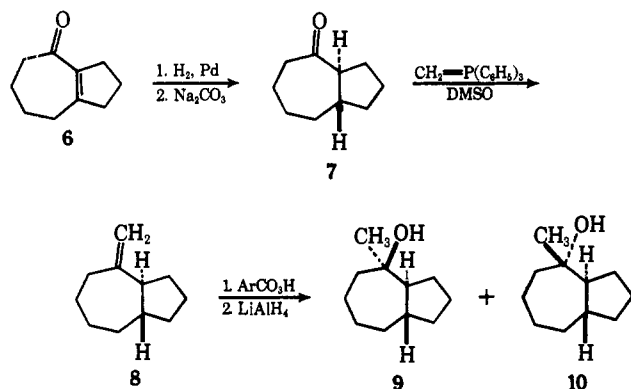


in 60% yield, presumably *via* the decalinboronate **2**.<sup>5</sup> Solvolysis of the *p*-nitrobenzoate derivative **4**<sup>4</sup> [ $\delta_{\text{TMS}}^{\text{CCl}_4}$  1.55 (vinyl CH<sub>3</sub>), 4.97 (carbinyl H, multiplet), 5.44, and 8.23 ppm (vinylic H's, multiplets)] in aqueous dioxane afforded the hydroazulenol **5**<sup>4</sup> [ $\delta_{\text{TMS}}^{\text{CCl}_4}$  1.22 (vinyl CH<sub>3</sub>) and 5.36 ppm (vinyl H, multiplet)] in 70% yield, along with 20% of unsaturated hydrocarbons according to gas chromatographic analysis. Several peaks possibly arising from isomers of **5** were also observed, but each of these accounted for less than 2% of the total product.

The structure of the major solvolysis product was ascertained through hydrogenation to the dihydro compound **10**<sup>4</sup> [ $\delta_{\text{TMS}}^{\text{CCl}_4}$  1.05 ppm (CH<sub>3</sub>);  $\lambda_{\text{max}}^{\text{filim}}$  2.97  $\mu$  (OH)], which was independently synthesized as outlined in Scheme II. The known *trans*-hydroazulene **7**,<sup>6</sup> se-

Scheme II



cured *via* hydrogenation of enone **6** followed by basic equilibration (85:15 *cis*:*trans*  $\rightarrow$  20:80 *cis*:*trans*) afforded the olefin **8**<sup>4</sup> [ $\delta_{\text{TMS}}^{\text{CCl}_4}$  4.64 ppm (vinyl H multiplet);  $\lambda_{\text{max}}^{\text{filim}}$  6.02 and 11.34  $\mu$  (C=CH<sub>2</sub>)] upon treatment with methylenetriphenylphosphorane in DMSO.<sup>7</sup> Epoxidation with *m*-chloroperoxybenzoic acid (Na<sub>2</sub>HPO<sub>4</sub> buffer) and reduction of the resulting 45:55 epoxide mixture with lithium aluminum hydride afforded a 45:55 mixture of the alcohols **9** and **10**. The former alcohol<sup>4</sup> [ $\delta_{\text{TMS}}^{\text{CCl}_4}$  1.15 ppm (CH<sub>3</sub>);  $\lambda_{\text{max}}^{\text{filim}}$  2.91  $\mu$  (OH)] was also obtained (over 90% yield) through the addition of methyl-lithium to ketone **7**.

The above described transannular cyclization approach to hydroazulenes is predicated upon the specific electrophilic activation of one cyclodecadiene double bond through formation of an incipient allylic cation.<sup>8</sup> *A priori* a number of structural possibilities could be envisioned for the product(s) of such a cyclization process. The remarkable selectivity actually observed can be rationalized on the basis of the following scheme wherein the aforementioned ion is preferentially formed in the "sickle" as opposed to the "W" or "U" arrangement.<sup>9</sup> The crossed (*vs.* aligned) orientation of the transannular double bond systems presumably minimizes steric interactions in the transition state thereby

(5) Cf. J. A. Marshall and G. L. Bundy, *J. Amer. Chem. Soc.*, **88**, 4291 (1966).

