

Table I. Sulfur 2p Binding Energies^a

Oxidized cytochrome <i>c</i>	167.8	163.0
Cyanocytochrome <i>c</i>	—	162.8
Lyophilized cytochrome <i>c</i>	—	162.5
Methionine	—	162.2

^aCytochrome *c* concentration was 10 mg/ml in 0.01 *M* phosphate buffer pH 6.9. For the cyano derivative, a sufficient amount of a neutralized KCN solution was added to make a final CN⁻ concentration of 0.08 *M*. Because of the inherent asymmetry of the sulfur 2p peaks all binding energy values are ± 0.5 eV.

sulted in the formation of a thick layer of ice on the surface of the protein thus increasing the time required for data acquisition.

The lyophilized sample was prepared by examining the sample at 190 K. Examination of the sample after analysis indicated that lyophilization had occurred. Another sample was studied at room temperature and gave an analogous spectrum. Between 2 and 3 hr of running time was required for each spectrum.

The XPS spectrum of a frozen (173 K), concentrated aqueous solution of oxidized horse heart cytochrome *c* clearly shows two peaks in the sulfur 2p region, differing in energy by 3.8 eV (see Table I). The one at lower binding energy (163.0 eV) corresponds closely with that of free methionine, and agrees with the literature value for a thioether.⁴ The peak at higher binding energy must be due to the coordinate methionine sulfur which, because of its electron donation to the Fe(III), would be expected to show a higher binding energy. This seemingly large shift is reasonable in light of the recent work of Solomon et al. with plastocyanin, a "blue" copper protein.⁵ In addition, if a shift of 5.2 eV corresponds to a one-electron transfer,⁶ then, in the case of cytochrome *c*, 0.7 electron is transferred from the bound methionine sulfur to the iron.

Evidence that the peak at higher binding energy is actually the bound methionine comes from the x-ray photoelectron spectrum of the cyano derivative of cytochrome *c*, for which only one sulfur 2p peak is observed. The binding energy of this peak is 162.8 eV which corresponds to the peak of lower binding energy in the spectrum of native cytochrome *c*. This is consistent with the fact that CN⁻ replaces the coordinated methionine sulfur.⁷ Furthermore, lyophilization of cytochrome *c* also resulted in the disappearance of the peak at high binding energy which is in accord with the belief that lyophilization causes the rupture of this bond.⁸ The absorption spectrum of cytochrome *c* after x-ray irradiation showed no evidence of any structural alteration of the native protein.

We conclude that XPS is a valuable tool in determining the integrity of the Fe-S bond in cytochrome *c*. In addition, XPS may be of potential use in determining whether sulfur is liganded to the metals of various other metalloproteins. These include cytochrome *f*,⁹ cytochrome p-450,¹⁰ and the copper "blue" proteins.¹¹

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References and Notes

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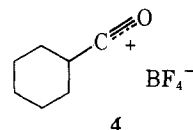
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Acylation of Acetylenes. I. Observation of an Intramolecular 1,5-Hydride Shift in a Vinyl Cation Intermediate¹

Sir:

We recently reported a new and unusual reaction leading to the formation of cyclopent-2-enones via alkyne acylation with acyl tetrafluoroborates in a nonnucleophilic solvent.² The purpose of the present communication is to report yet a different reaction pathway that predominates in the acylation of alkynes with the cycloacyl tetrafluoroborate **4**.³



The formation of the previously reported cyclic substitution products² is unusual in that it necessarily involves the saturated chain of the acyl residue. The results can be rationalized in terms of the reactive vinyl cation intermediate **A** with subsequent conversion, via transition state **B**, either

