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Electric Discharge Synthesis of Phosphorus Compounds

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Low-pressure silent electric discharge has been found to be a versatile tool for the synthesis of reactive and unstable phosphorus compounds. Phosphine gives diphosphine in fair yields and conversion. Methylphosphine gives, among other products, the novel diphosphines CH_3PHPH_2 and $CH_3PHPHCH_3$. Diphosphines are also found in the products from CF_3PH_2 and $(CF_3)_2PH$. Discharge through a mixture of phosphine and acetylene gives the novel compound ethynylphosphine, $HC{\equiv}CPH_2$.

Silent electric discharges have been frequently employed in the preparation of thermodynamically unstable but kinetically isolable products of structural and chemical interest.[1,2] There have, however, been relatively few studies of the use of this technique in preparing phosphorus compounds. The best known previous work in this area is perhaps the preparation of diphosphorus tetrachloride by electric discharge of mixtures of phosphorus trichloride and hydrogen.[3] Because of the dearth of work in this area and because of our interest in reactive and unstable molecules containing phosphorus, we have initiated a survey of the utility of high-energy processes, like electric discharge, in the preparation of phosphorus compounds.

Experimental Section

Materials. Phosphine was a commercial sample (Rocky Mountain Research Inc.) which was found, by mass spectrometry, to be at least 99.5% pure. Methylphosphine,[4] trifluoromethylphosphine,[5] and bis(trifluoromethylphosphine)[6] were prepared by published methods. Commercial acetylene (Air Products) was distilled on a conventional vacuum line through traps held at -95° to remove acetone.

Instrumentation. Materials were handled and products separated on a vacuum line fitted with greaseless poly(tetrafluoroethylene) needle valves; the vacuum line was connected to a low-temperature distillation column[7] and to a gas chromatograph modified for the introduction and collection of gaseous samples.

Infrared (ir) spectra were determined on Beckman IR-5 and IR-12 spectrophotometers; nuclear magnetic resonance (nmr) spectra were determined on Varian A-60 (^1H) and HA-100 (^{19}F, ^1H) spectrometers and on a Bruker HX-90 spectrometer (^{31}P). Mass spectra were determined on CEC Model 21-620 and Varian-MAT CH5 spectrometers.

The electric discharge apparatus was a Siemens type apparatus[2] supplied with high voltage at 60 Hz from a 15-kV neon sign transformer; the output voltage was controlled by a variable transformer at the primary winding of the high-voltage transformer. Discharges were run in the batch mode, with reagents being run from a storage bulb through the discharge vessel, where the pressure was approximately 1 Torr, and with the products being trapped at -196°.

Discharge Reactions. Phosphine. PH_3 was run through the discharge apparatus at rates of around 10 mmol/hr (See Table I). The products were collected in a trap at -196°; hydrogen was allowed to pump away. The products were fractionated through traps at -95 and -196°; diphosphine collected in the trap at -95°. It was characterized by comparing its infrared,[8] ^1H nmr,[9] ^{31}P nmr,[9] and mass spectra[10] with published spectra. The diphosphine was transferred to a small weighing tube for determination of the yield. The contents of the -196° trap were identified by ir spectroscopy as recovered PH_3.

Table I. P_2H_4 Synthesis Conditions

Discharge voltage, kV	Flow rate, mmol/hr	% conversion of PH_3	% yield of P_2H_4
2.63	9	5.4	27.1
5.00	10	21.0	46.1
5.00	12	18.7	48.7
5.00	14	20.1	28.7
6.90	12	30.1	36.0
7.50	8.5	41.3	29.3
7.50	8.7	38.4	17.1
10.0	9.2	47.9	20.5
10.0	10.5	43.8	34.8
10.0	15	49.7	23.8
13.8	18	46.6	31.0

