	Assignment	K (dynes/cm. 10 ⁹)
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 ⁶	C-H bend	

the HCP spectrum at 1354 cm.^{-1} which appears to be the first overtone of the C-H bending vibration and a weak broad band at 812 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 HCl at -110° . Under these conditions, CH_3PCl_2 was the sole product.

(6) The value for HCN(g) is 712 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 perchlorate¹ (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).

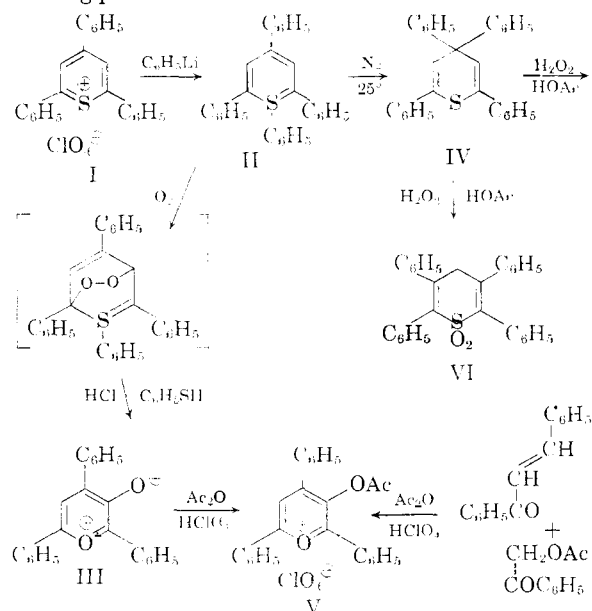
Analysis indicated the retention of some ether. Purification was obstructed by the chemical reactivity and the non-crystalline character of the product. The principal ultraviolet maxima occurred at 244 and $524 \text{ m}\mu$ (ethanol), the major in-

frared bands at 6.28, 6.70, 6.95, 7.05, 8.05 and 14.40μ .

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 evident² 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° (0.7 g.) and 280° (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).

