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Oxidative Generation of 1-Nitroalkyl Radicals and Their Addition Reaction to Olefins[#]

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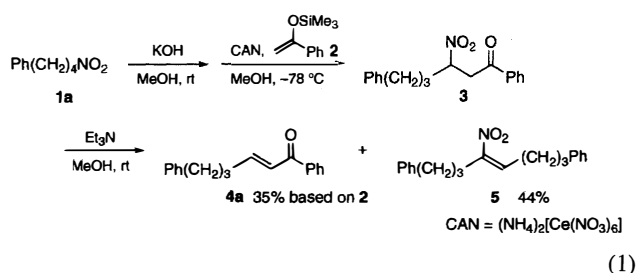
1-Nitroalkyl radicals are generated by oxidation of potassium salt of 1-*aci*-nitroalkanes with ammonium hexanitratocerate(IV). When the oxidation is carried out in the presence of electron-rich olefins, such as silyl enol ethers, intermolecular addition of the radicals onto the olefins proceeds to afford β -nitro ketones, which are further converted to α,β -unsaturated ketones in high yield. Stereoselective construction of fused ring systems is achieved by intramolecular addition of 1-nitroalkyl radicals.

Carbon–carbon bond-forming reactions by using radical species are recently attracting much attention in synthetic chemistry because of their unique reactivity, distinct from that of ionic species.^{1,2)} Though one-electron oxidation of carbanions is considered to be one of the simplest methods for generation of carbon-centered radicals, this method has rarely been employed as a synthetic tool. That is, although several reactions are known to form carbon–carbon bonds by the use of radicals generated by one-electron oxidation of carbanions, most of them afford self-coupling products and few examples have been reported concerning the intermolecular carbon–carbon bond forming reactions.^{3–8)} In these intermolecular reactions, the yield of the products is not sufficiently high, even with the use of large excess amounts of radical acceptors. Recently, we found that 1-nitroalkyl radicals are generated by oxidation of *aci*-nitro anions with ammonium hexanitratocerate(IV) (CAN), and the intermolecular addition reaction proceeds with electron-rich olefins.⁹⁾ In this paper, we would like to report the details of this reaction and the application to the construction of fused ring systems by intramolecular addition reaction of thus generated 1-nitroalkyl radicals.

Results and Discussion

Intermolecular Addition Reaction between 1-Nitroalkyl Radicals and Electron-Rich Olefins. Though it has been known that one-electron oxidation of *aci*-nitro anions with a metallic oxidant generates 1-nitroalkyl radicals, their addition reaction to olefins has rarely been reported.^{10–14)} Recently, Bowmann et al. reported an intramolecular cyclization of 1-nitroalkyl radical using a norbornene derivative, but, the yield of the cyclized product was not satisfactory.¹⁵⁾ In the course of our study on generation of reactive species by oxidation with high valent metallic compounds, we found

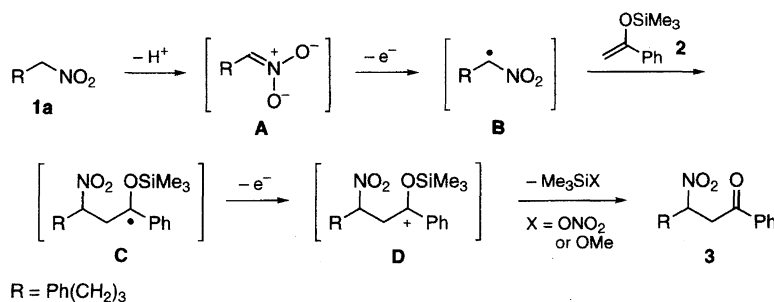
an intermolecular addition reaction of 1-nitroalkyl radical to electron-rich olefins. When a solution of potassium salt of 1-nitro-4-phenylbutane (**1a**) in methanol, prepared by treating **1a** with potassium hydroxide, was added to a solution of CAN and (1-trimethylsiloxyethenyl)benzene (**2**) in methanol at $-78\text{ }^{\circ}\text{C}$ (**1a**:KOH:CAN:**2** = 1:1.3:1.9:0.85; 0.1 mol dm⁻³ for **1a**), the reaction proceeded to give 3-nitro-1,6-diphenyl-1-hexanone (**3**) as a crude product. Since purification of the β -nitro ketone **3** by preparative TLC (silica gel) caused a partial elimination of nitrous acid from **3**, the crude product was purified after converting to 1,6-diphenyl-2-hexen-1-one (**4a**). Thus, by treatment of the crude nitro ketone **3** with triethylamine, the α,β -unsaturated ketone **4a** was obtained in 35% yield based on the silyl enol ether **2**, accompanied by the formation of a self-coupling product **5** (44%) (Eq. 1).



This reaction is considered to proceed as follows (Scheme 1). A potassium salt of 1-*aci*-nitroalkane **A** is oxidized with CAN to generate a 1-nitroalkyl radical **B**. The radical species **B** adds to the enol ether **2**, affording a radical intermediate **C**. Oxidation of the intermediate **C** with CAN gives a cation **D**, desilylation of which affords the β -nitro ketone **3**. It is well known that, in the alkylation of *aci*-nitro anions with alkyl halides, generally *O*-alkylation proceeds predominantly over *C*-alkylation.^{16–18)} In the present radical addition to the silyl enol ether, *C*-alkylation proceeded exclusively.

In order to optimize the reaction conditions, effects of the

[#] Dedicated to Professor Dieter Seebach on the occasion of his 60th birthday.



Scheme 1. Mechanism for the addition reaction of the nitroalkane to the silyl enol ether.

Table 1. Temperature and Concentration Effect on the Yield of **4a**^{a)}

Entry	Temp °C	Concn mol dm ⁻³	Yield/%		
			4a ^{b)}	5	6 ^{b)}
1 ^{c)}	-78	0.1	35	44	11
2 ^{d)}	-78	0.05	74	13	2
3	-78	0.03	99	15	0
4	-61	0.03	85	5	20
5	-45	0.03	55	15	37

a) **1a**: KOH: CAN: **2**=1.0: 1.3: 1.9: 0.85. b) Based on the silyl enol ether **2**. c) A small amount (3% based on **1a**) of 3,4-dihydro-1(2*H*)-naphthalenone was obtained. d) A small amount (8% based on **1a**) of 3,4-dihydro-1(2*H*)-naphthalenone was obtained.

concentration and the reaction temperature were examined first. As shown in Table 1, when the concentration became lower, formation of the self-coupling product **5** was diminished and the product was obtained in higher yield (Entries 1, 2, and 3). The reaction temperature is crucial for the selective preparation of **4a**. At higher temperature, the yield of the dimer **6** of the enol ether was increased considerably (Entries 3, 4, and 5). The enone **4a** was obtained quantitatively by the reaction at -78 °C (Entry 3).

The reaction was investigated with some oxidizing agents such as $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]\text{PF}_6$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mn}(\text{pic})_3$, or

$\text{Ag}(\text{pic})_2$ (pic = 2-pyridinecarboxylato). The addition product **4a** was obtained in 12% yield only when $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]\text{PF}_6$ was employed. The use of other oxidizing agents gave only the self-coupling product **5**, or brought about oxidation or hydrolysis of the silyl enol ether **2**.

In addition to potassium hydroxide, sodium or lithium hydroxides and potassium methoxide can be used as a base to generate the *aci*-nitro anion, giving **4a** in more than 93% yield. No reaction took place, however, when a weak base such as triethylamine was used.

Under the optimum reaction conditions found as above, the nitroalkane **1a** reacted with various silyl enol ethers to afford the corresponding addition products in good yield (Table 2, Entries 2, 3, and 4). The reactions with a tetrasubstituted silyl enol ether (Entry 5) and cyclic silyl enol ethers (Entries 6 and 7), however, gave poor yields of the products. In addition to silyl enol ethers, a vinyl ether, a styrene derivative, and an allylsilane could be employed successfully to give the corresponding products in moderate to good yield (Entries 8, 9, and 10). The formation of the unexpected hydroxy ketone **15a** is explained as follows (Scheme 2): A cation intermediate **E** is formed by the addition of the 1-nitroalkyl radical to α -methylstyrene and successive oxidation. Trapping of the cation species **E** by the solvent (MeOH) affords the product **14a**, while intramolecular capture of **E** by the nitro group gives a cyclic compound **F**. Hydrolysis of **F** in $\text{S}_{\text{N}}1$ manner under acidic work-up conditions would easily take place to generate *aci*-nitro compound **G**, which is hydrolyzed to the ketone **15a** by Nef-type reaction.

The reactions of various nitroalkanes and silyl enol ethers were examined as shown in Table 3. When primary nitroalkanes such as 5-nitropentyl acetate (**1b**) and a silyl ether of

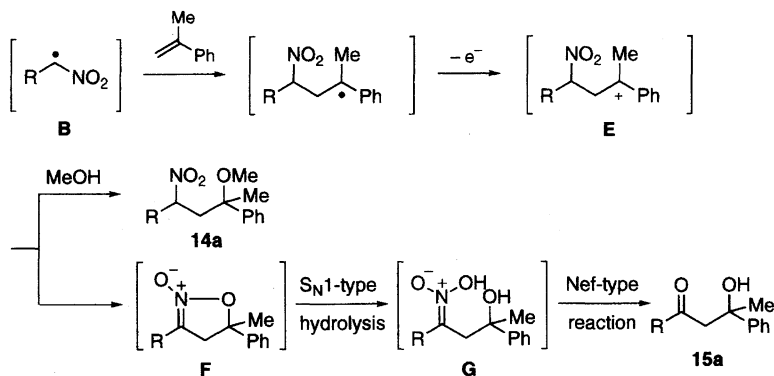
Scheme 2. Formation of the hydroxy ketone **15a**.

