

appear to be significantly broader than the other resonances. Thus, the low-temperature spectra (Figure 1) give no evidence of freezing out of a "classical" norbornyl cation. This means only that if one views the spectra in terms of rapidly equilibrating classical ions, the barrier of that equilibration must be lower than about 3 kcal mol⁻¹. Within this limitation, one can adopt a different view. The recent studies of the appropriately deuterium labeled norbornyl cation by Saunders show very small isotopic splittings owing to perturbation of symmetry.¹⁵ This result is stronger support, albeit less direct, for the "nonclassical" symmetrical norbornyl cation. We anticipate that we shall be able to conduct MAS ¹³C NMR spectroscopy in the 30 K range in the future and look forward to additional studies of this and other cations over this extended temperature range.

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Stable Vinyl Cations. Direct Spectroscopic Observation of Vinyl-Substituted Vinyl Cations

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Vinyl cations, although well established as reactive intermediates^{1a} and predicted to be rather stable thermodynamically,^{1b} have been rather elusive toward direct spectroscopic observation. Attempts to generate vinyl cations via SbF₅-assisted heterolysis of α -arylvinyli halides resulted in attack of SbF₅ at the alkene π system and formation of σ complexes.² Protonation of alkynes under strongly acidic conditions also failed to give stable vinyl cation solutions;³ rapid inter-⁴ and intramolecular⁵ sequential reactions took place instead. Hitherto the only spectroscopic evidence comes from treatment of α -alkynyl alcohols with superacids, leading to alkynylcarbenium ions, which may be regarded as vinyl cations if the allenic resonance structure is important.⁶

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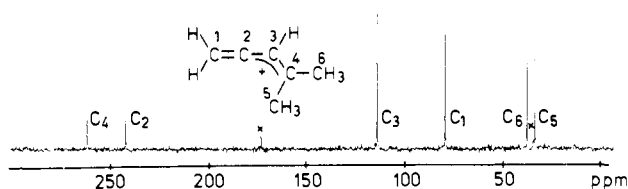
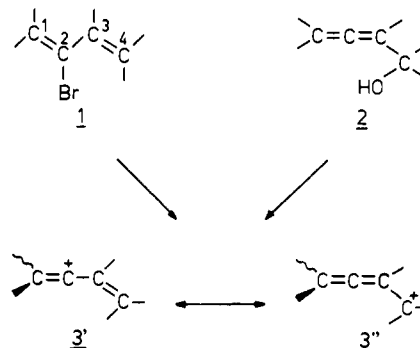


Figure 1. ¹³C NMR spectrum of cation **3a** in SO₂ClF/SO₂F₂ (2:1) at -120 °C. Peaks marked * are due to CD₃COCl used as capillary lock.

We now report the first generation and NMR spectroscopic observation of α -vinyl-substituted vinyl cations **3**, which have previously been encountered as short-lived intermediates.

Grob and Spaar studied solvolysis reactions of 2-bromo-1,3-butadienes and found particularly large rate enhancements through methyl groups at C₄, in accord with intermediate vinyl cations **3'** \leftrightarrow **3''**.⁷ Reactions of α -allenyl alcohols **2** with aqueous acid



to give α,β -unsaturated ketones were also suggested to proceed via vinyl cations **3**.⁸ Since conjugated double bonds are more stable than cumulated double bonds, vinyl cations **3** can be expected to form more readily from **2** than from **1**.

Clean solutions of **3a-c** in SO₂ClF/SO₂F₂ were obtained by reaction of alcohols **2a-c** with SbF₅ using Saunders' "molecular beam" method.¹⁰ The ¹³C NMR spectra (Table I) were recorded at -120 °C and assigned by off-resonance and proton-coupled spectra (Figure 1). Single-frequency proton-decoupled spectra were used to confirm the assignments.

In all cations, C₂ and C₄ absorb at very low field, indicating location of positive charge at these positions. Contribution of both resonance structures **3'** and **3''** is thus confirmed. The small chemical shift difference between C₃ in **3** and **2** shows that this position does not carry significant charge. The C₁ resonances are also quite similar in cations **3** and precursors **2**, since the C₁C₂ π system cannot interact with the electron-deficient orbital at C₂. Hindered rotation around the C₃-C₄ bond is responsible for the nonequivalence of C₅ and C₆.

Small, but significant, effects on chemical shifts are generated by methyl substitution at C₁. The shift of C₁ corresponds to the normal α^{σ} -CH₃ effect in allenes (≈ 10 ppm/CH₃ group)¹¹ and is almost identical for alcohols **2a-c** and cations **3a-c**. While C₃ is practically unaffected by C₁ substituents, the chemical shifts of C₂ and C₄ show opposite trends in series **2** and **3**. In the alcohols **2**, C₁-methyl groups exert the normal β^{σ} -CH₃ effect on C₂ (≈ -3 ppm/CH₃ group) in allenes¹¹ and do not influence the remote C₄. In cations **3**, however, C₂ is deshielded and C₄ is shielded by methyl groups at C₁. CC hyperconjugation, which is more effective than CH hyperconjugation, can account for this effect since the C₁-CH₃ bond is ideally oriented (dihedral angle of 0°) for interaction with

