pathway, whereas vinylphosphorane formation will predominate when α fluorines are present in this intermediate. Our work continues to explore these unusual phosphoranes and carbanions.

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(5) For a general discussion of the role of fluorine in polyfluorinated carbanions, see R. D. Chambers, "Fluorine in Organic Chemistry", Wiley-Interscience, New York, 1973, pp 84-93.

(6) The facile conversion of the phosphonium tetrafluoroborate (unpublished work) and the ammonium tetrafluoroborate salts[3] into the ylide by reaction with KF suggests that the initial reaction is merely another example of the typical addition-elimination process common to the reaction of fluoro olefins with nucleophiles.

(7) Triphenylphosphine does not react with HFP under normal reaction conditions. Trisdimethylaminophosphine reacts violently with HFP.

(8) It is possible that transitory fromation of ylide occurred followed by collapse to vinylphosphorane. However, at no time was any evidence of ylide detected by NMR.

(9) Depending on the dilution, rate of addition of phosphine, and temperature control, the amount of *E* isomer varied from 0 to 10%. By careful control of the above parameters, the *Z* isomer could be formed exclusively.

(10) The *Z* phosphorane exhibited four sets of signals in the ^{19}F NMR spectrum at ϕ^* 16.7 (d, F_c, J_{P,F_c} = 609 Hz), 67.6 (d, d, CF_3, J_{CF_3,F_a} = 23, J_{CF_3,F_b} = 11 Hz), 142.0 (d, pentets, F_a, J_{F_a,F_b} = 131, J_{F_a,F_c} = 23 Hz), 170.0 ppm (br d, F_b). The ^{31}P NMR spectrum of the *Z* phosphorane exhibited a doublet of doublets at 63.7 ppm (relative to external H_3PO_4) (J_{P,F_b} = 7.5 Hz). In all of the stable fluorinated phosphonium ylides that we have examined the ^{31}P NMR chemical shift is always negative (downfield from external H_3PO_4).

(11) Further confirmation of the vinylphosphorane structure was achieved by stereospecific hydrolysis to the reduced olefin, $CF_3CF{=}CFH$. Full details of this novel reduction method will be reported elsewhere. The stable cyclic fluorinated ylides do not hydrolyze to give reduced olefins.[2,3]

(12) The ylide from *F*-2-butene exhibited three sets of signals in the ^{19}F NMR spectrum at ϕ^* 37.0 ("octet", $CF_{3(b)}$, J_{Cf_3,CF_2} = 16.7 J_{CF_3,CF_3} = 7.8 Hz), 85.5 (q, t, $CF_{3(a)}$, $J_{CF_{3(a)},CF_2}$ = 4.1 Hz), 90.7 ppm (q, q, CF_2). Computer simulation of this spectrum using the LAOCOON II program,[13] as modified by Professor W. E. Bennett of this department, was in good agreement with the experimentally determined spectrum. The ^{31}P NMR spectrum of this ylide exhibited a singlet at −23.7 ppm (relative to external H_3PO_4).

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(14) Additional confirmation of the ylide structure was obtained by selective cleavage of the ylide with bromine to give $CF_3CF_2CBr_2CF_3$. The cyclic *F*-alkenes exhibit similar behavior with bromine (unpublished work of P. D. Vander Valk).

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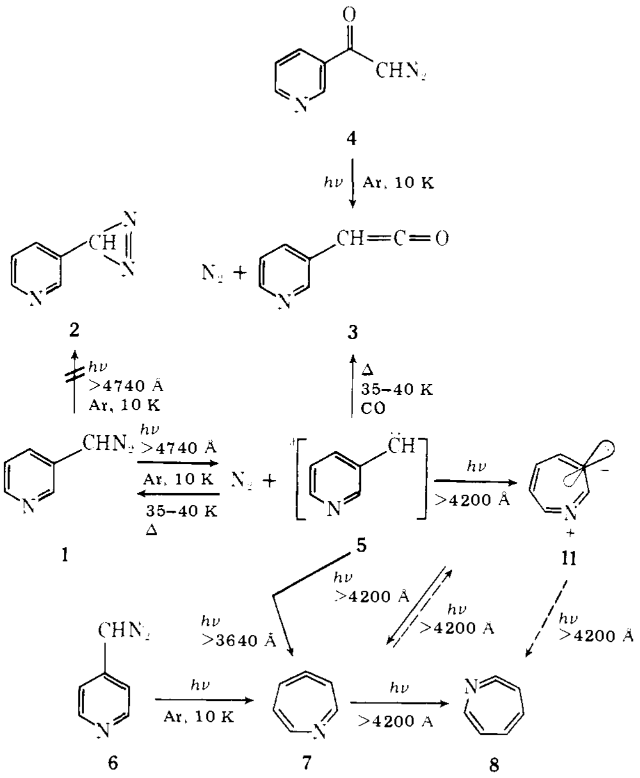
3-Pyridylmethylene: Infrared Spectrum and Photochemistry