Table 2. Reaction of 1-Nitro-4-phenylbutane (**1a**) with Various Olefins^{a)}

$\text{R}-\text{CH}_2\text{NO}_2 \xrightarrow[\text{MeOH, rt}]{\text{KOH}} \xrightarrow[\text{MeOH, -78 } ^\circ\text{C, 15 min}]{\text{CAN, Olefin}} \xrightarrow[\text{MeOH, rt}]{\text{Et}_3\text{N}} \text{Product}$				
1a R = Ph(CH ₂) ₃				
Entry	Olefin	Product		Yield/% ^{b)}
1			4a	99
2			7a	81
3			8a	78
4			9a	79
5			10a	5
6			11a	28
7			12a	38
8 ^{d)}			13a	96
9 ^{d)}			14a 15a	48 ^{e)} 25 ^{e)}
10 ^{d)}			16a	45

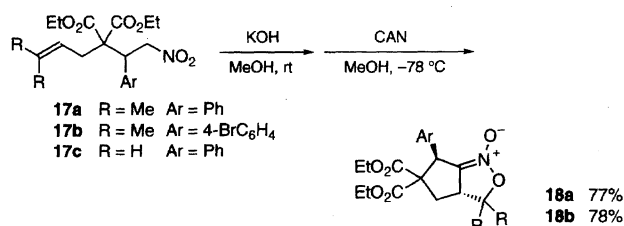
a) **1a**: KOH: CAN: olefin = 1.0: 1.3: 1.9: 0.85. b) Based on the olefin. c) *Z/E* = 95/5 (determined by ¹H NMR). d) The crude products were not treated with triethylamine. e) The yield was based on the nitroalkane **1a**, since 4 molar amounts of olefin were used.

3-nitro-1-propanol **1c** were employed, the addition products were obtained in moderate yield (Entries 2, 3, 4, and 5). A secondary nitroalkane **1d** and a cyclic nitroalkane **1e** also afforded α,β -unsaturated ketones in excellent yield in the reaction with **2** (Entries 6 and 8), while the reactions with an aliphatic silyl enol ether resulted in poor yield of the products (Entries 7 and 9). Phenylnitromethane (**1f**) gave a complex mixture (Entry 10). Although the oxidation of nitromethane (**1g**) afforded the corresponding β -nitro ketone, the isolated yield was hard to determine because of the instability of the β -nitro ketone and the volatility of acrylophenone (**4g**) which was formed by the elimination of nitrous acid from the β -nitro ketone. Only NMR yield of **4g** was shown in the table (Entry 11).¹⁹⁾ When the initially formed β -nitro ketones resist the elimination to α,β -unsaturated ketones, the use of DBU is preferable. In these cases, methanol should not be employed as solvent, since its Michael addition proceeds on produced α,β -unsaturated ketones.

Construction of Fused Ring Systems by the Intramolecular Cyclization of 1-Nitroalkyl Radicals.

As described above, the oxidation of *aci*-nitro anions with CAN in the presence of an electron-rich olefin affords the correspond-

ing addition products. This carbon-carbon bond-forming reaction was applied for constructing fused ring systems by intramolecular cyclization. When nitro compounds **17a** and **17b** were treated with potassium hydroxide, followed by oxidation with CAN, the cyclized products **18a** and **18b** were obtained, respectively, as a single stereoisomer (Eq. 2). The relative configuration of **18b** was unambiguously determined as *trans* by X-ray crystallographic analysis.²⁰⁾ Introduction of substituents on the olefinic moiety is essential for stabilizing intermediate radical species. In fact, a terminal vinyl compound **17c** did not give desired cyclized products cleanly but a mixture which was difficult to separate.



(2)

This cyclization was further applied to six-membered ring

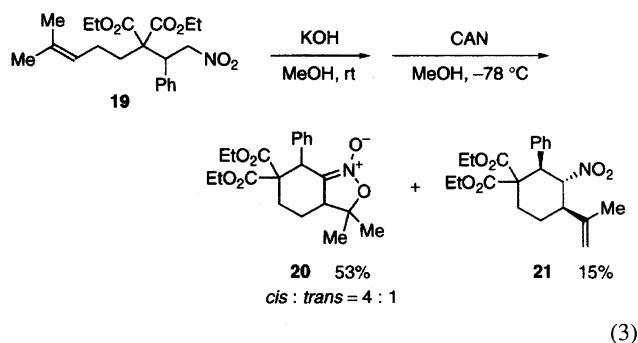
Table 3. Reaction of Various Nitroalkanes with Silyl Enol Ethers^{a)}

$\text{Nitroalkane} \xrightarrow[\text{MeOH, rt}]{\text{KOH}} \xrightarrow[\text{MeOH, } -78^\circ\text{C}]{\text{CAN, Olefin, 15 min}} \xrightarrow[\text{CH}_2\text{Cl}_2, \text{rt}]{\text{DBU}} \text{Product}$				
Entry	Nitroalkane	Olefin	Product	Yield/% ^{b)}
1	$\text{Ph}(\text{CH}_2)_3\text{NO}_2$ 1a	OSiMe_3 $\text{CH}=\text{Ph}$	$\text{Ph}(\text{CH}_2)_3\text{CH}=\text{CH}-\text{C}(=\text{O})\text{Ph}$ 4a	99 ^{d)}
2	$\text{AcO}(\text{CH}_2)_4\text{NO}_2$ 1b	OSiMe_3 $\text{CH}=\text{Ph}$	$\text{AcO}(\text{CH}_2)_4\text{CH}=\text{CH}-\text{C}(=\text{O})\text{Ph}$ 4b	69
3	$\text{AcO}(\text{CH}_2)_4\text{NO}_2$ 1b	OSiMe_3 $\text{CH}=\text{n-Pr}$	$\text{AcO}(\text{CH}_2)_4\text{CH}=\text{CH}-\text{C}(=\text{O})\text{n-Pr}$ 7b	60
4	$\text{AcO}(\text{CH}_2)_4\text{NO}_2$ 1b	$\text{Me}-\text{CH}=\text{OSiMe}_3$ ^{c)} $\text{CH}=\text{Ph}$	$\text{AcO}(\text{CH}_2)_4\text{CH}=\text{CH}-\text{C}(=\text{O})\text{Ph}$ 9b	65
5	$\text{TBSO}(\text{CH}_2)_2\text{NO}_2$ 1c	OSiMe_3 $\text{CH}=\text{Ph}$	$\text{TBSO}(\text{CH}_2)_2\text{CH}=\text{CH}-\text{C}(=\text{O})\text{Ph}$ 4c	52
6	Me_2CHNO_2 1d	OSiMe_3 $\text{CH}=\text{Ph}$	$\text{Me}_2\text{CHCH}=\text{CH}-\text{C}(=\text{O})\text{Ph}$ 4d	98
7	Me_2CHNO_2 1d	OSiMe_3 $\text{CH}=(\text{CH}_2)_2\text{Ph}$	$\text{Me}_2\text{CHCH}=\text{CH}-\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{Ph}$ 8d	20
8	$\text{C}_6\text{H}_{11}\text{NO}_2$ 1e	OSiMe_3 $\text{CH}=\text{Ph}$	$\text{C}_6\text{H}_{11}\text{CH}=\text{CH}-\text{C}(=\text{O})\text{Ph}$ 8d	90
9	$\text{C}_6\text{H}_{11}\text{NO}_2$ 1e	OSiMe_3 $\text{CH}=(\text{CH}_2)_2\text{Ph}$	$\text{C}_6\text{H}_{11}\text{CH}=\text{CH}-\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{Ph}$ 8e	43
10	PhCH_2NO_2 1f	OSiMe_3 $\text{CH}=\text{Ph}$	$\text{PhCH}=\text{CH}-\text{C}(=\text{O})\text{Ph}$ 4f	10 ^{d)}
11	CH_3NO_2 1g	OSiMe_3 $\text{CH}=\text{Ph}$	$\text{CH}_2=\text{CH}-\text{C}(=\text{O})\text{Ph}$ 4g	14 ^{e)}

a) nitroalkane : KOH : CAN : olefin = 1.0 : 1.3 : 1.9 : 0.85. b) Based on the olefin.

c) Z/E = 95/5 (determined by ¹H NMR). d) The crude products were treated with triethylamine instead of DBU. e) Determined by ¹H NMR using Ph₃CH as an internal standard.

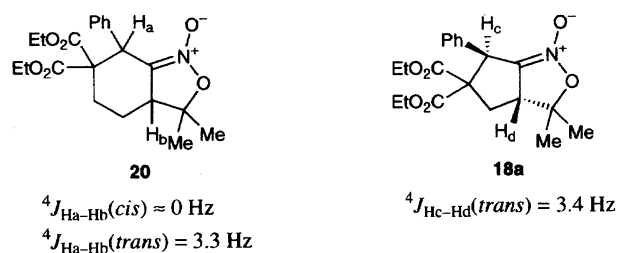
formation. For example, potassium salt of a nitro compound **19** cyclized to cyclohexanes **20** and **21** in good total yield (Eq. 3).