Methylphosphine. An 18.0-mmol amount of methylphosphine was passed through the discharge apparatus at a rate of 6 mmol/hr. The discharge was maintained at 7500 V. The products were collected at -196° and were then fractionated through traps at -95, -130, and -196°. The -130° trap contained methylphosphine, identified by its ir spectrum (10.3 mmol of CH_3PH_2 recovered; 7.7 mmol, 43%, converted to products). The -196° trap contained mostly PH_3, identified by its ir spectrum, contaminated with a small amount of an unidentified hydrocarbon (total yield in this trap 2.3 mmol, 30% based on the amount of methylphosphine used in the reaction). Low-temperature column distillation of the contents of the -95° trap yielded three fractions; the first, collected at column head temperature -100 to -80°, was identified by ir spectra as a mixture of CH_3PH_2 and $(CH_3)_2PH$ (totaling 1.0 mmol); the second, collected at -70 to -57° (totaling 1.0 mmol) was shown by ir, nmr, and mass spectra (see Results and Discussion) to contain $(CH_3)_2PH$ (10%), P_2H_4 (30%), and CH_3PHPH_2 (60%); the third fraction, collected at -55 to -40° contained the diastereomers of $CH_3PHPHCH_3$ (1.0 mmol), identified spectrally (see text). At the conclusion of the discharge, the discharge tube was coated with an adherent yellow-brown coating which did not appear to change when exposed to air.

Trifluoromethylphosphine. A 17.8-mmol amount of CF_3PH_2 was passed through the discharge apparatus at a rate of 7 mmol/hr and at a discharge voltage of 10,000 V. The products were collected at -196° and were fractionated through traps at -78, -105, -130, and -196°. The -196° trap contained (ir spectra) perfluorinated hydrocarbons (primarily C_2F_6, as gauged by mass spectra) together with a small amount of PH_3 (total content 5.2 mmol). The -130° trap contained recovered CF_3PH_2 (ir and ^{19}F nmr spectra) (3.1 mmol; 14.7 mmol of CF_3PH_2 converted, 83%). The -105° trap contained (ir and ^{19}F nmr spectra) $(CF_3)_2PH$, 1.2 mmol, CF_3PH_2, 0.1 mmol, and $(CF_3)_3P$, about 0.02 mmol. The -78° trap contained about 0.02 ml of liquid product which was found (^{31}P, ^{19}F nmr) to be 50% P_2H_4, 35% $CF_3PHPHCF_3$, and 15% $(CF_3)_2PH$.

Bis(trifluoromethylphosphine). A 21.0-mmol amount of $(CF_3)_2PH$ was passed through the discharge apparatus at a rate of 7 mmol/hr and at a discharge voltage of 10,000 V. The products were collected at -196° and were fractionated through traps at -78, -105, -130, and -196°. The -196° trap contained (ir spectra) perfluorinated hydrocarbons, primarily C_2F_6 (5.3 mmol). The -130° trap contained pure CF_3PH_2 (ir spectrum) (1.2 mmol). The -105° trap contained 10.7 mmol of recovered $(CF_3)_2PH$ (10.3 mmol, 49%, converted). The -78° trap contained 0.5 ml of liquid shown (^{19}F nmr) to contain $(CF_3)_4P_2$, $(CF_3)_2PH$, and $(CF_3)_3P$.

Acetylene–Phosphine Mixture. A mixture of phosphine (11.4 mmol) and acetylene (12.0 mmol) was passed through the discharge apparatus at a rate of 8 mmol/hr and at a discharge voltage of 10,000 V. The products were collected at -196° and were fractionated through traps at -78, -130, and -196°. The -196° trap contained (ir spectrum) an approximately equimolar mixture of phosphine and acetylene (14.5 mmol; 8.9 mmol, 38%, converted). The -78° trap contained (ir spectrum) P_2H_4 (0.1 mmol). The -130° trap contained (see text below) a mixture of ethynylphosphine and 1,3-butadiyne. This mixture was separated by gas chromatography. At 25° on a 5 m × 5 mm aluminum column packed with 5% SE30 silicone on 45–60 mesh acid-washed Chromosorb W, with a helium flow rate of 100 cm^3/min, retention times were 2.5 min (C_4H_2) and 3.3 min ($HC{\equiv}CPH_2$). The final yield of ethynylphosphine was 0.4 mmol, 9%.

