Reaction of 3-Chloro-3-methyldiazirines with Hydrogen Atoms

Sir:

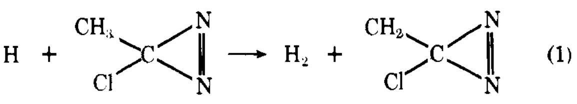
The chemistry of diazirines has been the subject of investigation for many years.[1-5] The unimolecular pathways and their relationship to the diazo isomers have been elucidated[6-8] and the photochemistry of these compounds continues to be an active research field.[9-12] From a practical point of view the 3-halodiazirines are convenient sources of halocarbenes.[13]

The recent observation by Maeda and Ingold[14] of the formation of diazirinyl radicals by abstraction of bromine from 3-bromodiazirines is in remarkable contrast to the lack of reactivity of these compounds toward a variety of reagents.[15-17] We now report on the reaction of 3-chloro-3-methyldiazirine (**1**) with hydrogen atoms which gives acetonitrile as expected from the reactions of Maeda and Ingold,[14] but by a different mechanism.

1 was prepared as described by Graham[18] and other gases were obtained from commercial sources and were determined to be pure by mass spectroscopy. The preparation of trideuterated **1** (**1**-d_3) will be reported elsewhere.[19] The mass spectra were obtained in a TOF system[20] at an ionization voltage of 20 eV and trap current of 0.3 μA. Typical flow conditions through walls poisoned with phosphoric acid were 27 μmol s^{-1} at 0.25 Torr. He + H_2 was swept away by a 425 L min^{-1} pump at a linear velocity of 880 cm s^{-1} and reaction time of 6.2×10^{-2} s. The flow rates were the following: He, 20 μmol s^{-1}; H_2/D_2, 6 μmol s^{-1}; **1**, 0.5-1.0 μmol s^{-1}. H or D atoms were produced by microwave discharge.

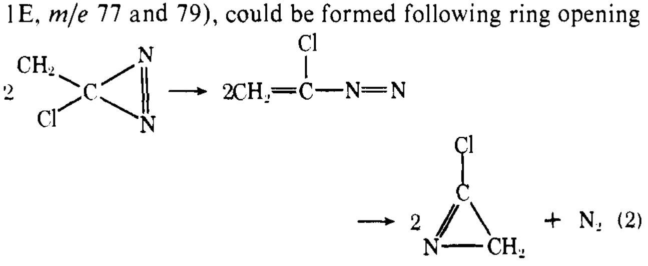
Four types of experiments were performed: **1** with hydrogen atoms, **1** with deuterium atoms, **1**-d_3 with hydrogen atoms, and **1**-d_3 with deuterium atoms (Figures 1B-E, respectively). (No reaction was observed from **1** with metastable He or Ar atoms or from hydrogen gas without discharge.) As expected from the work of Maeda and Ingold,[14] acetonitrile and HCl are major products. In contrast to their work, however, we observe the formation of deuterated acetonitriles in the reaction of **1** with deuterium atoms (Figure 1C) under conditions where acetonitrile itself would not be expected to produce them[21,22] and also several fragments which still contain the chlorine atom. In the absence of **1**, the peak for HD in the deuterium flow increased when the discharge was switched on because of reaction with the walls.[23] When **1** was admitted to the flow, HD decreased by 10%, implying the formation of radicals which decreased the D concentration. When the fully deuterated diazirine, **1**-d_3, reacted with hydrogen atoms, the HD peak height doubled.

In view of these results and the known reactions of hydrogen atoms as recently reviewed,[24] we propose as the first step abstraction from the methyl group (eq 1).



1

As suggested by Maeda and Ingold for their system,[14] loss of nitrogen may follow dimerization. In this case, for example, the high mass chlorinated product, **2** (Figures 1B and 1C, *m/e* 75 and 77; Figures 1D and 1E, *m/e* 77 and 79), could be formed following ring opening (eq 2).