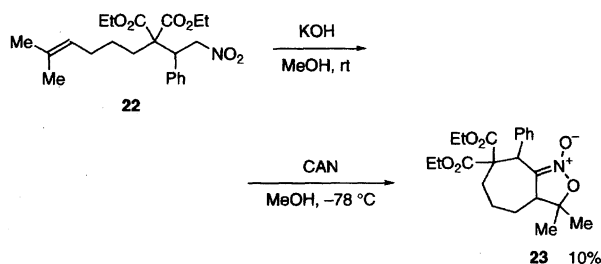


The product **20** was obtained as a mixture of two stereoisomers (*cis* : *trans* = 4 : 1). The isomer ratio was determined by the integration value of ¹H NMR. Relative configuration was determined by comparing the coupling-constant between H_a and H_b with that of **18a**, whose relative configuration was

determined as mentioned above (Fig. 1). It was confirmed by molecular mechanics calculation that the location of H_a and H_b in the most stable conformer of the *trans*-**20** is similar to that of H_c and H_d in **18a**, so that each coupling-constant is expected to have nearly the same value.²¹⁾

Though we tried a seven-membered ring formation from **22**, the desired cyclized product **23** was obtained only in low yield (Eq. 4).

Fig. 1. Comparison of ⁴J_{H-H}.



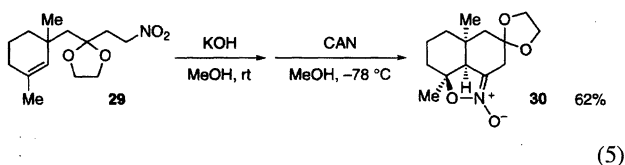
(4)

It is known that six-membered ring formation is not favorable in the radical cyclization reaction mediated by tributylstannane, because of the relatively small rate constant of the cyclization of an intermediate radical (e.g. 6-heptenyl radical) compared to that of its hydrogen abstraction from the stannane.²²⁾ According to the above results, on the contrary, the intramolecular cyclization of the 1-nitroalkyl radical is found to be a useful method for the construction of a six-membered ring as well as a five-membered ring. So this method is applied for the construction of decalin skeleton from a cyclohexene derivative **29**.

The precursor **29** for the cyclization was expected to be prepared by carbon chain elongation of an allylic alcohol **24**. To introduce a side chain to **24**, the model reaction with the silyl enol ether **2** was examined in the presence of various Lewis acids. The results are summarized in Table 4, which shows that the use of trifluoroborane–diethyl ether (1/1) affords the expected product **25** in high yield (Entries 1, 2, and 3). The product **25** was obtained in comparable yield even with a catalytic amount of trifluoroborane–diethyl ether (1/1) (Entries 4 and 5).

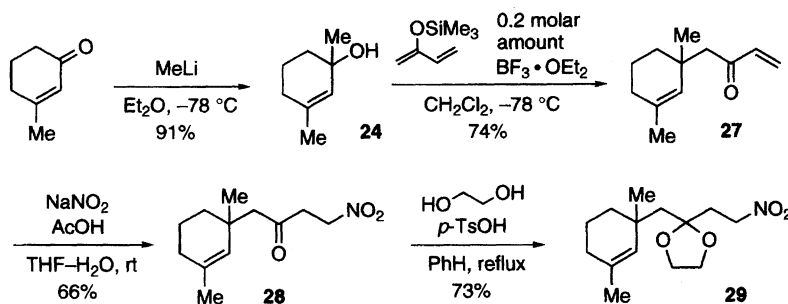
By using this carbon–carbon bond forming reaction, the precursor **29** was prepared in 4 steps starting from 3-methyl-2-cyclohexen-1-one (Scheme 3).

When the precursor **29** was treated with potassium hydroxide followed by oxidation with CAN, the cyclized product **30** was obtained as a single stereoisomer in 62% yield (Eq. 5).

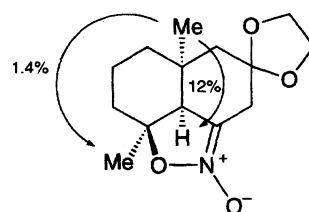


(5)

The relative configuration was determined by the differential NOE experiment (Fig. 2). This revealed that *cis*-decalin was constructed by this radical cyclization.



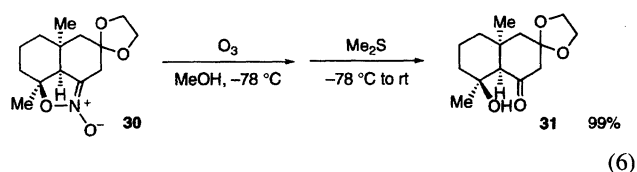
Scheme 3. Preparation of the precursor for the decalin skeleton.

Fig. 2. Observed NOE for the compound **30**.Table 4. Reaction of **24** with Silyl Enol Ether Catalyzed by Lewis Acid

Entry	Lewis Acid	Molar amounts	Yield/%	
			25	26
1 ^{a)}	Me ₃ SiOTf	1.5	57	11
2 ^{a)}	EtAlCl ₂	1.5	70	0
3 ^{a)}	BF ₃ ·OEt ₂	1.5	90	2
4 ^{b)}	BF ₃ ·OEt ₂	0.2	86	0
5 ^{b)}	BF ₃ ·OEt ₂	0.1	84	0

a) 1.5 molar amounts of the silyl enol ether **2** were employed.b) 1.1 molar amounts of the silyl enol ether **2** were employed.

The *aci*-nitro ester **30** was converted quantitatively into a hydroxy ketone **31** by ozonolysis (Eq. 6), which would be a useful intermediate for the synthesis of *cis*-decalin derivatives.



(6)

In conclusion, oxidation of potassium salt of 1-*aci*-nitroalkanes with CAN generates 1-nitroalkyl radicals which react with various electron-rich olefins to afford the corresponding addition products. This radical addition reaction is also utilized for the intramolecular cyclization. That is, even six-membered fused ring systems, which are difficult to obtain by the conventional radical cyclization by using stannane, are constructed in good yield as well as five-membered ring systems.

Experimental

General. ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker AM 500 spectrometer in CDCl_3 solutions using CHCl_3 (for ^1H , $\delta = 7.24$) and CDCl_3 (for ^{13}C , $\delta = 77.00$) as an internal standard. IR spectra were recorded on a Horiba FT 300-S spectrophotometer. High-resolution mass spectra were obtained with a JEOL JMS-SX102A mass spectrometer at an ionization energy of 70 eV. X-Ray diffraction intensities were collected on a Rigaku AFC-7R goniometer with graphite monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71069 \text{ \AA}$) radiation. The melting points were uncorrected. Elemental analyses were carried out at The Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo. Methanol was distilled from magnesium methoxide and stored under argon atmosphere. Dichloromethane was distilled from P_2O_5 , then from CaH_2 , and dried over Molecular Sieves 4Å. CAN (Kanto Chemical Co., Inc., guaranteed grade) was dried under vacuum at 80°C for 10–12 h before use. $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]\text{PF}_6$, $^{23}\text{Mn}(\text{pic})_3$, 24 and $\text{Ag}(\text{pic})_2$ 25 were prepared according to the literature procedure. Preparative TLC was performed on a silica gel (Wakogel B-5F).

Typical Procedure for the Reaction of Nitroalkanes with Olefins. To a solution of CAN (119.5 mg, 0.218 mmol) in methanol (1 ml) was added a solution of (1-trimethylsiloxyethyl)benzene (**2**) (18.6 mg, 0.0981 mmol) in methanol (1.5 ml) at -78°C under an argon atmosphere. At the same temperature, a mixture of KOH (1.05 mol dm^{-3} in methanol, 0.15 ml, 0.158 mmol) and 1-nitro-4-phenylbutane (**1a**) (20.8 mg, 0.116 mmol) in methanol (1.5 ml) was gradually added. The orange-yellow solution immediately turned dark brown and the color faded to pale yellow within 4 to 5 min. After 15 min, the reaction was quenched by adding 0.1 mol dm^{-3} aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (a few drops) and water. The mixture was extracted with dichloromethane (10 ml \times 4) and the combined extracts were dried over anhydrous Na_2SO_4 . After evaporation of the solvent, the residue was treated with triethylamine (ca. 0.2 ml) in methanol at ambient temperature for 20 min. The reaction mixture was diluted with water and acidified with 1 mol dm^{-3} aqueous HCl. After the extraction and evaporation in the same way, chromatographic purification afforded 1,6-diphenyl-2-hexen-1-one (**4a**) (24.0 mg, 0.0959 mmol, 99%).

A large scale run (**1a**, 208.3 mg, 1.16 mmol; **2**, 188.6 mg, 0.981 mmol; **1a**, KOH soln, 1.5 ml, 1.58 mmol; CAN, 1.21 g, 2.21 mmol) afforded almost the same result (**4a**, 234.1 mg, 0.935 mmol, 95% yield).

