Tetrahedron Vol. 46, No. 21, pp. 7393-7402, 1990
Printed in Great Britain

0040-4020/90 $3.00+.00

HARD ACID AND SOFT NUCLEOPHILE SYSTEMS. PART 12.[1,2] REGIOSELECTIVE FUNCTIONALIZATION OF 1,3-DIENES THROUGH THE LEWIS ACID MEDIATED THIENIUM CATION DIELS-ALDER REACTION

Kaoru Fuji,*[a] Subhash P. Khanapure,[b] Manabu Node,[a] Takeo Kawabata,[a] Akichika Itoh,[c] and Yukio Masaki[c]

Institute for Chemical Research,[a] Kyoto University, Uji, Kyoto 611, Japan. Department of Chemistry,[b] Southern Methodist University, Dallas Texas 75275, U.S.A. Gifu Pharmaceutical University,[c] Mitahora, Gifu 502, Japan.

(*Received in USA* 8 *February* 1990)

Abstract: Reaction of α-Ethylthio-β-nitroolefins with 1,3-dienes under acidic Diels-Alder conditions afforded *Z*-olefins through stereoselective 1,4-functionalization.

Since carbon-oxygen bonds may be regarded as made up of a soft acid and a hard base, combination reagent systems[3] consisting of a hard acid and a soft nucleo-phile should cleave those bonds according to the hard and soft acids and bases (HSAB) principle.[4,5] A combination of aluminum chloride, as a hard Lewis acid, and ethanethiol[6] or sodium iodide,[7] as a soft nucleophile, has been proven to be remarkably useful for cleaving methyl ethers. This method greatly facilitates the use of the methyl group as a protecting group for alcohols. A reaction that gives rise to carbon-carbon bond formation may be achieved when a carbon nucleophile is employed as a component in such a combination system. We selected a combination of aluminum chloride, as a hard acid, and a diene, as a soft carbon nucleophile, since this should achieve such a transformation. α-Ethylthio-β-nitroalkenes were used as substrates, because the synthetic utility of nitroalkenes as Michael acceptors and dienophiles in the Diels-Alder cycloaddition is well-documented.[8] However, substitution by the electron-donating sulfur atom at the β-position may depress the normal reactivity of nitroalkenes toward dienes in the Diels-Alder reaction. Here, we report the unusual reactivity of α-ethylthio-β-nitroalkenes[9] with 1,3-dienes under the influence of aluminum chloride. This process leads to *Z*-olefins by regioselective 1,4-functionalization of 1,3-dienes through the Diels-Alder cycloaddition involving a thienium cation.[10,11]

Results

The reaction of 1-ethylthio-2-nitro-1-cyclohexene (**1a**) with a combination of aluminum chloride and 2,3-dimethyl-1,3-butadiene (**2**), as a soft nucleophile, afforded no Diels-Alder product **3** but the unusual product **4** which was formed in 70% yield. ^{13}C-NMR signals [δ 147.0 (s) and 138.2 (s)] characteristic to the α,β-unsaturated nitro group and ultra violet (UV) absorption at 264 nm clearly exclude the normal Diels-Alder product **3**. The *Z*-stereochemistry at the side chain double bond was confirmed by the nuclear Overhauser effect (7%) between two vinyl methyl groups.

In order to study the scope and limitation of this unusual reaction, cyclic nitroolefins **1a** and **1b** and acyclic nitroolefins **1c** and **1d** were employed to react with a variety of dienes **2** and **5**-**10** under the influence of aluminum chloride.

Scheme 1.

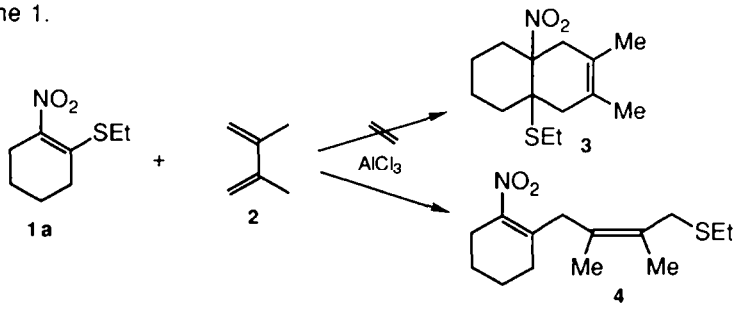


Table I. Reaction of Cyclic Nitroolefins **1a** and **1b** with Dienes.

