Table 1. Polymerization of Phenylacetylene by $MoCl_5$-$HC{\equiv}CCH_2OH$ Catalyst System[a]

Experiment number	Catalyst system[b] (mole ratio)	Polymer yield[c] (%)	Molecular weight[d] (M_w)
1	$MoCl_5$	34	6850
2	$MoCl_5$-$HC{\equiv}CCH_2OH$ (1 : 1)	43	6580
3	$MoCl_5$-$HC{\equiv}CCH_2OH$ (1 : 3)	54	7030
4	$MoCl_5$-$HC{\equiv}CCH_2OH$ (1 : 5)	58	7200
5	$MoCl_5$-$EtAlCl_2$-$HCl{\equiv}CCH_2OH$ (1 : 2 : 4)	33	6840
6	$Mo(OEt)_5$-$HC{\equiv}CCH_2OH$ (1 : 4)	trace	–
7	WCl_6	84	10800
8	WCl_6-$HC{\equiv}CCH_2OH$ (1 : 4)	8	3160

[a]Polymerized in chlorobenzene at 60℃ for 24 h; $[monomer]_o$ = 1.0 M, [monomer]/[catalyst] = 50. [b]Mixture of catalyst and cocatalyst was aged at 20℃ for 15 min before use. [c]Methanol-insoluble polymer. [d]Measured by GPC-150C of waters using the calibration curves for polystyrene standard.

were carried out under dry nitrogen atmosphere in chlorobenzene at 60℃, $[monomer]_o$ = 1.0 M, monomer to catalyst mole ratio (M/C) = 50, for 24 h.

Table 1 shows the results for the polymerization of phenylacetylene by $MoCl_5$ activated by $HC{\equiv}CCH_2OH$. In most cases, $HC{\equiv}CCH_2OH$ activated $MoCl_5$ for the polymerization of phenylacetylene by $MoCl_5$. As the mole ratio of $HC{\equiv}CCH_2OH$ to $MoCl_5$ was increased, the polymer yield was increased, and then over $[HC{\equiv}CCH_2OH]/[MoCl_5] = 5$ the polymer yield was decreased. When $EtAlCl_2$, a typical cocatalyst for the polymerization of acetylene derivatives by $MoCl_5$ and WCl_6,[4,5] was used, the catalytic activity was decreased. Fully substituted molybdenum ethoxide, $Mo(OEt)_5$, showed no catalytic activity even when $HC{\equiv}CCH_2OH$ was used as a cocatalyst. When $HC{\equiv}CCH_2OH$ was used as a cocatalyst in the WCl_6-catalyzed polymerization of phenylacetylene, the polymer yield was notably decreased than the polymer yield (84%) obtained by WCl_6 alone. It can be deduced that the oxygen atom of $HC{\equiv}CCH_2OH$ deactivate WCl_6. The deactivation phenomena of WCl_6 by the oxygen atom-containing acetylene monomers was also observed in the polymerization of propiolic acid,[13] dipropargyl ether,[14] and dipropargyl sulfone.[15]

The average molecular weight ($\overline{M}_w$)s of poly(phenylacetylene) prepared by $MoCl_5$-$HC{\equiv}CCH_2OH$ catalyst system were similar to that of poly(phenylacetylene) obtained by $MoCl_5$ alone. These molecular weights were somewhat lower than that ($\overline{M}_w$ = 10800) of poly(phenylacetylene) prepared by WCl_6 alone under the same reaction conditions.

The initial purple color of $MoCl_5$ catalyst solution was disappeared as soon as the $HC{\equiv}CCH_2OH$ solution was injected. The resulting poly(phenylacetylene) prepared by $MoCl_5$-$HC{\equiv}CCH_2OH$ was yellow and light-brown colored powder.

The elemental analyses agreed well with the calculated value (*e.g.*, $MoCl_5$-$HC{\equiv}CCH_2OH$ (1 : 5) catalyzed poly(PA), calcd for $(C_8H_6)_n$: C, 94.08%; H, 5.92%. Found: C, 93.21%; H, 5.83%).