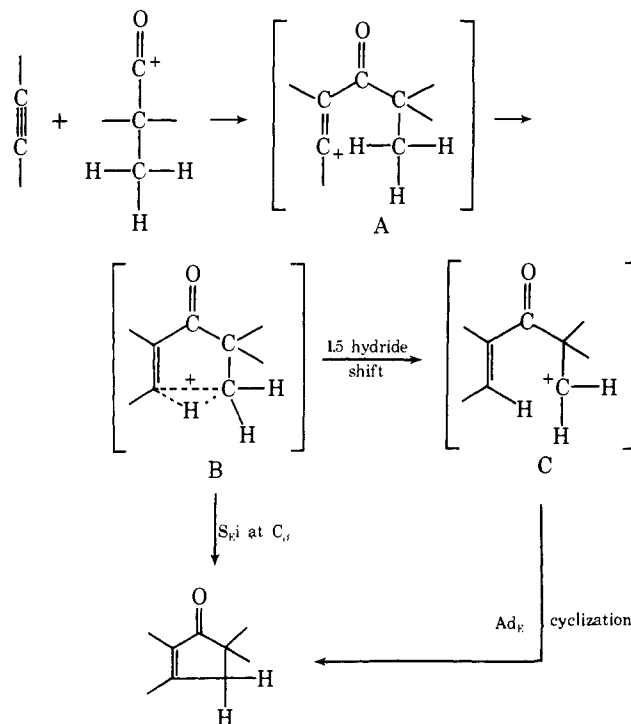
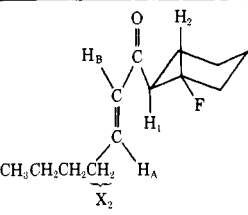
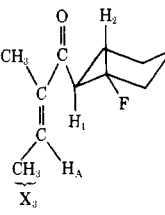
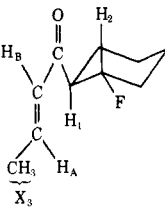


Table I. Hydride Shifted Products in the Acylation of Alkynes

Fluoride obs ^{d,a,b}	¹ H NMR spectra ^c				Ir, ^d cm ⁻¹	U ^e (λ _{max}), nm (ε)
	H _A	H _B	H ₂	H ₁		
 5a	406 Hz dt J _{AB} = 16.1 J _{A,X} = 6.8	361 Hz dd J _{AB} = 16.1 J _{B,X} = 1	272 Hz m J _{H₂,F} = 50 ^f J _{H₁,H₂} ~ 13 ^g	160 Hz m J _{H₁,H₂} ~ 13 ^g	1695 1670 ^h 1628	228 (11700)
 5b	403 Hz q J _{AX} = 6.7 ⁱ (J _{allylic} < 1)		276 Hz m J _{H₂,F} = 49 ^f J _{H₁,H₂} ~ 13 ^g	187 Hz m J _{H₁,H₂} ~ 13 ^g	1715 1680 ⁱ 1648	232 (8550)
 5c	410 Hz dq J _{AB} = 15.5 J _{AX} = 6.5 ⁱ	365 Hz dq J _{AB} = 15.5 J _{BX} = 1	274 Hz m J _{H₂,F} = 49 J _{H₁,H₂} ~ 13 ^g	165 Hz m J _{H₁,H₂} ~ 13 ^g	1698 1675 ^h 1635	225 (9000)