Results and Discussion

Phosphine. Electric discharge in phosphine gave as products diphosphine, hydrogen (which was not estimated quantitatively), and an adherent coating on the discharge apparatus, which did not seem to change when exposed to air. A study (Table I) of the dependence of the variation of the diphosphine yield and the phosphine conversion on voltage and flow rate showed that increased voltage gave increased conversion of phosphine but that the yield of diphosphine peaked at around 5000 V. Increased flow rate generally gave lower yields. Under the optimum conditions we explored, yields of nearly 50% based on phosphine consumed could be achieved.

The conventional preparation of diphosphine is by the hydrolysis of calcium phosphide, Ca_3P_2. This reaction gives erratic and unpredictable yields of diphosphine; the major product of the hydrolysis is phosphine.[11] The present electric discharge synthesis would seem to offer a convenient alternative for the batchwise preparation of small amounts of diphosphine. By adapting it to a continuous circulation apparatus the process might even be useful for the preparation of large amounts of P_2H_4. In addition to infrared and mass spectral identification, diphosphine was also characterized by its ^{31}P and ^1H nmr spectra, which have previously been analyzed.[9] However the ^{31}P chemical shift of diphosphine does not appear to have been published previously, δ +212 ppm (from 85% H_3PO_4(ext) = 0; positive sign means an upfield shift). This is some 28 ppm downfield from the resonance position of phosphorus in PH_3 (δ +240 ppm).

Methylphosphine. Discharge in methylphosphine led to extensive cleavage and to a wide range and a high yield of volatile products. Of mechanistic, though not of preparative, interest, is the appearance of phosphine, diphosphine, and dimethylphosphine among the products, together with traces of unidentified hydrocarbons. (If methane, bp −161°, had been produced in the discharge reaction, it would not have been trapped or detected under the conditions of our experiments.) The most interesting products are the novel diphosphines methyldiphosphine, CH_3PHPH_2, and the diastereomers of 1,2-dimethyldiphosphine, $CH_3PHPHCH_3$.

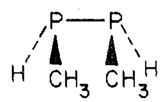
Methyldiphosphine was present in one fraction of the reaction products; it could not be separated by distillation from the other components of the same fraction, diphosphine and dimethylphosphine. Since methyldiphosphine is thermally unstable, it was not found possible to purify it by chromatography. However its presence in this fraction was demonstrated unambiguously by ^{31}P nmr spectroscopy. The proton-decoupled spectrum of the fraction showed, in addition to the peaks expected for P_2H_4 (δ +212 ppm) and dimethylphosphine (δ +99.5 ppm), an AB quartet with δ_A + 137.0 ppm and δ_B +175.3 ppm; J_{AB} = 152 Hz. Without proton decoupling, each line of the low-field half of the AB quartet at +137 ppm is composed of a doublet ($^1J_{P_AH}$ = 187 Hz) of multiplets (poorly resolved quadruplet of triplets due to coupling with the methyl protons and the PH_2 protons). Thus the signal at +137 ppm must be assigned to the alkylated phosphorus atom. In turn the lines of the higher field half of the AB quartet at +175.3 ppm are composed of a triplet ($^1J_{P_BH}$ = 185 Hz) of multiplets (poorly resolved quadruplet of doublets due to coupling with the protons of the CH_3PH group) and must be assigned to the PH_2 phosphorus atom of CH_3PHPH_2.

Values and signs of $^1J_{PP}$ for a number of diphosphines have been determined.[12] In P_2H_4 $^1J_{PP}$ = −108 Hz and in $(CH_3)_4P_2$ $^1J_{PP}$ = −179.7 Hz. It seems reasonable to suggest that the observed $^1J_{PP}$ of 152 Hz in $CH_3P_2H_3$ is negative, but a fuller spectral analysis is needed to confirm this. The chemical shift of the protons of the CH_3 group in CH_3PHPH_2 is 1.31 ppm downfield from internal $(CH_3)_4Si$.