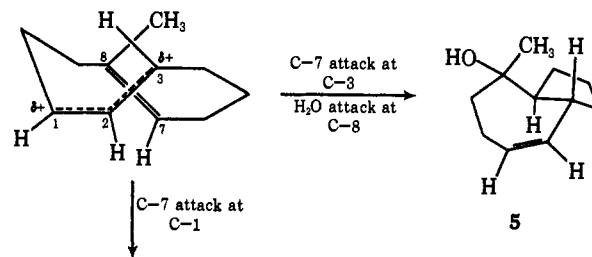
(6) W. Hüchel and L. Schnitzspahn, *Justus Liebigs Ann. Chem.*, **505**, 274 (1933).

(7) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

(8) Cf. W. S. Johnson, *Accounts Chem. Res.*, **1**, 1 (1968).

(9) For previous usage of these terms, see A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **89**, 3914 (1967); R. B. Bates, R. H. Carnighan, and C. E. Staples, *ibid.*, **85**, 3031; 3033 (1963).

favoring the *trans* fused product.<sup>10</sup> Attack of the isolated double bond at C-1 (*vs.* C-3) of the allylic cation would afford a hydroazulenic product containing a *trans*-cycloheptene double bond. The high degree of strain inherent in such an intermediate would expectedly prohibit this mode of cyclization.

[a *trans*-cycloheptene]

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(10) An alternative pathway involving stereospecific S<sub>N</sub>2' attack by the isolated double bond on the allylic *p*-nitrobenzoate could also account for the observed specificity of the cyclization reaction.

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## Preparation of Difluoroaminodifluorophosphine

Sir:

Many workers have examined the physical and chemical properties of aminophosphines. Some of the results have been rationalized by suggesting that the N-P bond, which arises from hybridized atomic orbitals forming a  $\sigma$  molecular orbital, is supplemented by additional  $\pi$  molecular orbitals which arise from the delocalization of the lone pair of electrons on nitrogen into the empty d orbitals of phosphorus (a  $(p \rightarrow d)\pi$  bond).<sup>1</sup> The most reliable support for the theory of a  $(p \rightarrow d)\pi$  interaction in the P-N bond comes from stereochemical evidence. The results of two detailed structural studies are available. Morris and Nordman<sup>2</sup> have found through a single-crystal X-ray diffraction study of (CH<sub>3</sub>)<sub>2</sub>NPF<sub>2</sub> that nitrogen, when bonded to a PF<sub>2</sub> moiety, can achieve planarity. A detailed microwave spectral analysis of H<sub>2</sub>NPF<sub>2</sub><sup>3,4</sup> indicates that nitrogen also is planar in this compound.

We wanted to prepare an aminophosphine which would be suitable for gas-phase structural investigations and which would have very electronegative groups

(1) A. B. Burg and P. J. Slota, *J. Amer. Chem. Soc.*, **80**, 1107 (1958); G. Ewart, D. S. Payne, A. L. Porte, and A. P. Lane, *J. Chem. Soc.*, 3984 (1962); R. R. Holmes and R. P. Carter, *Inorg. Chem.*, **2**, 1146 (1963); W. A. Hart and H. H. Sisler, *ibid.*, **3**, 617 (1964); R. Schmutzler, *ibid.*, **3**, 415 (1964); A. H. Cowley and R. P. Pinnell, *J. Amer. Chem. Soc.*, **87**, 4454 (1965); A. H. Cowley and M. H. Hnoosh, *ibid.*, **88**, 2595 (1966); K. Cohn and R. W. Parry, *Inorg. Chem.*, **7**, 46 (1968); J. E. Clune and K. Cohn, *ibid.*, **7**, 2067 (1968); J. F. Nixon and M. D. Sexton, *J. Chem. Soc. A*, 1089 (1969); R. M. Kren and H. H. Sisler, *Inorg. Chem.*, **9**, 836 (1970).

(2) E. D. Morris and C. E. Nordman, *ibid.*, **8**, 1673 (1969).

(3) J. E. Smith and K. Cohn, *J. Amer. Chem. Soc.*, in press.

(4) A. H. Brittain, J. E. Smith, and R. H. Schwendeman, unpublished results.