entry	nitroolefin	diene	reaction time (min)	product	yield, %
1	**1a**	**2**	15	**4**	70
2	**1a**	**5**	60	**11**	79
3	**1a**	**6**	90	a	68
4	**1a**	**7**	60	**14**	61(83)[b]
5	**1a**	**8**	90	**15**	54
6	**1a**	**9**	420	**16**	54
7	**1a**	**10**	15	**17**	48(91)[b]
8	**1b**	**2**	15	**18**	86
9	**1b**	**7**	15	**19**	82

[a]A 10:1 mixture of **12** and **13**. [b]Numbers in parentheses are the yields based on the consumed nitroolefin.

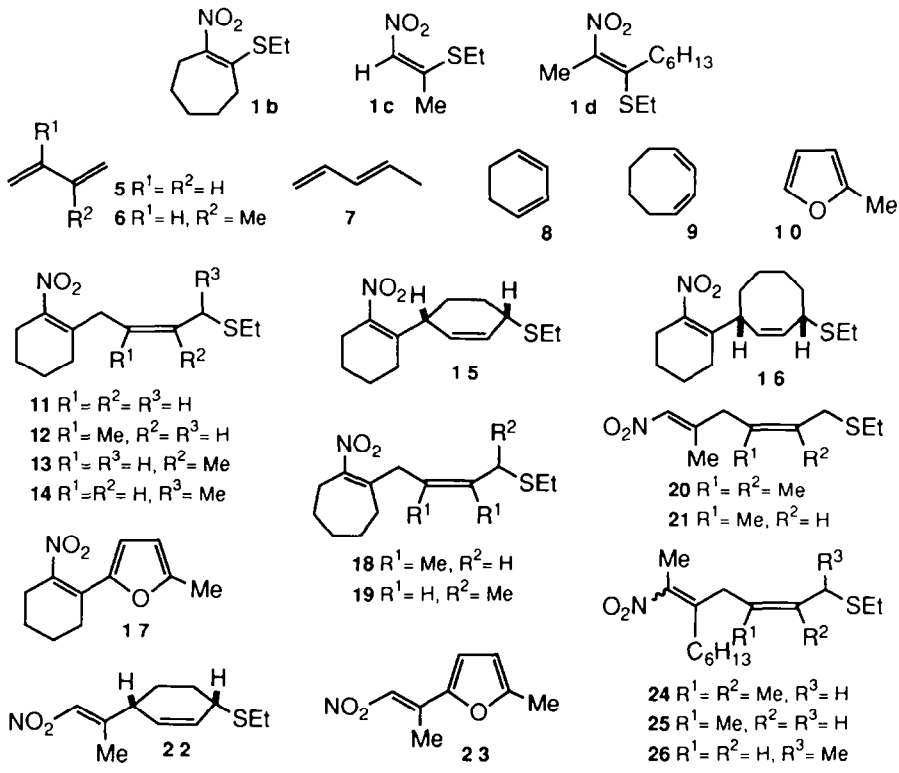


Table I lists the results with cyclic nitroolefins **1a** and **1b**. A 10:1 mixture of regioisomers **12** and **13** was obtained when 2-methyl-1,3-butadiene (**6**) was used as a diene (entry 3). The structure of the major isomer **12** was unambiguously confirmed by conversion into the known diketone **28**[12] through the three steps involving the reduction with $NaBH_4$, ozonization, and the Nef reaction. Another unsymmetrical diene **7** gave **14** and **19** as a sole product when it reacted with **1a** and **1b**, respectively (entries 4 and 9). Cyclic dienes **8** and **9** afforded **15** and **16**, respectively, in which the nitroolefin moiety and the ethylthio group is *cis* each other. The reaction of **1a** and 2-methyl furan (**10**) gave 5-substituted product **17**.

The reaction of acyclic nitroolefins **1c** and **1d** is more complicated than that of cyclic ones, because both *E*- and *Z*-isomers at the nitroolefinic double bond can exist. Results of the reactions of **1c** and **1d** with dienes are summarized in Table II. All the products **20–23** have the *E*-geometry at the double bond bearing the nitro group, when **1c** was employed (entries 1-4 in Table II), while nitroolefin **1d** provided approximately 1:1 mixture of *E*- and *Z*-isomers at the nitroolefinic double bond (entries 5-7 in Table II).

