and references therein.
13. B. Chase, N. Herron, and E. Holler, *J. Phys. Chem.*, **96**, 4262 (1992) and references therein.
14. D. W. McKee, *Carbon*, **29**, 1057 (1991).
15. H. S. Chen, A. R. Kortan, R. C. Haddon, and D. A. Fleming, *J. Phys. Chem.*, **96**, 1016 (1992).
16. J. D. Saxby, S. P. Chatfield, A. J. Palmisano, A. M. Vasallo, M. A. Wilson, and L. S. K. Pang, *J. Phys. Chem.*, **96**, 17 (1992).
17. G. H. Lee, S. B. Hong, S. S. Kim, and I. C. Jeon, to be published.
18. P. N. Keizer, J. R. Morton, K. F. Preston, and A. K. Sugden, *J. Phys. Chem.*, **95**, 7117 (1991).

A Mechanistic Study for the Addition Reaction of Secondary Amines to Methyl Propiolate

Ik-Hwan Um*, Kyung-Hee Kim, and Dong-Sook Kwon

Department of Chemistry, Ewha Womans University, Seoul 120-750

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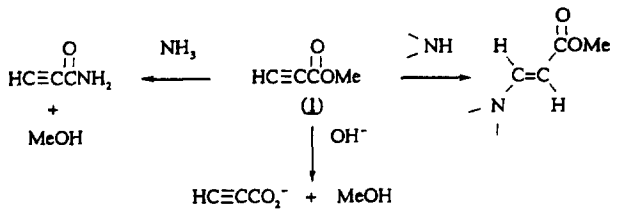
Nucleophilic addition to triple bonds has been extensively studied for a variety of synthetic interests.[1-3] Particularly, additions of amines to acetylenes with a strong electron withdrawing substituent have intrigued synthetic chemists due to the high versatility of the addition products, enamines.[4,5] However, mechanistic studies for reactions of electron deficient acetylenes with amines have not been systematically investigated, although scattered informations on kinetic studies are available.[6,7]

For a systematic study, we have investigated the reaction of methyl propiolate (**1**) with 7 different secondary amines whose pK_a range is over 5.5 in the pK_a unit. A preliminary study has revealed that the enamines obtained in the present reactions are exclusively the trans isomers. In addition, the reaction of **1** with ammonia or hydroxide ion was found to proceed in a different manner, *i.e.*, a substitution reaction occurred at the carbonyl carbon to give an amide or a carboxylate and methanol instead of an addition product as shown below.



The observed rate constants (k_{obs}) were measured spectrophotometrically by monitoring the appearance of the product at a fixed wavelength corresponding to the maximum absorption of respective enamines. All the reactions were carried out under pseudo-first-order conditions in which the concentration of amines was in large excess of **1**. Second order constants (k_2) were obtained from the slopes of the linear plots of k_{obs} *vs.* amine concentrations.

Table 1. Summary of the Second-Order Rate Constants (k_2) for the Addition Reaction of Secondary Amines to Methyl Propiolate in H_2O at 25.0℃

Amine	pK_a[a]	λ_{max} of enamine, nm	k_2, $M^{-1}s^{-1}$
1. piperazine	5.68[c]	277	0.040
2. morpholine	8.36	283	0.233(0.308)[b]
3. piperazine	9.82[d]	285	0.505
4. diethylamine	10.98	284	0.568
5. 3-Me piperidine	11.07	287	1.41
6. piperidine	11.22	289	1.24
7. pyrrolidine	11.27	291	6.94

[a] pK_a of conjugate acid of the amine: pK_a data taken from reference 13. pH of the reaction medium is kept near the pK_a of respective amines by keeping the buffer ratio with unit, *i.e.* [amine H^+]/[amine] = 1. [b] The rate constant for the reaction run in D_2O. [c] $pK_{a(1)}$. [d] $pK_{a(2)}$.

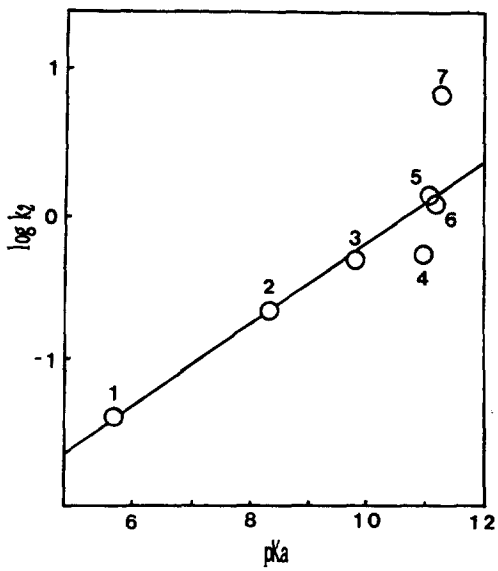


Figure 1. A Brϕnsted plot for the addition reaction of secondary amines to methyl propiolate in H_2O at 25℃. The numbers refer to the amines of Table 1.

