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A Novel Strategy for the Synthesis of 4,5-Dihydroisoxazoles via Conjugate Additions to α-Nitroalkenes

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ABSTRACT

Michael condensation of α-nitroalkenes with various nucleophiles, followed by the addition of trimethylchlorosilane, led to novel syntheses of 4,5-dihydroisoxazoles via cycloadditions of silyl nitronates.

INTRODUCTION

As one of the most important classes of heterocycles, 4,5-dihydroisoxazole derivatives have been found to be important tools for natural product total syntheses [1–3]. As synthetic equivalents of β-hydroxy ketones, 1,3-diketones, γ-aminoalcohols, α,β-unsaturated ketones, and other related functions, 4,5-dihydroisoxazoles play an important role in organic synthesis. Furthermore, intramolecular nitrile oxide–olefin cycloadditions (INOC) exhibit high stereoselectivities and can lead to the construction of polycyclic compounds [3,4]. These results have stimulated the discovery of novel and convenient methods for the synthesis of various 4,5-dihydroisoxazoles [5–11].

While 4,5-dihydroisoxazole rings can be constructed by two possible routes, i.e., nitrile oxide–olefin cycloaddition and silyl nitronate–olefin cycloaddition [12], the latter has been investigated far less intensively than the former. Many problems concerning silyl nitronate reactivities and stereoselectivities, for example, remain unsolved. Herein, we wish to report our successful findings with respect to these conditions. Our work started with the conjugate additions of various nucleophiles to α-nitroalkenes.

α-Nitroalkenes have received attention in recent years because of their versatile applications in organic synthesis [13,14]. Michael condensations of various nucleophiles with α-nitroalkenes have led to convenient syntheses of many types of organic compounds [15,16], in particular, heterocycles [17–19].

RESULTS AND DISCUSSION

As a part of our systematic investigations of the chemical behavior and transformations of tetraethyl methylenebisphosphonate and its derivatives [20–23], we carried out their reactions with α-nitroalkenes, aiming at the preparation of cyclopropane-1,1-diylbisphosphonates. α-Cyanoacetates gave the corresponding 1-cyanocyclopropane-1-carboxylates on reaction with α-nitroalkenes [14]. To our surprise, no such products **3** could be isolated. On the other hand, with the addition of trimethylchlorosilane (TMSCl), 4,5-dihydroisoxazole-5,5-diylbisphosphonates **6** were obtained in high yields. The reaction mechanism was in each case thought to proceed through the formation of the appropriate ethenylidenebisphosphonate **4** and silyl nitronate **5**, which then underwent 1,3-dipolar cycloaddition to give the corresponding product **6**, as indicated in Scheme 1. An interesting phenomenon was that in each case, the bisphosphonate anion **2** eliminated a nitronate anion rather than a nitrite

Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

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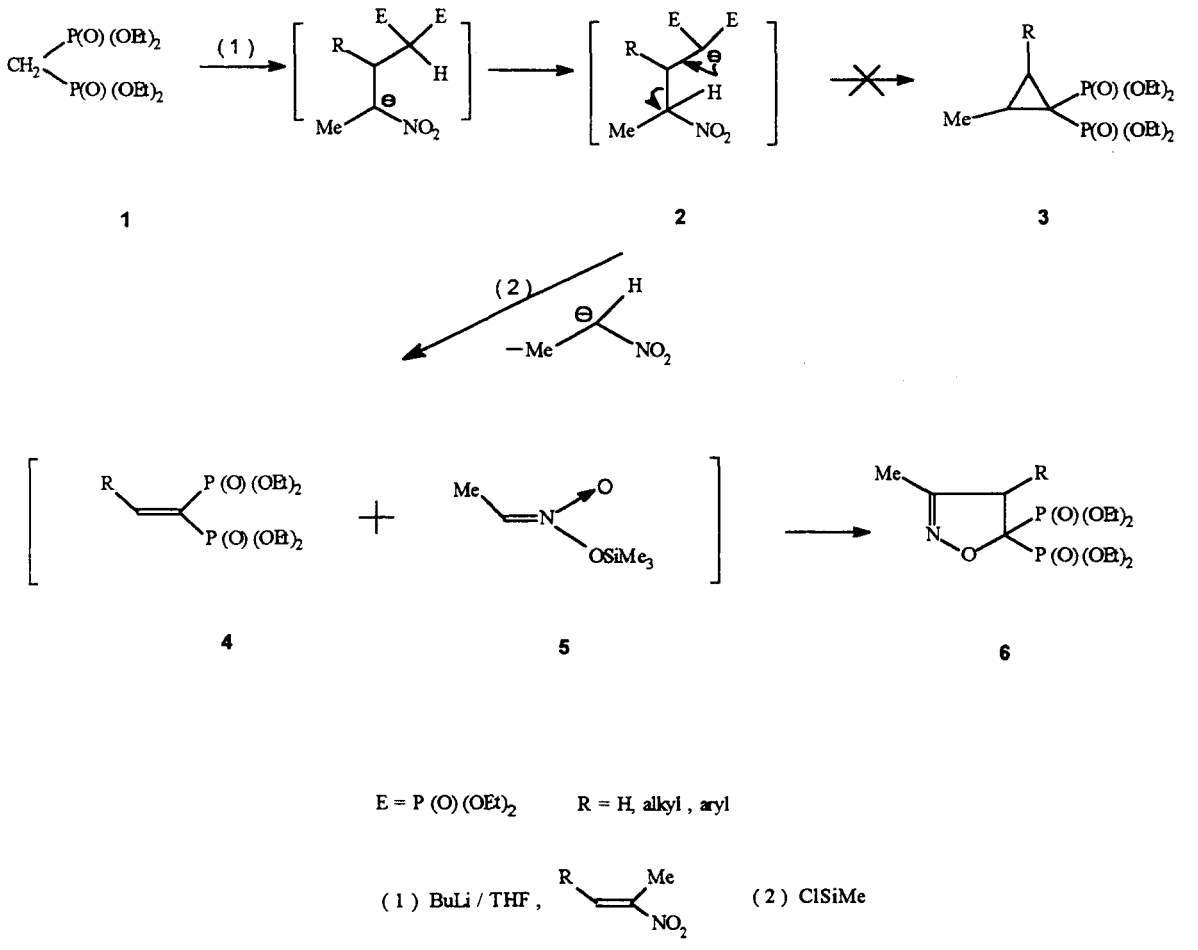
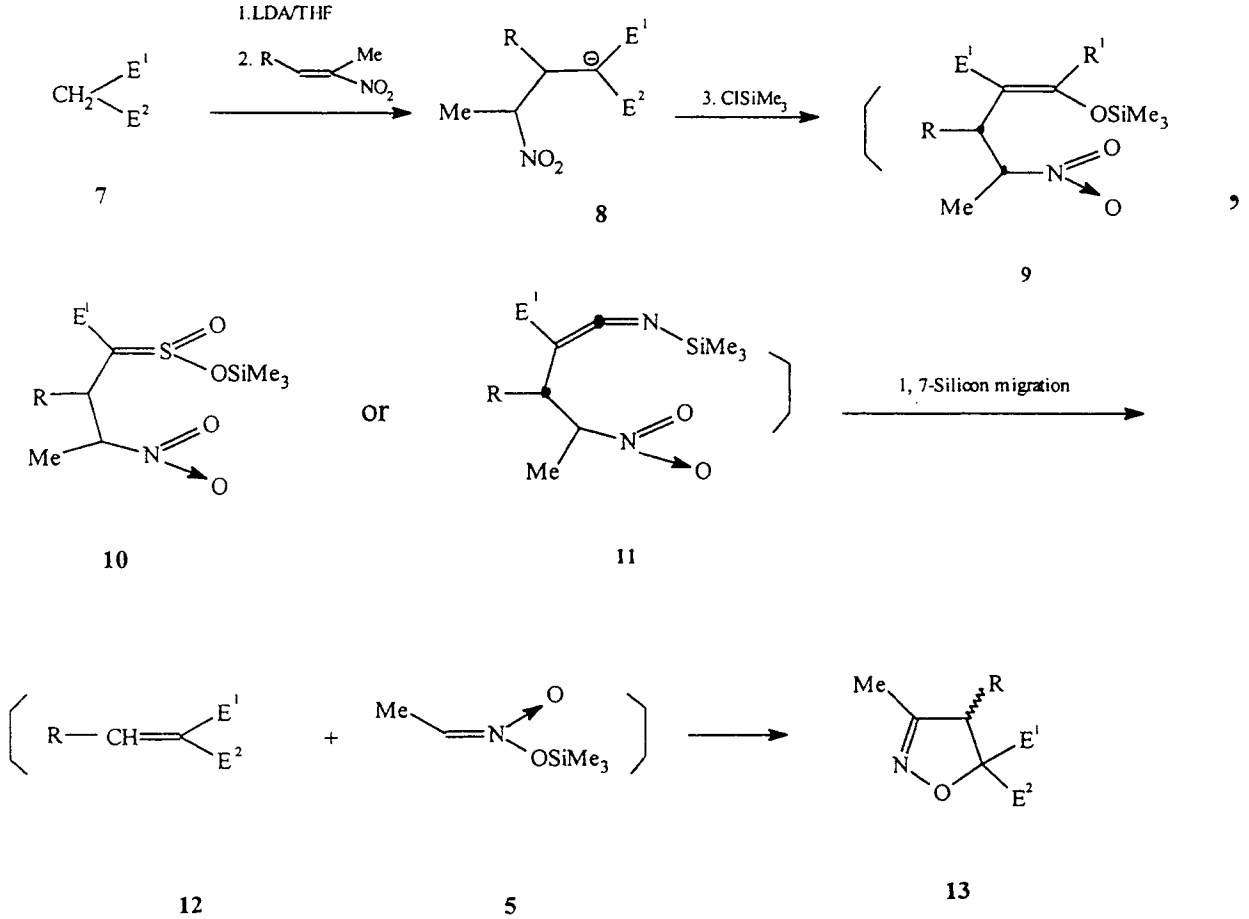


SCHEME 1

ion, which thereupon gave rise to the unexpected result [24].

As an extension, the possibility for these types of reactions was further investigated by the use of other active methylene compounds instead of the methylenebisphosphonate as the nucleophile [25]. As shown in Scheme 2, with the introduction of TMSCl after the Michael additions of the active methylene compounds to the α-nitroalkenes, silylation occurred at the carbonyl, sulfonyl, or cyano groups of intermediates **8** and the corresponding new intermediates **9**, **10**, and **11**, respectively, were formed. Treatment of these intermediates with acid gave the corresponding nitro compounds, while base-catalyzed reactions led to the isolation of the 4,5-dihydroisoxazoles **13** in high yields in one-pot procedures. These results could be rationalized by the occurrence of novel 1,7-silicon migration processes of **9**, **10**, and **11**, by which the alkenes **12** and silyl nitronates **5** were formed. Therefore, compounds bearing an active methylene group were shown to react with α-nitroalkenes, followed by the addition of TMSCl to provide a novel and convenient syntheses of 4,5-dihydroisoxazoles having two electron withdrawing substituents at C-5 (Equation (1)). The advantages of this method become more evident by comparison with the corresponding nitrile oxide–olefin cycloaddition approach. The latter variation gives rather low yields of or, in some cases, no desired products due to the low reactivity of polysubstituted alkenes **4** or **12** and the high reactivity of nitrile oxides, which mainly lead to 1,3-dipolar self-cycloaddition reactions [23,26]. These results also indicate the necessity for the relatively low reactivity of silyl nitronates.