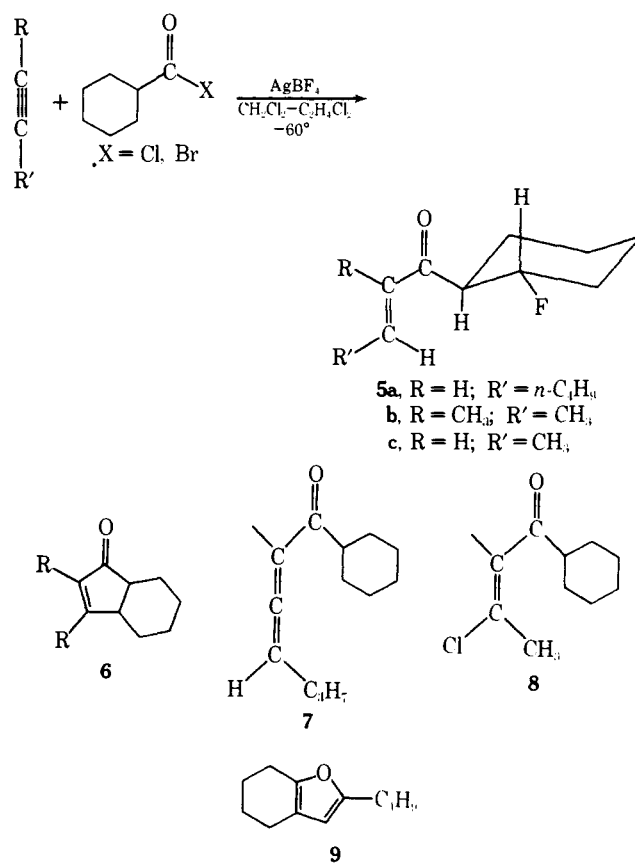
^aMicroanalysis confirmed by mass spectral analysis. ^bIsolated yields, after preparative GLC and TLC, were about 20% in each instance. An analytical GLC of the crude products showed products 5a–c to be clearly the major ones (at least 50%) and the low isolated yields reflect the narrow bands that were taken to get pure products. ^c¹H NMR spectra recorded with Varian DL-60 with the internal standard HMDS. ^dIr spectra recorded for CCl₄ solutions. ^eUv spectra obtained with ethanol solutions. ^fThe presence of fluorine is confirmed by ¹⁹F magnetic resonance where J_{H₂,F} is again observed. ^gThe trans diaxial coupling is confirmed by saturation of H₁ and observing a collapse of about 13 Hz in the width of the components of H₂. ^hThe twin carbonyl absorption, of roughly equal intensities, is attributed to the syn and anti conformations of the α,β-unsaturated system. ⁱAs in 5c except carbonyl absorption at 1680 cm⁻¹ is of greater intensity. ^jThis interaction is further confirmed by double resonance.

directly into the substitution product or to the intermediate carbenium ion C via a hydride shift. The involvement of a triangular transition state such as B is consistent with recently developed concepts on electrophilic substitution at saturated carbon.^{4–6}

The possibility of obtaining the carbenium ion intermediate C, which corresponds to a novel 1,5-intramolecular hydride shift of an intermediate vinyl cation,⁷ prompted us to examine the acylation of alkynes with cyclohexylcarbonyl cation (4). It was felt that cyclization leading to the formation of the fused ring system would be accompanied by some strain and therefore that the probability of observing products derived from the hydride shifted intermediate C would be enhanced.

We wish here to report our results with the acylation of methylacetylene, dimethylacetylene, and *n*-butylacetylene with cyclohexanecarboxylic acid chloride (and bromide) and silver tetrafluoroborate in a nonnucleophilic solvent medium. In each case the major product was the fluoride 5 with the indicated geometry about the olefinic center and also the trans configuration in the ring. These results are summarized in Table I.

Significantly, no products corresponding to the cyclized substitution products 6 could be isolated and, if present at all, they must be there in exceedingly small amounts as an effort was made to identify minor components. The identified secondary products are trivial in that they corresponded to allenic or β-chlorovinyl ketones.^{8,9} These products vary in an expected fashion as the acetylation is changed. Thus with *n*-butylacetylene the allenic compound 7 was detected and with methylacetylene the β-chlorovinyl



ketone **8** was identified. Furthermore small quantities of the furan **9** were observed in the acylation of *n*-butylacetylene, but **9** could be shown to arise from isomerization of the alkene **7**.

The somewhat surprising failure to isolate any of the substitution products **6** upon reaction with **4** suggests a significant change in some energy parameter in going from the acyclic acyl to cycloacyl cations. While the enhanced strain in forming a fused ring system may be important, the fact that the intermediate carbenium ion C in the present case is secondary, whereas in the substitution reactions with the acyl tetrafluoroborates it would have to be primary, is also undoubtedly significant. Studies are presently underway to examine these various possibilities.

