sulting solution produced only white solid A·2HClO$_4$[13] instead of the complex. We were also unsuccessful in isolating any Co(II), Co(III), or Fe(II) complex of A from the reaction of A and the metal ion. The electronic spectra (Figure 1) of the methanol solution containing the ligand and Ni(II) ion are also very similar to that containing the metal ion only. Moreover, no spectral change is observed even by heating (>45℃) the mixture for more than six hours. The similar result was also observed in the spectra of the mixture of A and Co(II) or Fe(II) ion ($[M^{2+}]=5.0\times10^{-3}$ M; $[A]=2.5\times10^{-3}$ M). This result is quite different from the fact that the addition of A to the solution of Cu(II) acetate even at room temperature changes its spectrum. The stability constant of the Cu(II) complex calculated by the method of continuous variation[14] at 25℃ is more than 1.0×10^6. The results indicate that the ligand A is highly selective for complex formation with Cu(II) over Ni(II) and other 3d-metal ions. The high selectivity for Cu(II) against Ni(II) ion in the complex formation has not been observed for other per-N-methylated 14-membered tetraaza macrocycles such as D, G, and H.[9,15,16] Although it has been reported that D exhibits some selectivity for Cu(II) over Ni(II) ion,[9] both $[Cu(D)]^{2+}$ and $[Ni(D)]^{2+}$ are readily isolated by the reaction of the metal ions and the ligand in methanol solution.[8] The Ni(II) complex of D or F is also obtained by the reaction of $[Ni(C)]^{2+}$ or $[Ni(E)]^{2+}$ with MeI and KOH in DMSO solution.[17] However, in all attempts to prepare Ni(II) complex of A from $[Ni(B)]^{2+}$ by the similar reaction, the complex with four N-methyl groups was never isolated.[18] To our knowledge, the new ligand A prepared in this work is a rare 14-membered tetraaza macrocycle that exhibits the clear-cut recognition of Cu(II) against Ni(II) ion in the complex formation.

The reason for the high selectivity for complexation of A toward Cu(II) over Ni(II) ion is not clearly understood. However, it is likely that the selectivity is caused in part by the presence of the cyclohexane rings and C-methyl groups in addition to the N-methyls in the ligand, that sterically hinder the binding of the metal ion, and the acidity of the metal ions(Cu(II)≫Ni(II)).[19] Further studies on selective extraction, separation, and transport of the transition metal ions by using the noble ligand are in progress.

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References

1. Y. Inoue and G. W. Gokel, Cation Binding by Macrocycles, Marcel Dekker, Inc., New York, 1990 and references therein.
2. R. M. Izatt and J. J. Christenen, Synthesis of Macrocycles, John Wiley & Sons, Inc., New York, 1987 and references therein.
3. H. Tsukube, T. Yoden, T. Iwachido, and M. Zenki, *J. Chem. Soc. Chem. Commun.*, 1069 (1991).
4. M. Hujiwara, J. Matsuda, and H. Wakita, *Polyhedron*, **9**, 2491 (1990).
5. R. C. Luckay and R. D. Handcock, *J. Chem. Soc. Dalton Trans.*, 1491 (1991).
6. E. Kimura, Y. Kurogi, S. Wada, and M. Shionoya, *J. Chem. Soc. Chem. Commun.*, 781 (1989).
7. M. D. Casa, L. Fabbrizzi, A. Perotti, A. Poggi, and P. Tundo, *Inorg. Chem.*, **24**, 1611 (1985).
8. C. M. Madeyski, J. P. Michael, and R. D. Handcock, *Inorg. Chem.*, 1487 (1984).
9. E. K. Barefield and F. Wagner, *Inorg. Chem.*, **12**, 2435 (1973).
10. E. Kimura, C. A. Dalimunte, A. Yamashita, and R. Machida, *J. Chem. Soc. Chem. Commun.*, 1041 (1985).
11. S.-G. Kang, J. K. Kweon, and S.-K. Jung, *Bull, Korean Chem. Soc.*, **12**, 483 (1991).
12. Anal. Calcd for $[Cu(A)](ClO_4)_2\cdot H_2O$: C, 42.8; H, 7.47; N, 8.08% Found: C, 42.9; H, 7.34; N, 8.08%. λ_{max}: 563 nm ($\varepsilon=286\ M^{-1}cm^{-1}$) in MeCN. Λ_M: 278 ohm^{-1}mol^{-1}cm^2 in MeCN.
13. Elemental analysis. Calcd for $C_{24}H_{50}N_4Cl_2O_8$: C, 47.2; H, 8.20; N, 9.19%. Found: C, 46.8; H, 8.27; N, 9.39%.
14. D. T. Sawyer, W. R. Heineman, and J. M. Beebe, Chemistry Experiments for Instrumental Methods, John Wiley & Sons, Inc., New York, 1984, pp. 198-201.
15. D.-E. Klaehn, H. Paelus, R. Grewe, and H. Elias, *Inorg. Chem.*, **23**, 483 (1984).
16. S.-G. Kang and J. K. Kweon, Unpublished results.
17. F. Wagner and E. K. Barefield, *Inorg. Chem.*, **15**, 408 (1976).
18. In all attempts, the reaction product was a Ni(II) complex containing three N-methyl groups, which was identified with elemental analyses and infrared and NMR spectra of the product and mass spectrum of the free ligand.
19. F. Basolo and R. G. Pearson, Mechanisms of Inorganic Reactions, 2nd Ed., John Wiley and Sons, Inc., New York, 1968, p. 32.