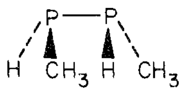
Table II. Mass Spectral Cracking Pattern of $(CH_3PH)_2$

m/e	Rel intens	*m/e*	Rel intens
94	0.55	47	17.02
64	0.87	46	100
63	1.91	45	49.16
62	39.5	44	21.94
61	7.92	43	2.60
59	13.83	34	1.33
58	2.72	33	1.90
57	8.82	32	3.87
56	2.53	31	2.66
48	33.98		

1,2-Dimethyldiphosphine could be obtained in a reasonably pure state as the highest boiling fraction of the volatile discharge products. Both ^1H and ^{31}P nmr spectra showed the presence of the expected pair of diastereomers (shown here, for clarity, in the eclipsed conformation)

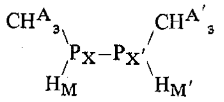


meso



and mirror image (*dl*)

The full nmr spectral analysis of these complex $A_3A'_3MM'XX'$ systems



is not yet accomplished, but a number of spectral parameters are available. The phosphorus-decoupled proton spectrum shows the two chemical shifts for the methyl groups in the diastereomers as δ 1.21 ppm and δ 1.16 ppm (relative intensities 60:40, low field:high field isomer). In each diastereomer $J_{H_AH_M}$ + $J_{H_AH_M'}$ = 7.6 Hz; since $J_{H_AH_M'}$, a $^4J_{HH}$, is expected to be rather small, it is likely that $^3J_{H_AH_M} \simeq$ 7.6 Hz. In each diastereomer δ_M is at about 3 ppm and $^1J_{H_MP_X} + {}^2J_{H_MP_X'} \simeq$ 200 Hz. The proton-decoupled ^{31}P spectrum shows the chemical shifts for the diastereomers to be +112.5 and +120.3 ppm (two single lines of intensities 57:43, low field:high field isomer).

Without proton decoupling, each of these lines is composed of a complex pattern, the main features of which are a doublet (spacing = $^1J_{P_XH_M} + {}^2J_{P_XH_M}$, *ca.* 200 Hz) of septets (spacing = $^1/_2(^2J_{P_XH_A} + {}^3J_{P_XH_A'})$, *ca.* 10 Hz). The additional lines expected for a $A_3A'_3MM'XX'$ system, inside and outside of this main doublet, were observed and the spacing between these "inner" and "outer" lines shows that ($^1J_{P_XP_X'} \pm {}^3J_{H_MH_M'}$) must lie between 150 and 200 Hz. A full analysis of these $AA'_3MM'XX'$ systems is under way.

The fact that two methyl group signals with $\Delta\nu$ = 5 Hz at 100 MHz are seen in the proton spectrum at the highest temperatures used in the nmr study (240 K) indicates that there is not a rapidly established equilibrium between the two diastereomers under these conditions either by intermolecular hydrogen exchange or by thermal pyramidal inversion at phosphorus. It is possible to estimate,[13] therefore, that the free energy of activation for each of these processes must be greater than 13 kcal/mol. This is not unexpected since an activation energy of 22 kcal/mol has been evaluated for the interconversion of the diastereomers of 1,2-diphenyldiphosphine.[14]

The mass spectrum of 1,2-dimethyldiphosphine (Table II) is in agreement with its structure. There is a low-intensity parent peak at *m/e* 94; peaks of substantial intensity (with possible assignments indicated) include those at 48 ($CH_3PH_2^+$), 47 (CH_3PH^+), 46 (the base peak; CH_3P^+), 45 (CH_2P^+), and 44 (HCP^+). It is possible that the peak at *m/e* 62 is due to $(CH_3)_2PH^+$, produced from dimethylphosphine which arises by thermal rearrangement of the 1,2-dimethyldiphosphine in the spectrometer inlet system. The intensity of this peak (39% of base) seems too high for it to be P_2^+, especially since other peaks which may represent fragments containing two phosphorus atoms (*m/e* 64, $P_2H_2^+$?; *m/e* 63, P_2H^+?) are only observed at low intensity.

