Table I. Coupling Constants (Gauss) of Hexakis(trifluoromethyl)benzene Anion in Tetrahydrofuran

Temp, °K	a^F	a^{C_1}	a^{C_2}
299		4.721	5.836
297	7.530		
274		4.669	5.775
273	7.554		
243		4.603	5.743
239	7.596		
216		4.559	5.701
208	7.615		
207		4.540	5.651
185	7.643		

Bolton and Fraenkel[5] indicate that line-width variations among sets of equivalent ^{13}C nuclei having the same statistical weights can be used in assigning coupling constants. The lines belonging to the set of nuclei having the larger local π-electron spin density should be broader under conditions where the anisotropic dipole interactions affect the line width. As the temperature was lowered, the amplitudes of the ^{13}C satellites with the larger splitting were found to decrease more than the amplitudes of the other pair. Therefore, we assign the larger coupling constant to the ring carbon nuclei, since only these atoms should have a significant local π-electron spin density.

Of particular interest in these data is the magnitude of a^{C_2}. Bolton[6] has reported a value of 2.8 gauss for a^C in the benzene anion at $-100°$. Our extrapolated value of 5.62 is about twice as large. This larger coupling may be explained if the benzene ring of I is slightly nonplanar. In this case, either changes in hydridization or bond polarization effects could influence the magnitude of a^C. Karplus and Fraenkel[7] predict an increase of about 20 gauss in the ^{13}C splitting for a 5° deviation from planarity of the methyl radical. At lower temperatures an increase in the planarity of the benzene ring would cause a decrease in the ^{13}C coupling constant, as observed here.

It has been suggested[1,8] that a p orbital of fluorine can undergo direct conjugation with the π orbital containing the unpaired spin. An enhancement of the conjugation as the temperature is lowered would lead to an increase in a^F. Our results are thus consistent with those obtained by Scheidler and Bolton[1] for II.

The decrease in a^{C_1} and a^{C_2} as the temperature is lowered could then arise partially from a transfer of π-spin density to the fluorine p orbitals. It is difficult to draw any quantitative conclusions from this work and that of Scheidler and Bolton, however, because of the possibility of at least two mechanisms contributing to the temperature dependence of the coupling constants.

Acknowledgment. This work was supported by the National Science Foundation through Grant GP-3398.

(5) J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, 41, 944 (1964).
(6) J. R. Bolton, *Mol. Phys.*, 6, 219 (1963).
(7) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, 35, 1312 (1961).
(8) W. A. Sheppard, *J. Am. Chem. Soc.*, 87, 2410 (1965).

J. C. Danner, A. H. Maki
Department of Chemistry, University of California
Riverside, California 92502
Received June 16, 1966

A Thiopolyphosphine Heterocycle[1]

Sir:

The existence of the homocyclic polyphosphines $(CF_3P)_4$ and $(CF_3P)_5$[2] suggests the possibility of heterocycles in which CF_3P is replaced by another bifunctional unit. However, various attempts to make CF_3P–O heterocycles have failed, and recent attempts toward CF_3P–NR heterocycles fared no better.[3] One may argue that the $(CF_3P)_n$ rings are stabilized by circumannular delocalization of the phosphorus lone-pair electrons *via* the P_{3d} orbitals (enhanced by the electron-withdrawing CF_3 groups), whereas the insertion of N or O into the ring would block such delocalization. Hence a $(CF_3P)_nO$ or $(CF_3P)_nNR$ ring might be far less stable than other arrangements of the same atoms.

However, the insertion of sulfur into the P_n ring would not block the 3d delocalization; rather, S_{3d} would contribute only a little less π-bonding energy than P_{3d} aided by CF_3.

Accordingly, the stable compound $(CF_3P)_4S$ can be made by direct addition of S_8 to $(CF_3P)_4$ at temperatures in the μ-sulfur range. Although this inorganic thiophene analog is the first clearly recognized product of the reaction, other P–S heterocycles apparently are formed in larger yield.

Synthesis. Each of the two main experiments employed 1 g-atom of sulfur[4] per $(CF_3P)_4$, in sealed tubes at 170–250° for as long as 5 hr. The colorless liquid mixture consisted mostly of an oil which could be refluxed under high vacuum only by heating toward 100°. However, about 15% of it was a liquid having 1-mm vapor tension at 25°, separable from the 27–35% of unconsumed $(CF_3P)_4$ by a high-vacuum microcolumn (boiler, 50°; reflux, 0°). It showed the vapor-phase molecular weight (437 or 432) and chemical behavior expected for a heterocyclic $(CF_3P)_4S$. Its strong infrared spectrum in the C–F stretching region lacked certain intense peaks characteristic of $(CF_3P)_n$: the tetramer had been removed and the pentamer had not been formed at the reaction temperature.

