factors, bond distances, angles, hydrogen bonds and selected nonbonding distances, least-squares planes, anisotropic thermal parameters, and root-mean-square amplitudes of thermal vibration (27 pages); tables of values of F_{obsd} and F_{calcd} (13 pages). Ordering information is given on any current masthead page.

The Ionization of Terminal Acetylenes: Pseudoacid Behavior

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The acid ionization of terminal acetylenes, eq 1, generates

$$\mathrm{RC{\equiv}CH \rightleftarrows R{\equiv}C{:}^- + H^+} \qquad (1)$$

carbanions whose basic electron pairs reside in sp orbitals localized on single carbon atoms. Such carbanions thus resemble "normal"[1] oxygen and nitrogen bases, whose basic electron pairs are also localized on single atoms, and acetylenes might therefore be expected to show "normal" acid–base behavior. Recent evidence in support of this idea comes from Brønsted relations for the thermodynamically uphill ionization of phenylacetylene[2] and several other terminal monoalkynes:[3] these Brønsted relations have unit slopes and thus resemble the unit-slope uphill legs of Eigen plots[1] for "normal" acid–base reactions, in which proton transfer is rapid and separation of the proton-transfer products is rate determining, eq 2. We wish to report that we have now

$$\mathrm{B + HA \overset{fast}{\rightleftarrows} BH^+{\cdot}A^- \xrightarrow{r.d.} BH^+ + A^-} \qquad (2)$$

found other terminal acetylenes whose uphill ionizations give Brønsted relations with slopes decidedly less than unity. This plus additional isotope effect evidence indicates that proton transfer is rate determining in these acid–base reactions; these acetylenes are therefore not functioning as "normal" acids but rather are showing the regular "pseudoacid" behavior typical of most carbon acids.

We measured rates of detritiation of cyanoacetylene in aqueous solution catalyzed by amines and carboxylate ions, eq 3. The

$$\mathrm{CNC{\equiv}CT \xrightarrow[B]{H_2O} CNC{\equiv}CH} \qquad (3)$$

data give separate Brønsted relations for the two kinds of catalyst, whose slopes are $\beta = 0.65 \pm 0.04$ (amines) and $\beta = 0.83 \pm 0.03$ (carboxylate ions).[4,5] We also examined the detritiation of two conjugated diacetylenes catalyzed by amines, eq 4, and find $\beta = 0.79 \pm 0.04$ (Ar = 4-$CH_3C_6H_4$) and $\beta = 0.79 \pm 0.06$ (Ar = 3-$CH_3OC_6H_4$).[4]

$$\mathrm{ArC{\equiv}C{-}C{\equiv}CT \xrightarrow[B]{H_2O} ArC{\equiv}C{-}C{\equiv}CH} \qquad (4)$$

We have, in addition, measured rates of dedeuteriation of cyanoacetylene in aqueous formic acid–formate buffers. The results, when combined with detritiation rate constants measured in the same buffer system, give isotope effects which, by way of the relationship $k_H/k_D = (k_D/k_T)^{2.26}$,[7] are equivalent to $(k_H/k_D)_{HCO_2^-} = 5.44 \pm 0.99$ and $(k_H/k_D)_{HO^-} = 2.41 \pm 0.34$. We have also determined $(k_H/k_D)_{HO^-} = 2.13 \pm 0.11$ and $(k_H/k_D)_{HO^-} = 1.48 \pm 0.23$ for hydron transfer from the hydroxide ion to phenylacetylene and chloroform, respectively; chloroform is a carbon acid whose conjugate base also contains a localized electron pair, and whose unit-slope Brønsted relation[2] implies normal acid behavior.

Table I. Analysis of Isotope Effects

substrate	pK_a	base	$\phi^\ddagger$	$\lvert\Delta pK\rvert^a$
$CHCl_3$	24	HO^-	0.75 ± 0.12	8
PhC≡CH	20	HO^-	0.30 ± 0.02	4
NCC≡CH	8	HO^-	0.27 ± 0.04	8
NCC≡CH	8	HCO_2^-	0.12 ± 0.02	4

[a] Absolute value of pK_a(substrate) - pK_a(base).