A close inspection of Table I and II reveals the following noteworthy features of this reaction. 1) 1,4-Addition of the ethylthio group and the nitro-olefinic moiety onto the 1,3-dienes was totally regioselective. 2) Formation of *Z*-alkene from 1,3-dienes was inevitable in all cases. 3) Cyclic 1,3-dienes afforded 1,4-*cis*-disubstituted cycloalkenes with complete stereoselectivity. 4) The nitro-olefinic moiety predominantly added to the electron rich terminus, when unsymmetrical dienes were used. 5) 2-Methyl furan (**10**) provided the corresponding 5-substituted furans **17** and **23**.

Table II. Reaction of Acyclic Nitroolefins **1c** and **1d** with Dienes.

entry	nitroolefin	diene	reaction time (min)	product	yield, %
1	**1c**	**2**	40	**20**	65
2	**1c**	**6**	30	**21**	56[a]
3	**1c**	**8**	60	**22**	71
4	**1c**	**10**	15	**23**	46
5	**1d**	**2**	30	**24**[b]	84(93)[c]
6	**1d**	**6**	60	**25**[b]	72
7	**1d**	**7**	120	**26**[b]	63(73)[c]

[a]A 4:1 mixture of **21** and its streoisomer. [b]A 1:1 mixture of *E*- and *Z*-isomers. [c]Numbers in parentheses are the yields based on the consumed nitroolefin.

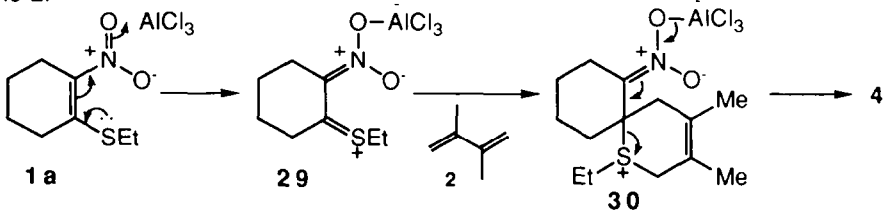
Discussion

All of the characteristic features described above can be explained by the intervention of the Diels-Alder reaction of a thienium cation with a diene, as shown in Scheme 2. 1-Ethylthio-2-nitro-1-cyclohexene (**1a**) has two basic groups involving the sulfur and the oxygen. The hard Lewis acid aluminum chloride should not interact strongly with the sulfur atom but rather with the oxygen atom to form the thienium cation **29**, because the oxygen lone pair is harder than sulfur. The thienium cation **29** possesses two dienophilic groups in the molecule, of which the carbon-sulfur double bond is softer than the carbon-nitrogen double bond. Thus, the diene **2**, which is a soft nucleophile, selects the thienium cation as a counter part of the Diels-Alder cycloaddition to provide the cyclic sulfonium salt **30**. The carbon-sulfur bond cleavage of the resulting ring under the reaction conditions gives the final product **4**, in which an overall *Z*-functionalization across the 1,3-diene is completed.

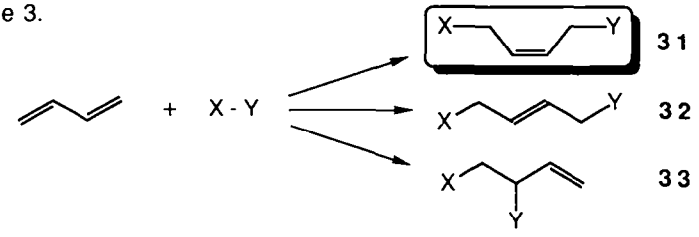
Functionalization of acyclic 1,3-dienes may provide three type of products **31**, **32**, and **33** as shown in Scheme 3. In electrophilic additions, a 1,2-addition product **33** is predominant under the kinetically controlled conditions,[13] while 1,4-