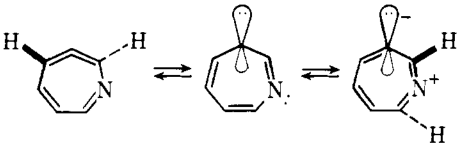
Sir:

Scheme I



We describe here the first infrared spectrum of an aryl carbene, 3-pyridylmethylene, and the photochemistry of this intriguing intermediate. Irradiation (>4740 Å) of 3-diazomethylpyridine (**1**) matrix isolated in argon gives a new product with infrared absorption bands at 1595, 1520, 1379, 1325, 1233, 1221, 1110, 1015, 990, 983, 943, 788, 688, 628, 600, 550, 505, 441, and 430 cm^{-1} (Figure 1). The presence of intense bands at 788 and 688 cm^{-1} shows that the 3-substituted pyridine ring is still intact. Comparison of the infrared spectrum of 3*H*-(3-pyridyl)diazirine (**2**)[1] matrix isolated in argon with that of the photoproduct established that the photoproduct was not the diazirine. Irradiation (>4740 Å) of **1** in an argon matrix containing carbon monoxide (1.5%) gave the same photoproduct and a trace of 3-pyridylketene (**3**) (Scheme I). When the matrix was warmed to 35-40 K, the bands due to the photoproduct decreased, and the bands due to **1** and **3** increased. The identity of **3** was established by an alternate synthesis. Irradiation of matrix isolated 3-pyridyl diazomethyl ketone (**4**)[2] gave **3** identical in infrared absorption with that obtained in the thermal reaction of the photoproduct. It is thus clear that the photoproduct is 3-pyridylmethylene (**5**). The electron spin resonance spectrum of **5** (triplet ground state) has been described.[3] The species observed in the electron spin resonance experiment has the same behavior with respect to wavelength effects in its formation and destruction (vide infra) as the species observed in the infrared experiment. Irradiation (>4740 Å) of 3-(deuteriodiazomethyl)pyridine[4] gave 3-pyridyldeuteriomethylene. The infrared spectra of **5** and its deuterio derivative are strikingly similar. Bands at 505 and 441 cm^{-1}, however, are shifted to 353 and 305 cm^{-1} in the deuterio derivative. This suggests that the bands at 505 and 441 cm^{-1} are due to deformation modes of the methylene C-H. Pacanksy[5] has assigned similar low frequency (550-500 cm^{-1}) bands in the infrared spectra of alkyl radicals to the deformation modes of the C-H bonds at the radical center, and cyanomethylene shows a deformation mode at 458 cm^{-1}.[6]

Irradiation (>3640 Å) of 3-diazomethylpyridine (**1**), 3-pyridylmethylene (**5**), or 4-diazomethylpyridine (**6**) gives 1-aza-1,3,4,6-cycloheptatetraene (**7**).[3] Irradiation of **5** with longer wavelength light (>4200 Å) gives **7** and a new species