It is instructive to analyze these isotope effects in terms of fractionation factor theory.[8] This gives $k_H/k_D = \phi_s/\phi^\ddagger$, where ϕ_s is the D:H fractionation factor for the isotopically substituted hydrogen of the substrate in the initial state and $\phi^\ddagger$ is the fractionation factor of this hydrogen in the transition state. The value of ϕ_s for chloroform is 1.11 ± 0.01,[9] and use of that with $k_H/k_D = 1.48$ leads to $\phi^\ddagger = 0.75 \pm 0.12$. Values as close to unity as this are not characteristic of hydrogens undergoing transfer, but this value of $\phi^\ddagger$ is reasonable for the hydrogen atom of a water molecule solvating the negative charge of an already fully formed trichloromethyl carbanion, as shown in the product of eq 5; for

$$\mathrm{Cl_3CL + HO^- \rightarrow Cl_3C{:}^-LOH} \qquad (5)$$

example, $\phi = 0.7$ for the hydrogens of a water molecule performing the same function in the solvated hydroxide ion.[8c,10] Similar analysis of the isotope effects on ionization of the acetylenes, using $\phi_s = 0.64$ for the acetylenic hydrogen,[8c,11] gives $\phi^\ddagger = 0.30$ to 0.12 (Table I). Such low values *are* characteristic of hydrogens undergoing transfer; they represent sizable primary kinetic isotope effects.

This difference between chloroform and the acetylenes might be a consequence of differences in the energetics of these reactions: the proton-transfer step of energetically balanced systems with ΔpK near zero will be slower than that of imbalanced systems with ΔpK substantially removed from zero,[12] and the difference may be sufficient to change normal acid to pseudoacid behavior. Examination of this hypothesis requires information on the pK_a's of the present substrates. Directly measured values for aqueous solution are not available, but the estimates pK_a = 24 for chloroform and pK_a = 20 for phenylacetylene have been made from hydrogen-exchange rates.[2] Use of this method for cyanoacetylene can give only an upper limit, pK_a < 13, but this is enough to place the pK_a of this substance between that of the conjugate acids of the two bases, HO^- and HCO_2^-, used here to determine isotope effects; the assumption that these isotope effects vary in magnitude with ΔpK according to the Melander–Westheimer principle[13] then leads to pK_a = 8. These estimates give the ΔpK values listed in Table I.

It may be seen that the normal acid behavior indicated by $\phi^\ddagger = 0.75$ for proton transfer from chloroform to hydroxide ion is indeed associated with a greater value of ΔpK than the pseudoacid

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behavior indicated by $\phi^{\ddagger} = 0.30$ for proton transfer from phenylacetylene to hydroxide ion. Phenylacetylene, moreover, changes from its pseudoacid behavior toward hydroxide ion, where ΔpK is only 4, to normal acid behavior toward the considerably weaker bases used in constructing its unit-slope Brønsted plot, where ΔpK = 10–14. Differences in reaction energetics would thus appear to play a decisive role in determining normal acid and pseudoacid behavior.

This, however, cannot be the sole determining factor in the present case, for $|\Delta pK|$ is the same for cyanoacetylene plus hydroxide ion as for chloroform plus hydroxide ion, and yet isotope effects indicate the former to be a pseudo, and the latter a normal, acid–base system. Moreover, the value of ΔpK for phenylacetylene plus hydroxide ion is the same as that for cyanoacetylene plus formate ion, but the isotope effect in the latter system is twice as strong as that in the former.

It is not clear why cyanoacetylene should be so much more inclined to act as a pseudoacid: proton transfer from its C–H bond leaves behind a basic electron pair localized on a single atom, just as in the case of chloroform and the monoacetylenes. A difference which could be significant, however, is the presence of two conjugated triple bonds in cyanoacetylene, and in the diacetylenes as well: this provides a highly polarizable π-electron system through which an appreciable shift of negative charge could be induced upon formation of the acetylide ion, and this change in charge distribution would require reorganization of solvent molecules which might slow proton transfer sufficiently to convert normal acid behavior into pseudoacid behavior.

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High Diastereofacial Selectivity in Nucleophilic Additions to Chiral Thionium Ions[1]

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In a recent publication,[2] we presented computational evidence in favor of a theory of diastereofacial selectivity in additions to α-chiral carbonyl compounds. The calculations show that nucleophiles will tend to attack the carbonyl group in a compound RCOR* along a trajectory that is displaced from the normal plane (the plane perpendicular to the R–C–R* plane and containing the C=O bond) in the direction of the sterically less demanding R and R* (Figure 1). If R* is a stereocenter, the diastereofacial preference of the chiral carbonyl compound should then be related to steric bulk on the same side of the normal plane as R, as is observed in reduction of chiral ketones PhCH(Me)COR (R = Me, Et, *i*-Pr, and *t*-Bu)[3] and in the Lewis acid mediated additions of silyl enol ethers and silyl ketene acetals to chiral aldehydes.[4] Similar ideas have been advanced by Liotta, Burgess, and Eberhardt[5] and by Nguyên Trong Anh and Bui Tho Thanh.[6] In this communication, we present further experimental results that are consistent with this theory.