The spectral data of the products are as follows:

(E)-1,6-Diphenyl-2-hexen-1-one (4a): Colorless oil; IR (neat) 3028, 2931, 1670, 1620, 1290, 1225, 748, 696 cm^{-1} ; ^1H NMR $\delta = 1.83$ – 1.89 (2H, m), 2.32–2.37 (2H, m), 2.66–2.69 (2H, m (t-like)), 6.88 (1H, dt, $J_d = 15.4$, $J_t = 1.4$ Hz), 7.07 (1H, dt, $J_d = 15.4$, $J_t = 6.9$ Hz), 7.17–7.20 (3H, m), 7.27–7.30 (2H, m (t-like)), 7.44–7.47 (2H, m (t-like)), 7.52–7.55 (1H, m (t-like)), 7.90–7.92 (2H, m (d-like)); ^{13}C NMR $\delta = 29.75$, 32.22, 35.32, 125.93, 126.18, 128.38, 128.42, 128.49, 128.49, 132.59, 137.92, 141.66, 149.35, 190.80. Found: C, 86.06; H, 7.32%. Calcd for $\text{C}_{18}\text{H}_{18}\text{O}$: C, 86.36; H, 7.25%.

(Z)-4-Nitro-1,8-diphenyl-4-octene (5): Colorless oil; IR (neat) 3026, 2937, 1518, 1454, 1335, 748, 700 cm^{-1} ; ^1H NMR $\delta = 1.76$ – 1.84 (4H, m), 2.11–2.16 (2H, m), 2.53–2.56 (2H, m), 2.61–2.66 (4H, m), 7.09 (1H, t, $J = 7.9$ Hz), 7.13–7.22 (6H, m), 7.26–7.31 (4H, m); ^{13}C NMR $\delta = 25.91$, 27.23, 29.30, 29.93, 35.25, 35.25, 126.04, 126.13, 128.30, 128.34, 128.41, 128.47, 136.07, 141.02, 141.16, 151.76. HRMS: m/z 309.1714. Calcd

for $\text{C}_{20}\text{H}_{23}\text{NO}_2$: M, 309.1729.

(E)-9-Phenyl-5-nonen-4-one (7a): Colorless oil; IR (neat) 2933, 1693, 1672, 1629, 1456, 978, 746, 700 cm^{-1} ; ^1H NMR $\delta = 0.92$ (3H, t, $J = 7.4$ Hz), 1.58–1.65 (2H, m), 1.76–1.82 (2H, m), 2.20–2.25 (2H, m), 2.48 (2H, t, $J = 7.4$ Hz), 2.63 (2H, t, $J = 7.6$ Hz), 6.08 (1H, dt, $J_d = 15.8$, $J_t = 1.5$ Hz), 6.80 (1H, dt, $J_d = 15.8$, $J_t = 6.9$ Hz), 7.14–7.19 (3H, m), 7.25–7.28 (2H, m); ^{13}C NMR $\delta = 13.81$, 17.72, 29.70, 31.84, 35.28, 42.04, 125.94, 128.38, 128.41, 130.62, 141.65, 146.62, 200.75. HRMS: m/z 216.1509. Calcd for $\text{C}_{15}\text{H}_{20}\text{O}$: M, 216.1514.

(E)-1,8-Diphenyl-4-octen-3-one (8a): Colorless oil; IR (neat) 3026, 2931, 1693, 1672, 1630, 1495, 1452, 978, 746, 700 cm^{-1} ; ^1H NMR $\delta = 1.74$ – 1.80 (2H, m), 2.19–2.24 (2H, m), 2.60–2.63 (2H, m (t-like)), 2.82–2.86 (2H, m), 2.90–2.94 (2H, m), 6.09 (1H, dt, $J_d = 15.8$, $J_t = 1.4$ Hz), 6.80 (1H, dt, $J_d = 15.8$, $J_t = 6.9$ Hz), 7.14–7.21 (6H, m), 7.25–7.28 (4H, m); ^{13}C NMR $\delta = 29.63$, 30.07, 31.85, 35.24, 41.66, 125.94, 126.05, 128.34, 128.38, 128.40, 128.45, 130.53, 141.25, 141.59, 147.08, 199.45. HRMS: m/z 278.1665. Calcd for $\text{C}_{20}\text{H}_{22}\text{O}$: M, 278.1671.

(E)-2-Methyl-1,6-diphenyl-2-hexen-1-one (9a): Colorless oil; IR (neat) 3026, 2931, 1645, 1598, 1448, 1315, 1282, 748, 704 cm^{-1} ; ^1H NMR $\delta = 1.73$ – 1.79 (2H, m), 1.93 (3H, d, $J = 0.73$ Hz), 2.27–2.32 (2H, m), 2.62–2.65 (2H, m (t-like)), 6.27–6.30 (1H, m), 7.14–7.19 (3H, m), 7.25–7.28 (2H, m), 7.38–7.41 (2H, m (t-like)), 7.46–7.50 (1H, m (t-like)), 7.59–7.61 (2H, m (d-like)); ^{13}C NMR $\delta = 12.50$, 28.62, 30.25, 35.56, 125.93, 128.01, 128.36, 128.37, 129.24, 131.32, 136.77, 138.72, 141.67, 146.18, 198.99. HRMS: m/z 264.1513. Calcd for $\text{C}_{19}\text{H}_{20}\text{O}$: M, 264.1514.

The configuration of this compound was determined as *E*, since a cross peak was observed between the protons of methyl group and those at 4-position by NOESY experiment.

2,2-Dimethyl-3-nitro-1,6-diphenyl-1-hexanone (10a): Colorless oil; IR (neat) 2939, 1678, 1549, 1462, 1367, 1257, 960, 700 cm^{-1} ; ^1H NMR $\delta = 1.37$ (3H, s), 1.42 (3H, s), 1.53–1.67 (3H, m), 2.11–2.15 (1H, m), 2.54–2.61 (2H, m), 5.17 (1H, dd, $J = 1.9$, 11.3 Hz), 7.09–7.11 (2H, m (d-like)), 7.15–7.18 (1H, m (t-like)), 7.23–7.26 (2H, m (t-like)), 7.39–7.42 (2H, m (t-like)), 7.47–7.50 (1H, m (t-like)), 7.53–7.54 (2H, m (d-like)); ^{13}C NMR $\delta = 20.74$, 23.83, 28.21, 28.91, 34.90, 50.72, 93.41, 126.05, 127.48, 128.29, 128.40, 128.43, 131.43, 137.89, 141.02, 205.54. HRMS: m/z 279.1770. Calcd for $\text{C}_{20}\text{H}_{23}\text{O}$: M–NO₂, 279.1749.

(E)-2-(4-Phenylbutylidene)cyclopentanone (11a): Colorless oil; IR (neat) 3026, 2935, 1718, 1649, 1454, 1232, 1203, 746, 700 cm^{-1} ; ^1H NMR $\delta = 1.75$ – 1.82 (2H, m), 1.87–1.94 (2H, m), 2.13–2.18 (2H, m), 2.31 (2H, t, $J = 7.8$ Hz), 2.50–2.54 (2H, m), 2.60–2.64 (2H, m (t-like)), 6.53–6.57 (1H, m), 7.14–7.18 (3H, m), 7.26–7.28 (2H, m); ^{13}C NMR $\delta = 19.77$, 26.75, 29.07, 29.93, 35.40, 38.59, 125.88, 128.34, 128.39, 135.63, 137.60, 141.74, 207.19. HRMS: m/z 214.1355. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}$: M, 214.1358.

(E)-2-(4-Phenylbutylidene)cyclohexanone (12a): Colorless oil; IR (neat) 3026, 2935, 1718, 1685, 1610, 1454, 748, 700 cm^{-1} ; ^1H NMR $\delta = 1.69$ – 1.73 (2H, m), 1.74–1.78 (2H, m), 1.80–1.85 (2H, m), 2.09–2.13 (2H, m), 2.39–2.43 (4H, m), 2.60–2.63 (2H, m), 6.61–6.65 (1H, m), 7.12–7.18 (3H, m), 7.24–7.29 (2H, m); ^{13}C NMR $\delta = 23.31$, 23.57, 26.70, 27.20, 30.01, 35.45, 40.15, 125.84, 128.32, 128.39, 136.51, 138.99, 141.83, 201.09. HRMS: m/z 228.1520. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}$: M, 228.1514.

1,1-Dimethoxy-3-nitro-1,6-diphenylhexane (13a): Colorless crystals; mp 62.0 – 63.0°C (hexane); IR (KBr) 2945, 1552, 1549, 1450, 1338, 1286, 1184, 1134, 1049, 768, 704 cm^{-1} ; ^1H NMR $\delta = 1.40$ – 1.46 (3H, m), 1.74–1.80 (1H, m), 2.01 (1H, dd, $J = 3.1$, 15.5 Hz), 2.38–2.47 (2H, m), 2.89 (1H, dd, $J = 8.7$, 15.5 Hz),

3.07 (3H, s), 3.14 (3H, s), 4.17—4.22 (1H, m), 6.98—7.00 (2H, m (d-like)), 7.14—7.19 (1H, m (t-like)), 7.21—7.24 (2H, m), 7.31—7.34 (1H, m), 7.35—7.39 (2H, m), 7.41—7.44 (2H, m); ^{13}C NMR δ = 26.91, 34.06, 34.52, 40.49, 48.85, 49.04, 84.17, 101.94, 125.97, 126.86, 128.24, 128.36, 128.36, 128.40, 139.12, 140.88. Found: C, 69.88; H, 7.30; N, 4.14%. Calcd for $\text{C}_{20}\text{H}_{25}\text{NO}_4$: C, 69.95; H, 7.34; N, 4.08%.