1,2-Dimethyldiphosphine is thermally unstable and decomposes readily at room temperature, even at moderate pressure in the gas phase, to give methylphosphine and a highly viscous liquid of probable composition $(CH_3P)_n$. It is likely that this "decomposition" is actually an equilibrium of the type:

$$CH_3PHPHCH_3 \rightleftharpoons CH_3PH_2 + (1/n)(CH_3P)_n$$

An analogous equilibrium has been established for 1,2-diphenyldiphosphine.[14]

Trifluoromethylphosphines. In some respects the discharge products of trifluoromethylphosphine parallel those of methylphosphine. However, in addition to all the possible monophosphorus products, PH_3, $(CF_3)_2PH$, and $(CF_3)_3P$, only one diphosphine was obtained. This was the mixture of the diastereomers of 1,2-bis(trifluoromethyldiphosphine), $CF_3PHPHCF_3$. This compound has been previously obtained[15] by the partial hydrolysis of the cyclopolyphosphine $(CF_3P)_4$, but its nuclear magnetic resonance spectra were not reported at that time.

The ^{19}F nmr spectrum of each diastereomer of $CF_3PHPHCF_3$ shows primarily a doublet (large spacing = $^2J_{PCF} + {}^3J_{PCCF}$) of doublets (small spacing = $^3J_{HPCF} + {}^4J_{HPPCF}$) plus weaker peaks of the type expected[12] for the A part of an $A_3A'_3KK'XX'$ spectrum; the values observed are as follows: for the lower field diastereomer (δ +40.7 ppm from CCl_3F(int)), large spacing 69 Hz, small spacing 12.5 Hz; for the higher field diastereomer (δ +41.3 ppm), large spacing 61 Hz; small spacing 11.5 Hz. Fuller analysis of these spectra is being undertaken.

Discharge of bis(trifluoromethylphosphine) again yielded CF_3PH_2 and $(CF_3)_3P$. The only diphosphine observed was the well-characterized compound[16] $(CF_3)_4P_2$.

Ethynylphosphine. This interesting and novel compound was produced, along with diphosphine and 1,3-butadiyne, in the discharge of acetylene–phosphine mixtures. It could be separated in a pure state by a combination of low-temperature distillation and gas–liquid chromatography.

The new phosphine is thermally unstable. Above –20° it undergoes irreversible polymerization to an involatile, and as yet uncharacterized, material. Consequently it was not possible to obtain reasonable vapor pressure data on the compound. It is premature to speculate on the nature of the polymerization reaction of ethynylphosphine, but it is perhaps worth noting that phosphines are known to undergo base-catalyzed addition to activated alkynes.[17]

Ethynylphosphine was fully characterized by its spectral properties. The most significant high frequency peaks in the infrared spectrum are at 3290 cm^{-1} (ν(H–C≡)) and 2280 cm^{-1} (ν(P–H)). In the proton nmr spectrum the ethynyl proton of the AB_2X system

$$H^A{-}C{\equiv}CP^XH^B{}_2$$

is at 1.82 ppm, with $^3J_{PH_A} = 0.8$ Hz and $^4J_{H_AH_B} = 3.2$ Hz; the H_B protons are at 3.12 ppm with $^1J_{PH_B} = 214.5$ Hz. This is an unusually large coupling constant for a $^1J_{PH}$; thus[18] in CH_3PH_2, $^1J_{PH} = 188$ Hz; however introduction of electron-withdrawing groups on the α carbon generally leads to increased values of $^1J_{PH}$, as is seen[18] for $ClCH_2PH_2$, $^1J_{PH} = 206$ Hz, or CF_3PH_2, $^1J_{PH} = 201$ Hz. This increase can be rationalized by the simple hybridization argument that s character concentrates in bonds to more electropositive groups and that increased s character leads to a higher *J* value. It seems that in ethynylphosphine the ethynyl substituent, linked to phosphorus by a rather electronegative sp-hybridized carbon atom, is quite effective in increasing p character in the carbon–phosphorus bond and is thus increasing s character in the phosphorus–hydrogen bond.

