strong P − 38⁺(P − F₂) peak is observed. The most intense peak in the spectrum is that of the CF_3^+ ion.

Based on this work and other work in progress, it appears that for a given system there exists a temperature significantly higher than −196° where fluorine will not react with a delicate organic or inorganic reactant for thermodynamic and kinetic reasons. Just above that temperature, there may be a region in which the reaction rate may be controlled solely by careful control of the temperature. This would suggest that in certain cases one may be able to use pure fluorine at 1 atm pressure and control the reaction solely by temperature regulation. Cryogenic control does extend the applications of the La-Mar direct fluorination process. The major by-products of the fluorination of hexamethylethane are partially fluorinated species rather than fragments, and yields considerably higher than 10% could be achieved by recycling the products, by automating the process, or by using a longer cold reactor.

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Structure of a New Isopolymolybdate–Cyclophosphazene Complex

Sir:

We report the first identification and structure analysis of the $[Mo_6O_{19}^{2-}]$ anion, together with the first X-ray structure proof of a ring-protonated dimethylaminocyclotriphosphazene cation. The anion structure resolves the question of bonding in this and related species.

Hexakis(dimethylamino)cyclotriphosphazene, $[NP(NMe_2)_2]_3$, reacts with molybdenum trioxide in boiling water to give a yellow-green, water-insoluble, crystalline material (I). Conductance measurements of dilute acetonitrile solutions indicated that I was a strong electrolyte. Microanalysis followed by an X-ray single-crystal determination of this compound has shown that the correct formulation for I is $[HN_3P_3(NMe_2)_6^+]_2[Mo_6O_{19}^{2-}]$. Crystals of I, grown as prisms from a dichloromethane–hexane solvent mixture, were monoclinic, space group $P2_1/c$, $a = 13.571$ (13), $b = 10.966$ (11), $c = 21.069$ (19) Å; $\beta = 108.36(10)°$; and $Z = 2$. Intensity data were collected on a Picker FACS-I system using Mo Kα radiation. The structure was solved by Patterson and Fourier methods using the 3126 unique observed reflections collected up to $2\theta = 47.5°$. Least-squares refinement of the atomic positional and thermal parameters for all but the methyl hydrogen atoms gave $R = 0.030$.

The molecular arrangement within each cation unit is shown in Figure 1. The bond distances within the six-membered ring are as follows: N(1)–P(1), 1.675 (5); P(1)–N(2), 1.563 (5); N(2)–P(2), 1.597 (5); P(2)–N(3), 1.599 (5); N(3)–P(3), 1.560; P(3)–N(1), 1.662 (5) Å. The difference Fourier map clearly revealed a hydrogen atom bonded to a ring nitrogen atom with the N(1)–H(N1) bond distance equal to 0.86 (6) Å. The six exocyclic P–N bonds had a mean length of 1.640 Å (range 1.623–1.658 Å) and the 12 N–C bonds of the amine groups had a mean length of 1.46 Å (range 1.43–1.47 Å). The principal bond angles are shown in the figure. The 12 N(ring)–P–N(exo) bond angles were in the range of 105.4–117.1° with a mean value of 110.1°. The ring adopts a highly distorted chair configuration. The displacements of the ring atoms from the least-squares plane were as follows: N(1), −0.08; P(1), 0.11; N(2), −0.09; P(2), 0.03; N(3), 0.00; P(3), 0.03 Å. The combined results confirm that the site of protonation is a ring nitrogen rather than an exocyclic nitrogen atom.[1] The ring hydrogen atom is directed toward one of the oxygen atoms of the molybdate anion, the distance H(N1)–O is 2.03 (6) Å and the angle N(1)–H(N1)–O is 172 (6)°.

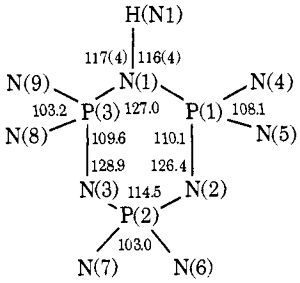

Figure 1. Molecular geometry and bond angles for the phosphazadiene cation. The standard deviations for the bond angles are 0.4° unless otherwise indicated.