2-Methoxy-4-nitro-2,7-diphenylheptane (14a): One of the two diastereomers (68 : 32) could be isolated in pure form by TLC. Colorless oil; IR (neat) 2941, 1550, 1452, 1375, 1169, 1074, 702 cm^{-1} ; ^1H NMR δ = 1.47—1.53 (3H, m), 1.51 (3H, s), 1.77—1.81 (1H, m), 1.84 (1H, dd, J = 2.0, 15.4 Hz), 2.46—2.51 (2H, m), 2.63 (1H, dd, J = 9.0, 15.4 Hz), 3.07 (3H, s), 4.61—4.62 (1H, m), 7.02—7.03 (2H, m (d-like)), 7.13—7.16 (1H, m (t-like)), 7.20—7.22 (2H, m (d-like)), 7.25—7.28 (1H, m (t-like)), 7.31—7.37 (4H, m); ^{13}C NMR δ = 22.50, 27.10, 34.70, 34.88, 46.87, 50.53, 77.87, 84.16, 125.84, 125.97, 127.27, 128.32, 128.38, 128.48, 141.08, 143.95. Found: C, 73.50; H, 7.59; N, 4.52%. Calcd for $\text{C}_{20}\text{H}_{25}\text{NO}_3$: C, 73.37; H, 7.70; N, 4.28%.

2-Hydroxy-2,7-diphenyl-4-heptanone (15a): Colorless oil; IR (neat) 3471, 3026, 2933, 1697, 1494, 1450, 1375, 764, 748, 702 cm^{-1} ; ^1H NMR δ = 1.49 (3H, s), 1.74—1.80 (2H, m), 2.24 (1H, dt, J_d = 17.4, J_t = 7.2 Hz), 2.34 (1H, dt, J_d = 17.4, J_t = 7.2 Hz), 2.42—2.52 (2H, m), 2.76 (1H, d, J = 16.8 Hz), 3.10 (1H, d, J = 16.8 Hz), 4.61 (1H, s), 7.05—7.07 (2H, m (d-like)), 7.15—7.18 (1H, m (t-like)), 7.19—7.26 (3H, m), 7.29—7.32 (2H, m (t-like)), 7.38—7.39 (2H, m (d-like)); ^{13}C NMR δ = 24.51, 30.67, 34.72, 43.63, 53.23, 73.35, 124.31, 125.98, 126.71, 128.26, 128.38, 128.39, 141.26, 147.22, 212.64. HRMS: m/z 282.1600. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_2$: M, 282.1620.

4-Nitro-7-phenyl-1-heptene (16a): Colorless oil; IR (neat) 2929, 1550, 1454, 1373, 928, 750, 700 cm^{-1} ; ^1H NMR δ = 1.62—1.68 (2H, m), 1.71—1.78 (1H, m), 1.95—2.03 (1H, m), 2.42—2.48 (1H, m), 2.61—2.67 (3H, m), 4.47—4.52 (1H, m), 5.10—5.13 (2H, m), 5.62—5.70 (1H, m), 7.12—7.13 (2H, m), 7.16—7.19 (1H, m), 7.25—7.28 (2H, m); ^{13}C NMR δ = 27.35, 32.69, 35.03, 37.90, 88.02, 119.49, 126.11, 128.32, 128.47, 131.43, 141.03. Found: C, 70.91; H, 7.67; N, 6.60%. Calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2$: C, 71.21; H, 7.81; N, 6.39%.

(E)-7-Oxo-7-phenyl-5-heptenyl Acetate (4b): Colorless oil; IR (neat) 2945, 1738, 1670, 1622, 1242, 696 cm^{-1} ; ^1H NMR δ = 1.57—1.61 (2H, m), 1.65—1.69 (2H, m), 2.03 (3H, s), 2.32—2.36 (2H, m), 4.07 (2H, t, J = 6.5 Hz), 6.87 (1H, dt, J_d = 15.4, J_t = 1.4 Hz), 7.02 (1H, dt, J_d = 15.4, J_t = 6.9 Hz), 7.43—7.46 (2H, m (t-like)), 7.52—7.55 (1H, m (t-like)), 7.89—7.91 (2H, m (d-like)); ^{13}C NMR δ = 20.94, 24.57, 28.14, 32.27, 64.02, 126.26, 128.49, 128.50, 132.64, 137.88, 148.90, 171.12, 190.72. HRMS: m/z 246.1260. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3$: M, 246.1256.

(E)-7-Oxo-5-decenyl Acetate (7b): Colorless oil; IR (neat) 2962, 2935, 1739, 1672, 1631, 1367, 1240, 1045 cm^{-1} ; ^1H NMR δ = 0.91 (3H, t, J = 7.4 Hz), 1.49—1.57 (2H, m), 1.58—1.68 (4H, m), 2.02 (3H, s), 2.20—2.24 (2H, m), 2.48 (2H, t, J = 7.2 Hz), 4.04 (2H, t, J = 6.5 Hz), 6.08 (1H, dt, J_d = 15.9, J_t = 1.4 Hz), 6.78 (1H, dt, J_d = 15.4, J_t = 6.9 Hz); ^{13}C NMR δ = 13.78, 17.66, 20.93, 24.50, 28.10, 31.88, 42.08, 64.00, 130.66, 146.15, 171.12, 200.65. HRMS: m/z 212.1432. Calcd for $\text{C}_{12}\text{H}_{20}\text{O}_3$: M, 212.1412.

(E)-6-Methyl-7-oxo-7-phenyl-5-heptenyl Acetate (9b): Colorless oil; IR (neat) 2937, 1738, 1645, 1446, 1365, 1240, 1045, 708 cm^{-1} ; ^1H NMR δ = 1.45—1.51 (2H, m), 1.61—1.67 (2H, m), 1.94 (3H, s), 2.01 (3H, s), 2.27—2.32 (2H, m (q-like)), 4.04 (2H, t, J = 6.5 Hz), 6.24 (1H, t, J = 7.3 Hz), 7.37—7.41 (2H, m (t-like)), 7.46—7.49 (1H, m (t-like)), 7.58—7.60 (2H, m (t-like)); ^{13}C NMR δ = 12.51, 20.92, 25.01, 28.33, 28.63, 64.04, 128.02, 129.23, 131.36, 136.88,

138.61, 145.58, 171.10, 198.91. HRMS: m/z 260.1427. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$: M, 260.1412.

(E)-5-(*t*-Butyl)dimethylsiloxy-1-phenyl-2-penten-1-one (4c): Colorless oil; IR (CCl_4) 2931, 1674, 1626, 1228, 1101 cm^{-1} ; ^1H NMR δ = 0.04 (6H, s), 0.87 (9H, s), 2.49—2.53 (2H, m), 3.78 (2H, t, J = 6.4 Hz), 6.91 (1H, d, J = 15.6 Hz), 7.02 (1H, dt, J_d = 15.6, J_t = 6.9 Hz), 7.43—7.46 (2H, m (t-like)), 7.52—7.55 (1H, m (t-like)), 7.89—7.91 (2H, m (d-like)); ^{13}C NMR δ = -5.37, 25.84, 36.28, 53.36, 61.59, 127.59, 128.33, 128.46, 128.53, 132.56, 146.44, 190.83. HRMS: m/z 233.0990. Calcd for $\text{C}_{13}\text{H}_{17}\text{O}_2\text{Si}$: M - C_4H_9 (*t*-Bu), 233.0998.

3-Methyl-1-phenyl-2-buten-1-one (4d):²⁶ Colorless oil; IR (neat) 3060, 2912, 1660, 1614, 1448, 1248, 1011, 700 cm^{-1} ; ^1H NMR δ = 2.00 (3H, s), 2.19 (3H, s), 6.72—6.73 (1H, m), 7.41—7.44 (2H, m), 7.48—7.52 (1H, m), 7.90—7.91 (2H, m); ^{13}C NMR δ = 21.15, 27.96, 121.19, 128.16, 128.41, 132.24, 139.26, 156.64, 191.53.

5-Methyl-1-phenyl-4-hexen-3-one (8d): Colorless oil; IR (neat) 3060, 2931, 1687, 1622, 1446, 1111, 700 cm^{-1} ; ^1H NMR δ = 1.86 (3H, d, J = 1.0 Hz), 2.14 (3H, d, J = 0.90 Hz), 2.71—2.74 (2H, m (t-like)), 2.88—2.91 (2H, m (t-like)), 6.04—6.05 (1H, m), 7.15—7.18 (3H, m), 7.24—7.27 (2H, m); ^{13}C NMR δ = 20.76, 27.66, 30.08, 45.75, 123.65, 125.93, 128.33, 128.40, 141.47, 155.39, 199.82. HRMS: m/z 188.1212. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}$: M, 188.1201.

2-Cyclohexylidene-1-phenyl-1-ethanone (4e): Colorless oil; IR (neat) 2929, 1658, 1614, 1446, 1219, 702 cm^{-1} ; ^1H NMR δ = 1.59—1.65 (4H, m), 1.69—1.73 (2H, m), 2.28—2.31 (2H, m), 2.74—2.76 (2H, m (t-like)), 6.58 (1H, s), 7.41—7.44 (2H, m), 7.49—7.52 (1H, m), 7.91—7.93 (2H, m); ^{13}C NMR δ = 26.27, 27.97, 28.85, 30.63, 38.39, 118.72, 128.72, 128.31, 128.37, 132.30, 139.27, 162.75, 192.36. HRMS: m/z 200.1212. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}$: M, 200.1201.