addition predominates over 1,2-addition under the thermodynamic control.[14] 1,4-Functionalization is a predominant mode in palladium-catalyzed diacetoxyla-tion,[15] dialkoxylation,[16] and acetoxychlorination.[17] Electrochemical nitroacet-amidation of 1,3-dienes also gave a 1,4-adduct as the major product.[18] Exclusive or predominant formation of an *E*-isomer **32** has been realized in these reactions. Since the selective formation of a *Z*-olefin **31** is difficult to attain in the direct 1,4-functionalization of 1,3-dienes, the two-step process involving the Diels-Alder cyloadditions with heterodienophiles followed by the cleavage of the resulting ring is the most promising method for this purpose.[19] A noteworthy feature of our reactions is the totally regio- and stereoselective transformation of a 1,3-diene into a *Z*-olefin **31**, where X is a nitroolefinic moiety and Y is an ethylthio group. 1,4-Functionalization of cyclic 1,3-dienes may be attended with another stereochemical problem involving *cis*- or *trans*- addition. The selective formation of 1,4-*cis*-disubstituted products **15**, **16**, and **22** was remarkable, when cyclic dienes were used. Bäckvall *et al*[15,20] have developed an elegant method for the stereoselective *cis*- and *trans*-1,4-addition of oxygen functional groups onto cyclic 1,3-dienes.

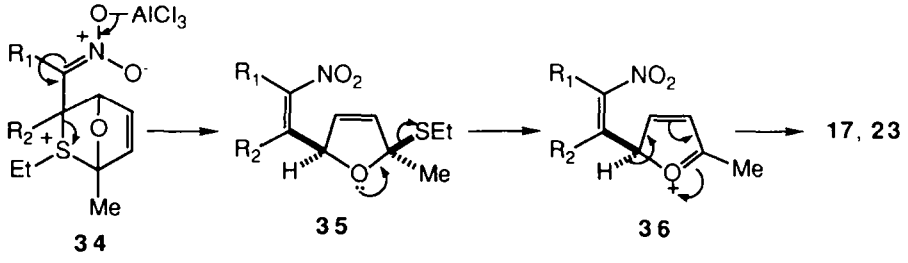
Scheme 2.



Scheme 3.



Scheme 4.



A rational explanation for the formation of 5-substituted furans **17** and **23** from 2-methylfuran (**10**) is shown in Scheme 4. Cleavage of carbon-sulfur bond in the primary adduct **34** provides the 1,4-*cis*-disubstituted dihydrofuran **35**. Rearomatization of **35** via **36** gives the final products.

Experimental

General Procedure. Melting points were taken with a micro hot-stage apparatus (Yanagimoto) and are uncorrected. Boiling points were determined on a micro distillation apparatus. The infrared (IR) spectra were recorded with a JASCO A-202 diffraction grating infrared spectrophotometer and ^{1}H-NMR spectra were obtained with a JEOL JNM-FX-100 spectrometer or JEOL JNM-GX-270 spectrometer or JEOL JNM-GX-400 spectrometer with tetramethylsilane as an internal standard. Mass spectra (MS) were determined on a JEOL JMS-01SG mass spectrometer. A Buchi GKR-50 apparatus was used for Kugelrohr distillation. Kieselgel 60 (0.063-0.2 mm Merck) was used for column chromatography, and Kieselgel 60 F-254 plates for thin layer chromatography (TLC) and preparative TLC.

Material. 1-Ethylthio-2-nitro-1-cyclohexene (**1a**) and (*Z*)-2-ethylthio-1-nitropropene (**1c**) are known compounds.[9]

1-Ethylthio-2-nitrocyclo-1-heptene (**1b**) and (*E*)-3-ethylthio-2-nitro-2-nonene (**1d**) were prepared by the reported method.[9]

1-Ethylthio-2-nitro-1-cycloheptene (1b). IR($CHCl_3$) 2950, 1560, 1470, 1290 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 1.32 (t, J=7.3 Hz, 3H), 1.60-1.80 (6H), 2.90 (q, J=7.3 Hz, 2H), 2.90-3.10 (m, 2H). Anal. Calcd. for $C_9H_{15}NO_2S$: C, 53.70, H, 7.51, N, 6.96. Found: C, 53.31, H, 7.42, N, 6.84.

(*E*)-3-ethylthio-2-nitro-2-nonene (1d). IR($CHCl_3$) 2950, 2925, 2850, 1560, 1465, 1380, 1285 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 0.92 (t, J=7.5 Hz, 3H), 1.31 (t, J=7.5 Hz, 3H), 1.30-1.42 (5H), 1.51-1.59 (m, 3H), 2.30 (s, 3H), 2.52 (t, J=7.5 Hz, 2H), 2.81 (q, J=7.5 Hz, 2H). Anal. Calcd. for $C_{11}H_{21}O_2NS$: C, 57.10, H, 9.15, N, 6.05. Found: C, 57.51, H, 9.12, N, 6.18.