The anion $[Mo_6O_{19}^{2-}]$ is a new member of the group of discrete isopolymolybdate anions. Its structure can be considered as an octahedral array of molybdenum atoms with an oxygen atom O_a bonded to each molybdenum and pointing away from the center of the octahedron, an oxygen O_b spanning each edge and thus joining two molybdenum atoms, and one oxygen O_c at the center of the octahedron. Alternatively, the structure can be visualized as formed from six MoO_6 octahedra that have condensed so that they all share a common vertex. A similar structure has been proposed[2,3] for $Nb_6O_{19}^{8-}$ on the basis of the metal atom locations. The structure can also be considered as a subunit of the $V_{10}O_{28}^{6-}$ structure.[4] The central oxygen atom lies at the origin of the unit cell at an inversion center. The mean bond distances, bond angles, and ranges (in parentheses) for the atoms in the asymmetric unit are as follows: Mo–O_a, 1.678 Å (1.676–1.679); Mo–O_b, 1.928 (1.856–2.007); Mo–O_c, 2.319 (2.312–2.324); Mo–Mo, 3.274 (3.258–3.288); Mo–O_c–Mo, 89.8° (89.4–90.1); Mo–O_b–Mo, 116.5° (116.3–116.8); O_c–Mo–O_a, 177.8° (176.5–179.7). The standard deviations are 0.005 Å for the individual bond distances and 0.4° for the individual bond angles.

An optical spectrum believed to originate from the $Mo_6O_{19}^{2-}$ ion has been reported elsewhere,[5] with maxima at 222, 255, and 324 nm. Compound I in acetonitrile shows maxima at 257 and 325 nm with ϵ values of 6120 and 3080, respectively. This isolation

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(3) J. Lindqvist, *ibid.*, 7, 49 (1953).
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and structure study of the polymolybdate species in I is of considerable interest in view of recent discussions about the structure of related heteropoly and isopoly anions.[5–7]

Acknowledgments. We thank the donors of the Petroleum Research Fund administered by the American Chemical Society for the support of part of this work.

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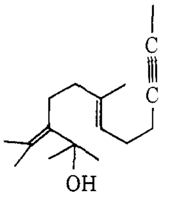
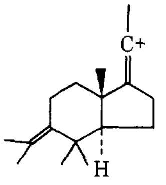
Acetylenic Bond Participation in Biogenetic-Like Olefinic Cyclizations.[1] Wagner–Meerwein Rearrangement of a Linear to a Bent Vinyl Cation

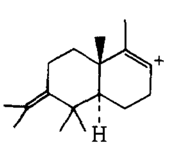
Sir:

Recently we discovered that the diolefinic acetylenic alcohol I undergoes a facile, acid-catalyzed, stereospecific cyclization to produce the bicyclic vinyl cation II which can be captured by various nucleophiles, *i.e.*, formic acid, acetonitrile, and an olefinic bond (supplied intramolecularly in a modification of I where the acetylenic methyl is replaced by an alkenyl side chain).[2,3]

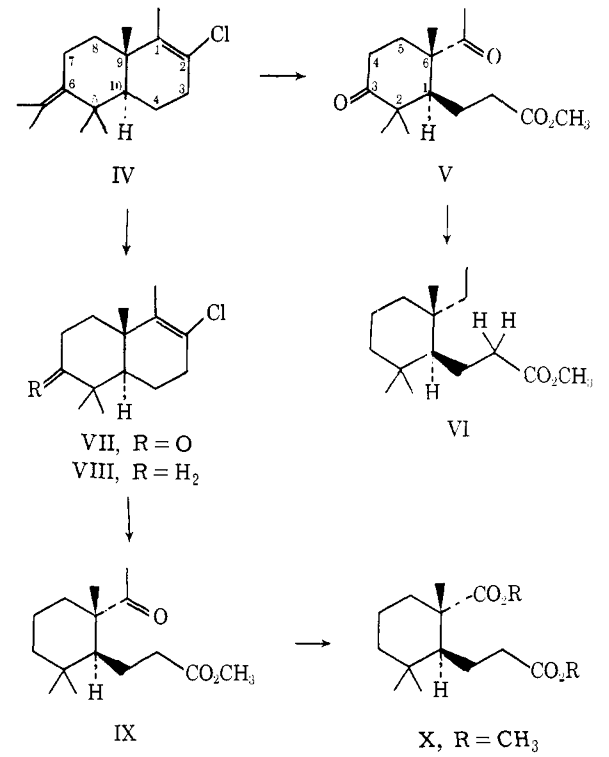
It is noteworthy that a vinyl cation can actually be produced efficiently under extremely mild conditions (see below) from a relatively stable ditertiary allylic cation, the energy being provided by the conversion of π to σ bonds.