1-Cyclohexylidene-4-phenyl-2-butanone (8e): Colorless oil; IR (neat) 2935, 1687, 1622, 1448, 702 cm^{-1} ; ^1H NMR δ = 1.57—1.64 (6H, m), 2.13—2.15 (2H, m), 2.72—2.75 (2H, m), 2.78—2.80 (2H, m), 2.88—2.92 (2H, m), 5.94 (1H, s), 7.15—7.19 (3H, m), 7.24—7.27 (2H, m); ^{13}C NMR δ = 26.23, 27.89, 28.78, 30.01, 30.14, 38.10, 45.92, 120.85, 125.91, 128.34, 128.39, 141.46, 162.22, 200.59. HRMS: m/z 228.1512. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}$: M, 228.1514.

(E)-1,3-Diphenyl-2-propen-1-one (4f):²⁷ ^1H NMR δ = 7.40—7.65 (9H, m), 7.80 (1H, d, J = 15.7 Hz), 8.02—8.05 (2H, m (d-like)).

Typical Procedure for the Preparation of Substrates for Intramolecular Cyclization. To a suspension of sodium hydride (60% oil dispersion, 0.22 g, 5.5 mmol), washed with petroleum ether before use) in tetrahydrofuran (10 ml) was added a solution of diethyl (3-methyl-2-butenyl)malonate (1.14 g, 4.99 mmol) in tetrahydrofuran (2 ml) at 0 °C under an argon atmosphere. After stirring at 0 °C for 15 min, the mixture was cooled to -78 °C, and then a solution of ((*E*)-2-nitroethyl)benzene (0.746 g, 5.00 mmol) in tetrahydrofuran (3 ml) was added. Stirring was continued for 2 h at -78 °C, and the reaction was quenched by adding pH 7 phosphate buffer solution. The mixture was extracted with ethyl acetate (20 ml \times 4) and dried over anhydrous Na_2SO_4 . After evaporation of the solvent, chromatographic purification of the residue afforded diethyl (3-methyl-2-butenyl)(2-nitro-1-phenylethyl)malonate (**17a**) (1.09 g, 2.89 mmol, 58%).

The spectral data of the products are as follows:

Diethyl (3-Methyl-2-butenyl)(2-nitro-1-phenylethyl)malonate (17a): Pale yellow oil; IR (neat) 2983, 1730, 1556, 1450, 1377,

1294, 1227, 1184, 704 cm^{-1} ; $^1\text{H NMR}$ δ =1.23 (3H, t, J =7.1 Hz), 1.30 (3H, t, J =7.1 Hz), 1.41 (3H, s), 1.70 (3H, s), 2.20 (1H, dd, J =7.9, 15.4 Hz), 2.50 (1H, dd, J =6.1, 15.4 Hz), 4.14—4.22 (3H, m), 4.24—4.31 (2H, m), 4.92 (1H, dd, J =11.2, 13.4 Hz), 5.04 (1H, br t), 5.11 (1H, dd, J =3.0, 13.4 Hz), 7.06—7.08 (2H, m), 7.24—7.26 (3H, m); $^{13}\text{C NMR}$ δ =13.97, 14.00, 18.02, 26.09, 32.32, 46.20, 60.27, 61.86, 61.89, 78.63, 116.93, 128.30, 128.69, 128.90, 135.21, 136.16, 169.85, 170.12. HRMS: m/z 378.1924. Calcd for $\text{C}_{20}\text{H}_{28}\text{NO}_6$: $M+H$, 378.1917.

Diethyl (3-Methyl-2-butenyl)[2-nitro-1-(4-bromophenyl)ethyl]malonate (17b): Colorless crystals; mp 82.0—82.5 °C (hexane-diethyl ether); IR (KBr) 2991, 1736, 1666, 1549, 1450, 1383, 1308, 1220, 1192, 1173 cm^{-1} ; $^1\text{H NMR}$ δ =1.23 (3H, t, J =7.1 Hz), 1.29 (3H, t, J =7.1 Hz), 1.43 (3H, s), 1.70 (3H, s), 2.19 (1H, dd, J =7.9, 15.5 Hz), 2.50 (1H, dd, J =6.1, 15.5 Hz), 4.15—4.22 (3H, m), 4.23—4.30 (2H, m), 4.87 (1H, dd, J =11.3, 13.5 Hz), 5.01 (1H, br t), 5.10 (1H, dd, J =3.0, 13.5 Hz), 6.96 (2H, d, J =8.5 Hz), 7.40 (2H, d, J =8.5 Hz); $^{13}\text{C NMR}$ δ =13.94, 14.00, 18.08, 26.06, 32.26, 45.61, 60.04, 62.01, 62.01, 78.27, 116.62, 122.46, 130.58, 131.85, 134.33, 136.45, 169.67, 169.90. Found: C, 52.38; H, 5.68; N, 3.20%. Calcd for $\text{C}_{20}\text{H}_{26}\text{BrNO}_6$: C, 52.64; H, 5.74; N, 3.07%.

Diethyl (4-Methyl-3-pentenyl)(2-nitro-1-phenylethyl)malonate (19): Pale yellow oil; IR (neat) 2979, 1728, 1556, 1450, 1377, 1221, 704 cm^{-1} ; $^1\text{H NMR}$ δ =1.28 (3H, t, J =7.2 Hz), 1.29 (3H, t, J =7.2 Hz), 1.44—1.49 (1H, m), 1.51 (3H, s), 1.61 (3H, s), 1.71—1.77 (1H, m), 1.86—1.91 (1H, m), 1.95—2.02 (1H, m), 4.19 (1H, dd, J =3.0, 11.0 Hz), 4.22—4.31 (4H, m), 4.90 (1H, br t), 4.94 (1H, dd, J =11.0, 13.4 Hz), 5.05 (1H, dd, J =3.0, 13.4 Hz), 7.09—7.11 (2H, m), 7.26—7.30 (3H, m); $^{13}\text{C NMR}$ δ =13.98, 14.07, 17.58, 23.04, 25.59, 33.82, 46.78, 60.20, 61.81, 61.95, 78.84, 122.61, 128.40, 128.79, 128.79, 132.68, 135.24, 169.86, 170.32. HRMS: m/z 392.2052. Calcd for $\text{C}_{21}\text{H}_{30}\text{NO}_6$: $M+H$, 392.2073.

Diethyl (5-Methyl-4-hexenyl)(2-nitro-1-phenylethyl)malonate (22): Colorless oil; IR (neat) 2976, 1728, 1556, 1452, 1377, 1209, 704 cm^{-1} ; $^1\text{H NMR}$ δ =1.44—1.22 (1H, m), 1.26 (3H, t, J =7.2 Hz), 1.29 (3H, t, J =7.2 Hz), 1.33—1.40 (1H, m), 1.41—1.46 (1H, m), 1.50 (3H, s), 1.62 (3H, d, J =0.6 Hz), 1.72—1.75 (1H, m), 1.82—1.91 (2H, m), 4.18 (1H, dd, J =3.0, 11.1 Hz), 4.21—4.29 (4H, m), 4.93 (1H, dd, J =11.1, 13.5 Hz), 4.97 (1H, br t), 5.06 (1H, dd, J =3.0, 13.5 Hz), 7.07—7.09 (2H, m), 7.26—7.28 (3H, m); $^{13}\text{C NMR}$ δ =13.98, 14.06, 17.59, 24.40, 25.63, 27.84, 33.26, 46.39, 60.25, 61.78, 61.39, 78.75, 123.45, 128.37, 128.73, 128.73, 132.28, 135.25, 169.93, 170.34. HRMS: m/z 405.2136. Calcd for $\text{C}_{22}\text{H}_{31}\text{NO}_6$: M , 405.2151.

Typical Procedure for the Intramolecular Cyclization. To a solution of CAN (113.6 mg, 0.207 mmol) in methanol (2 ml) was added a solution of potassium salt of *aci*-nitro compound (prepared by adding KOH (1.05 mol dm^{-3} in methanol, 0.10 ml, 0.105 mmol) to a solution of diethyl (3-methyl-2-butenyl)(2-nitro-1-phenylethyl)malonate (17a) (38.0 mg, 0.101 mmol) in methanol (2 ml)) at -78°C under an argon atmosphere. The orange-yellow solution immediately turned dark brown and the color faded to pale yellow within 4 to 5 min. After 15 min, the reaction was quenched by adding 0.1 mol dm^{-3} aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (a few drops) and water. The mixture was extracted with dichloromethane (10 ml \times 4) and dried over anhydrous Na_2SO_4 . After evaporation of the solvent, the residue was purified by TLC (hexane-ethyl acetate, 3:1 (v/v)) to afford the product **18a** (29.3 mg, 0.0780 mmol, 77%).