The NMR (^1H- and ^{13}C-), IR, UV-visible spectral data were similar to those of poly(phenylacetylene) obtained by $MoCl_5$ and $MoCl_5$-*n*-Bu_4Sn.[16-18] The higher catalytic activity of $MoCl_5$-$HC{\equiv}CCH_2OH$ catalyst system was deduced that the partially substituted molybdenum compounds by $HC{\equiv}CCH_2OH$ are active species though the mechanism is not fully understood.

Further works for the polymerization mechanism and the effect of 2-propyn-1-ol homologues are in progress.

References

1. T. Masuda, K-I. Hasegawa, and T. Higashimura, *Macromolecules*, **7**, 728 (1974).
2. M. G. Voronkov, V. B. Pukhnaevich, S. P. Suchchinskaya, V. Z. Annenkova, V. M. Annenkova, and N. J. Andreeva, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 53 (1980).
3. T. Higashimura, Y-X. Deng, and T. Masuda, *Macromolecules*, **15**, 234 (1982).
4. Y. S. Gal, H. N. Cho, and S. K. Choi, *J. Polym. Sci. Polym. Chem. Ed.*, **24**, 2021 (1986).
5. Y. S. Gal, H. N. Cho, and S. K. Choi, *Polymer (Korea)*, **9**, 361 (1985).
6. W. C. Lee, J. E. Sohn, Y. S. Gal, and S. K. Choi, *Polymer (Korea)*, **12**, 720 (1988).
7. Y. S. Gal, B. Jung, W. C. Lee, and S. K. Choi, *Polymer (Korea)*, **14**, 597 (1992).
8. B. N. Kuzentsov, A. N. Startsev, and Y. I. Yermakov, *J. Mol. Cat.*, **8**, 135 (1980).
9. R. Nakamura, S. Fukuhara, S. Matsumoto, and K. Komatsu, *Chem. Lett.*, 253 (1976).
10. R. Nakamura, S. Matsumoto, and E. Echigoya, *Chem. Lett.*, 1019 (1976).
11. G. C. Bazan, R. R. Schrock, H. N. Cho, and V. C. Gibson, *Macromolecules*, **24**, 4495 (1991).
12. G. C. Bazan, J. H. Oskam, H. N. Cho, L. Y. Park, and R. R. Schrock, *J. Am. Chem. Soc.*, **113**, 6899 (1991).
13. T. Masuda, M. Kawai, and T. Higashimura, *Polymer*, **23**, 744 (1982).
14. Y. S. Gal and S. K. Choi, *Polymer (Korea)*, **11**, 563 (1987).
15. Y. S. Gal and S. K. Choi, *J. Polym. Sci. Polym. Chem. Ed.*, **31**, in press (1993).
16. T. Masuda, N. Sasaki, and T. Higashimura, *Macromolecules*, **8**, 717 (1975).
17. A. C. Chiang, P. F. Waters, and M. H. Aldridge, *J. Polym. Sci. Polym. Chem. Ed.*, **20**, 1807 (1982).
18. C. P. Tsonis and M. F. Farona, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 1779 (1979).

Reformatsky Reactions of *N*-Alkylidenebenzenesulfenamides

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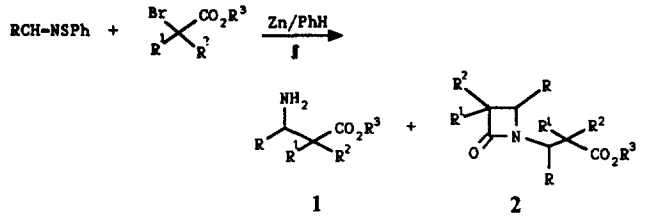
Among various approaches to the preparation of primary



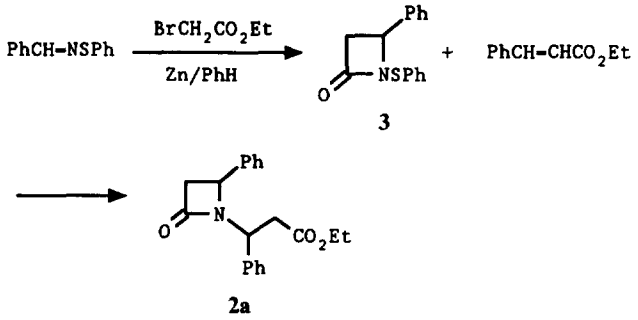
Scheme 1.