The kinetic results for the reaction of **1** with seven secondary amines are summarized in Table 1 and demonstrated graphically in Figure 1. As shown in Figure 1, six-membered cyclic amines show a good Brönsted correlation while the other two (an acyclic and a five-membered cyclic amines) exhibit significant deviations from the linearity.

It has been generally believed that a linearity obtained from a Brönsted plot is suggestive of a common reaction mechanism for a series of reactants.[8] Similary, a break in Brönsted plot has been considered as an indication of a change in reaction mechanism.[8] However, this would be valid only when the reactants in the system are structurally similar.[9] Since pyrrolidine and diethylamine are structurally different from the other amines, it is not necessary to invoke

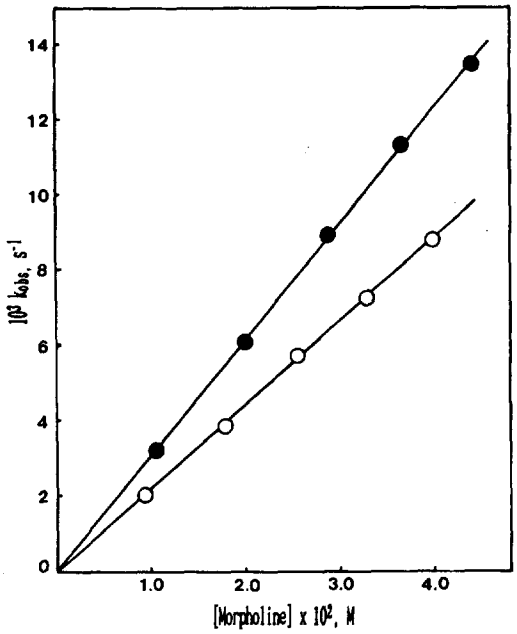
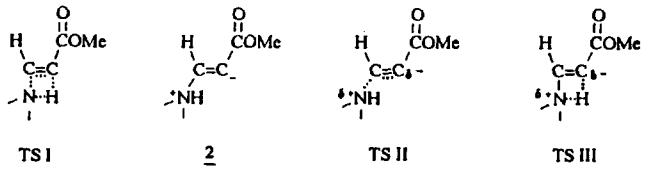


Figure 2. Plots showing inversed isotope effect for the reaction of methyl propiolate with morpholine in H_2O (○) and D_2O (●) at 25℃.

a mechanistic change in the present system. Instead, one would attribute the deviations shown by the two amines to differences in their structures rather than a change in the reaction mechanism. This is consistent with the fact that a five-membered ring compound experiences more ring strain than a six membered (e.g., cyclopentane *vs.* cyclohexane), while acyclic compounds do not experience ring strain at all. Therefore, the difference in the ring strain would affect the ground-state energy of these amines, which, in consequence, is considered to cause the present deviations in the Brönsted plot.

Based on the present results, three different reaction pathways would be suggested for the addition reaction *i.e.*, a one-step concerted mechanism with a transition state similar to TS I or stepwise processes with an intermediate **2**. The latter mechanism has two different transition states. *i.e.* TS II represent the transition state structure in the rate-determining formation of the intermediate **2**, and TS III applies to the rate-determining proton transfer to yield the product.



The one-step mechanism *via* TS I is favored by the fact that only the trans isomer has been produced. In this mechanism, one would expect to see a large primary isotope effect, since the N-H bond cleavage is involved in the rate-determining step. In fact, the reaction of **1** with morpholine (as an example) is found to be faster in D_2O than in H_2O resulting in an inversed isotope effect ($k_H/k_D=0.76$) as shown in Figure 2. This is contrary to what would have been expected if the N-H bond cleavage were involved in the rate-determining step. Therefore, the inversed isotope effect observed in the present system clearly rules out the one-step concerted mechanism.

