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(16) Analyses for the fully hydrated crystals were not possible because of their tendency to lose water. Drying a sample in air overnight gave the following: Anal. Calcd for $Na_2(C_7H_{18}N)[Cr(C_7H_5NOS)_3]\cdot\frac{1}{2}NaH_3O_2\cdot 11H_2O$: C, 37.82; H, 6.40, N, 6.30; S, 10.79. Found: C, 37.8; H, 5.5; N, 6.3; S, 10.1. After drying under high vacuum at room temperature for 12 h, the dried sample gave the following: Anal. Calcd for $Na_2(C_7H_{18}N)[Cr(C_7H_5NOS)_3]\cdot\frac{1}{2}NaH_3O_2\cdot 2H_2O$: C, 46.24; H, 5.34; N, 7.70; S, 13.20; Na, 7.91. Found: C, 45.74; H, 5.05; N, 7.67; S, 12.98; Na, 7.92. In order to establish the formulation as a hemihydroxide double salt, the dried crystals were dissolved in water and potentiometrically titrated with standard HCl solution. The first break in the pH-volume plot occurred at pH 9.7, which corresponds to the end point of the hydroxide content. Equiv wt: calcd, 1.47×10^3; found, 1.46×10^3.
(17) The structure was solved by direct phasing methods, followed by full-matrix least-squares refinement and Fourier techniques. In the final refinement, the 4136 independent data with $F^2 > 3\sigma(F^2)$ were used.
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The Role of α and β Fluorine in Product Determination of Fluoro Olefin-Tertiary Phosphine Reactions. Ylide vs. Vinylphosphorane Formation[1]

Sir:

Recent reports have documented the facile conversion of cyclic *F*-alkenes into stable phosphonium and ammonium ylides.[2-4] The stability of these unusual fluorinated carbanions has been attributed to the inductive effect of the difluoromethylene groups adjacent to the carbanionic site[3] (β-fluorine stabilization). Since the structure of these systems did not permit the incorporation of a fluorine atom on the ylidic carbon (carbanion site), it was not possible to assess the role of α fluorine (destabilization)[5] on the fate of the initial addition-elimination product.[6]

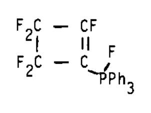


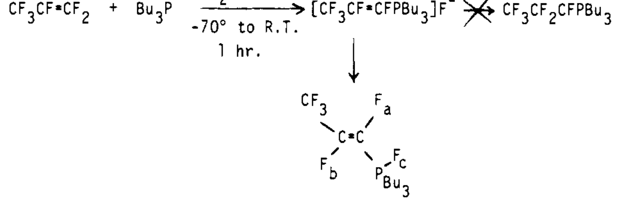
Table I

$$F\text{-1-alkene} + Bu_3P \xrightarrow[-70\text{ to RT}]{Et_2O} \text{vinylphosphorane}$$

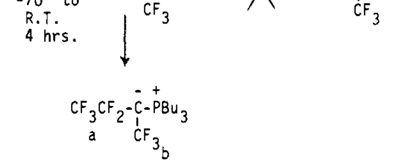
olefin	vinylphosphorane (%)[a]	*E/Z*[a]
F-1-pentene	$CF_3(CF_2)_2CF{=}CFP(F)Bu_3$ (81)	100% *Z*
F-1-heptene	$CF_3(CF_2)_4CF{=}CFP(F)Bu_3$ (83)	100% *Z*
2-phenyl-*F*-1-propene	$CF_3(C_6H_5)C{=}CFP(F)Bu_3$ (84)	91/9
2-phenyl-*F*-1-butene	$CF_3CF_2(C_6H_5)C{=}CFP(F)Bu_3$ (87)	92/8

[a] Determined by ^{19}F NMR vs. internal $C_6H_5CF_3$.

We now report the first example of the role of α fluorine in the mechanistic course of the reaction of *F*-1-alkenes with tertiary phosphines, When hexafluoropropene (HFP) was allowed to react with *n*-tributylphosphine,[7] no evidence of any stable ylide could be obtained.[8] Instead, the *F*-vinylphosphorane was obtained in nearly quantitative yield—with the *Z* isomer formed stereoselectively.[9-11] Table I summarizes the data for several related systems that behave analogously to HFP. The reactions are facile, clean, and give excellent yields of the vinylphosphoranes. Note, that, with *F*-1-pentene, *F*-1-heptene, and 2-phenyl-*F*-1-butene, that *only* the terminal vinylphosphorane is formed. No isomeric phosphoranes, which could be formed by an S_N2' reaction, were ever observed.



However, when *F*-2-butene was employed under similar conditions in this reaction, *only* the phosphonium ylide was observed; no vinylphosphorane was detected.[12,14] Thus, the *F*-2-butene behavior is analogous to the cyclic *F*-alkenes. Comparison of the potential phosphonium ylides that could be formed from the reaction of *F*-1-alkenes, *F*-2-alkenes, and cyclic *F*-alkenes with tertiary phosphines, and the respective stability of these ylides, illustrates the role of α and β fluorine in the determination of the fate of the reaction course. When only β fluorines are present (*F*-2-butene and cyclic *F*-alkenes), the initial addition-elimination adduct is converted into the phosphonium ylide. However, when both α and β fluorines are present, the ylide is either not formed or exhibits only transient stability, and the vinylphosphorane becomes the stable product.



Consequently, the fate of the initially formed addition-elimination product in *F*-alkene-tertiary phosphine reactions can be confidently predicted by assessment of the α and β fluorines in this intermediate. When no α fluorines are present, conversion into the phosphonium ylide will become the major

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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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(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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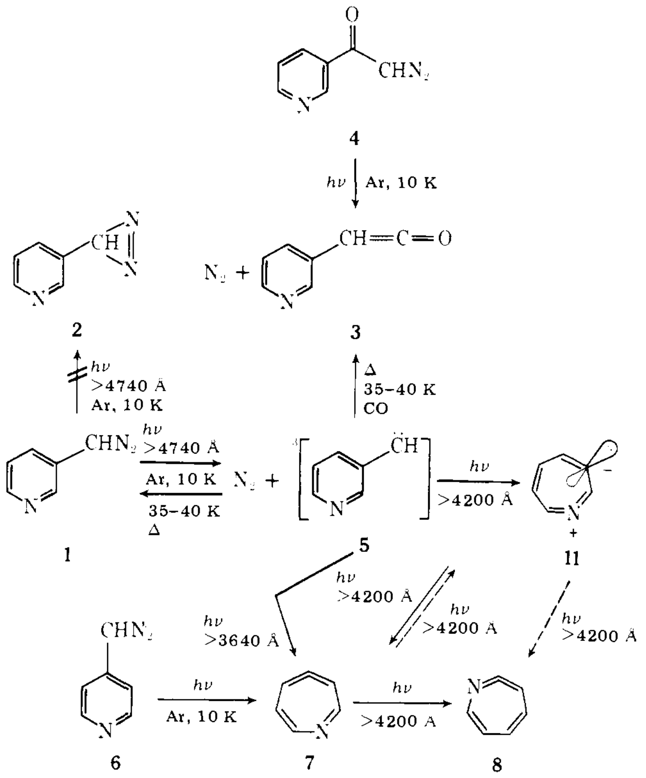
3-Pyridylmethylene: Infrared Spectrum and Photochemistry

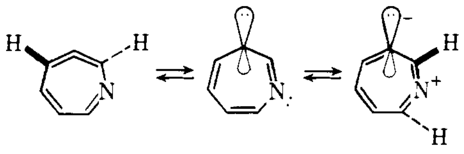
Sir:

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]

Scheme I



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**

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