The spectral data of the products are as follows:

Diethyl (6*R, 3*aR**)-(\pm)-3*a*,4,5,6-Tetrahydro-3,3-dimethyl-6-phenyl-3*H*-cyclopenta[*c*]isooxazole-5,5-dicarboxylate 1-Oxide (18a):** Colorless crystals; mp 87.0—87.5 °C (hexane); IR (KBr)

2983, 1753, 1724, 1676, 1460, 1369, 1261, 1198, 1093, 1095, 773 cm^{-1} ; $^1\text{H NMR}$ δ =0.70 (3H, t, J =7.1 Hz), 1.26 (3H, t, J =7.1 Hz), 1.40 (3H, s), 1.59 (3H, s), 1.92 (1H, dd, J =11.0, 12.8 Hz), 2.54 (1H, dd, J =7.5, 12.8 Hz), 3.29 (1H, dq, J_a =10.7, J_q =7.1 Hz), 3.67 (1H, dq, J_a =10.7, J_q =7.1 Hz), 4.21 (1H, dq, J_a =10.8, J_q =7.1 Hz), 4.31 (1H, dq, J_a =10.8, J_q =7.1 Hz), 4.43 (1H, ddd, J =3.4, 7.5, 11.0 Hz), 5.01 (1H, d, J =3.4 Hz), 7.19—7.27 (5H, m); $^{13}\text{C NMR}$ δ =13.20, 13.98, 22.67, 26.99, 32.76, 47.18, 57.37, 61.65, 62.15, 70.98, 85.20, 123.89, 127.88, 128.41, 128.61, 134.68, 169.17, 169.94. Found: C, 63.86; H, 6.55; N, 3.83%. Calcd for $\text{C}_{20}\text{H}_{25}\text{NO}_6$: C, 63.99; H, 6.71; N, 3.73%.

Diethyl (6*R, 3*aR**)-(\pm)-3*a*,4,5,6-Tetrahydro-3,3-dimethyl-6-(4-bromophenyl)-3*H*-cyclopenta[*c*]isooxazole-5,5-dicarboxylate 1-Oxide (18b):** Colorless crystals; mp 138.0 °C (hexane-diethyl ether); IR (KBr) 2976, 1751, 1728, 1674, 1263, 1230, 1188, 1061 cm^{-1} ; $^1\text{H NMR}$ δ =0.67 (3H, t, J =7.1 Hz), 1.25 (3H, t, J =7.1 Hz), 1.38 (3H, s), 1.58 (3H, s), 1.91 (1H, dd, J =11.1, 12.8 Hz), 2.51 (1H, dd, J =7.5, 12.8 Hz), 3.41 (1H, dq, J_a =10.7, J_q =7.1 Hz), 3.72 (1H, dq, J_a =10.7, J_q =7.1 Hz), 4.19 (1H, dq, J_a =10.8, J_q =7.1 Hz), 4.30 (1H, dq, J_a =10.8, J_q =7.1 Hz), 4.41 (1H, ddd, J =3.5, 7.5, 11.1 Hz), 4.94 (1H, d, J =3.5 Hz), 7.13 (2H, d, J =8.4 Hz), 7.39 (2H, d, J =8.4 Hz); $^{13}\text{C NMR}$ δ =13.23, 13.93, 22.61, 26.85, 32.70, 46.65, 57.10, 61.81, 62.26, 70.84, 85.56, 121.95, 123.34, 130.35, 131.49, 133.68, 168.94, 169.74. Found: C, 52.99; H, 5.26; N, 3.16%. Calcd for $\text{C}_{20}\text{H}_{24}\text{BrNO}_6$: C, 52.87; H, 5.32; N, 3.08%.

Diethyl 3*a*,4,5,6,7-Hexahydro-3,3-dimethyl-7-phenylcyclohexa[*c*]isooxazole-6,6-dicarboxylate 1-Oxide (20): Colorless oil, obtained as a mixture of two diastereomers (80:20). In the assignment of $^{13}\text{C NMR}$ described below, the sign of *cis* and *trans* refers to (7*R**, 3*aS**)-(\pm) and (7*R**, 3*aR**)-(\pm)-isomers respectively. IR (neat) 2978, 1730, 1649, 1454, 1371, 1291, 704 cm^{-1} ; $^1\text{H NMR}$ δ =0.97 (3H \times 0.8, t, J =7.1 Hz), 1.02 (3H \times 0.2, t, J =7.1 Hz), 1.19 (3H \times 0.2, t, J =7.1 Hz), 1.25 (3H \times 0.2, t, J =7.1 Hz), 1.28 (3H, s), 1.35—1.42 (1H \times 0.8, m), 1.38 (3H \times 0.2, s), 1.45 (3H \times 0.8, s), 1.71—1.76 (1H \times 0.2, m), 1.86—1.90 (1H \times 0.8, m), 1.90—2.00 (1H \times 0.2, m), 2.18—2.24 (1H \times 0.2, m), 2.37—2.47 (2H \times 0.8+1H \times 0.2, m), 3.27—3.31 (1H \times 0.2, m), 3.36 (1H \times 0.8, dd, J =6.3, 12.2 Hz), 3.71—3.78 (1H, m), 3.84—3.91 (1H, m), 4.17—4.24 (1H, m), 4.25—4.30 (1H, m), 4.60 (1H \times 0.2, d, J =3.3 Hz), 4.74 (1H \times 0.8, s), 7.19—7.24 (5H, m); $^{13}\text{C NMR}$ δ =13.57 (*cis*), 13.62 (*trans*), 13.89 (*trans*), 14.03 (*cis*), 18.09 (*trans*), 20.61 (*cis*), 21.50 (*trans*), 22.00 (*cis*), 25.87 (*trans*), 26.41 (*cis*), 26.50 (*trans*), 26.70 (*cis*), 43.14 (*cis*), 44.70 (*trans*), 48.40 (*trans*), 50.30 (*cis*), 58.36 (*cis*), 58.60 (*trans*), 61.42 (*cis*), 61.49 (*trans*), 62.05 (*trans*), 62.11 (*cis*), 82.76 (*cis*), 83.22 (*trans*), 116.14 (*trans*), 116.36 (*cis*), 127.87 (*trans*), 127.99 (*cis*), 128.22 (*trans*), 128.59 (*cis*), 129.02 (*cis*), 129.35 (*trans*), 134.05 (*trans*), 135.44 (*cis*), 168.48 (*cis*), 170.13 (*cis*), 171.02 (*trans*). HRMS: m/z 389.1833. Calcd for $\text{C}_{21}\text{H}_{27}\text{NO}_6$: $M+H$, 389.1838.

Diethyl *c*-4-Isopropenyl-*t*-3-nitro-*r*-2-phenylcyclohexanedicarboxylate (21): Colorless oil; IR (neat) 2981, 1724, 1649, 1556, 1450, 1369, 1269, 1240, 1108, 750, 702 cm^{-1} ; $^1\text{H NMR}$ δ =0.82 (3H, t, J =7.1 Hz), 1.18 (3H, t, J =7.1 Hz), 1.57—1.66 (1H, m), 1.76 (3H, s), 1.84—1.89 (1H, m), 2.24—2.31 (1H, m), 2.33—2.37 (1H, m), 2.79—2.84 (1H, m), 3.53 (1H, d, J =11.5 Hz), 3.71 (1H, dq, J_a =10.7, J_q =7.1 Hz), 3.92 (1H, dq, J_a =10.7, J_q =7.1 Hz), 4.14—4.20 (2H, m), 4.82 (2H, s), 5.80 (1H, t, J =11.5 Hz), 7.18—7.22 (3H, m), 7.35—7.37 (2H, m); $^{13}\text{C NMR}$ δ =13.39, 13.90, 17.94, 25.84, 33.15, 51.17, 52.74, 60.49, 61.29, 61.38, 88.78, 114.80, 127.98, 128.02, 129.84, 135.09, 142.79, 169.87, 169.97. HRMS: m/z 359.1820. Calcd for $\text{C}_{21}\text{H}_{27}\text{O}_5$: $M-\text{NO}$, 359.1858.

Diethyl 3*a*,4,5,6,7,8-Hexahydro-3,3-dimethyl-8-phenyl-3*H*-

cyclohepta[c]isooxazole-7,7-dicboxylate 1-Oxide (23): Colorless oil, obtained as a mixture of two diastereomers (80:20). ^{13}C NMR of the major isomer is only shown. IR (neat) 2979, 1732, 1620, 1452, 1371, 1207, 702 cm^{-1} ; ^1H NMR δ =1.10 (3H \times 0.83, t, J =7.1 Hz), 1.14 (3H \times 0.83, t, J =7.1 Hz), 1.19 (3H \times 0.17, t, J =7.1 Hz), 1.257 (3H \times 0.17, s), 1.264 (3H \times 0.17, t, J =7.1 Hz), 1.32 (3H \times 0.83, s), 1.37 (3H \times 0.83, s), 1.46 (3H \times 0.17, s), 1.65—1.88 (4H, m), 2.08—2.17 (1H \times 0.17, m), 2.26—2.30 (1H \times 0.83, m), 2.30—2.37 (1H \times 0.17, m), 2.42—2.47 (1H \times 0.82, m), 3.22—3.24 (1H \times 0.83, m), 3.29—3.32 (1H \times 0.17, m), 4.00—4.18 (4H \times 0.83+2H \times 0.17, m), 4.19—4.24 (1H \times 0.17, m), 4.27—4.33 (1H \times 0.17, m), 4.75 (1H \times 0.83, s), 4.78 (1H \times 0.17, s), 7.21—7.34 (5H, m); ^{13}C NMR δ =13.84, 20.81, 22.51, 26.56, 26.73, 32.11, 48.11, 53.15, 61.07, 61.40, 61.77, 81.90, 120.59, 127.75, 128.31, 128.47, 129.44, 129.91, 136.16, 169.46. HRMS: m/z 403.1997. Calcd for $\text{C}_{22}\text{H}_{29}\text{NO}_6$: M, 403.1995.