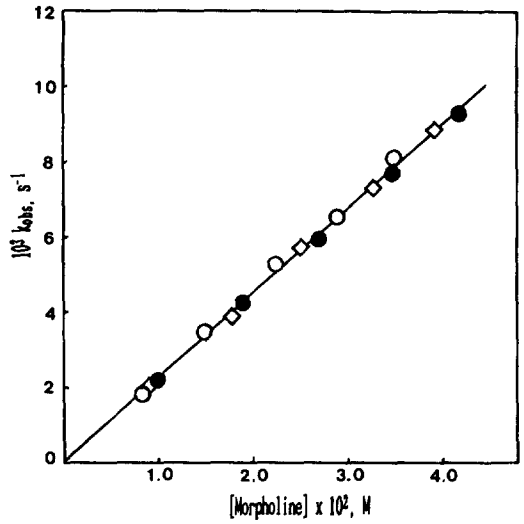


Figure 3. Plots showing absence of general acid/base catalysis for the reaction of methyl propiolate with morpholine in pH 8.06 (□), 8.34 (○) and 8.66 (●) at 25℃.

Previously, solvent effects on the reaction rate were observed to be significant in the present type of reactions performed in various organic solvents, *i.e.*, the reaction rate was found to be significantly increasing with increasing solvent polarity, and this led to a conclusion that the reaction proceeds *via* an intermediate similar to **2**.[7] Therefore, one would consider that a stepwise mechanism with TS III is plausible for the present system. Such a stepwise mechanism has often been reported to be operative in the addition reaction of amines to activated ethylenes.[10] Besides, this mechanism is further supported by the small Brönsted β_{nuc} value ($\beta_{nuc}=0.28$) obtained in the present system (Figure 1). In this mechanism, the rate of addition of amines to **1** would be significantly accelerated as the basicity of amines increases. This would result in a large Brönsted β_{nuc} value. In opposition to such an effect, the rate-determining proton transfer from the positively charged nitrogen to the negatively charged carbon would be greatly retarded as the pK_a of the amine increases and, therefore, a large negative Brönsted β_{nuc} value would be obtained. In consequence, the β_{nuc} value should become small when the reaction proceeds *via* TS III due to the compensating effect. In fact, such a compensating effect has often been observed in aminolysis of various carboxylic esters.[11]

However, the above mechanism also requires a large primary isotope effect, since a proton transfer is involved in the rate-determining. Thus, the inversed isotope effect observed in the present system (Figure 2) is clearly against TS III. Furthermore, if the proton transfer is the rate-determining step, one would also expect to see a large general acid/base catalysis.[12] In fact, general acid/base catalysis is not observed for the reaction of **1** with morpholine performed in three different pH's (pH=8.06, 8.34, 8.66) by varying buffer ratio as shown in Figure 3. This result clearly supports that the proton transfer is not involved in the rate-

determining step, and, therefore, the TS III mechanism is ruled out.

Korzhova *et al.* found no correlationship between the reactivities of amines and their basicities for the reaction of activated acetylenes with various aliphatic secondary amines.[6a] Instead, the steric factors of amines were found to determine the reactivity. Therefore, the steric hindrance has been suggested to be important in the present type of reactions. This is consistent with the preliminary results in this study, *i.e.* sterically less hindered bases such as NH_3, RNH_2 and HO^- attack only the carbonyl carbon of **1** while the secondary amines attack only the sterically less hindered acetylenic carbon of **1**. Generally, large steric effect has been observed when the degree of bond formation at the transition state has advanced significantly.[10] Thus, the reaction, in which steric hindrance plays an important role like the present system, would proceed without significant bond formation at the rate-determining step in order to avoid steric hindrance. This would explain the small β_{nuc} value obtained in this system. Therefore, it is proposed that the addition of secondary amines to **1** proceeds *via* a stepwise mechanism with a transition state similar to TS II. The absences of primary isotope effect and general acid/base catalysis are clearly consistent with this proposed mechanism.