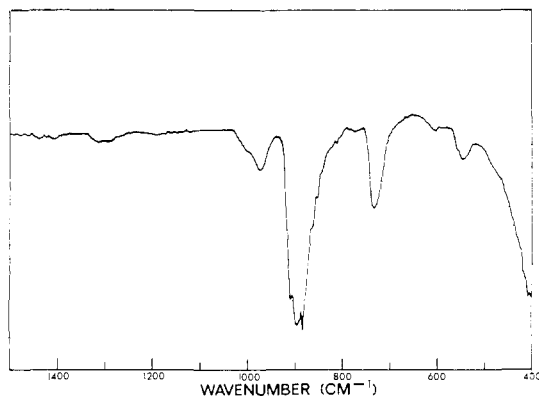
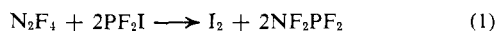


Figure 1. The ir spectrum of  $F_2NPF_2$  at 10 mm of pressure in a 8.5-cm cell (AgCl windows).

attached to nitrogen. These groups should compete for the lone pair of electrons on nitrogen and reduce the extent of  $(p \rightarrow d)\pi$  bonding. This reduction should be reflected in an increased P-N bond length and a loss of planarity about nitrogen. In this communication we report the preparation of  $F_2NPF_2$ , which was prepared by allowing  $PF_2I$  and  $N_2F_4$  to interact at  $23^\circ$ . The interaction of  $(CF_3)_2PI$  and  $N_2F_4$  under conditions similar to those employed for the preparation of  $F_2NPF_2$  did not result in the formation of  $F_2NP(CF_3)_2$ .

*Difluoroaminodifluorophosphine,  $F_2NPF_2$ , is an exceedingly explosive and treacherous compound.* Samples of the compound have detonated in the gas, liquid, and solid phases, and at temperatures as low as  $-196^\circ$ .

In a typical reaction a 4.4-mmol sample of  $PF_2I$  was condensed at  $-196^\circ$  into a previously dried 1000-ml round-bottom flask equipped with a Teflon high-vacuum valve (Kontes). A 4.5-mmol sample of  $N_2F_4$  (Air Products Co.) was condensed on top of the sample of  $PF_2I$ . The reaction mixture was allowed to warm to  $23^\circ$  for a period of 45 hr. After 15 min the formation of a purple vapor ( $I_2$ ) indicated a reaction was occurring. The volatile products were separated by codistillation.<sup>6</sup> Only three volatile compounds were obtained from the reaction mixture. Two of these,  $N_2F_4$  and  $PF_2I$ , were easily identified by their characteristic infrared spectra. Elemental iodine, identified by a starch test and mass spectral data, remained in the reaction flask. The boiling point of the third volatile compound,  $F_2NPF_2$ , lies between those of  $PF_2I$  and  $N_2F_4$ . No other products were obtained. In another reaction, in which  $N_2F_4$  was removed by passing the volatile products through a trap held at  $-140^\circ$ , the yield of  $F_2NPF_2$  was 26% (based on the amount of  $PF_2I$  used).<sup>7</sup> Although we were unable to obtain detailed stoichiometric data, we suggest the reaction can be represented by



Difluoroaminodifluorophosphine was unequivocally characterized by spectral data. The  $^{19}F$  nmr spectrum at  $-60^\circ$  consists of a broad low-field doublet ( $\delta$  from  $CFCl_3 - 2.0$  ppm,  $^2J_{FNP} = 120$  Hz) of area 1 which is assigned to the fluorines attached to nitrogen. The

(5) J. G. Morse, K. Cohn, R. W. Rudolph, and R. W. Parry, *Inorg. Syn.*, **10**, 147 (1967).

(6) C. H. Cady and D. P. Siegarth, *Anal. Chem.*, **31**, 618 (1959).

(7) We believe higher yields can be obtained by careful photolysis; however, the reaction mixture exploded when we attempted irradiation with a sunlamp in a Pyrex vessel for longer than 1 hr.

broadening arises from the spin-lattice relaxation of the resonances by the quadrupole moment of the nitrogen. In addition to the low-field doublet there is also a high-field doublet ( $\delta$  from  $CFCl_3 + 71.8$  ppm,  $^1J_{PF} = 1336$  Hz) of area 1 which is assigned to the fluorines attached to phosphorus. Each member of the doublet is further split into a 1:2:1 triplet ( $^3J_{FPNF} = 13.2$  Hz) by the fluorines attached to nitrogen. The  $^{31}P$  nmr spectrum consists of a triplet ( $\delta - 127$  ppm from  $H_3PO_4$ ;  $^1J_{PF} = 1345$  Hz), each member of which is split into a triplet ( $^2J_{FNP} = 126$  Hz). Both the coupling constants and chemical shifts are consistent with the proposed formulation and are similar to values previously reported for alkylaminodifluorophosphines<sup>8a</sup> and difluoroamino derivatives.<sup>8b</sup>