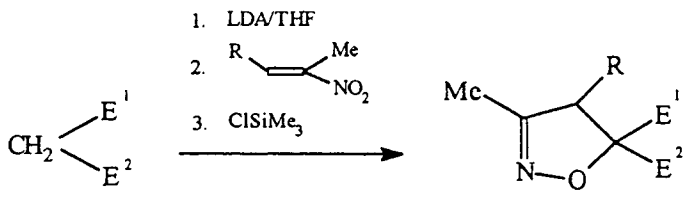
As new derivatives of 4,5-dihydroisoxazoles, some of these compounds underwent interesting transformations in the presence of base. For example, compounds **13a** and **13b** bearing a sulfonyl group at C-5 eliminated $PhSO_2H$ in the presence of NaOEt, yielding the corresponding isoxazoles **14a** and **14b**, respectively (Equation (2)). In the presence of a catalytic amount of triethylamine, compounds **13c** and **13d** underwent equilibration with **16c** and **16d** through the elimination and readdition of HCN, as depicted in Equation (3). Com-



SCHEME 2

pounds **13e** and **13f** underwent novel rearrangements in the presence of triethylamine and furan derivatives **18e** and **18f**, respectively, were isolated, as indicated in Equation (4). These results also demonstrated high acidity of the proton at C-4 of compounds **13** and helped to explain why the rings could be easily destroyed, especially under mass spectroscopy testing conditions [23,27].

As for ordinary carbonucleophiles, their behaviors were quite different from those of active methylene compounds. Michael condensations of each carbonucleophile **19** with a nitroethylene, followed by the addition of TMSCl, led to O-silylation of the resulting nitro group, and the corresponding functionalized silyl nitronate **20** was isolated rather than the 4,5-dihydroisoxazole. However, when we added



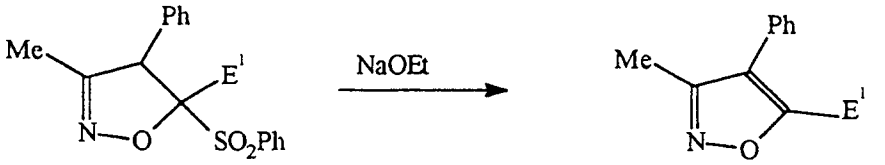
(1)

E^1, E^2 = COOEt, COMe, CN, SO_2Ph, $P(O)(OEt)_2$, SO_2Me R = H, alkyl, aryl

another portion of alkenes to the reaction mixture, 1,3-dipolar cycloaddition between the appropriate **20** and the alkene occurred, and a functionalized 4,5-dihydroisoxazole was isolated in moderate to good yield [28] (Equation (5)). The cycloadditions proceeded well with activated alkenes, such as methyl vinyl ketone or methyl acrylate, while other electron-rich alkenes such as styrene or 1-hexene did not undergo the reaction. These results could be ascribed to the lower reactivities of silyl nitronates than those of the corresponding nitrile oxides. Nevertheless, the reaction did take place in a tandem process, and various functionalized 4,5-dihydroisoxazoles **21** could easily be obtained, which should be of importance in organic synthesis.

Another example using diethyl phosphite as the nucleophile gave similar results, and 3-(18-diethoxyphosphorylalkyl) substituted 4,5-dihydroisoxazoles **24** were isolated in moderate yields [29] (Equation (6)). This one-pot procedure was much better than the literature method [11].

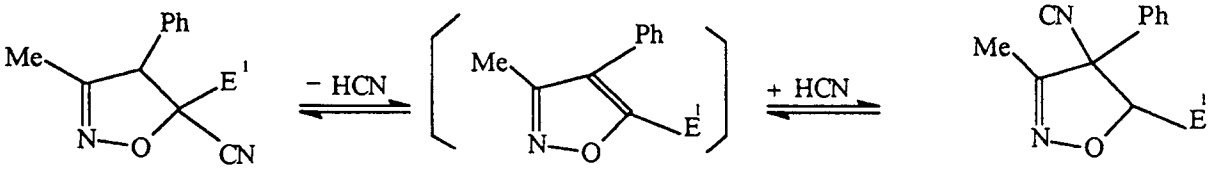
Further investigations on the previously mentioned reaction systems led us to pay attention to intramolecular cycloaddition reactions of silyl nitronates, which are relatively uninvestigated [30]. Based on this idea, we carried out the reactions of diethyl but-3-en-1-ylphosphonate with α-nitroalkenes. Condensation of the but-3-en-1-yl-phosphonate with α-nitroalkenes, followed by the addition of TMSCl, led to stereoselective syntheses of fused carboisoxazole derivatives **26**. In the case of aryl substituted α-nitroalkenes, compounds **26a** were obtained as the sole products (Equation (7)). These results could be rationalized by preferential formation of transition states **27** of the least steric hindrance during the Michael addition step, which gave rise to the exclusive formation of erythro isomers. With alkyl-substituted α-nitroalkenes, the diastereoselectivity was not obvious due to minor steric differences of the related groups. In the intramolecular silyl nitronate–olefin cycloaddition (ISOC) step, the substituent at C-6 showed the predominant role in the stereoselectivity, while the phosphonate group had no significant influence on it. This stereoselectivity could best be rationalized by the preferential formation of the less sterically hindered transition states **28**. The products **26** with



(2)

13 a (E^1 = P(O)(OEt)$_2$) **14** a, b

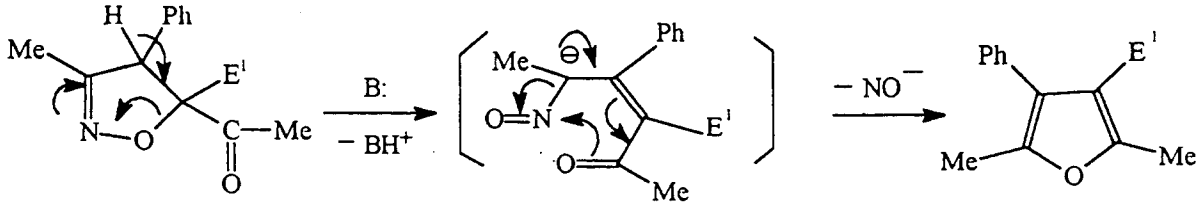
b (E^1 = COOEt)