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References

1. (a) W. E. Truce and L. M. Markley, *J. Org. Chem.*, **35**, 3275 (1970); (b) W. E. Truce and D. G. Brady, *J. Org. Chem.*, **31**, 3543 (1966).
2. V. A. Breus, S. A. Neklyudov, B. N. Solomonov, and A. I. Konovalove, *Zh. Org. Khim.*, **19**, 1613 (1983).
3. (a) B. Singaram, M. V. Rangaishenvi, H. C. Brown, C. T. Goralski, D. L. Hasha, *J. Org. Chem.*, **56**, 1543 (1991); (b) R. H. Mueller and M. E. Thompson, *Tetrahedron Lett.*, **21**, 1093 (1980).
4. B. Singaram, C. T. Goralski, and G. B. Fisher, *J. Org. Chem.*, **56**, 5691 (1991).
5. (a) J. A. Marshall and D. A. Flynn, *J. Org. Chem.*, **44**, 1391 (1979); (b) P. A. Wender and M. A. Eissenstat, *J. Am. Chem. Soc.*, **100**, 292 (1978).
6. (a) N. V. Korzhove, V. S. Pisareva, S. P. Korshunov, and L. L. Kucherenko, *Zh. Org. Khim.*, **10**, 2542 (1972); (b) N. V. Korzhova, V. S. Pisareva, and S. P. Korshunov, *Zh. Org. Khim.*, **11**, 1030 (1975).
7. B. Giese and R. Huisgen, *Tetrahedron Lett.*, **20**, 1889 (1967).
8. (a) E. Buncel, I. H. Um, and S. Hoz, *J. Am. Chem. Soc.*, **111**, 971 (1989); (b) N. B. Chapman and J. Shorter Eds., *Advances in Linear Free Energy Relationships*, Plenum, London, 1972; (c) C. F. Bernasconi Ed., *Techniques of Organic Chemistry*, Vol. 6, 4th ed., Wiley, New York, 1986.
9. E. Buncel, S. S. Shaik, I. H. Um, and S. Wolfe, *J. Am. Chem. Soc.*, **110**, 1275 (1988).
10. A. F. Popov, I. F. Perepichka, and L. I. Kostenko, *J. Chem. Soc., Perkin Trans. 2*, 395 (1989).
11. F. M. Menger and J. H. Smith, *J. Am. Chem. Soc.*, **94**, 3824 (1972).
12. P. Sykes Ed., *A Guidebook to Mechanism in Organic Chemistry*, 6th ed., John Wiley & Sons, Inc., New York, 1986.
13. W. P. Jencks and F. Regenstein in *Handbook of Biochemistry. Selected data for Molecular Biology*, H. A. Sober ed., The Chemical Rubber Co., OH, 1968.

A Novel Procedure for the Synthesis of α,β-Disubstituted β-Fluorovinyl and β-Trifluoromethylvinyl Sulfides[1]

In Howa Jeong*, Yong Ki Min†, Young Sup Kim†, Kwang Yun Cho†, and Keun Jae Kim‡

Department of Chemistry, Yonsei University, Kangwondo 222-701
†Korea Research Institute of Chemical Technology, Taejon 305-606
‡Department of Chemistry, Hannam University, Taejon 300-791

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Recently, considerable effort has been paid to the development of fluorine-containing synthetic building blocks[2,3] because of their potential to give new synthetic routes to a variety of fluoroorganic compounds, some of which exhibit unique biololgical properties in the areas of agrochemicals and pharmaceuticals.[4,5] Of particular interests in this conjunction are fluorinated vinyl sulfides which are possible synthons of vinyl fluorides and α-fluorinated ketones.[6,7] Although the synthesis and transformations of nonfluorinated vinyl sulfides have been well established,[8] there are only limited reports on the synthesis of fluorinated vinyl sulfides and most of these methods[9-11] refer to the synthesis of vinyl sulfides which do not contain an alkyl or aryl substituent at olefin carbon atoms. On the other hand, a couple of examples[12,13] has been reported on the preparation of alkyl or aryl substituted vinyl sulfides, but these methods lack generality or efficiency.

As part of our continuing studies on the chemistry and utilities of perfluoroalkylated dithioketals **1**,[14,15] we have found that **1a** and **1b** were smoothly reacted with organolithium compounds, such as alkyllithium, phenyllithium, vinyllithium and lithium alkyl or aryl acetylide, to afford α,β-disubstituted β-fluorovinyl and β-trifluoromethylvinyl sulfides **3** and **4**, but reaction of **1c** with *n*-BuLi at −78℃ resulted in the formation of β,β-difluorovinyl sulfide **2**. From the isolation of alkyl, aryl, vinyl, and acetyl phenyl sulfides in quantitative yield, reaction pathway seems likely that the initial reactions of **1** with organolithium compounds *via* attack of sulfur atom by nucleophiles provide carbanion bearing perfluoroalkyl group, which quickly undergo β-defluorination[9] to give β,β-perfluorinated vinyl sulfides **2**. The intermediate **2** is so reactive that they quickly undergo addition-elimination reac-