A less volatile fraction (*ca.* 0.5 mm at 25°) showed a different infrared spectrum (*e.g.*, a single main C–F stretching peak at 1153 cm^{-1}). It was heated in a sealed tube with mercury (48 hr, 145°), forming HgS and nearly pure $(CF_3P)_4S$, but no $(CF_3P)_n$. Removal of one S from a P–S–S–P situation is suggested.

Chemical Proof of Formula. The most direct proof of the formula $(CF_3P)_4S$ is described by the following equation with mmole stoichiometry.

$$(CF_3P)_4S + (CH_3)_3P \longrightarrow (CH_3)_3PS + 4CF_3P$$

0.359	0.399	0.352	1.432
	−0.036		(99.7%)
	0.363		

The sample was from the mercury-treated product. A more direct column distillate (mol wt obsd 432) slowed slightly more sulfur and less CF_3P per mole, suggesting impurities such as $(CF_3P)_4S_2$ and $(CF_3P)_3S$. The principle of the method relates to the reversible

(1) Supported by Grant No. GP-3812 from the National Science Foundation, which contributed also through Grants GP-199 and G-14665 toward the purchase of the Beckman IR7 spectrophotometer with NaCl and CsI optics.
(2) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, 80, 6161 (1958).
(3) J. Heners and A. B. Burg, *ibid.*, 88, 1677 (1966).
(4) A spectroscopically pure crystalline product of American Smelting and Refining Co., kindly supplied by Professor J. Donohue.

formation of $(CH_3)_3PPCF_3$ and the consequent catalysis of the $(CF_3P)_4$–$(CF_3P)_5$ equilibrium.[5] The reaction occurred in a weighed stopcocked bulb, during warming to 25°, and was completed at 50°. The CF_3P was distilled out as the tetramer–pentamer mixture (identified by infrared spectra and basic hydrolysis to give $0.5HCF_3$ per CF_3P).[2] The less volatile $(CH_3)_3PS$ was weighed as a residue and characterized as described later.

The P–S–P situation of the sulfur was proved by basic hydrolysis. If the sulfur were P=S bonded outside the ring, the products should be a trifluoromethyl phosphonate and the consequences of $H_2(CF_3P)_3$, leading to only one HCF_3 per $(CF_3P)_4S$. But from the P–S–P situation hydroxyl would displace sulfide and form two P–O bonds, so that the rules of basic hydrolysis[2] would predict $2.5HCF_3$ per $(CF_3P)_4S$. Actually, a 24.6-mg sample gave 0.140 mmole of HCF_3, or 2.50 per mole. The recovery of H_2S from the acidified solution was 95%.

The neutral methanol reaction of $(CF_3P)_4S$ was slow and complex, apparently with P–S bonds cleaving scarcely more easily than P–P. Thus CF_3PH_2 was formed almost as soon as H_2S, suggesting the possibility of isolating intermediate P_nS open-chain compounds, analogous to the cleavage products of the $(CF_3P)_n$ rings.[6] After 11 hr at 90°, a mixture of CF_3PH_2 and H_2S was delivered through a high-vacuum trap at −120° and resolved by means of lead acetate solution. The yield of CF_3PH_2 was 39%; predicted, 37.5%. The demonstrable yield of H_2S was 89%. The expected 62.5% yield of $(CF_3HPOOH)_2$ and $CF_3P(OCH_3)_2$[7] could not be isolated from the excess methanol. Dimethyl ether was a large product of the 90° heating.

Physical Properties. The volatility of pure $(CF_3P)_4S$ is represented by the equation $\log P_{mm} = 6.8222 + 1.75 \log T - 0.005T - 2881/T$ ($t_{760} = 183°$; Trouton constant, 21.9 eu); examples, 0.94 mm at 24.1°, 2.67 mm at 40.1°, 8.91 mm at 61.17°, and 14.22 mm at 70.20° (calcd, 0.94, 2.67, 8.92, and 14.20 mm).

The ultraviolet spectrum of the vapor of $(CF_3P)_4S$ showed a fairly broad maximum at 2400 A, a shallow minimum at 2280 A, and a sharp maximum at 2050 A, with molar extinction coefficients respectively 3500, 3100, and 8300.