General Procedure for the Thienium Cation Diels-Alder Reaction. To a solution of the α-ethylthio-β-nitroalkene (1 mmol) in anhydrous dichloromethane (5 ml) was added sublimed aluminum chloride (2 mmol) and the mixture was stirred at 0°C for 5 min. Then, the 1,3-diene (10 mol eq.) in anhydrous dichloromethane was added and stirring was continued for another hour at 0°C.

Extractive workup with dichloromethane afforded a crude material which was purified by column chromatography over silica gel.

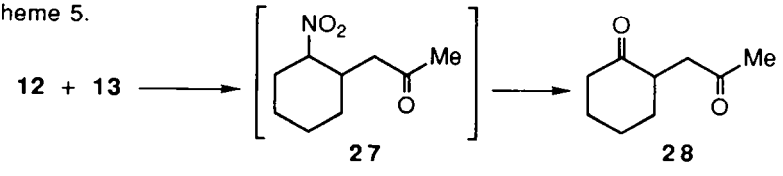
4: IR($CHCl_3$) 2975, 2900, 1555, 1525, 1460, 1365 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 1.25 (t, J=7.3 Hz, 3H), 1.58 (s, 3H), 1.60 (m, 2H), 1.73 (m, 2H), 1.79 (s, 3H), 2.09(m, 2H), 2.48(q, J=7.3 Hz, 2H), 2.59 (m, 2H), 3.18(s, 2H), 3.23(s, 2H). UV(MeOH) λ_{max} 361 (ε 270), 262 (ε 3500), 207 nm (ε 29500). HRMS m/z 269.1455. $C_{14}H_{23}NO_2S$ requires 269.1450.

11: ^{1}H-NMR($CDCl_3$) δ 1.26 (t, J=7.3 Hz, 3H), 1.60-1.67 (m, 2H), 1.70-1.78 (m, 2H), 2.24 (m, 2H), 2.53 (q, J=7.3 Hz, 2H), 2.58 (m, 2H), 3.12 (d, J=6.8 Hz, 2H), 3.23(d, J=8.3 Hz, 2H), 5.50 (m, 1H), 5.64 (m, 1H).

12: Contaminated with 10% of **13**. The following ^{1}H-NMR signals were extracted from those of a 10:1 mixture of **12** and **13**. ^{1}H-NMR ($CDCl_3$) δ 1.25 (t, J=7.3 Hz, 3H), 1.59-1.65 (m, 2H), 1.65 (s, 3H), 1.72-1.78 (m, 2H), 2.10-2.15 (m, 2H), 2.51 (q, J=7.3 Hz, 2H), 2.59 (m, 2H), 3.14 (d, J=6.8 Hz, 2H), 3.18 (d, J=7.8 Hz, 2H), 5.45 (t, J=7.8 Hz, 1H). Anal. Calcd. for $C_{13}H_{21}O_2NS$: C, 61.14; H, 8.28, N, 5.48. Found: C, 61.54; H, 8.34, N, 5.68.

2-(2'-Oxopropyl)cyclohexanone (28). To a solution of $NaBH_4$ (270mg, 7.1 mmol) in EtOH was added a mixture of **12** and **13** (490mg, 2.3 mmol) and the reaction mixture was stirred overnight at room temperature. After evaporation of EtOH under reduced pressure, extractive workup with CH_2Cl_2 under acidic conditions afforded a crude material, which was purified by chromatography over a silica gel column to give an oil (291 mg, 63%). A part of this oil (50mg) was ozonized in CH_2Cl_2 (2.5 ml) and MeOH (4 ml) for 2 h at 0°C. The product obtained by usual workup with Me_2S followed by preparative TLC afforded **27** (21 mg). To a solution of **27** (32 mg, 0.18 mmol) in THF (1 ml) was added aqueous 20% $TiCl_3$ solution (620 mg) in THF (1 ml) slowly and the reaction mixture was stirred for 15 h at room temperature. After being poured over crashed ice, the mixture was extracted with dichloromethane. The crude product thus obtained was purified by preparative TLC to give **28**, whose spectral data were identical with the authentic sample.[12]

Scheme 5.