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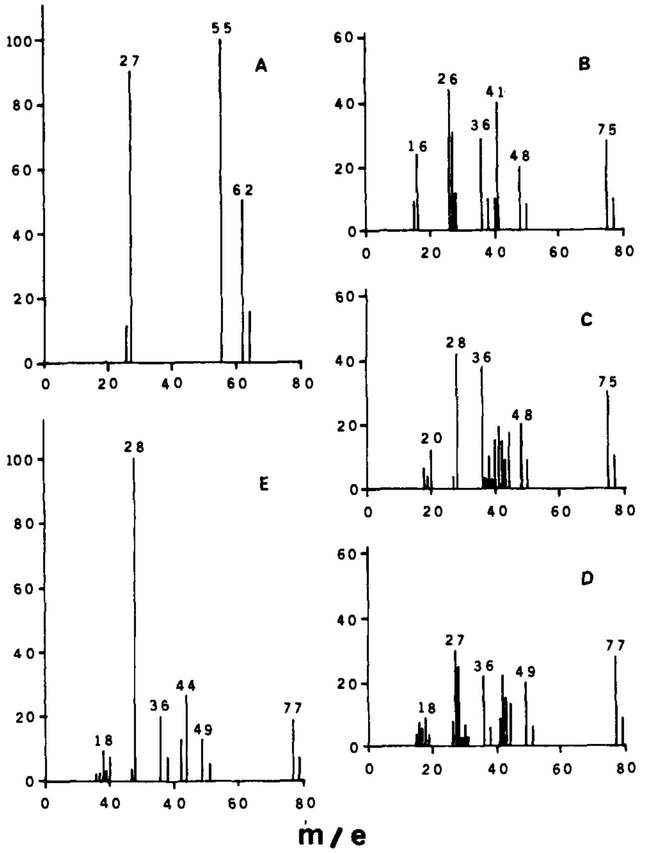
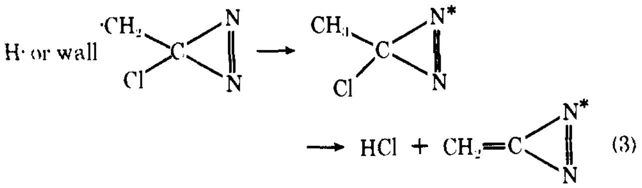


Figure 1. (a) Mass spectrum of **1** (see text for conditions). The vinyl chloride peaks are from thermal or electron impact cracking in the analyzer. Independent checks by IR and GLC showed **1** to be free of all but traces of vinyl chloride. (b) Reaction of **1** with hydrogen atoms. (c) Reaction of **1** with deuterium atoms. (d) Reaction of **1**-d_3 with hydrogen atoms. (e) Reaction of **1**-d_3 with deuterium atoms.

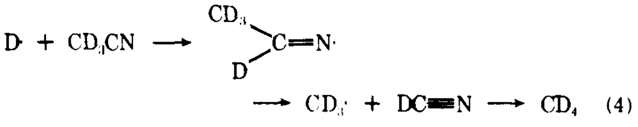
In a second pathway, the acetonitrile and HCl may be formed by a sequence of reactions which begins with steps known for activation of alkyl halides[25-27] (eq 3) (* indicates excitation of internal energy levels).



Intermediate **3**, which probably carries with it a considerable fraction of the available energy,[28,29] isomerizes easily to diazoethene according to MINDO/3 calculations.[30] Dimerization would lead to acetonitrile radicals and, hence, deuterated acetonitriles in the presence of deuterium:

$$2CH_2{=}\overset{-}{C}{-}\overset{+}{N}_2 \rightarrow 2{\cdot}CH_2{-}CN + N_2$$

Support for these products may be found by comparing the mass spectrum of the products from reaction of **1**-d_3 with deuterium atoms (Figure 1E) with the results using hydrogen atoms (Figure 1D). In the acetonitrile region in the deuterium atom reaction *m/e* 44, corresponding to fully deuterated acetonitrile, becomes the main peak. The peak at *m/e* 28 (DCN) increases at the expense of *m/e* 27 (HCN) and fully deuterated methane at *m/e* 20 is seen as a result of reaction 4.[21] Part of



$$D\cdot + CD_3CN \longrightarrow \overset{CD_3}{\underset{D}{>}}C{=}N\cdot \longrightarrow CD_3\cdot + DC{\equiv}N \longrightarrow CD_4 \quad (4)$$

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the *m/e* 28 peak is nitrogen, of course, and some could be ethyne-d_2 formed by facile isomerization[31,32] of ethenylidene which would arise by loss of nitrogen from **3**.

Work on the kinetics and key intermediates is underway. If the initial steps proposed prove correct, this is further testimony to the lack of reactivity of the diazirine ring.

Acknowledgments. Financial support from the National Sciences and Engineering Research Council of Canada to W.E.J. and M.T.H.L. is gratefully acknowledged.

References and Notes

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Received July 5, 1979

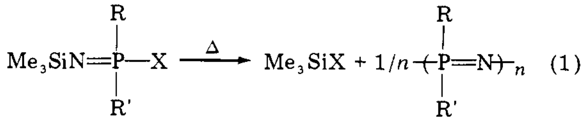
Poly(dimethylphosphazene), $(Me_2PN)_n$

Sir:

The synthesis of fully alkyl- or aryl-substituted polyphosphazenes $(R_2PN)_n$ is a prime objective in phosphazene chemistry because of their anticipated high thermal stability. We report here a new, direct method for the preparation of phosphazenes including the first fully alkylated polyphosphazene, $(Me_2PN)_n$.

