

and -lithium^{3,16,21} compounds is difficultly reconcilable with such an intermediate. Intramolecular insertion thus becomes the third of three "diagnostic carbene reactions" now shown to be characteristic, instead, of a precursor.

It is clear that the carbene need arise no more often in reactions of an organometallic carrying a labile alkoxide,²² halide, or other Lewis base in the α -position than does its conjugate acid in reactions of a similar substrate which lacks the metal atom. By analogy with carbonium ion chemistry then, one might hope to achieve both deeper understanding and more reliable predictions if the carbene were no longer routinely invoked in α -eliminations but, rather, only after its many precursors had first been excluded from their simpler role: immediate precursors of the product.

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Concerning the Acid-Catalyzed Hydration of Acetylenes

Sir:

We wish to report evidence indicating the rate-determining formation of a vinylic cation in the acid-catalyzed hydration of phenylpropionic acids and phenylacetylenes.

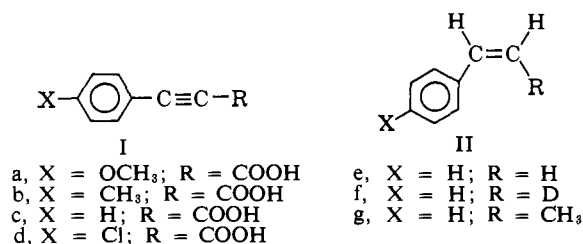
Table I. Hydration of Phenylpropionic Acids in H₂SO₄ at 25°

Compound	10 ⁶ k, sec. ⁻¹ ^a	Acidity range, % H ₂ SO ₄	-d log k/dH ₀	k _{H₂SO₄}/k_{D₂SO₄} ^b}}
Ia	2820	23.6-43.8	1.13	3.93
Ib	13.5	48.4-61.3	0.98	3.70
Ic	0.444	62.3-70.4	0.96	4.07
Id	0.165	64.8-73.4	0.97	3.75

^a At 50% H₂SO₄ (H₀ = -3.38), extrapolated where necessary.

^b Compared at that mole fraction SO₄²⁻ at which the hydration rate in H₂SO₄ is 1 × 10⁻³ sec.⁻¹.

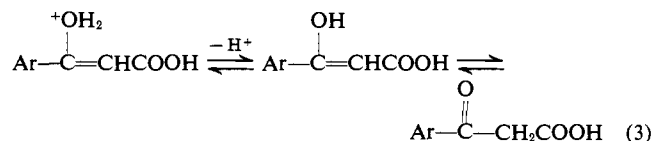
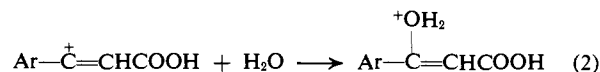
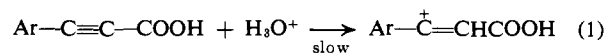
Pseudo-first-order rate constants (measured spectrophotometrically) for the hydration of four phenylpropionic acids (Ia-d) in H₂SO₄ and D₂SO₄ are summarized in Table I, with derived information.



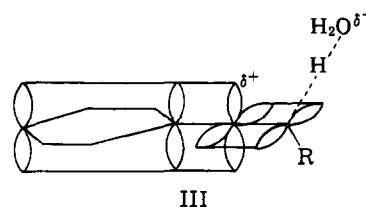
The rate data for the phenylpropionic acids correlate with σ^+ , $\rho = -4.79 \pm 0.02$, indicating a high degree of positive charge on the benzylic carbon at the transition state. The solvent kinetic isotope effects indicate rate-

determining proton transfer to the α -carbon atom; they are similar to those occurring in olefin hydration¹ and aromatic exchange.²

The experimental data thus rule out a mechanism involving 1,4-addition of water to phenylpropionic acid and support the following mechanism.



The large negative ρ shows that C-OH₂ bond formation (2) lags appreciably behind proton transfer. The addition of the two fragments to the triple bond is thus not simultaneous, and the transition state can be described best as a solvated vinylic cation of the following geometry.



Additional evidence (Table II) supporting this interpretation is provided by rate data on hydration of phenylacetylene, phenylacetylene-*d*₁, and methylphenylacetylene.

Table II. Phenylacetylene Hydration in H₂SO₄ at 25°

Compound	10 ⁶ k, sec. ⁻¹ ^a	Acidity range, % H ₂ SO ₄	k _{H₂SO₄}/k_{D₂SO₄} ^b}}
Ie	83.0	32.4-48.4	2.98
If	75.0	31.8-46.5	...
Ig	2.82	48.7-56.7	2.25

^a At 44.0% H₂SO₄, H₀ = -2.78 (solvent 5% ethanol). ^b Compared at that mole fraction SO₄²⁻ at which the hydration rate in H₂SO₄ is 1 × 10⁻³ sec.⁻¹.