The infrared peaks of $(CF_3P)_4S$ vapor (heated as high as 85°) had the following frequencies (cm^{-1}) with relative intensities in parentheses: C–F stretching, 1153 (190) and 1139 (240); CF_3 deformations, 743 (6.5) and 551 (0.8); P–S–P asymmetric stretching, 511 (2.3); P–CF_3 stretching, 431 (6) and 418 (2.3); CF_3 rocking, 315 (0.9); overtones and combinations, 2265 (0.64), 1874 (0.24), 1895 (0.14); unassigned, 1279 (1.1), 843 (0.20), 822 (0.22), 537 sh, 483 (1.0), 464 (0.95), 407 sh, 352 (0.20), and 337 (0.34). The P–S–P band was obvious from the literature,[8] and there was no band assignable to a P=S bond.

Trimethylphosphine Sulfide. The $(CH_3)_3PS$ from the analytical reaction was sublimed from the weighing bulb at 50° into an immersible tensimeter wherein the vapor tensions were measured: $\log P_{mm} = 10.545 - 3670/T$; examples, 3.30 mm at 92.8°, 9.80 mm at 111.0°, and 16.97 mm at 120.8° (calcd, 3.29, 9.81, and 16.97). Its infrared spectrum showed distinct (although unresolved) P, Q, and R branches for the vapor phase up to 115°—understandably deviant from the solid-phase spectrum.[8] The frequencies of the peaks, with relative intensities in parentheses, were as follows: C–H stretching, 3035 (0.5), 3002R (1.9), 2993Q (2.4), 2985 shP (1.5), 2932R (1.9), 2923Q (2.8), 2914 shP (1.6), 2883 (0.31); CH_3 deformations, 1445 sh (0.67), 1435R (1.1), 1422Q (1.7), 1410 shP (0.9), 1320 (1.2), 1313 (2.0), 1300R (2.5), 1289Q (3.8), 1280 shP (1.8); CH_3 rocking and wagging, 973R (5.6), 971Q (10), 961P (7.5), 939 (5.5), 862R (0.56), 852Q (1.2), 843P (0.48), 822 (0.13); P=S stretching, 731R (6.7), 725P (6.9); P—C stretching, 591R (0.9), 582Q (1.7), 575P (0.8).

(5) A. B. Burg and W. Mahler, *J. Am. Chem. Soc.*, **83**, 2388 (1961).
(6) L. K. Peterson and A. B. Burg, *Inorg. Chem.*, **5**, 943 (1966).
(7) A. B. Burg and J. E. Griffiths, *J. Am. Chem. Soc.*, **83**, 4333 (1961).
(8) F. N. Hooge and P. J. Christen, *Rec. Trav. Chim.*, **77**, 911 (1958).

Anton B. Burg
Department of Chemistry, University of Southern California
Los Angeles, California 90007
Received July 5, 1966

Continuous Synthesis of Optically Active α-Hydroxynitriles

Sir:

The flavoprotein D-oxynitrilase (E.C. 4.1.2.10), the preparation and properties of which have been described by us,[1,2] combines with cellulose-based ion exchangers to form a very active, stable catalyst, which gives excellent results in the continuous synthesis of D-α-hydroxynitriles from aldehydes and hydrocyanic acid.[3] The products, which are optically almost homogeneous, can be prepared on the kilogram scale by means of milligram quantities of the enzyme.

Preparation of the Catalyst. ECTEOLA cellulose (coarse-fiber product for technical use) charged with chloride ions is slurried in a column (1 × 5 cm). The exchanger adsorbs the D-oxynitrilase quantitatively from its salt-free aqueous solution (enzyme concentration 5–10 mg/ml), which is slowly passed through the column. Before the substrate is added, the catalyst is equilibrated with the reaction medium. Suitable solvents for the stereospecific synthesis are salt-free methanol–water mixtures.

D-(+)-Mandelonitrile. A mixture of very pure benzaldehyde (0.2 *M*) and hydrogen cyanide (0.3 *M*) in cold 50% methanol is passed through a catalyst column containing 50–80 mg of D-oxynitrilase at a rate of 10–15 ml/min. (The reservoir is cooled to avoid evaporation of HCN. When larger quantities are used, the experiment should be carried out under nitrogen to avoid oxidation of the benzaldehyde since benzoic acid is a strong inhibitor for the enzyme). The solvent and excess hydrocyanic acid are evaporated under vacuum at 50°. The residual clear colorless oil, when cold, crystallizes on rubbing with a glass rod, and gives colorless needles, mp 28–29°; $[\alpha]^{20}D$ +46° (*c* 5, $CHCl_3$); yield 95%.

(1) W. Becker, U. Benthin, E. Eschenhof, and E. Pfeil, *Biochem. Z.*, **337**, 156 (1963) (older method for the preparation of the enzyme).
(2) W. Becker and E. Pfeil, *ibid.*, in press (improved method of preparation).
(3) W. Becker and E. Pfeil, Federal German Patent Application P 36473 IV b/12 o (April 7, 1965).