14: IR($CHCl_3$) 2940, 2860, 1510, 1450, 1340, 1320 cm^{-1}. ^1H-NMR($CDCl_3$) δ 1.20 (t, J=7.3 Hz, 3H), 1.30 (d, J=8 Hz, 3H), 1.50-1.80 (m, 4H), 2.10-2.30 (m, 4H), 2.50 (q, J=7.3 Hz, 2H), 3.10 (bd, J=5.5 Hz, 2H), 3.80 (m, 1H), 5.40 (m, 2H). HRMS m/z 255.1272. $C_{13}H_{21}NO_2S$ requires 255.1292.

15: IR($CHCl_3$) 2950, 2860, 1510, 1450, 1340 cm^{-1}. ^1H-NMR($CDCl_3$) δ 1.24 (t, J=7.3 Hz, 3H), 1.50-2.00 (8H), 2.12 (m, 2H), 2.60 (q, J=7.3 Hz, 2H), 2.50-2.70 (m, 2H), 3.30-3.70 (2H), 5.44 (br.d, J=10.5 Hz, 1H), 5.90 (ddd, J=10.5, 5, and 2.5 Hz, 1H). HRMS m/z 206.1187. $C_{14}H_{21}NO_2S$-SEt requires 206.1181.

16: IR($CHCl_3$) 2925, 2850, 1560, 1290 cm^{-1}. ^1H-NMR($CDCl_3$) δ1.30 (t, J=7.3 Hz, 3H), 1.40-1.90 (10H), 1.95-2.30 (m, 2H), 2.50-3.20 (8H), 5.20 (dd, J=11 and 8 Hz, 1H), 5.63 (m, 1H). Anal. Calcd. for $C_{16}H_{25}NO_2S$: C, 65.06, H, 8.53, N, 4.74. Found: C, 65.35, H, 8.30, N, 4.77.

17: IR($CHCl_3$) 2950, 2850, 1600, 1555, 1530, 1450, 1360 cm^{-1}. ^1H-NMR ($CDCl_3$) δ 1.72 (4H), 2.14 (s, 3H), 2,40-2.70 (4H), 5.95 (dd, J=4 and 1 Hz, 1H), 5.26 (d, J=4Hz, 1H). Anal. Calcd. for $C_{11}H_{13}NO_3$: C, 63.75, H, 6.32, N, 6.76. Found: C, 63.57, H, 6.39, N, 6.44.

18: IR($CHCl_3$) 2925, 2850, 1520, 1440, 1340, 1260 cm^{-1}. ^1H-NMR($CDCl_3$) δ 1.24 (t, J=7.3 Hz, 3H), 1.60 (s, 3H), 1.45-1.66 (6H), 1.80 (s, 3H), 2.16 (m, 2H), 2.48 (q, J=7.5 Hz, 2H), 2.64-2.74 (m, 2H), 3.04 (s, 2H), 3.22 (s, 2H). Anal. Calcd. for $C_{15}H_{25}NO_2S$: C, 63.58, H, 8.89, N, 4.94. Found: C, 63.92, H, 8.82, N, 4.96.

19: IR($CHCl_3$) 2950, 2925, 2850, 1520, 1440, 1340 cm^{-1}. ^1H-NMR($CDCl_3$) δ 1.24 (t, J=7.3 Hz, 3H), 1.30 (d, J=7.0 Hz, 3H), 1.45-2.00 (6H), 2.25-2.36 (m, 2H), 2.50 (q, J=7.3 Hz, 2H), 2.64-2.76 (m, 2H), 3.00 (m, 2H), 3.78 (m, 1H), 5.42 (m, 2H). HRMS m/z 269.1464. $C_{14}H_{23}NO_2S$ requires 269.1449.

20: IR($CHCl_3$) 2975, 2925, 1520, 1380, 1350 cm^{-1}. ^1H-NMR($CDCl_3$) δ 1.24, 1.36 (2t, J=7.3 Hz, ratio=5:1, 3H), 1.63 (s, 3H) 1.70, 2.20 (2d, J=1.5 Hz, ratio=1:5, 3H), 2.50, 2.76 (2q, J=7.3 Hz, ratio=5:1, 2H), 2.98, 3.58 (2m, ratio=5:1, 2H), 3.16, 3.24 (2s, ratio=5:1, 2H), 6.84, 7.00 (2m, ratio=5:1, 1H). Anal. Calcd. for $C_{11}H_{19}NO_2S$: C, 57.62, H, 8.35, N, 6.11. Found: C, 57.98, H, 8.29, N, 6.12.