The enhanced reactivity of phenylacetylene relative to methylphenylacetylene parallels the difference in heats of hydrogenation of 1-propyne and 2-butyne.³ The major factor responsible for this effect would seem to be the difference in rehybridization energy involved in going from a C_{sp}-H bond to a C_{sp²}-H bond in the transition

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state for phenylacetylene as compared to the corresponding change from $C_{sp}-C_{sp}$ to $C_{sp^2}-C_{sp}$ for methylacetylene.⁴

The same type of bond hybridization change is incorporated in the model of Streitwieser, *et al.*,⁵ for calculating secondary deuterium isotope effects. This model predicts that deuteriophenylacetylene should hydrate some 1.3 times faster than phenylacetylene. The observed reactivity shows that additional effects must be operating. Two may be suggested. Increased hyperconjugative stabilization may occur in III, $R = H$, where both carbon-hydrogen bonds are *ideally* situated for overlap with the empty p-orbital. The importance of such an effect in hyperconjugative enhancement of geminal coupling constants in allenic and ketenic structures has recently been discussed.⁶ Alternatively, hydrogen bonding from the acetylenic hydrogen to solvent may provide more effective solvation in the transition state. Experimental work is in progress to clarify these points.

It is interesting to compare the relative ease of formation of vinylic and saturated carbonium ions from acetylenes and olefins, respectively. Rates of hydration of compounds reported here may be compared to those of cinnamic acids⁷ and styrene.^{1a}

Phenylpropionic acid is hydrated 19 times more rapidly than *cis*-cinnamic acid; phenylacetylene is hydrated 2.3 times more rapidly than styrene under comparable conditions. Vinylic cations are thus seen to be more readily accessible in moderately acidic solutions than are ordinary carbonium ions.

A growing body of evidence has appeared recently implicating vinylic cations as intermediates in a variety of reactions. The protonation of acetylenes to vinylic cations has been invoked in discussions of the hydration of acetylenic ethers,⁸⁻¹⁰ the hydration of 3-hexyne,¹¹ and the trifluoroacetic acid catalyzed reactions of 1- and 3-hexyne and 5-chloro-1-pentyne.¹² The acid-catalyzed cleavage of (phenylethynyl)triethylgermanes¹³ has also been proposed to take place through these intermediates. Finally, studies of the solvolyses of α -bromostyrene¹⁴ and α,β -unsaturated β -halocarboxylate ions¹⁵ indicate that these, too, may proceed by way of vinylic cations. The present work constitutes one more piece of evidence to show that vinylic cations are relatively common reactive intermediates.

Acknowledgment. Supported in part by a grant from the Petroleum Research Fund of the American

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(16) National Science Foundation Predoctoral Fellow, 1962-1965.

(17) National Science Foundation Predoctoral Fellow, 1964-1966.

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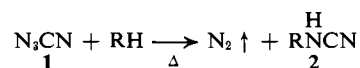
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Cyanonitrene. Reaction with Saturated Hydrocarbons

Sir:

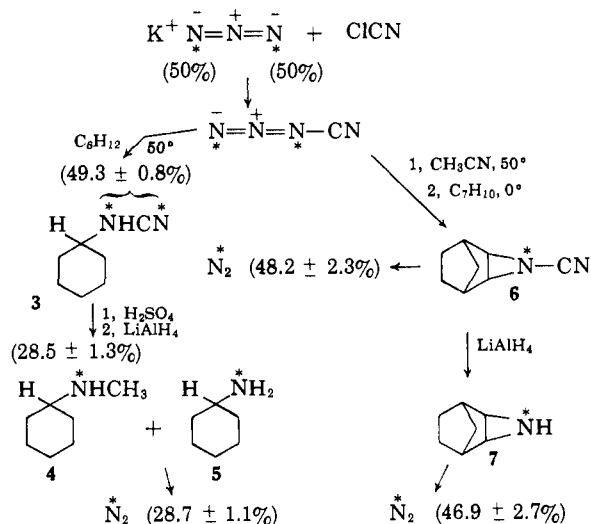
We wish to report on the thermally-induced reaction of cyanogen azide¹ with alkanes.

When solutions of cyanogen azide (1) in saturated hydrocarbons are heated at 40°, nitrogen is evolved and *primary* alkylcyanamides 2 are formed. A reasonable



mechanism for this reaction involves decomposition of cyanogen azide to nitrogen and cyanonitrene followed by insertion² of the latter into a C-H bond.

The transient existence of NCN was established by the use of isotopically labeled (¹⁵N) cyanogen azide, which was prepared from $\text{KN}^*=\text{N}=\text{N}^*$ and cyanogen chloride and was decomposed thermally in cyclohexane. The resulting cyclohexylcyanamide (3) was degraded as shown. Mass spectrometric analysis of 4 and of the nitrogen obtained from 4 and 5 on combustion afforded a value close to theory (25%) for complete scrambling, in keeping with the intermediacy of NCN. The possibility of prereaction scrambling was excluded by heating labeled cyanogen azide in acetonitrile, quenching with norbornene, and degrading the resulting cyanaziridine 6 as shown.



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(2) The term insertion is used here in a general way to indicate end result rather than mechanistic detail.