Typical Procedure for the Substitution of Allylic Hydroxy Group with Silyl Enol Ethers. To a solution of (1-trimethylsiloxyethenyl)benzene (**2**) (84.1 mg, 0.437 mmol) in dichloromethane (2 ml) was added a solution of trifluoroborane-diethyl ether (1/1) (0.95 mol dm^{-3} in methanol, 0.08 ml, 0.076 mmol), and then a solution of 1,3-dimethyl-2-cyclohexen-1-ol (**24**) (50.6 mg, 0.401 mmol) in dichloromethane (2 ml) slowly at -78°C . After stirring for 15 min, the reaction was quenched by adding a saturated aqueous solution of NaHCO_3 . The mixture was extracted with dichloromethane (10 ml \times 4) and dried over anhydrous Na_2SO_4 . After evaporation of the solvent, the residue was purified by TLC (hexane-ethyl acetate, 20:1 (v/v)) to afford the product, 2-(1,3-dimethyl-2-cyclohexen-1-yl)-1-phenyl-1-ethanone (**25**) (78.4 mg, 0.343 mmol, 86%).

The spectral data of the products are as follows:

2-(1,3-Dimethyl-2-cyclohexen-1-yl)-1-phenyl-1-ethanone (25): Colorless oil; IR (neat) 2925, 1687, 1674, 1597, 1448, 1011, 750, 692 cm^{-1} ; ^1H NMR δ =1.09 (3H, s), 1.40—1.47 (1H, m), 1.57 (3H, s), 1.61—1.66 (3H, m), 1.84—1.88 (2H, br), 2.83 (1H, d, J =14.5 Hz), 2.97 (1H, d, J =14.5 Hz), 5.25 (1H, br s), 7.39—7.42 (2H, m), 7.48—7.52 (1H, m), 7.89—7.91 (2H, m); ^{13}C NMR δ =19.44, 23.80, 27.68, 29.86, 35.12, 35.48, 49.26, 128.24, 128.34, 129.98, 132.56, 132.93, 138.68, 200.21. Found: C, 84.32; H, 8.85%. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}$: C, 84.16; H, 8.83%.

1,5-Dimethyl-3-phenyl-2-oxabicyclo[3.3.1]non-3-ene (26): Colorless oil; IR (neat) 3053, 2945, 1641, 1493, 1450, 1327, 1255, 1176, 1052, 750, 692 cm^{-1} ; ^1H NMR δ =1.12 (3H, s), 1.27—1.34 (1H, m), 1.35—1.40 (1H, m), 1.36 (3H, s), 1.45—1.58 (4H, m), 1.64—1.74 (1H, m), 1.90—1.95 (1H, br d), 4.97 (1H, d, J =1.7 Hz), 7.23—7.26 (1H, m (t-like)), 7.29—7.32 (2H, m (t-like)), 7.59—7.61 (2H, m (d-like)); ^{13}C NMR δ =20.44, 28.75, 29.16, 31.54, 38.42, 39.55, 44.25, 75.47, 103.82, 124.57, 127.54, 128.04, 136.23, 152.16. HRMS: m/z 228.1502. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}$: M, 228.1514.

1-(1,3-Dimethyl-2-cyclohexenyl)-3-buten-2-one (27): Colorless oil; IR (neat) 2929, 1689, 1612, 1454, 1400, 989 cm^{-1} ; ^1H NMR δ =1.03 (3H, s), 1.35—1.40 (1H, m), 1.53—1.62 (3H, m), 1.59 (3H, s), 1.81—1.83 (2H, m), 2.45 (1H, d, J =13.7 Hz), 2.52 (1H, d, J =13.7 Hz), 5.19 (1H, s), 5.69 (1H, dd, J =1.1, 10.6 Hz), 6.12 (1H, dd, J =1.1, 17.5 Hz), 6.32 (1H, dd, J =10.6, 17.5 Hz); ^{13}C NMR δ =19.36, 23.80, 27.72, 29.81, 35.04, 35.23, 51.44, 127.39, 129.66, 133.11, 137.93, 200.40. HRMS: m/z 177.1272. Calcd for $\text{C}_{12}\text{H}_{17}\text{O}$: M—H, 177.1279.

β -Nitro ketone **28** was prepared from **27** according to the literature.²⁸⁾

1-(1,3-Dimethyl-2-cyclohexenyl)-4-nitro-2-butanone (28): This compound easily decomposed by elimination of HNO_2 to reproduce **27**, so that it was immediately used for the next reaction.

Colorless oil; ^1H NMR δ =1.06 (3H, s), 1.38—1.43 (1H, m), 1.49—1.55 (1H, m), 1.57—1.62 (2H, m), 1.63 (3H, s), 1.85 (2H, br), 2.42 (1H, d, J =14.2 Hz), 2.46 (1H, d, J =14.2 Hz), 3.01—3.04 (2H, m), 4.58 (2H, t, J =6.0 Hz), 5.21 (1H, br s); ^{13}C NMR δ =19.34, 23.87, 27.82, 29.80, 34.97, 35.04, 40.52, 54.45, 68.99, 128.95, 134.12, 205.37.

Acetal **29** was prepared from **28** according to the literature.²⁹⁾

1-(1,3-Dimethyl-2-cyclohexenyl)-4-nitro-2-butanone Ethylene Acetal (29): Pale yellow oil; IR (neat) 2927, 1556, 1437, 1382, 1144, 1043 cm^{-1} ; ^1H NMR δ =1.00 (3H, s), 1.27—1.31 (1H, m), 1.57—1.85 (7H, m), 1.61 (3H, s), 2.45 (2H, t, J =6.8 Hz), 3.86—3.92 (4H, m), 4.38 (2H, t, J =6.8 Hz), 5.19 (1H, br s); ^{13}C NMR δ =19.44, 23.88, 29.31, 29.78, 33.93, 35.28, 35.86, 48.33, 64.42, 64.59, 71.06, 110.17, 130.52, 132.53. Found: C, 62.46; H, 8.55; N, 5.36%. Calcd for $\text{C}_{14}\text{H}_{23}\text{NO}_4$: C, 62.43; H, 8.61; N, 5.20%.

Compound **30** was prepared from **29** according to the procedure for the intramolecular cyclization described before.

(5aR*,8aR*,8bR*)-(±)-4,4-Ethylenedioxy-4,5,5a,6,7,8,8a,8b-octahydro-5a,8a-dimethyl-3H-naphtho[1,8-cd]isooxazole 2-Oxide (30): Colorless crystals; mp 165.0—166.0 $^\circ\text{C}$ (hexane-dichloromethane); IR (KBr) 2958, 1653, 1556, 1440, 1381, 1242, 1103, 785 cm^{-1} ; ^1H NMR δ =1.04 (3H, s), 1.13—1.17 (1H, m), 1.30—1.36 (1H, m), 1.54 (3H, s), 1.54—1.65 (3H, m), 1.69—1.75 (1H, m), 1.78—1.82 (1H, m), 2.09—2.16 (1H, m), 2.29 (1H, dd, J =4.1, 16.8 Hz), 2.74 (1H, d, J =4.1 Hz), 2.92 (1H, d, J =16.8 Hz), 3.81—3.85 (1H, m), 3.90—3.94 (1H, m), 3.96—4.00 (2H, m); ^{13}C NMR δ =17.83, 25.05, 28.75, 31.77, 33.35, 33.76, 34.18, 47.40, 55.77, 63.74, 64.95, 82.50, 107.60, 116.90. Found: C, 62.70; H, 7.69; N, 5.34%. Calcd for $\text{C}_{14}\text{H}_{21}\text{NO}_4$: C, 62.90; H, 7.92; N, 5.24%.

Procedure for the Ozonolysis of 30. Ozone was passed through a solution of **30** (17.9 mg, 0.0700 mmol) in methanol (1 ml) at -78°C , until the solution was colored blue. The reaction vessel was purged with argon, and then dimethyl sulfide (0.05 ml) was added to the mixture, this was allowed to warm to room temperature. After removal of the solvent, the residue was partitioned with water-ether and the aqueous phase was extracted with ether (10 ml \times 4). The combined extracts were dried over anhydrous Na_2SO_4 , and then the solvent was evaporated. The residue was purified by flash column chromatography (hexane-ethyl acetate, 2:1 (v/v)) to afford the product **31** (17.6 mg, 0.0692 mmol, 99%).

The spectral data of the product are as follows:

(4aR*,8aR*,8aS*)-(±)-3,3-Ethylenedioxy-3,4,4a,5,6,7,8,8a-octahydro-8-hydroxy-4a,8-dimethyl-1(2H)-naphthalenone (31): Colorless crystals; mp 118.0—120.0 $^\circ\text{C}$ (hexane-dichloromethane); IR (KBr) 3404, 2931, 1684, 1171, 1101 cm^{-1} ; ^1H NMR δ =0.97 (3H, s), 1.13—1.17 (2H, m), 1.17 (3H, s), 1.31—1.34 (1H, m), 1.35—1.46 (2H, m), 1.57—1.61 (2H, m), 1.82—1.91 (2H, m), 2.52—2.56 (1H, m), 2.79 (1H, br d), 3.22 (1H, br d), 3.81—3.88 (2H, m), 3.93—3.96 (2H, m); ^{13}C NMR δ =17.39, 30.87, 31.06, 33.98, 39.61, 40.93, 41.06, 51.58, 63.62, 64.67, 64.75, 70.16, 110.84, 210.71. Found: C, 65.82; H, 8.72%. Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_4$: C, 66.12; H, 8.72%.

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