(3)

13 c (E^1 = COOEt) **15** **16** e, d

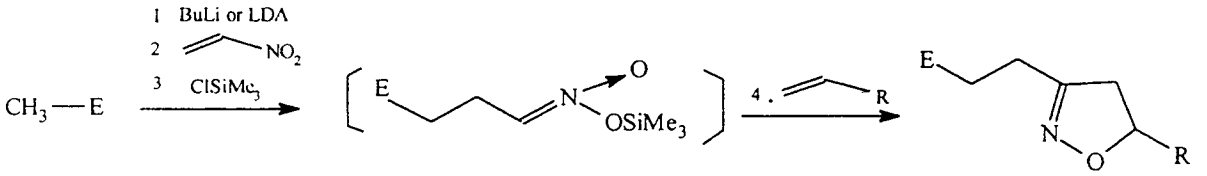
d (E^2 = CN)



(4)

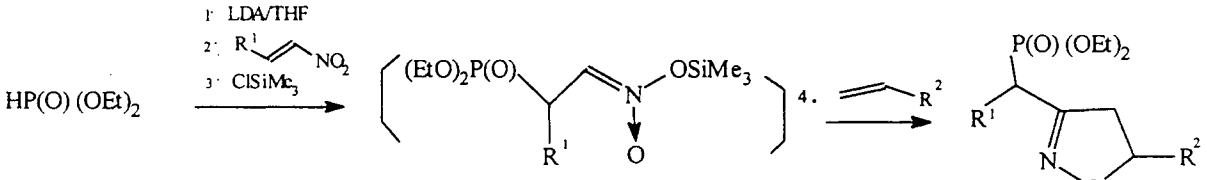
13 e (E^1 = COOEt) **17** **18** e, f

f (E^2 = COMe)



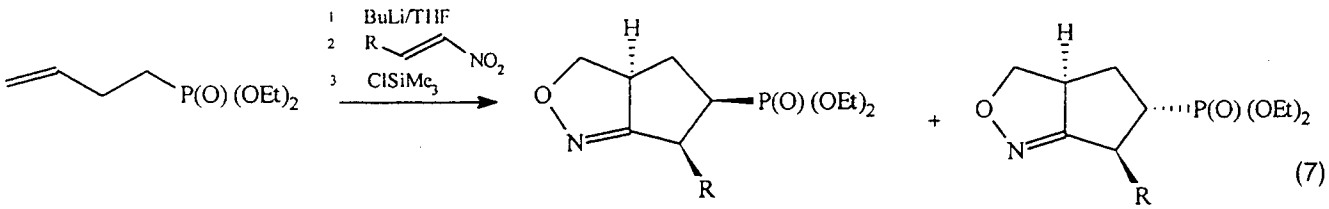
19 20 21 (5)

E = NO_2, CN, COOEt, COME, COPh, $P(O)(OEt)_2$, R = COMe, CO_2Me



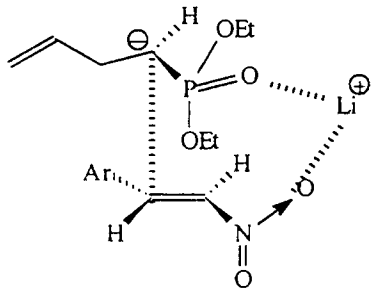
22 23 24 (6)

R^1 = H, alkyl, Ph R^2 = COMe, CO_2Me



25 26 a 26 b (7)

R = H, alkyl, aryl



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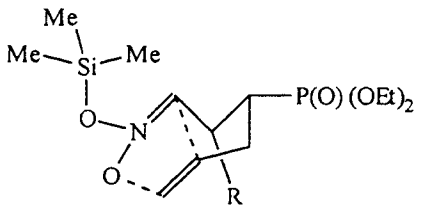
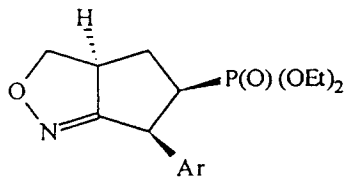
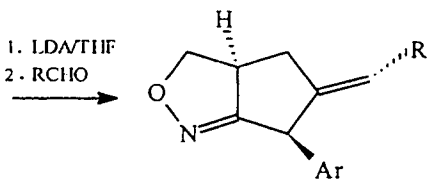
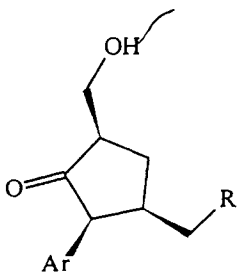


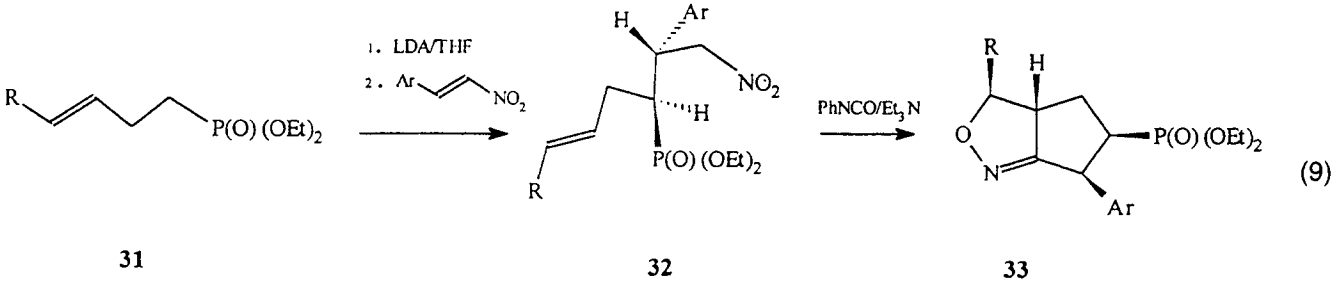
28 (8)