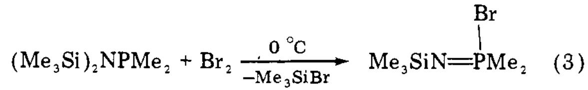
Currently, high molecular weight poly(organophosphazenes) of general formula $[(RO)_2PN]_n$, $[(RHN)_2PN]_n$, and $[(R_2N)_2PN]_n$ are prepared by the nucleophilic replacement of halogen in poly(dihalophosphazene) as developed by Allcock and co-workers.[1] This approach, however, is not generally applicable to the preparation of polymeric phosphazenes containing alkyl or aryl groups linked directly to phosphorus through P-C bonds. Reactions of Grignard and other organometallic reagents with $(Cl_2PN)_n$[2] or $(F_2PN)_n$[3] yield only partially substituted high polymers. If forcing conditions and excess organometallic reagent are employed, significant degradation of the P-N backbone occurs.

Alternatively, our approach is based on the thermal decomposition (eq 1) of suitably constructed *N*-silylphosphinimines. For example, a straightforward sequence of reactions (eq 2-4)[4,5] provides the phosphinimines **1** and **2**, both of which are precursors to the dimethylphosphazenes $(Me_2PN)_n$. Details of the synthesis and characterization of **1** and **2** are reported elsewhere.[5]



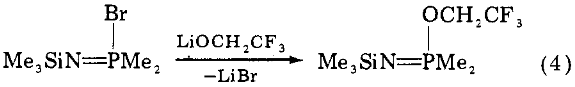
$$Me_3SiN{=}P(R)(R')\text{—}X \xrightarrow{\Delta} Me_3SiX + 1/n\,\text{—}\!(P(R)(R'){=}N)\!\text{—}_n \quad (1)$$

$$PCl_3 \xrightarrow[2.\ 2MeMgBr]{1.\ (Me_3Si)_2NLi} (Me_3Si)_2NPMe_2 \quad (2)$$



$$(Me_3Si)_2NPMe_2 + Br_2 \xrightarrow[-Me_3SiBr]{0\ °C} Me_3SiN{=}P(Br)Me_2 \quad (3)$$

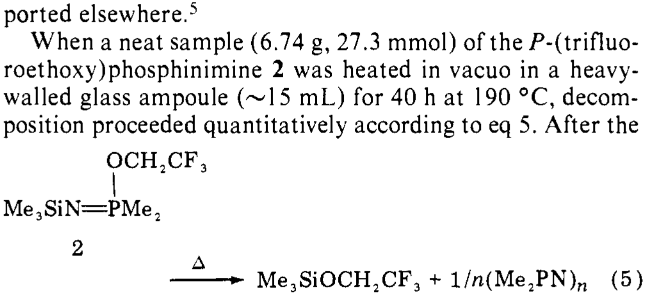
1



$$Me_3SiN{=}P(Br)Me_2 \xrightarrow[-LiBr]{LiOCH_2CF_3} Me_3SiN{=}P(OCH_2CF_3)Me_2 \quad (4)$$

2

When a neat sample (6.74 g, 27.3 mmol) of the *P*-(trifluoroethoxy)phosphinimine **2** was heated in vacuo in a heavy-walled glass ampoule (~15 mL) for 40 h at 190 °C, decomposition proceeded quantitatively according to eq 5. After the ampoule was opened, $Me_3SiOCH_2CF_3$ (identified by ^1H NMR) was removed in vacuo leaving a gummy white solid which was dissolved in CH_2Cl_2 and removed from the ampoule. Solvent evaporation gave $(Me_2PN)_n$ as an opaque, flexible, polymeric film (2.02 g, 100% yield). The polymer is soluble in CH_2Cl_2, $CHCl_3$, and ethanol, but insoluble in H_2O, acetone, THF, and hexane, A floculent, white, power-like form of the compound (mp 148-149 °C) precipitates when a CH_2Cl_2 solution of the film is poured into hexane. By light scattering, the $\overline{M}_w$ molecular weight is 50 000 corresponding to roughly 650 repeating units. The glass transition temperature of the polymer is −40 °C. By comparison, the polymers of formula $[(RO)_2PN]_n$ and $[(RHN)_2PN]_n$ generally have an average of ~10 000 repeating units. Hence, the glass transition and melting temperatures quoted for $(Me_2PN)_n$ may not represent the limiting values and further efforts are in progress to raise the chain length into the high polymer region. Elemental analysis[6] and IR and NMR spectra are consistent with the formula $(Me_2PN)_n$: ^1H NMR ($CDCl_3$) δ 1.43 (d, J_{PH} = 12.5 Hz); ^{13}C NMR ($CDCl_3$) δ 22.46 (d, J_{PC} = 90.23 Hz); ^{31}P NMR ($CDCl_3$) δ 8.26; IR (thin film) 1300 (s), 1275 (s), 1200 (br, vs) cm^{-1} (P=N). The NMR signals are all sharp lines and there is no indication of the presence of any small ring compounds such as $(Me_2PN)_{3,4}$.



$$Me_3SiN{=}P(OCH_2CF_3)Me_2\ (\mathbf{2}) \xrightarrow{\Delta} Me_3SiOCH_2CF_3 + 1/n(Me_2PN)_n \quad (5)$$

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