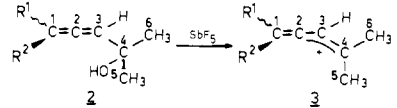
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Table I. ^{13}C NMR Chemical Shifts of Vinyl Cations 3a-c and Their Precursors 2a-c^a


| compd | R ¹ | R ² | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | C ₁ -CH ₃ |
|-------|-----------------|-----------------|--------|--------|--------|--------|--------------------|--------------------|---------------------------------|
| 3a | H | H | 79.01 | 241.88 | 113.68 | 261.58 | 32.81 | 36.91 | |
| 3b | CH ₃ | H | 90.34 | 243.97 | 114.43 | 259.16 | 32.64 | 36.63 | 9.46 |
| 3c | CH ₃ | CH ₃ | 101.55 | 245.39 | 113.97 | 257.64 | 32.43 | 36.44 | 16.29 |
| 2a | H | H | 77.28 | 205.24 | 99.90 | 68.89 | 29.33 | | |
| 2b | CH ₃ | H | 88.55 | 201.28 | 100.39 | 69.36 | 29.52 ^b | 29.59 ^b | 13.99 |
| 2c | CH ₃ | CH ₃ | 97.86 | 197.92 | 99.01 | 69.54 | 29.51 | | 20.10 |

^a Specific assignments of C-5 and C-6 in the ions 3a-c tentatively analogous to allyl cations. ^b Assignment tentative.

Table II. Calculated Bond Lengths (Å) and π Densities ρ of Vinyl Cations 3^a

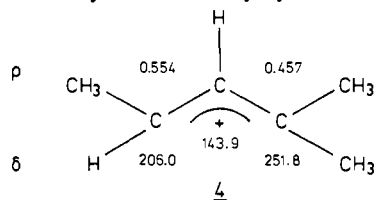
| compd | C ¹ -C ² | C ² -C ³ | C ³ -C ⁴ | ρ_2 | ρ_3 | ρ_4 |
|-------|--------------------------------|--------------------------------|--------------------------------|----------|----------|----------|
| 3a | 1.285 | 1.352 | 1.410 | 0.543 | 1.162 | 0.458 |
| 3b | 1.287 | 1.358 | 1.403 | 0.518 | 1.167 | 0.481 |
| 3c | 1.289 | 1.363 | 1.398 | 0.496 | 1.171 | 0.500 |

^a All calculations were carried out with the Gaussian 76 series of programs¹⁴ at the STO-3G basis set level.¹⁵ C-C bond lengths were optimized; standard values were selected for angles and C-H bond lengths.

the electron-deficient orbital at C₂.¹² If corrections for the precursors are considered, 10.8-ppm deshielding of C₂ and 4.6-ppm shielding of C₄ can be attributed to the hyperconjugative electron donation of two methyl groups at C₁. As in ordinary allyl cations, electron donation at one end increases the positive charge at this terminus (C₂) and decreases the charge at the opposite end (C₄).¹³

This interpretation of spectroscopic data is supported by ab initio MO calculations¹⁷ (Table II). The optimized bond lengths show that C₁-C₂ is identical with that in allene (1.288 Å),¹⁶ whereas C₂-C₃ and C₃-C₄ are similar as in allyl cations,¹³ in accord with the delocalized structure 3. The positive charge is located at C₂ and C₄, the termini of the allylic cation.

Hyperconjugative electron donation by C₁ methyl groups is also confirmed by the calculations. As derived from the ^{13}C NMR spectra, electron density increases at C₄ and decreases at C₂ when methyl groups are added at C₁. Simultaneously elongation of C₂-C₃ and shortening of the C₃-C₄ bond takes place. In valence bond terminology the contribution of resonance structure 3' increases from 3a to 3c. Calculated π densities indicate similar charge distributions in cation 3a and allyl cation 4.¹³ This is verified by the similarity of the ^{13}C chemical shifts of the tertiary carbons in both species. The other carbons cannot directly be compared, since they are differently hybridized.



As part of an allene unit, C₃ and C₂ absorb at higher or lower field, respectively, than the corresponding allyl carbons of 4. C₂

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in 3a-c is, to our knowledge, the most deshielded sp hybridized carbon reported so far for carbocations. Experiment and theory are thus in good agreement concerning the delocalized structure of vinyl cations 3a-c.

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Preparation, Structural Characterization, and Reactivity of (PEt₃)₂(CO)Rh-Co(CO)₄. A Quantitative Study of the Reversible Heterolytic Cleavage of the Polar Rh-Co Bond

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A large number of heteronuclear metal-metal bonded compounds have been prepared and characterized, but relatively few have had their chemistry explored and even less have been shown to express catalytic activity.²⁻⁴ This is surprising in view of the unique reactivity features which should accrue as a result of adjacent metals with differing sets of chemical properties. The lack of catalytic activity appears to be due in part to the absence of open coordination sites or easily dissociable ligands in the complexes examined and the fact that relatively few contain one of the more active second-row metals such as rhodium. Another problem inherent with low-valent metal-metal bonded complexes is their susceptibility to cleavage of the metal-metal bond during reaction.^{2,5,6} A number of examples of such cleavage reactions have been reported but little quantitative data are available.⁵⁻¹⁰ We describe herein the preparation and characterization of (PEt₃)₂(CO)Rh-Co(CO)₄ (1), a coordinatively unsaturated polar

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