21: IR($CHCl_3$) 2950, 2925, 2850, 1520, 1450, 1380, 1350 cm^{-1}. ^1H-NMR ($CDCl_3$) δ 1.26, 1.37 (2t, J=7.3 Hz, ratio=5:1, 3H), 1.69,1.70 (2d, J=1.5 Hz, ratio=1:5, 3H), 1.85, 2.22 (2d, J=1.5 Hz, ratio=1:5, 3H), 2.52, 2.54 (2q, J=7.3 Hz, ratio=1:5, 2H), 2.96, 3.57 (2s, ratio=5:1, 2H), 3.16, 3.21 (2d, J=7.8 Hz, ratio=5:1, 2H), 5.52, 5.59 (2t,

J=7.8 Hz, ratio=1:5, 1H), 6.95, 7.05 (m, ratio=5:1, 1H). Anal. Calcd. for $C_{10}H_{17}NO_2S$: C, 55.80, H, 7.96, N, 6.51. Found: C, 55.44, H, 7.80, N, 6.57.

22: IR($CHCl_3$) 2950, 2925, 2850, 1630, 1520, 1440, 1380, 1350 cm^{-1}. ^1H-NMR ($CDCl_3$) δ 1.28 (t, J=7.3 Hz, 3H), 1.60 - 2.20 (m, 4H), 2.20 (d, J=1.5 Hz, 3H), 2.60 (q, J=7.3 Hz, 2H), 2.90 (m, 1H), 3.40 (m, 1H), 5.50 (bd, J=10 Hz, 1H), 5.95 (ddd, J=10, 4.5 and 2 Hz, 1H), 6.94 (s, 1H). Anal. Calcd. for $C_{11}H_{17}NO_2S$: C, 58.13, H, 7.54, N, 6.16. Found: C, 58.23, H, 7.51, N, 6.33.

23: IR($CHCl_3$) 1605, 1535, 1500, 1320 cm^{-1}. ^1H-NMR($CDCl_3$) δ 2.38 (s, 3H), 2.52 (d, J=1Hz, 3H), 6.16 (dd, J=4 and 1Hz, 1H), 6.80 (d, J=4 Hz, 1H), 7.60 (s, 1H). HRMS m/z 167.0567. $C_8H_9NO_3$ requires 167.0582.

24 (1:1 mixture): IR($CHCl_3$) 2950, 2925, 2850, 1535, 1520, 1455, 1380, 1355 cm^{-1}. ^1H-NMR($CDCl_3$) δ 0.88, 0.90 (br.t, J=7.3 Hz, 3H), 1.24, 1.26 (t, J=7.3 Hz, 3H), 1.00-1.44 (8H), 1.56 (s, 3H), 1.78, 1.80 (s, 3H), 1.84-2.07 (2H), 2.18, 2.22 (s, 3H), 2.46, 2.50 (q, J=7.3 Hz, 2H), 2.98, 3.06 (s, 2H), 3.22, 3.24 (s, 2H). Anal. Calcd. for $C_{17}H_{31}NO_2S$: C, 65.13, H, 9.97, N, 4.47. Found: C, 65.37, H, 9.88, N, 4.37.

25 (1:1 mixture): IR($CHCl_3$) 2950, 2925, 2850, 1520, 1455, 1380, 1355 cm^{-1}. ^1H-NMR($CDCl_3$) δ 0.88, 0.90 (br.t, J=7.3 Hz, 3H), 1.24, 1.26 (t, J=7.3 Hz, 3H), 1.10-1.50 (8H), 1.64, 1.66 (s, 3H), 1.80-2.16 (2H), 2.16, 2.21 (s, 3H), 2.52, 2.54 (q, J=7.3 Hz, 2H), 2.94, 3.02 (s, 2H), 3.14, 3.22 (d, J=1.5 Hz, 2H), 5.46 (m, 1H). Anal. Calcd. for $C_{16}H_{28}NO_2S$: C, 64.17, H, 9.76 N, 4.68. Found: C, 64.62, H, 9.48, N, 4.54.