twisted 9 planar 10 twisted 11

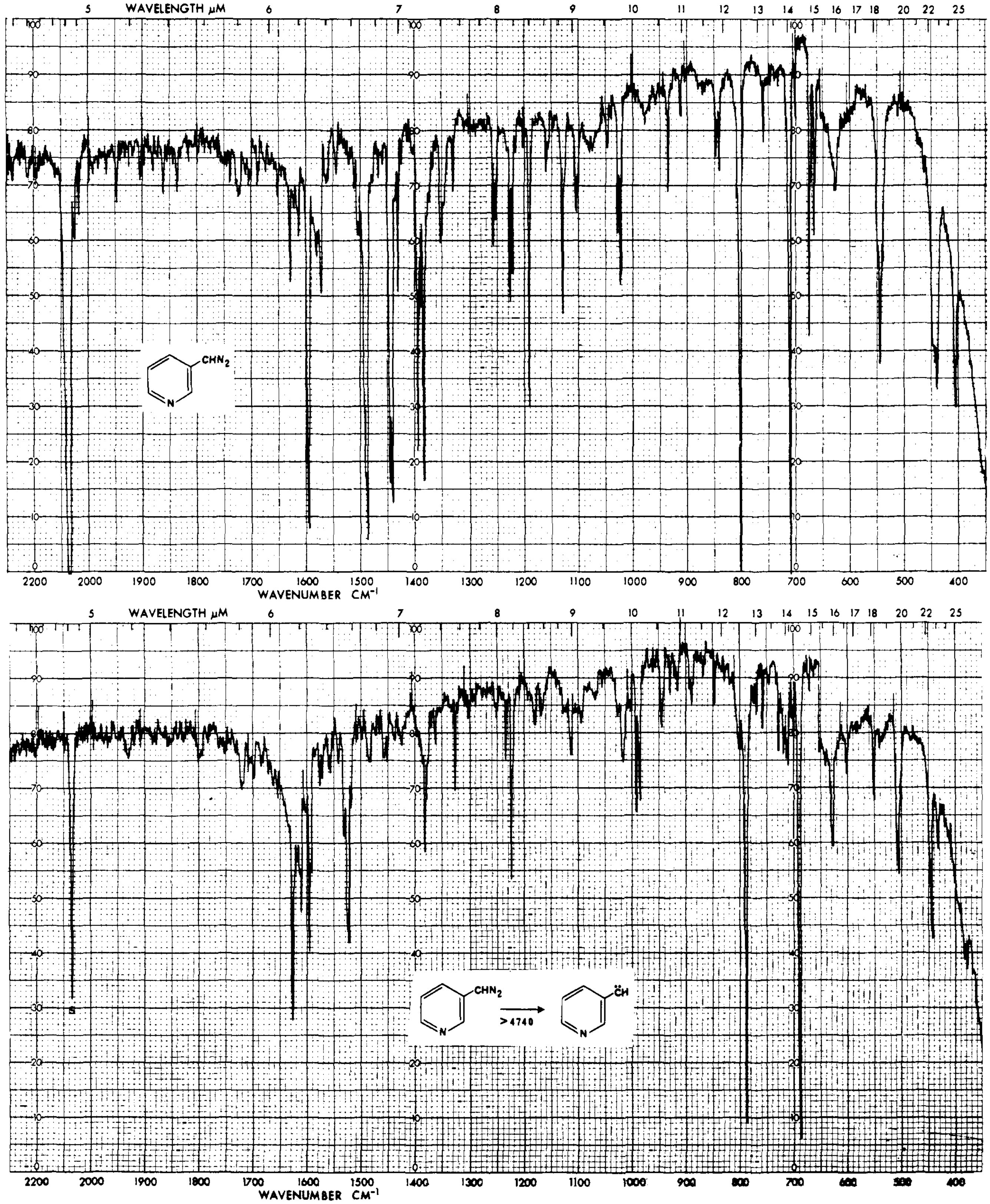


Figure 1. Top: infrared spectrum of 3-diazomethylpyridine (**1**) matrix isolated in argon at 10 K before irradiation. Bottom: infrared spectrum of 3-pyridylmethylene (**5**) obtained by irradiation (>4740 Å) of the sample shown above; the residual diazo band of starting material is marked with an s.

with an intense band at 1935 cm^{-1} and other significant bands at 1514, 1402, 1370, 1195, 1100, 995, 920, 870, 792, 718, and 410 cm^{-1}. Continued irradiation (>4200 Å) converts the 1935-cm^{-1} species to **7**. If the irradiation of **5** is monitored as a function of time, it is clear that the major portion of **7** is formed directly from **5** and only a minor amount is formed via the 1935-cm^{-1} species. The identity of the 1935-cm^{-1} species poses a difficult problem. The presence of an intense 1935-cm^{-1} band suggests the presence of a strained heterocumulene (cf. $\nu_{C=C=N}$ = 1895 cm^{-1} for 1-aza-1,2,4,6-cycloheptatetraene (**8**)[7]) and the absence of a strained allene (cf. $\nu_{C=C=C}$ = 1810 cm^{-1} (weak) for **7**[3]). Ring expansion of **5** could, in principle, occur in two regiochemically different ways. One ring expansion has been shown to give **7**. Ring expansion in the regiochemically opposite sense might be expected to give a different allene (**9**). The 1935-cm^{-1} band in the infrared spectrum shows that the new product is not the allene **9**, and the other ring-expanded structures (**10** and **11**) must be considered. The planar carbene (**10**, singlet or triplet) has no functionality which could account for the 1935-cm^{-1} band. The zwitterionic heterocumulene (**11**), however, should show a band in this region. The model zwitterionic heterocumulene (**12**) shows an intense band at 1930 cm^{-1} in an argon matrix.[7] Calculations by Salem[8] suggest that the C=N=C system in $\text{HC}^{-}{=}\text{N}^{+}{=}\text{CH}_2$ should be bent with an equilibrium angle of ~157° (the potential well is very broad). The relationship of **9**, **10**, and **11** is of considerable interest. These structures are topological isomers and can be interconverted by a series of single-bond rotations. The barriers to rotation are probably small, and at room temperature **9**, **10**, and **11** may be interconverting rapidly. The barriers are sufficiently large, however, to make **7** and **11** unique compounds at 10 K. It is not clear whether the nature of the compound formed is determined by the nuclear configuration at the point of entry to the energy surface in our experiments or by subtle electronic factors in the molecule. The zwitterionic heterocumulene (**11**) occupies the position assigned to the postulated allene (**9**) in our published scheme for the interconversion of the isomeric pyridylmethylenes and phenylnitrene.[3]