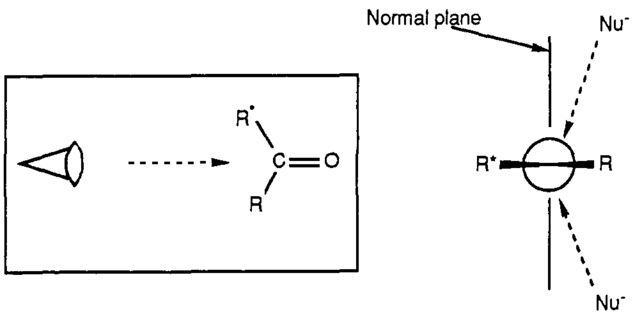
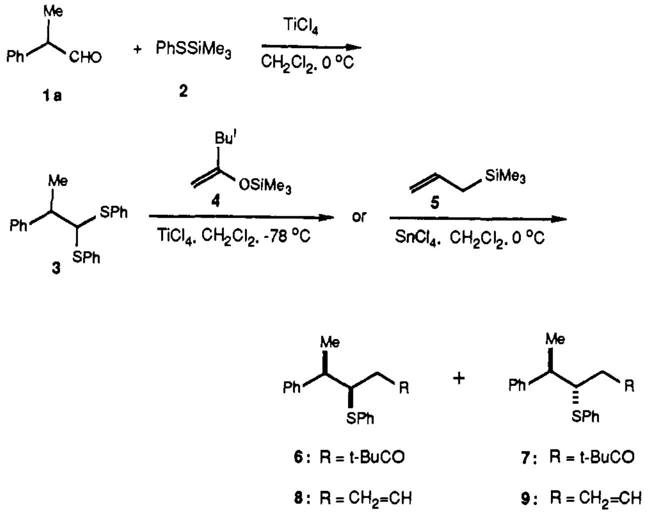
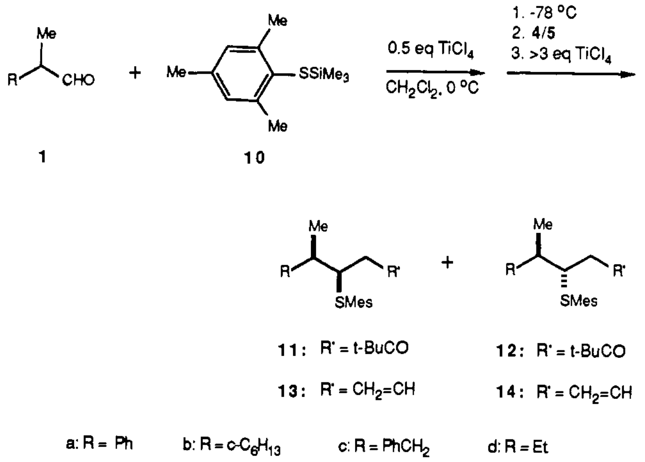


Figure 1. Proposed trajectory of attack of a nucleophile Nu⁻ on carbonyl compound R*COR, where R* is larger than R.

2-Phenylpropanal (**1a**) reacts with the trimethylsilyl derivative of thiophenol **2**[7] under the influence of $TiCl_4$ to provide the dithioacetal **3**. Treatment of this derivative with the trimethylsilyl enol ether of pinacolone **4** in the presence of several equivalents of $TiCl_4$ in CH_2Cl_2 at −78 °C affords sulfides **6** and **7** in a ratio of 4:1 (77% yield); when the nucleophilic alkene is allyltrimethylsilane (**5**) and the reaction is carried out in the presence of $SnCl_4$ in CH_2Cl_2 at 0 °C, sulfides **8** and **9** are obtained in a ratio of 3:1 (56% yield).[8]



In contrast, treatment of aldehyde **1a** with the corresponding trimethylsilyl derivative of 2,4,6-trimethylthiophenol **10**[9] gives a



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