Table 1. Formation of β-amino esters (**1**) and β-lactams (**2**) by the Reformatsky Reactions on *N*-alkylidenebenzenesulfenamides

R	R^1	R^2	R^3	Products, yields (%)
Ph	H	H	Et	**1a** 20, **2a** 25
	H	Me	Et	**1b** 33, **2b** 34
	Me	Me	Et	**1c** 34, **2c** 35
	H	H	*t*-Bu	**1d** 52
	H	Vinyl	Et	**1e** 20
Me	H	H	Et	**1f** 20
Et	H	H	Et	**1g** 23

amines, alkylation of imines is probably the most direct one.[1] Some imines such as *N*-alkoxycarbonylimines[2] and *N*-benzyloxyimines[3] have been employed for the synthesis of β-amino acids in recent years. However, some imines, such as *N*-trimethylsilylimines have been reported to yield β-lactames exclusively when they are reacted with lithium enolates.[4] Recently, we have examined several reactions of metal enolates with sulfenimines to develop a method producing β-amino esters in high yields. During this study, we have found that addition of Reformatsky reagents to *N*-alkylidenebenzenesulfenamides[5] gives rise to β-amino esters (**1**) and/or to unexpected β-lactams (**2**) as shown in Scheme 1, and we wish to report the results in this paper.

As shown in Table 1, the reaction of the Reformatsky reagents formed from simple ethyl 2-bromoacetate or its derivatives of *N*-alkylidenebenzenesulfenamides yields β-amino esters (**1**) with unexpected β-lactam compounds (**2**). The experiment has been typically carried out as exemplified for the first entry in Table 1. A solution of ethyl 2-bromoacetate (4.0 mmol) in dry benzene (20 m*l*) was refluxed with a piece of sandpapered zinc-foil and a crystal of iodine. Then, *N*-benzylidenebenzenesulfenamide (3.0 mmol) was added and the mixture was refluxed at 80℃ further for 1 hr. The mixture was then cooled, washed with 20% ammonium hydroxide, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was distilled under vacuum to obtain an oil. It was chromatographed over silica gel to obtain a β-amino ester [**1a**, IR (neat): 1735, 3350 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.33 (t, J=7 Hz, 5H, CH_3+NH_2), 2.80 (d, J=7 Hz, 2H), 4.20 (q, J=7 Hz, 2H), 7.68 (s, 5H) ppm] in 20% yield, a β-lactam [**2a**, IR (neat): 1740, 1760 cm^{-1}, ^{1}H-NMR ($CDCl_3$): δ 1.19 (t, J=7 Hz, 3H), 2.60 (dd, J=16.2 and 6.7 Hz, 1H, CH-COOEt), 2.79 (dd, J=14.7 and 2.7 Hz, 1H, β-lactam C_3-H), 3.12 (dd, J=16.2 and 8.8 Hz, 1H, CH-COOEt), 3.25 (dd, J=14.7 and 5.3 Hz, 1H, β-lactam C_3-H), 4.10 (q, J=7 Hz, 2H), 4.40 (dd, J=2.7 and 5.3 Hz, 1H, β-lactam C_4-H), 5.03 (dd, J=8.8 and 6.7 Hz, 1H), 7.29 (br s, 10H) ppm; ^{13}C-NMR ($CDCl_3$); δ 14.03, 37.93, 46.19, 54.77, 54.93, 60.67, 126.75(2C), 127.57(2C), 127.94, 128.28, 128.45, 128.64(2C), 128.71(2C), 138.35, 138.95, 167.27, 170.42 ppm; M^+ *m/z* 323 (electron impact MS)] in 25% yield, and ethyl cinnamate in 14% yield. Reflux of the *N*-benzylidenebenzenesulfenamide with *t*-butyl bromoacetate in the presence of Zn yieled a β-amino ester in 52% yield exclusively. Reformatsky reactions of ethyl γ-bromocrotonate with *N*-benzylidenebenzenesulfenamide or ethyl 2-bromoacetate with *N*-ethylidene- or *N*-propylidenebenzenesulfenamide yieled only β-amino esters in low yields. The β-lactam compound seems to be the product of Michael addition of the β-lactam **3** formed first to ethyl cinnamate which might be formed from the β-amino ester with loss of ammonia. More ethyl cinnamate was isolated when the reaction mixture refluxed for a longer time (45% yield after 12 hr reflux). Similar elimination of water from the product formed from the reaction of acetophenone with ethyl 2-bromoacetate in the presence of Zn was reported in the literature.[6]