I


II


III

In the present communication we are concerned with the question of the fate of the vinyl cation II in the absence of a good nucleophile. A solution of 0.67 mmol of dienynol I in 50 ml of methylene chloride (under nitrogen) was cooled to −78°; then 0.5 ml of trifluoroacetic acid was added with vigorous stirring.[4] After 20 min at −78°, the mixture was poured into excess aqueous sodium bicarbonate. The product, isolated in 66% yield by tlc on silica gel (10% ethyl acetate in hexane), proved to be the chlorodiene IV. Bulb-to-bulb distillation gave a low-melting crystalline product (*Anal.* Found: C, 76.8; H, 10.25; Cl, 13.1): mass spectrum *m/e* 266, M^+; nmr[5] 0.95 (3 H, s), 1.12 (3 H, s), and 1.20 (3 H, s), methyls at C-5 and C-9, 1.66 (3 H, s) and 1.80 (3 H, s), methyls of isopropylidene group, 1.68 (3 H, s), methyl at C-1. The chlorodiene IV, which evidently is derived from the vinyl cation III, appeared to be homogeneous by vpc and tlc, and it contained at most (see below) very small proportions of that isomer derived from the unrearranged cation II and that derived from the cation of alternative rearrangement (*i.e.*, formula III in which the + charge and the adjacent methyl are interchanged).


IV
V
VII, R = O
VIII, R = H_2
VI
IX
X, R = CH_3
XI, R = H

Proof of the structure and isomeric purity of the chlorodiene IV was obtained as follows. Exhaustive ozonization in 1 : 3 methanol–ethyl acetate at −78° followed by treatment with dimethyl sulfide gave, after preparative tlc (50% ethyl acetate in hexane), a 40% yield of the diketo ester V. (There was no evidence by tlc or vpc for the presence of *trans*-4,4,8-trimethylhydrindan-1,5-dione,[2] which would have been produced from the chlorodiene arising from cation II.) Bulb-to-bulb distillation at 105° (0.07 mm) afforded an oil (*Anal.* Found: C, 67.1; H, 8.9): nmr[5] 1.13 (6 H, s), methyls at C-2, 1.3 (3 H, s), methyl at C-6, 2.22 (3 H, s), ketone methyl 3.66 (3 H, s), ester methyl. Wolff–Kishner reduction of the diketo ester V by the Huang-Minlon method, followed by esterification with diazomethane and preparative tlc (5% ethyl acetate in hexane), gave the ester VI in 31% yield. Bulb-to-bulb distillation at 65° (0.01 mm) afforded an oil (*Anal.* Found: C, 75.2; H, 11.6): mass spectrum *m/e* 240, M^+; nmr[5] 0.82 (3 H, s), methyl at C-6, 0.87 (3 H, s) and 0.88 (3 H, s), methyls at C-2, 2.23–2.53 (2 H, m), hydrogens α to carbomethoxy group, 3.68 (3 H, s), ester methyl.

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(1) For the previous paper of this series, see W. S. Johnson, M. B. Gravestock, and B. E. McCarry, *J. Amer. Chem. Soc.*, **93**, 4332 (1971). For the previous paper of the series on Nonenzymic Biogenetic-Like Olefinic Cyclizations, see G. D. Abrams, W. R. Bartlett, V. A. Fung, and W. S. Johnson, *Bioorg. Chem.*, **1**, 243 (1971).

(2) W. S. Johnson, M. B. Gravestock, R. J. Parry, R. F. Myers, T. A. Bryson, and D. H. Miles, *J. Amer. Chem. Soc.*, **93**, 4330 (1971).

(3) We appreciate the possibility that the process may be concerted, in which case the transition state may be regarded as having some degree of vinyl cationic character.

(4) Under these conditions the trifluoroacetic acid is sparingly soluble and is largely out of solution, in the solid phase.

(5) The nmr spectra (60 MHz, TMS internal standard, $CDCl_3$ solvent) are recorded in δ values (ppm). Only absorptions of special significance are recorded here.