Trimethylsilyl Triflate Promoted Conjugate Addition of Organozinc Compounds to α,β-Enones

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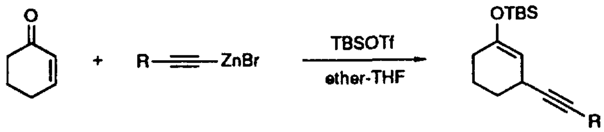
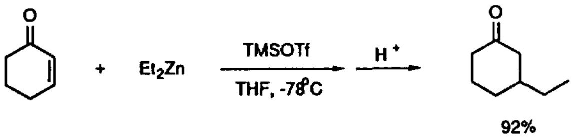
The conjugate addition of organometallic reagents to α,β-unsaturated carbonyl compounds is one of the most useful and reliable method for carbon-carbon bond formation. It has been normally achieved using organocopper reagents.[1] On the other hand, the use of Lewis acids such as titanium tetrachloride,[2] boron trifluoride etherate,[3] and trialkylsilyl triflate[4] makes it possible to use relatively mild allylsilanes and allylstannans in conjugate addition to α,β-enones. Organozinc compounds have mainly retained their synthetic usefulness in Reformatsky reaction[5] but several organozinc compounds such as triorganozincates[6] and zinc homoenolates[7] have been employed in conjugate addition to α,β-enones. Since organozinc compounds are less reactive than organometallic compounds derived from lithium, magnesium, and copper, their additions to α,β-enones have been achieved through the transmetallation of organozinc compounds to organocopper compounds[8] or the use of nickel as a catalyst.[9]

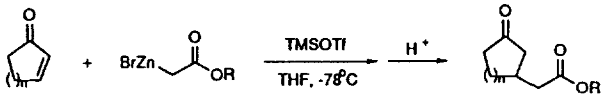


(1)



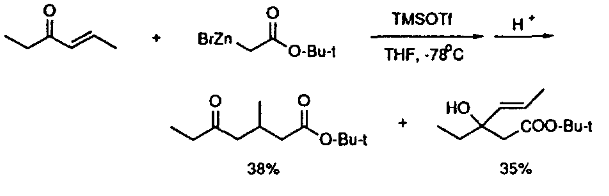
(2)

Recently, we have reported that the conjugate addition of alkynylzinc compounds to α,β-enones proceeds smoothly in the presence of trialkylsilyl triflate (Eq. 1)[10] and the success of the reaction may be attributed to an initial strong coordination of the carbonyl group by trialkylsilyl triflate and preferential conjugate addition of alkynyl group to α,β-enones. This initial encouraging result prompted us to investigate the possibility of the conjugate addition of several different types of organozinc compounds to α,β-enones. We have studied the conjugate addition reactions with commercially available diethylzinc in the presence of Lewis acid. Among several Lewis acids tested in this study, trimethylsilyl triflate (TMSOTf) gave the best result. Thus, the reaction of an equimolar mixture of 2-cyclohexen-1-one and TMSOTf with 1.2 equiv of diethylzinc in tetrahydrofuran at −78°C for 2 h gave 3-ethylcyclohexanone in 92% isolated yield after acidic workup (Eq. 2). Similarly, the reaction of carvone with diethylzinc gave the conjugate addition product in 86% yield. However, the use of trimethylsilyl chloride and boron trifluoride etherate gave 3-ethylcyclohexanone in 4% and 40% yield, respectively. The effort to extend the utility of the present reaction with alkylzinc halides was not promising. The reaction of 2-cyclohexen-1-one with *n*-butylzinc bromide, generated from equimolar amounts of *n*-butyllithium and zinc bromide, in the presence of TMSOTf in tetrahydrofuran at −78°C afforded 3-*n*-butylcyclohexanone in 32% yield and attempts to improve the yield under various reaction conditions were unsuccessful.