$$\text{Ph}\overset{-}{\text{C}}{=}\overset{+}{\text{N}}{=}\text{CH}_2$$

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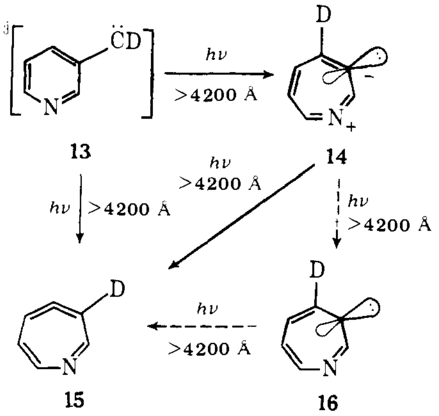
Irradiation (>4200 Å) of the zwitterionic heterocumulene (**11**) gives the allene **7** rapidly. This is the reason that only **7** is observed in the irradiation (>3640 Å) of 3-diazomethylpyridine. Irradiation (>4200 Å) of **7** slowly gives **8**. This amazing rearrangement may involve **11** (dashed arrows, Scheme I), but we have not been able to find evidence for the conversion of **11** into **8**. Irradiation (>4200 Å) of 3-pyridyldeuteriomethylene (**13**) gives a larger steady-state concentration of deuterated zwitterionic heterocumulene (**14**). The increase in the steady-state concentration of **14** is due to an increase in its rate of formation relative to the rate of its destruction. The change in stationary-state concentration of **14** when hydrogen is replaced by deuterium suggests that the conversion of **14** into **15** might involve a hydrogen shift. It is probable that the hydrogen shift would occur in the planar carbene (**16**) produced by irradiation of **14**. Tunneling has been shown by Ingold[9] to be the most important mechanism in an intramolecular hydrogen shift in a free radical at 28 K. It is an intriguing question whether tunneling is an important mechanism in hydrogen shifts of carbenes at low temperature. It is, however, possible that the change in stationary-state concentration of **14** could be due to secondary isotope effects in the conversion of **13** into **14**.



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Spin Trapping in Electrochemistry. 1. On the Electrooxidation of Organoborides

Sir:

In the course of identifying supporting electrolytes having inert anions of low nucleophilicity and high anodic discharge potentials for use in oxidative electrochemical characterization of substrates in nonaqueous, aprotic media,[1] we have examined the anodic electrochemistry of analogues of the widely used tetraalkylammonium tetrafluoroboride, R_4NBF_4. In contrast to BF_4^- which undergoes oxidation at >+3 V,[2] tetraphenylboride anion (BPh_4^-) is oxidized at a platinum electrode in acetonitrile (MeCN) at a potential of +0.92 V.[3] We have observed that the tetra-*n*-butylboride anion (BBu_4^-), however, is more easily oxidized than BPh_4^- and exhibits a well-defined, monoelectronic oxidation wave at $E_{\text{p(a)}} = +0.35$ V.[5] Exhaustive electrooxidation of BBu_4^- in MeCN indicates a charge release of 1 faraday/mol and this *n* value is invariant over the concentration range of 80 μM to 10 mM. That the corresponding electrooxidation of BPh_4^- affords concentration dependent *n* values ranging from $n \simeq 2$ at low (80 μM) BPh_4^- concentrations to $n \simeq 1$ at high (10 mM) BPh_4^- concentrations[4,6] has led us to examine the mechanisms of electrooxidation of these two organoborides. The expectation that free-radical intermediates might be formed in both cases (Ph· in BPh_4^- oxidation and *n*-Bu· in BBu_4^- oxidation) suggested the use of spin trapping[7] as a technique with which these highly reactive species could be detected.

Bard has demonstrated the utility of α-phenyl-*N*-*tert*-butyl nitrone (PBN) as a spin trap in direct electroreductions[8] and in photoassisted oxidations.[9] The "potential window" of PBN and that of the corresponding nitroxides[10] make PBN well suited to the oxidative examination of these organoborides.

Controlled potential electrolysis (CPE)[11] of rigorously deoxygenated millimolar solutions of TBABBu_4 in MeCN containing 0.10 M TBAP and 0.10 M PBN afforded very persistent spin adducts whose ESR spectra are typified by that shown in Figure 1A. Identical spectra were obtained from the in situ electrolysis[12] of rigorously deoxygenated TBABBu_4/PBN solutions. CPE without deoxygenation of the TBABBu_4/PBN solution prior to electrolysis gave a mixture of two nitroxide spin adducts, one of which was spectrally identical with that obtained under oxygen-free electrolysis conditions (Figure 1B). CPE of oxygen-saturated solutions of TBABBu_4/PBN afforded the spectrum of a single nitroxide