The compound  $F_2NPF_2$  exhibits gas-phase ir absorptions (Figure 1) at 980 (w), 890 (vs), 725 (m), 540 (w), 410 (?)  $cm^{-1}$ . We tentatively assign the broad absorption at 980  $cm^{-1}$  to a N-F symmetric stretch. The frequencies of the asymmetric NF stretch and the symmetric and asymmetric PF stretches lie close together. We feel that these bands overlap and give rise to the rather intense bands centered at about 890  $cm^{-1}$ . The band at 725  $cm^{-1}$  is assigned to the  $NF_2P$  symmetric deformation. The band which appears at 410  $cm^{-1}$  may be assigned to a symmetric FPF deformation.<sup>9</sup>

All attempts to obtain a large enough sample of pure  $F_2NPF_2$  for molecular weight vapor density measurements failed because the sample detonated. The mass spectrum of a sample of  $F_2NPF_2$  which contained  $N_2F_4$  as an impurity consisted of peaks attributable to  $NF_2^+$  and  $PF_2^+$ . As expected, no parent ion was observed.

(8) (a) R. Schmutzler, *Advan. Fluorine Chem.*, **5**, 31 (1965); (b) W. H. Hale and S. M. Williamson, *Inorg. Chem.*, **4**, 1342 (1965), and references therein.

(9) The cell employed in this study was fitted with AgCl windows which absorb strongly in this region. A spectrum obtained for an empty cell showed no shoulder at 410  $cm^{-1}$ . The band at 410  $cm^{-1}$  is real.

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## Barrier to Inversion at Nitrogen in Imines. Configurational Studies on *O*-Methyl Imidates

*Sir:*

Inversion at nitrogen in compounds of the type  $XYC=NZ$  is a problem of long-standing interest.<sup>1a-v</sup>

(1) (a) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Amer. Chem. Soc.*, **88**, 2775 (1966); (b) H. A. Staab and F. Vögtle, *Chem. Ber.*, **98**, 2681 (1965); (c) H. A. Staab and F. Vögtle, *ibid.*, **98**, 2691, 2701 (1965); (d) H. A. Staab and F. Vögtle, *Tetrahedron Lett.*, **51** (1965); (e) G. Saucy and L. H. Sternbach, *Helv. Chim. Acta*, **45**, 2226 (1962); (f) S. C. Bell, G. L. Conklin, and S. J. Childress, *J. Amer. Chem. Soc.*, **85**, 2868 (1963); (g) G. Wettermark and L. Dogliotti, *J. Chem. Phys.*, **40**, 1486 (1964); (h) D. G. Anderson and G. Wettermark, *J. Amer. Chem. Soc.*, **87**, 1433 (1965); (i) E. Fisher and Y. Frei, *J. Chem. Phys.*, **27**, 808 (1967); (j) A. Rieker and H. Kessler, *Tetrahedron*, **23**, 3723 (1967); (k) H. Kessler, *Tetrahedron Lett.*, 2041 (1968); (l) H. Kessler and D. Liebfritz, *ibid.*, 427 (1969); (m) H. A. Staab and D. Lauer, *Chem. Ber.*, **101**, 864 (1968); (n) A. Rieker and H. Kessler, *Tetrahedron*, **23**, 3723 (1967); (o) E. Haselbach and E. Heilbronner, *Helv. Chim. Acta*, **51**, 17 (1968); (p) V. I. Minkin, Yu. Zhdanov, E. A. Medyantzenz, and Yu. A. Ostroumov, *Tetrahedron*, **23**, 3651 (1967); (q) H. Saito and K. Nukado, *ibid.*, **22**, 3313 (1966); (r) S. Andreades, *J. Org. Chem.*, **27**, 4163 (1962); H. A. Staab, F. Vögtle, and A. Mannschreck, *Tetrahedron Lett.*, 697 (1967); (s) F. A. L. Anet, J. C. Jochim, and C. H. Bradley, *J. Amer. Chem. Soc.*, **92**, 2557 (1970); (t) J.-M. Lehn and B. Munsch,