26 a 29 30



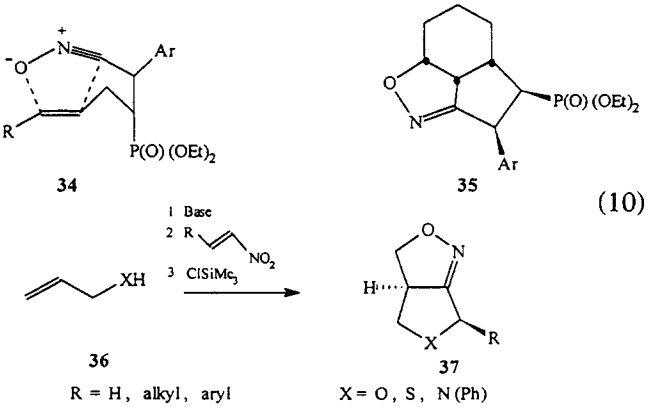
31 32 33 (9)

R = H, Me, Ph

fused isoxazole and carbocyclic rings bearing a phosphonate moiety should expand the applications of 4,5-dihydroisoxazoles in natural product synthesis. By subsequent transformations, cis-2,3,5-tri-substituted cyclopentanone derivatives **30** could easily be obtained (Equation (8)).

In comparison, the corresponding INOC reactions were also investigated [31]. Reactions of diethyl alk-3-en-1-ylphosphonates with aryl-substituted α-nitroalkenes gave diastereoselective formation of erythro isomers **32**. By use of the Mukaiyama–Hoshino method [26], compounds **32** underwent INOC reactions to give products **33** in high yield (Equation (9)). It could be seen that the stereoselectivity of ISOC reactions were the reverse of those of INOC reactions, which might be ascribed to the different transition states **34** formed in INOC reactions of **32**. The INOC reactions also gave the tricyclic compounds **35** with similar stereoselectivity. These results once again demonstrated the special properties of silyl nitronates in 1,3-dipolar cycloadditions.

An extension of the ISOC reactions was the use of heteroatom-centered nucleophiles **36** instead of alk-3-en-1-ylphosphonates in the foregoing reaction systems. The fused products **37** were obtained in one-pot procedures with high yields (Equation (10)). The stereoselectivity was also different from that of INOC reactions. Similar results were also reported by Dehean and Hassner [30].



34 35 (10)

36 37

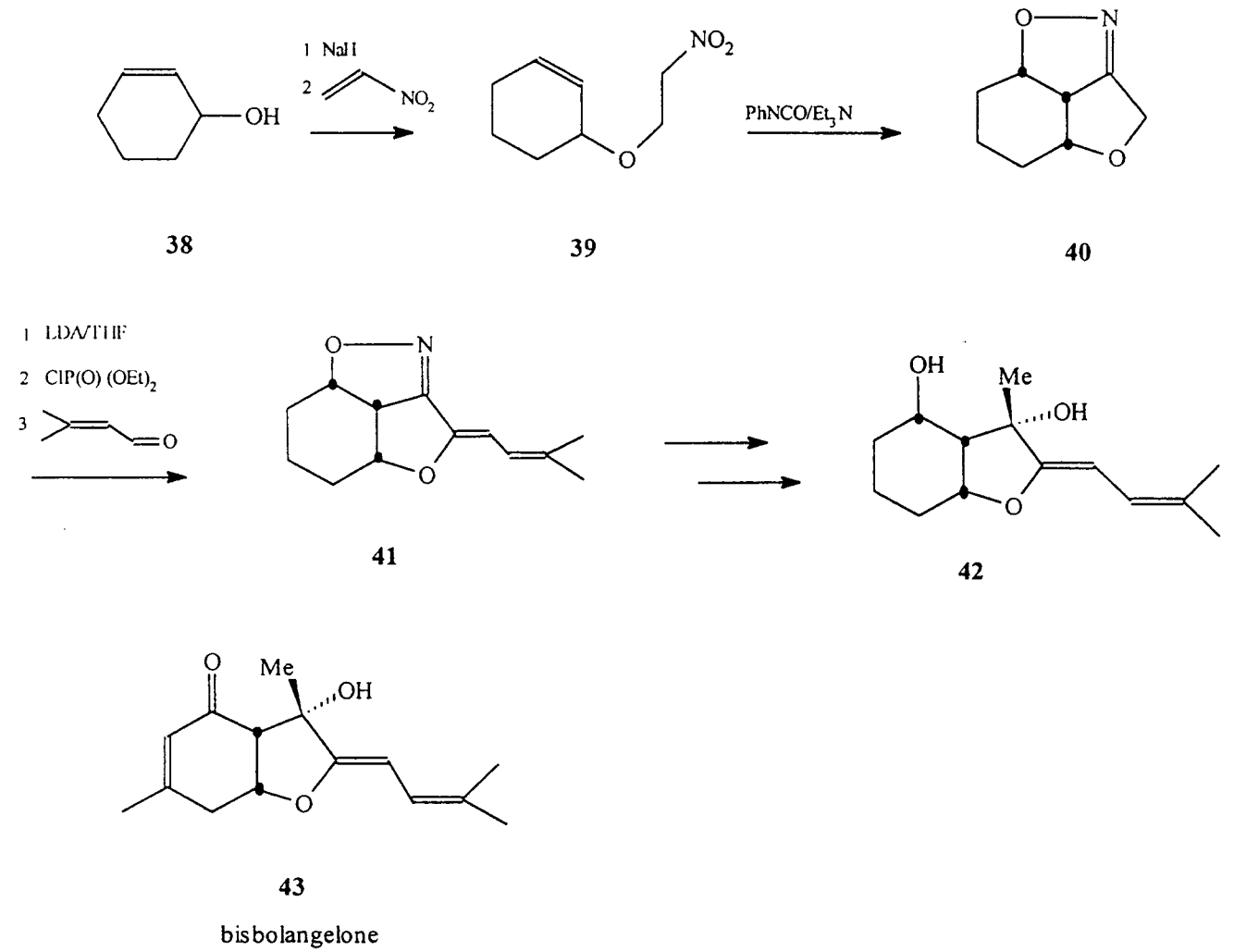
R = H, alkyl, aryl X = O, S, N(Ph)