Scheme 2.

When *N*-benzylidenebenzenesulfenamide was reacted with *t*-butyl lithioacetate, *t*-butyl 3-phenyl-3-phenylthioaminopropanoate (**4**) was isolated in 17% yield only, and with its cuprate, *t*-butyl 2-phenylthioacetate (**5**) was obtained in 93% yield. Cuprate seems to prefer nucleophilic attack on the sulfur atom of the sulfenimine.

Figure 1.

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References

1. (a) F. A. Davis and P. A. Mancinelli, *J. Org. Chem.*, **42**, 398 (1977); J. H. Lee, Y. Y. Lee, and Y. M. Goo, *J. Korean Chem. Soc.*, **35**, 592 (1991).
2. (a) T. Shono, N. Nise, F. Sanda, S. Ohi, and K. Tsubata, *Tetrahedron Lett.*, **29**, 231 (1988); (b) T. Shono, N. Kise, F. Sanda, S. Ohi, and K. Yoshioka, *Tetrahedron Lett.*, **30**, 1253 (1989).
3. (a) K. Ikeda, K. Achiwa, and M. Sekiya, *Tetrahedron Lett.*,

24, 4707 (1983); (b) D. A. Bunnett, D. J. Hart, and J. Liu, *J. Org. Chem.*, **51**, 1930 (1986).
4. D. C. Ha, D. J. Hart, and T. K. Yang, *J. Am. Chem. Soc.*, **106**, 4819 (1984).
5. F. A. Davis, W. A. R. Slegeir, S. Evans, A. Schwartz, D. L. Goff, and R. Palmer, *J. Org. Chem.*, **38**, 2809 (1973).
6. C. R. Hauser and W. H. Puterbaugh, *J. Am. Chem. Soc.*, **75**, 4756 (1953).

Determination of pK_a by Luminescence Quenching Method. pK_a of Conjugated Acids of 1-Alkyl-4,4'-Bipyridinium Ions

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The pK_a value of an acid is the most important parameter for the interpretation of pH-dependent physico-chemical properties of chemical species. Variety of methods have been used for determination of pK_a. Luminescence method is a very sensitive tool for chemical analysis of luminescent molecules. However, this method is rarely used for the determination of pK_a, as the pK_a of an excited state is usually remarkably different from that of ground state.[1] In this communication, we present a novel method for determination of pK_a based on luminescence quenching results.

1-Alkyl-4,4'-bipyridinium (RBPY) ions undergo the following acid-base equilibria.

acidic form basic form

The acidic form of RBPY is chemically similar to 1,1'-dialkyl-4,4'-bipyridinium (viologen) compounds which are widely used as electron relays in chemical[2] and photo-sensitized reduction[3] of substrates, and as active materials in electrochromic displays.[4] The basic form is a substituted pyridinium and is considered as a coenzyme NAD^+ analog.[5] Because of these interesting characters, the pH-dependent electrochemical[6-8] and spectroscopic[7-9] behaviors of the compounds as well as their ability as electron carriers in redox reactions[10,11] have been investigated.

