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).

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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%.

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The nmr and infrared spectra of the reaction product show that it is homogeneous. It contains 97% D- and 3% L-mandelonitrile (lit.[4] $[\alpha]_D$ +48.7° ($CHCl_3$) for optically pure D-(+)-mandelonitrile).

The method described for the synthesis of D-(+)-mandelonitrile can be used for the conversion of many aliphatic, aromatic, and heteroaromatic aldehydes into D-α-hydroxynitriles, which can be readily transformed into optically active D-α-hydroxycarboxylic acids, substituted ethanolamines,[5] or acyloins.[6] A table showing the aldehydes that can be used is given in ref 2.

Since both the reaction rate and the solubility in the reaction medium vary according to the aldehyde, the quantity of catalyst, flow rate, concentration of the reactants, and methanol–water ratio must be matched to the substrate in question in order to obtain optimum yields. A suitable pH range has been found to be 4.8–5.2; the H^+ concentration can be adjusted with volatile acids or bases.

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A Volatile Inorganic Salt, $Cs[Y(CF_3COCHCOCF_3)_4]$

Sir:

In the course of our investigation of a series of eight-coordinate β-diketonate complexes of yttrium and the rare earths, we made the rather surprising discovery that $Cs[Y(HFA)_4]$ (HFA = hexafluoroacetylacetonate) sublimes both in air and *in vacuo* without decomposition at temperatures ranging from 180 to 230°. In order to obtain further information about the identity of the chemical species in the vapor phase and in view of the current interest[1–5] in the mass spectra of various transition metal complexes, we have measured the mass spectrum of $Cs[Y(HFA)_4]$. Some preliminary results are reported here.

Analytically pure crystalline $Cs[Y(HFA)_4]$ was prepared in 60% yield from the reaction of Cs(HFA) with YCl_3 (4:1) in aqueous ethanol. *Anal.* Calcd for $CsYC_{20}H_4O_8F_{24}$: C, 22.86; H, 0.38; F, 43.43. Found: C, 22.9; H, 0.60; F, 42.6. A small quantity of the product was sublimed at 170° *in vacuo* (0.02 mm) onto a probe cooled with running water using the apparatus described previously.[6] The material obtained was analyzed (Found: C, 22.53; H, 0.58) and used in the mass spectrometric investigation.

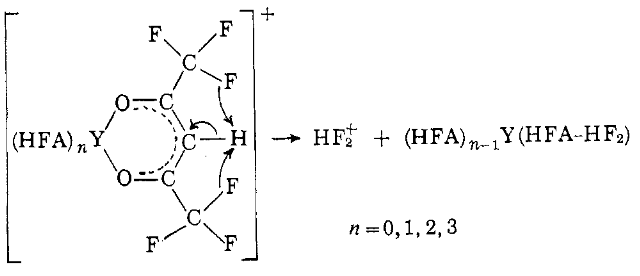
A list of several of the peaks observed in the mass spectrum of $Cs[Y(HFA)_4]$ may be found in Table I, along with their tentative assignments.[7] In addition to the peaks expected for the "molecular ion," $Cs[Y(HFA)_4]^+$, and its most likely decomposition daughters, Cs^+ and $Y(HFA)_4^+$, peaks corresponding to stepwise loss of ligand molecules to give $Y(HFA)_3^+$, $Y(HFA)_2^+$, and $Y(HFA)^+$ are quite prominent. The loss of β-diketonate ligand radicals has been previously observed for the iron, chromium, and aluminum acetylacetonates.[3,4]

Table I. Partial List of Peaks in the Mass Spectrum of $Cs[Y(HFA)_4]$

Mass number	Assignment	Intensity[a]
1050 ± 5	$Cs[Y(HFA)_4]^+$	vvw
917 ± 2	$Y(HFA)_4^+$	w
843	$Cs[Y(HFA)_3]^+$	s
807	$(CF_3CO)Y(HFA)_3^+$	m
738	$(CO)Y(HFA)_3^+$	s
710	$Y(HFA)_3^+$	s
641	$(COCHCOCF_3)Y(HFA)_2^+$	s
503	$Y(HFA)_2^+$	s
434	$(COCHCOCF_3)Y(HFA)^+$	w–m
340	Cs(HFA)	w
296	$Y(HFA)^+$	w–m
208	$H(HFA)^+$ (?)	w–m
133	Cs^+	vvs
69	CF_3^+	vvs
39	HF_2^+	vvs

[a] s = strong, m = medium, w = weak, v = very.

Of significance is the intense peak at mass 843 which may be assigned to the $Cs[Y(HFA)_3]^+$ ion. Apparently the cesium ion is held so strongly to the β-diketonate complex anion that loss of a ligand molecule can readily occur without the prior departure of Cs^+. This interaction may be formulated as a strong ion pair existing between the monopositive cesium ion and the sheath of electronegative fluorine atoms of the chelating ligands which surround the yttrium atom. Alternatively, the cesium ion could be bound directly to the methylene (=CH—) carbon atom of one of the β-diketonate ligands in a manner analogous to the interaction of silver ions with the β-diketonate anions chelated to nickel in the crystal structure of $AgNi(CH_3COCHCOCH_3)_3 \cdot 2AgNO_3 \cdot H_2O$.[8] Another interesting feature of the mass spectrum is the very strong peak at mass 39, which we tentatively assign to the HF_2^+ ion. This species may result in the following manner



a process made favorable by the close proximity of the hydrogen and two fluorine atoms of a chelated (*vs.* a free) HFA group.

The X-ray crystal structure of $Cs[Y(HFA)_4]$ is currently being determined in our laboratory,[9] the results

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