In conclusion, the aforementioned investigations provided novel and convenient strategies for the syntheses of various 4,5- dihydroisoxazole derivatives by conjugate addition reactions of α-nitroalkenes. With the easy availability of α-nitroalkenes [32–35] and fair performances in their utilization, these new strategies should be of wide application in organic syntheses. The synthesis of an analogue of a natural product, bisbolanelone [36], is an example and is shown in Scheme 3.

EXPERIMENTAL

Infrared spectra were obtained on an IR-440 infrared spectrometer. ^{1}H NMR spectra were recorded on an XL-200 spectrometer. ^{31}P and ^{13}C NMR were taken with broadband decoupling on an FX-90Q spectrometer using trimethylsilane (TMS) as the internal reference and 85% phosphoric acid as the external standard for ^{31}P NMR. Mass spectra were recorded on a Finnigan 4021 mass spectrometer. Butyllithium (2.5 M solution in hexanes) was purchased from Aldrich Chemical Co. Tetrahydrofuran (THF) was dried with metallic sodium and then freshly distilled from sodium-dibenzophenone under a nitrogen atmosphere. Other reagents were obtained from a local commercial source (Shanghai Chemical Reagents Co.) and purified by standard methods, prior to use.

Diethyl 5-Methoxycarbonyl-3-methyl-4-phenyl-2-isoxazoline-5-ylphosphonate. The following describes the general procedure of (**13**, R=C_6H_5, E^1=COOMe, E^2=P(O)$(OEt)_2$). Butyllithium (2.0 mL, 5 mmol, 2.5 M solution in hexane) was added to diisopropylamine (0.8 mL, 5.5 mmol) in dry, freshly distilled THF (25 mL) at −20°C, and the solution was stirred for 5 minutes under nitrogen in a 100 mL three-necked flask fitted with a drying tube and a rubber septum. The solution was cooled to −70°C, and methyl diethoxyphosphonoacetate (1.05 g, 5 mmol) was added dropwise. After the complete addition, the solution was stirred for 30 minutes, and 2-methyl-1-phenylpropene (0.82 g, 5.25 mmol) was added. The reaction temperature was allowed to



SCHEME 3

warm to room temperature (RT) and the solution stirred for an additional 5 hours. The solution was cooled to −40°C, and trimethylchlorosilane (0.70 mL, 5.5 mmol) was added. The temperature was then allowed to warm to RT again, and the solution was stirred for 60 hours. The resulting mixture was concentrated under vacuum, and the residue was poured into water. Hydrochloric acid (1 N) was added to the solution until the pH was slightly acidic. The mixture was extracted with CH_2Cl_2 (4 × 30 mL), the combined organic layers dried with anhydrous sodium sulfate, and concentrated in vacuo to leave the crude product, which was then purified by column chromatography on silica gel with ethyl acetate/acetone (5/1, v/v) as eluent to give the pure product as a colorless oil. Yield 1.45 g (82%). IR (film) ν: 3050, 1740, 1450, 1240, 1025, 940, 730, 700. ^{1}H NMR ($CDCl_3$) δ: 1.29, 1.32 (2 × 3H, 2t, J = 8, CH_3CH_2O), 1.80, 2.14 (3H, 2s (1/1), CH_3C=N), 3.40 (3H, s, CH_3O), 3.72 (1H, m, CH), 4.15 (4H, m, CH_2O), 7.24 (5H, m, C_6H_5). ^{31}P NMR ($CDCl_3$) δ: 21.51, 21.76 (1/1). ^{13}C NMR ($CDCl_3$) δ: 13.28 (C-C-N), 16.10, 16.20 (CH_3CH_2O), 30.39 (CH-Ph), 48.37 (d, J (C-P) = 97, C-P), 51.79, 52.04 (CH_3O), 62.86, 62.90 (CH_2O), 127.15, 128.4, 128.6, 128.8, 129.7, 138.1, 138.8 (Ph), 156.6 (C=N), 168.3 (C=O). Anal calcd for $C_{16}H_{22}NO_6P$: C, 54.09; H, 6.24; N, 3.94. Found: C, 54.20; H, 6.07; N, 3.88.

3a,4,6-Trihydro-3H-furano[3,4-c]isoxazole. The following describes the general procedure of (**37**, R=H, X=O). A solution of diisopropylamine (0.77 mL, 5.5 mmol) in THF (20 mL) was introduced to a 100 mL three-necked flask fitted with a thermometer, reflux condenser, and stirred under nitrogen. After the solution had been cooled to −40°C, butyllithium (3.125 mL, 5 mmol, 1.6 M solution in hexane) was added gradually from a syringe, and stirring was continued for an additional 30 minutes. Upon vigorous mixing, allyl alcohol (0.30 g, 5.5 mmol) was introduced, and then the reaction mixture was allowed to stir for another 30 min-

utes. Subsequently, a THF solution (4 mL) of nitroethene (0.40 g, 5.5 mmol) was added with stirring and the Dry-Ice bath was removed. The reaction mixture was then allowed to warm to RT and kept overnight with stirring. The mixture was cooled again to −50°C, followed by addition of TMSCI (0.70 mL, 5.5 mmol). When the mixture had warmed to RT, stirring was continued for another hour, and then the mixture was subjected to reflux for 8 hours. After cooling, the reaction mixture was treated with hydrochloric acid (1 N) to become slightly acidic and then extracted with ether (4 × 30 mL). The combined ether extracts were dried over anhydrous sodium sulfate, and the solvent was removed in a rotatory evaporator. The crude product thus obtained was purified by column chromatography on silica gel using petroleum ether/acetone (2/1, v/v) as eluent. The pure compound was a yellowish liquid, yield 0.34 g or 61%. IR (film) ν: 1470. ^{1}H NMR ($CDCl_3$) δ: 3.70–4.60 (5H, m, $2CH_2O$ + CH), 4.80 (2H, m, CH_2O). EIMS (m/z): 113 (M^+). HRMS calcd for $C_5H_7NO_2$: 113.0960. Found: 113.0964.