The ^{31}P chemical shift of ethynylphosphine is also unusual in being at +202.6 ppm, remarkably high field for an alkylated phosphine[18] (*cf.* CH_3PH_2, +163.5 ppm, and $C_2H_5PH_2$, +128 ppm). This may also indicate unusual bonding characteristics at phosphorus, but the interpretation of phosphorus chemical shifts does not seem yet to be well enough developed to interpret chemical shift values in unsymmetrically substituted phosphines.

Mechanisms and Conclusions. The basic physical chemistry of low-pressure discharges is extremely complex,[1] involving as it does interaction of very high energy electrons (of the order of several thousand electronvolts) with molecules at relatively high concentrations. Initial reaction processes may yield radical ions, neutral radicals, or ions in a variety of electronically excited states. Subsequent reaction possibilities are extremely varied. The importance of excited states is, of course, suggested by the light emission which is one of the most striking characteristics of discharge reactions.

One physicochemical study which indicates the potential complexity of reactions in discharge systems is a recent ion cyclotron resonance study of phosphine.[19] At low pressures (10^{-7} Torr) only products containing one phosphorus atom were seen, but at higher pressures (10^{-6}–10^{-5} Torr) processes leading to diphosphorus products were observed to occur with high efficiency, and the higher the electron energy, the more effective the pathways to diphosphorus products became. In our discharge conditions of pressures of the order of 1 Torr and very high electron energies a wide variety of different reaction options becomes available.

In fact, the results from the resent study can be empirically rationalized on a rather simple basis. Products which were isolable from single-component discharge reactions are those which conceptually can be formed by P–H and P–C bond cleavage and recombination of the resulting fragments (this statement is not intended as a mechanistic interpretation of the reactions, which are undoubtedly very complex). Thus we have the overall results

$$H{-}PH_2 \rightarrow H_2P{-}PH_2 + H_2$$

$$CH_3{-}PH{-}H \rightarrow PH_3,\ (CH_3)_2PH,\ P_2H_4,\ CH_3PHPH_2,\ (CH_3PH)_2$$

$$CF_3{-}PH{-}H \rightarrow CF_3{-}CF_3,\ PH_3,\ (CF_3)_2PH,\ (CF_3)_3P,\ P_2H_4,\ (CF_3PH)_2$$

$$(CF_3)_2PH \rightarrow CF_3{-}CF_3,\ CF_3PH_2,\ (CF_3)_3P,\ (CF_3)_2PP(CF_3)_2$$

In none of the single-component reactions were products isolated which conceptually require C–H or C–F bond cleavage for their rationalization. It should be noted, however, that one reaction product, namely, the inevitable yellow-brown unreactive film left on the surface of the discharge tube, is excluded from this discussion and perhaps, if its constitution could be established, it would appear as a product derived from C–H or C–F bond cleavage.

In the acetylene–phosphine reaction the observed products do involve C–H bond cleavage: $H_2C_2 + PH_3 \rightarrow P_2H_4$, $HC{\equiv}CPH_2$, $(HC{\equiv}C)_2$. While it seems to be true that, in neutral molecules, C–H bond dissociation energies are higher for acetylenic C–H than for saturated alkane C–H bonds,[20] it is not clear that bond dissociation energies have much to do with the mechanisms of discharge reactions. So much energy is available to the systems studied that it seems likely that kinetic rather than thermodynamic factors are responsible for the actual products obtained.

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Registry No. PH_3, 7803-51-2; CH_3PH_2, 593-54-4; CF_3PH_2, 420-52-0; $(CF_3)_2PH$, 460-96-8; acetylene, 74-86-2; P_2H_4, 13445-50-6; $(CH_3PH)_2$, 53684-00-7; CH_3PHPH_2, 53684-01-8; $CF_3PHPHCF_3$, 462-57-7; $HC{\equiv}CPH_2$, 34627-31-1.

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Carbon–Chalcogen Bonds in Organosilicon Pseudohalides[1]

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Kinetic studies show that the reaction between trialkylcyanosilanes and sulfur in 1-chloronaphthalene is second order. Ease of C–X bond cleavage increases sharply for the heavier chalcogens. Organoisotellurocyanatosilanes are not stable at room temperature.