26 (1:1 mixture): IR($CHCl_3$) 2950, 2925, 2850, 1560, 1460, 1380, 1290 cm^{-1}. ^1H-NMR($CDCl_3$) δ 0.89, 0.90 (br.t, J=7.3 Hz, 3H), 1.23, 1.26 (t, J=7.3 Hz, 3H), 1.29, 1.30 (d, J=6.5 Hz, 3H), 1.10-1.80 (9H), 2.18 (s, 3H), 2.00-2.24 (1H), 2.47, 2.50 (q, J=7.3 Hz, 2H), 2.96 (2H), 3.74 (m, 1H), 5.15-5.60 (2H). Anal. Calcd. for $C_{16}H_{29}NO_2S$: C, 64.18, H, 9.76, N, 4.68. Found: C, 64.45, H, 9.55, N, 4.66.

References

1. Part 11. Fuji, K.; Node, M.; Kawabata, T.; Fujimoto, M. *J. Chem. Soc , Perkin Trans. I* **1987**, 1043.
2. A part of this work has been published in a preliminary form: Fuji, K.; Khanapure, S. P.; Node, M.; Kawabata, T.; Ito, A. *Tetrahedron Lett.* **1985**, *26*, 779.
3. Fuji, K. "*Bond-Cleavage Reactions with Hard Acid and Soft Nucleophile Systems*" in *Nucleophilicity*; Advances in Chemistry Series 215; Harris, J. M.; McManus, S. P., Eds.; American Chemical Society: Washington, Dc, 1987, pp 219-231.

4. Pearson, R. G. *Hard and Soft Acids and Bases*; Dowden, Hutchinson, & Ross: Strousberg, 1977.
5. Saville, B. Angew. *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 928.
6. Node, M.; Nishide, K.; Fuji, K.; Fujita, E. *J. Org. Chem.* **1980**, *45*, 4275.
7. Node, M.; Ohta, K.; Kajimoto, T.; Nishide, K.; Fujita, E.; Fuji, K. *Chem. Pharm. Bull.* **1983**, *31*, 4178.
8. Seebach, D.; Colvin, E. W.; Lehr, F.; Weller, T. *Chimia* **1979**, *33*, 1.
9. Node, M.; Kawabata, T.; Fujimoto, M.; Fuji, K. *Synthesis* **1984**, 234.
10. Tamura, Y.; Ishiyama, K.; Mizuki, Y.; Maeda, H.; Ishibashi, H. *Tetrahedron Lett.* **1981**, *22*, 3773. Ishibashi, H.; Kitano, Y.; Nakatani, H.; Okada, M.; Ikeda, M.; Okura, M.; Tamura, Y. *Tetrahedron Lett.* **1984**, *25*, 4231. Ishibashi, H.; Okada, M.; Sato, K.; Ikeda, M.; Ishiyama, K.; Tamura, Y. *Chem. Pharm. Bull.* **1985**, *33*, 90. Ishibashi, H.; Okada, M.; Nakatani, H.; Ikeda, M.; Tamura, Y. *J. Chem. Soc. Perkin Trans. I* **1986**, 1763.
11. Corey, E. J.; Walinsky, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 8932.
12. Negishi, E.; Luo, F. *J. Org. Chem.* **1983**, *48*, 2427.
13. March, J. *Advanced Organic Chemistry*, (3rd ed.), J. Willy & Sons, Inc.: New York, 1985, pp 668.
14. Barluenga, J.; González, J. M.; Campos, P. J.; Asensio, G. *Tetrahedron Lett* **1988**, *29*, 6497, and references cited therein.
15. Bäckvall, J.; Byström, S.; Nordberg, R. E. *J. Org. Chem.* **1984**, *49*, 4619.
16. Bäckvall, J.; Vagberg, J. O. *J. Org. Chem.* **1988**, *53*, 5695.
17. Bäckvall, J.; Nyström, J.; Nordberg, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 3676.
18. Bloom, A. J.; Fleischmann, M.; Mellow, J. M. *Tetrahedron Lett.* **1984**, *25*, 4971.
19. Weinreb, S. M.; Garigipati, R. S. *J. Am. Chem. Soc.*, **1983**, *105*, 4499.
20. Bäckvall, J.; Nordberg, R. E.; Wilhelm, D. *J. Am. Chem. Soc.* **1985**, *107*, 6892.
21. Nakashita, Y.; Hesse, M. *Helv. Chim. Acta* **1983**, *66*, 845.