6-Methyl-3a,4,6-trihydro-3H-furano [3,4-c]isoxazole. (**37**, R=Me, X=O) was obtained analogously using allyl alcohol and 1-nitropropene as substrates. A pale yellow liquid was obtained, yield 65%. IR (film) ν: 1465. ^{1}H NMR ($CDCl_3$) δ: 1.40, 1.44 (3H, 2d, J = 7, CH_3), 3.60 (1H, m, CH), 3.8–4.80 (5H, m, $2CH_2O$ + CHO). EIMS (m/z): 127 (M^+). HRMS calcd for $C_6H_9NO_2$: 127.0633. Found: 127.0634.

6-Phenyl-3a,4,6-trihydro-3H-furano[3,4-c]isoxazole. (**37**, R=C_6H_5, X=O) was obtained analogously using allyl alcohol and 1-nitro-styrene as substrates. A pale yellow liquid was obtained, yield 80%. IR (film) ν: 1710, 1605, 1500, 1450, 740, 700. EIMS (m/z): 175, 159, 119, 77. ^{1}H NMR ($CDCl_3$) δ: 3.75–4.00 (2H, m, CH_2O), 4.40 (1H, dd, J = 4,9, CH), 4.61–5.10 (3H, m, CHPh + CH_2O), 7.35 (5H, m, Ph). ^{13}C NMR ($CDCl_3$) δ: 54.55 (CH), 69.98 (CH_2O), 77.12 (CH_2O), 80.39 (CHPh), 117.6, 127.5, 128.4, 129.1, 133.7 (C_6H_5), 170.3 (C=N). Anal calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.41. Found: C, 70.33; H, 5.59; N, 7.44.

3a, 4, 6-Trihydro-3H-thiopheno[3, 4-c]isoxazole. (**37**, R=H, X=S) was synthesized similarly using allyl mercaptan and nitroethene as substrates and with refluxing for 5 hours. Yield 77%. Yellowish liquid. IR (film) ν: 1460. EIMS (m/z): 129 (M^+). ^{1}H NMR ($CDCl_3$) δ: 2.70 (1H, d, J = 10, 4-H), 3.00 (1H, dd, J = 9, 11, 4-H), 3.95 (2H, s, 6-H), 4.05 (1H, d, J = 6, 3-H), 4.20 (1H, m, 3a-H), 4.50 (1H, dd, J = 8,9, 3-H). Anal calcd for C_5H_7NOS: C, 46.49; H, 5.46; N, 10.85. Found: C, 46.44; H, 5.76; N, 10.80.

6-Methyl-3a,4,6-trihydro-3H-thiopheno[3,4-c]isoxazole. (**37**, R=Me, X=H) was synthesized similarly using allyl mercaptan and 1-nitropropene as substrates and with refluxing for 5 hours. Yield 82% as yellowish liquid. IR (film) ν: 1470. EIMS (m/z): 143 (M^+). ^{1}H NMR ($CDCl_3$) δ: 1.55 (3H, ddd, J = 7, CH_3), 2.75 (1H, t, J = 10, 4-H), 3.07 (1H, dd, J = 9, 11, 4-H), 4.06 (1H, ddd, J = 1.1,6.8,13, 3-H), 4.30 (1H, m, 3a-H), 4.45 (1H, m, 6-H), 4.55 (1H, dd, J = 6,10, 3-H). Anal calcd for C_6H_9NOS: C, 50.32; H, 6.34; N, 9.78. Found: C, 50.44; H, 6.17; N, 9.77.

6-Phenyl-3a,4,6-trihydro-3H-thiopheno[3,4-c]isoxazole. (**37**, R=Ph, X=O) was synthesized similarly using allyl mercaptan and 1-nitro-styrene as substrates and with refluxing for 6 hours. Yield 90%, a yellowish liquid. IR (film) ν: 3030, 1710, 1605, 1460, 970. EIMS (m/z): 205 (M^+). ^{1}H NMR ($CDCl_3$) δ: 2.92 (1H, t, J = 9, 4-H), 2.22 (1H, dd, J = 8,10, 4-H), 4.15 (1H, dd, J = 8,10, 3-H), 4.35 (1H, m, 3a-H), 4.65 (1H, dd, J = 8,10, 3-H), 5.10 (1H, s, 6-H), 7.35 (5H, m, Ph). Anal calcd for $C_{11}H_{11}NOS$: C, 64.36; H, 5.40; N, 6.83. Found: C, 64.33; H, 5.43; N, 6.95.

5-N-Phenyl-3, 3a, 4, 6-tetrahydropyrro[3, 4-c]isoxazole. (**37**, R=H, X=PhN) was prepared similarly using N-allyl aniline and nitroethene as substrates under reflux for 10 hours. Yield 84%, a yellowish oily liquid. IR (film) ν: 3030, 1450, 740, 700. EIMS (m/z): 188 (M^+). ^{1}H NMR ($CDCl_3$) δ: 3.40–4.60 (5H, m, CH_2CHCH_2), 5.00 (2H, m, 6-H), 7.35 (5H, m, C_6H_5). HRMS calcd for $C_{11}H_{12}N_2O$: 188.2165. Found: 188.2166.