Introduction

Cyanotrimethylsilane reacts with molten sulfur to give $(CH_3)_3SiNCS$ as the sole product.[2-5] A similar reaction occurs with selenium.[4] In order to learn more about these systems, we have investigated the properties of the carbon–chalcogen bond in the series R_3SiNCX (X = O, S, Se) and have attempted to prepare the tellurium analog.

Results

I. Kinetic Studies. 1-Chloronaphthalene proved to be an excellent reaction medium; it had a high boiling point (263°) and would dissolve sulfur without solvolyzing the cyanosilanes. The reaction was monitored by following the growth of the NCS asymmetric stretching band (Table I; Figure 1).

When sulfur was allowed to react with a large excess of cyanotrimethylsilane, the reaction followed pseudo-first-order kinetics (Table II). At a stoichiometric ratio, as given by

$$8R_3SiCN + S_8 \rightarrow 8R_3SiNCS \qquad (1)$$

the reaction followed second-order kinetics. Similar results are found for triethylcyanosilane, triisopropylcyanosilanes, and *tert*-butyl isocyanide. The measured rate constants are given in Table III.

II. Tellurocyanate Studies. Downs[6] isolated $Et_4N^+TeCN^-$ and Austad, *et al.*,[7] isolated tetramethylammonium and tetraphenylarsonium tellurocyanates. The asymmetric stretching mode of $TeCN^-$ appears at 2082.0 ± 0.5 cm^{-1} in both acetone and acetonitrile (lit. 2079,[6] 2087 cm^{-1}). The saturation concentration in acetonitrile was $5.60 \pm 0.06 \times 10^{-3}$ *M*, giving a calculated molar extinction coefficient of 51 ± 2 l./(mm mol).

Triphenylphosphine readily extracts selenium from solutions of selenocyanate ion[8] to form triphenylphosphine selenide, which also can be made by direct combination. Triphenylphosphine does not react with tellurium.[9] Addition of triphenylphosphine to K^+TeCN^- in acetonitrile gave a yellow solution, which, upon evaporation, left a mixture of unreacted triphenylphosphine and $[(C_6H_5)_3P]_2Te$ recently reported by Austad, *et al.*[10] Attempts to remove the second triphenylphosphine molecule by recrystallization give rapid and complete decomposition. This compound also decomposes when dissolved in acetone, CCl_4, pentane, or THF, unless a large excess

Table I. Infrared Peaks (cm^{-1})

	-CN	-NCS
$(CH_3)_3Si$-	2189.5 (7.17)[a]	2076 (217.5)
$(C_2H_5)_3Si$-	2187.0 (6.8)	2072 (213)
$(i\text{-}C_3H_7)_3Si$-	2185.5 (5.43)	2069 (226)

[a] Molal extinction coefficient in kg/(mol mm).

Table II. $(CH_3)_3SiCN$–S_8 Kinetic Data

80.10°, $[Me_3SiCN] = 0.593$ *m*			100.20°, $[Me_3SiCN] = 0.06170$ *m*		
t, hr	$10^4[S_8]$, *m*	$-\ln [S_8]$	*t*, hr	$10^3[S_8]$, *m*	$1/[S_8]$, m^{-1}
0.00	8.15	7.11	0.0	7.636	131.0
0.50	7.32	7.22	29.8	6.311	158.4
2.08	5.15	7.57	145.6	4.011	249.3
3.42	3.71	7.90	175.4	3.669	272.5
5.75	2.16	8.44	317.1	2.581	387.4
25.20	(0.0235)[a]	(12.96)[a]	404.4	2.177	459.4

[a] Calculated.

Table III. Second-Order Rate Constants (80.10°)

	10^3k_2, kg/(mol hr)
$(CH_3)_3SiCN$	8.38 ± 0.38
$(C_2H_5)_3SiCN$	3.04 ± 0.14
$(i\text{-}C_3H_7)_3SiCN$	1.93 ± 0.14