(3)

n=1; R=t-Bu (92%), R=Et (68%)
n=2; R=t-Bu (96%), R=Et (40%)



(4)

The Reformatsky reaction with α,β-unsaturated carbonyl compounds was known to give mainly the 1,2-addition product, although the ratio of 1,2- and 1,4-addition product depended on the structure of the substrate.[5] The Reformatsky reagents were prepared from the reaction of *t*-butyl 2-bromoacetate and ethyl 2-bromoacetate with zinc dust in refluxing tetrahydrofuran for 1 h. The reaction of the Reformatsky reagent (R=*t*-Bu) with 2-cyclopenten-1-one in the presence of 1.2 equiv. of TMSOTf in tetrahydrofuran at −78°C proceeded cleanly, yielding 92% of the 1,4-addition product after acidic workup and no 1,2-addition product was detected. Similar results were obtained with 2-cyclohexen-1-one and carvone as shown in Eq. (3). In the case of the Reformatsky reagent (R=Et) prepared from ethyl 2-bromoacetate, the yields of the 1,4-addition product were considerably decreased. Thus, the reaction of the Reformatsky reagent (R=Et) with 2-cyclohexen-1-one and 2-cyclopenten-1-one gave the 1,4-addition product in 68% and 40% yield, respectively. The present method reaches a limit with α,β-acyclic enones, yielding a mixture of the 1,2- and 1,4-addition product. Thus, the Reformatsky reaction with 4-hexen-3-one under the same condition gave an equal ratio of the 1,2-and 1,4-addition product as shown in Eq. (4).

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References

1. For reviews, see: (a) G. H. Posner, *Org, React.*, **19**, 1 (1972); (b) G. H. Posner, An *Introduction to Synthesis Using Organocopper Reagents*, Wiley-Interscience, New York, 1980; (c) B. H. Lipshutz, *Synthesis*, 571 (1989).
2. (a) A. Hosomi and H. Sakurai, *J. Am. Chem. Soc.*, **99**, 1673 (1977); (b) D. Mobilio and B. D. Lange, *Tetrahedron Lett.*, **28**, 1483 (1987).
3. G. Majetich, R. Desmond, and A. M. Casares, *Tetrahedron Lett.*, **24**, 1913 (1983).
4. S. Kim and J. M. Lee, *Synth. Commun.*, **21**, 25 (1991).
5. M. W. Rathke, *Org. React.*, **22**, 423 (1975).
6. (a) M. Isobe, N. Nagasawa, and T. Goto, *Chem. Lett.*, 679 (1977); (b) W. Tuckmantel, K. Oshima, and H. Nozaki, *Chem. Ber.*, **119**, 1581 (1986).
7. (a) E. Nakamura, S. Aoki, K. Sekiya, H. Oshino, and I. Kuwajima, *J. Am. Chem. Soc.*, **109**, 8056 (1987); (b) E. Nakamura, K. Sekiya, and I. Kuwajima, *Tetrahedron Lett.*, **28**, 337 (1987).
8. (a) P. Knochel, M. C. P. Yeh, S. C. Berk, and J. Talbert, *J. Org. Chem.*, **53**, 2390 (1988); (b) P. Knochel and M. C. P. Yeh, *Tetrahedron Lett.*, **29**, 2395 (1988); (c) S. C. Berk, P. Knochel, and M. C. P. Yeh, *J. Org. Chem.*, **53**, 5791 (1988); (d) M. C. P. Yeh, P. Knochel, W. M. Bulter, and S. C. Berk, *Tetrahedron Lett.*, **29**, 6693 (1988).
9. (a) A. E. Greene, J. P. Lansard, J. L. Luche, and C. Petrier, *J. Org. Chem.*, **49**, 931 (1984); (b) J. C. S. Barboza, C. Petrier, and J. L. Luche, *Tetrahedron Lett.*, **26**, 829 (1985); (c) C. Petrier, J. C. S. Barbosa, C. Dupuy, and J. L. Luche, *J. Org. Chem.*, **50**, 5761 (1985).
10. S. Kim and J. M. Lee, *Tetrahedron Lett.*, **31**, 7627 (1991).