6-Methyl-5-N-phenyl-3, 3a, 4, 6-tetrahydropyrro-[3,4-c]isoxazole. (**37**, R=Me, X=PhN) was prepared similarly using N-allyl aniline and 1-nitro-2-propene as substrates under reflux for 10 hours. Yield 82%, a yellowish oily liquid. IR (film) ν: 3030, 1450. EIMS (m/z): 202 (M^+). ^{1}H NMR ($CDCl_3$) δ: 1.20, 1.25 (3H, 2d, J = 7, CH_3), 3.50–4.60 (5H, m, CH_2-$CHCH_2$), 5.20 (1H, m, 6-H), 7.35 (5H, m, C_6H_5). HRMS calcd for $C_{12}H_{14}N_2O$: 202.2426. Found: 202.2420.

6-Phenyl-5-N-phenyl-3, 3a, 4, 6-tetrahydropyrro-[3,4-c]isoxazole. (**37**, R=Ph, X=PhN) was prepared similarly using N-allyl aniline and 1-nitrostyrene as substrates under reflux for 10 hours. Yield 75%, a yellowish oily liquid. IR (film) ν: 3030, 1600, 1450. EIMS (m/z): 264 (M^+). ^{1}H NMR ($CDCl_3$) δ: 3.50–4.60 (5H, m, CH_2CHCH_2), 5.90 (1H, s, 6-H), 7.40 (5H, m, C_6H_5). Anal calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.34; H, 6.20; N, 10.33.

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REFERENCES

[1] K. G. B. Torssell: *Nitrile Oxides, Nitrones, and Nitronates in Organic Synthesis*, VCH Publishers, Inc., New York, 1988, pp. 129–255.
[2] W. Carruther: *Cycloaddition Reactions in Organic Synthesis*, Pergamon Press, New York, 1990, pp. 285–297.
[3] J. Mulzer, H.-J. Altenbach, M. Braun, K. Krohn, H.-U. Reissig: *Organic Synthesis Highlights*, VCH Publishers, Inc., New York, 1991, pp. 77–95.
[4] A. P. Kozikowski, *Acc. Chem. Res., 17*, 1984, 410.
[5] R. V. Stevens, C. G. Christensen, R. M. Cory, E., Thorsett, *J. Am. Chem. Soc., 97*, 1975, 5940.
[6] P. A. Wade, H. R. Hinney, *J. Am. Chem. Soc., 101*, 1979, 1319.
[7] T. Kametani, S.-P. Huang, M. Ihara, *Heterocycles, 12*, 1979, 1183.
[8] A. P. Kozikowski, A. K. Ghosh, *J. Am. Chem. Soc., 104*, 1982, 5788.
[9] A. P. Kozikowski, A. K. Ghosh, *Tetrahedron Lett.*, 24, 1983, 2623.
[10] A. P. Kozikowski, C.-S. Li, *J. Org. Chem., 50*, 1985, 778.
[11] O. Tsuge, S. Kanemasa, H. Suga, N. Nakagawa, *Bull. Chem. Soc. Jpn., 60*, 1987, 2463.
[12] K. Torssell, O. Zeuthen, *Acta Chem. Scand., B32(2)*, 1978, 118.
[13] A. G. M. Barrett, G. G. Graboski, *Chem. Rev., 86*, 1986, 751.
[14] R. Tamura, A. Kamimura, N. Ono, *Synthesis, 423*, 1991.
[15] For example, see: M. Miyashita, B. Z. E. Awen, A. Yoshikoshi, *Tetrahedron, 46*, 1990, 7569.
[16] G. H. Posner, R. D. Crouch, *Tetrahedron, 46*, 1990, 7509.
[17] D. H. R. Barton, M. Kervagoret, K. Maruyama, *Tetrahedron, 46*, 1990, 7587.
[18] G. Wang, C. Yuan, *Heteroatom Chem., 3*, 1992, 521.
[19] C. Yuan, W. Huang, *Synthesis*, 1993, 473.
[20] C. Yuan, C. Li, Y. Ding, *Synthesis*, 1991, 854.
[21] C. Li, C. Yuan, *Tetrahedron Lett., 34*, 1993, 1515.
[22] C. Li, C. Yuan, *Heteroatom Chem., 4*, 1993, 517.
[23] C. Li: Ph.D. Dissertation, Shanghai Institute of Organic Chemistry, Shanghai, China, 1993.
[24] C. Yuan, C. Li, Phosphorus, Sulfur and Silicon, *69*, 1992, 75.
[25] C. Yuan, C. Li, Phosphorus, Sulfur and Silicon, *78*, 1993, 47.
[26] T. Mukaiyama, T. Hoshino, *J. Am. Chem. Soc., 82*, 1960, 5339.
[27] C. Yuan, G. Fu, C. Li, to be published.
[28] C. Li, C. Yuan, *Synthesis*, 1993, 471.
[29] C. Li, D. Zhou, C. Yuan, *Chin. Chem. Lett., 4*, 1993, 391.
[30] W. Dehean, A. Hassner, *Tetrahedron Lett., 31*, 1990, 743.
[31] C. Yuan, C. Li, *Tetrahedron Lett., 34*, 1993, 5959.
[32] C. B. Gairaud, G. R. Lappin, *J. Org. Chem., 18*, 1953, 1.
[33] J. Melton, J. E. McMurry, *J. Org. Chem., 40*, 1975, 2138.
[34] E. J. Corey, H. Estreicher, *J. Am. Chem. Soc., B100*, 1978, 6294.
[35] G. D. Buckley, C. W. Scaife, *J. Chem. Soc.*, 1947, 1471.
[36] B. P. Riss, B. Muchenstrum, *Tetrahedron Lett., 27*, 1986, 4979.