Eour 1-alkyl-4,4'-bipyridinium (RBPY: R=methyl (C_1), *n*-octyl(C_8), *n*-dodecyl (C_{12}), benzyl (Bn)) salts were prepared by reacting 4,4'-bipyridine with corresponding alkyl halides as described in ref 10. Solution media were 0.10 M HCl, 0.01 M NaOH+0.09 M NaCl, or 0.01 M Na_2HPO_4+0.07 M NaCl. By appropriate mixing of these solutions, we obtained solutions of desired pH. The maximum change of ionic strength between pH 1 and 10 was less than 10%. Quenching of tris(2,2'-bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$, luminescence by RBPY was studied by steady-state luminescence measurement at 25℃ in aqueous media. At a given pH, the quenching data gave good linearity following Stern-Volmer equation (Eq. (1)), indicating dynamic nature of the queching reaction.

$$I_o/I = 1 + K_{SV}[\text{RBPY}] \quad (1)$$

I_o and I are luminescence intensities in the absence and presence of the quencher, respectively. The K_{SV} values obtained at pH 2 and 8 are summarized in Table 1: RBPY are present mostly as acidic forms at pH 2 and basic forms at pH 8 (note that pK_a values are about 3.5 from Table 1).

Table 1. Stern-Volmer Constant (K_{sv}) for Luminescence Quenching of $Ru(bpy)_3^{2+}$ by 1-Alkyl-4,4'-bipyridinium (RBPY) Ions and pK_a Values of the RBPY in Aqueous Solutions of Ionic Strength 0.10 M at 25.0℃

Compounds	K_{sv}		pK_a	
	pH 2.0	pH 8.0	SDS-free	10 mM SDS
C_1BPY	355	108	3.42 (3.60[a])	4.50
C_8BPY	400	135	3.65	4.96
C_{12}BPY	590	245	3.61	4.62
BnBPY	490	401	3.51	4.38

[a] Reported value from UV spectroscopic method.[9]

The quenching reactions are transfer of electron from photo-excited $Ru(bpy)_3^{2+}$ to the quenchers.[10,11] The K_{SV} values of the acidic forms are very similar to those of corresponding methyl alkyl viologens[12] and much greater than those of basic forms, though reactions with acidic forms are less favorable when one considers only electrostatic effect. Thus, our result reflects clearly facile reduction of the protonated (acidic) form of RBPY: the reduction potential of the protonated RBPY is *ca.* −0.7 V (*vs.* SCE) and similar to that of dialkyl viologen, whereas that of basic form is about −1.0 V.[6,7]

Because of the intrinsic difference in quenching efficiency between the acidic and basic forms of RBPY, the luminescence titration of a solution containing $Ru(bpy)_3^{2+}$ and RBPY shows spectral change similar to that observed in spectroscopic titration of a dye. In Figure 1, we present absorption spectra of RBPY and luminescence spectra of $Ru(bpy)_3^{2+}$ in the presence of RBPY taken at pH 1 and 10. The relative change in emission intensity produced by lowering pH to 1 from 10 is much greater than the corresponding change in absorbance: exception to this is absorption at $\lambda > 290$ nm, which is tail absorption region. The relative changes in absorbance of RBPY solution and luminescence intensity of a solution of $Ru(bpy)_3^{2+}$ and RBPY with pH are displayed in Figure 2. Good agreement between the absorbance and luminescence titration data is indicative of that the spectral changes arise from acid-base eqilibria of RBPY. The pK_a values of the quenchers were obtained from the titration data by using the relationship, $pH = pK_a + \log[\Delta I/(\Delta I_{max} - \Delta I)]$: the ΔAbs can be substituted for ΔI for absorbance data. The results are given in Table 1.

We also determined pK_a of RBPY in the presence of 10 mM sodium dodecylsulfate (SDS) and the results are included in Table 1. The pK_a value in the SDS micellar solution is about 1 pH unit higher than that in SDS-free solution. This is a typical result observed when the acid is bound