References and Notes

- (1) Portions of this work were reported at 169th National Meeting of the American Chemical Society, Philadelphia, Pa., April 6–11, 1975, and 9th Great Lakes Regional Meeting of the American Chemical Society, St. Paul, Minn., June 4–6, 1975.
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- (8) Origin of chlorine is abstraction from solvent: see W. S. Johnson, M. B. Gravestock, R. J. Parry, and D. A. O'Korie, *J. Am. Chem. Soc.*, **94**, 8604 (1972).
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Additions and Corrections

The Laser Initiated Oxidative Photoaddition of *p*-Benzoquinone to Cyclooctatetraene [*J. Am. Chem. Soc.*, **96**, 2955 (1974)]. By R. MARSHALL WILSON,* EDWARD J. GARDNER, R. C. ELDER, RICHARD H. SQUIRE, and L. ROXANE FLORIAN, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221.

Owing to an inadvertent interchange of data files, the final cycles of least-squares refinement of the crystal structure of **13** were performed on data not corrected for absorption. We anticipate that little, if any bias has been introduced into the reported atom positions or the bond lengths and angles derived therefrom. On the other hand, the anisotropic temperature parameters reported in Table II and the root-mean-square displacements in Table V are undoubtedly systematically biased by this error and should not be taken to describe the vibrational amplitudes in the crystalline sample of **13**.

Stereochemistry of Cobalt Porphyrins. I. The Structure and Characterization of 2,3,7,8,12,13,17,18-Octaethylporphinatobis(3-methylpyridine)cobalt(II) [*J. Am. Chem. Soc.*, **96**, 4440 (1974)]. By ROBERT G. LITTLE and JAMES A. IBERS,* Department of Chemistry, Northwestern University, Evanston, Illinois 60201.

The value of γ should be 66.72° rather than 113.28°.

Stereochemistry of Cobalt Porphyrins. II. The Characterization and Structure of meso-Tetraphenylporphinatobis(imidazole)cobalt(III) Acetate Monohydrate Monochloroformate, [(Co(Im)₂(TPP))[OAc]·H₂O·CHCl₃] [*J. Am. Chem. Soc.*, **96**, 4447 (1974)]. By JOSEPH W. LAUHER and JAMES A. IBERS,* Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois 60201.

The value of α should be 103.94° rather than 105.94°.

The following corrections should be made in Table III:
z for H of PB-C(4) should be -0.016 rather than 0.157.
z for PD-C(6) should be 0.5446 (12) rather than p.5446 (12).
y for H-C(2) should be -0.231 rather than 0.231.
y for H-C(3) should be -0.111 rather than 0.111.

Matrix Photolysis of 1,2,3-Thiadiazole. On the Possible Involvement of Thiirene [*J. Am. Chem. Soc.*, **96**, 6768 (1974)]. By A. KRANTZ* and J. LAURENI, Department of Chemistry, State University of New York, Stony Brook, New York 11790.

The sentence beginning on the sixth line in the left-hand column on page 6769 should read, "The assignment of these bands to a single species is most clearly evident upon irradiation with light of $\lambda > 220$ nm, which results in loss of the thioketene spectrum and the appearance of a band at 1520 cm⁻¹, perhaps due to a secondary product from carbon monosulfide."

A Sensitive Probe for Double Layer Structure. Potential Dependent Competitive Cyanation and Methoxylation of 1,4-Dimethoxybenzene [*J. Am. Chem. Soc.*, **97**, 1499 (1975)]. By N. L. WEINBERG,* D. H. MARR, and C. N. WU, Hooker Chemical and Plastics Corporation, Research Center, Grand Island, New York 14302.

Page 1501 (under eq 4): A solution of 0.5 M NaCN/CH₃OH will actually contain approximately 0.48 M cyanide and 0.02 M methoxide ions.

Page 1503 (left-hand column, line 4): Case II, $k_3/k_4 = 1/40$, and the ratio (CN⁻/CH₃O⁻) at $E = 1.35$ V is 0.48/0.02. Here an arbitrary potential is chosen midway in the potential region under consideration at which point the relative bulk concentration of nucleophiles is assumed to be equal to that available for reaction at the electrode. Significantly, a potential less than about $E = 1.15$ V cannot be se-