α-Alkylation of α,β-Unsaturated Aldehyde Dimethylhydrazones Accompanied with the Double Bond Migration to β,γ[1)]

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Lithiated α,β-unsaturated aldehyde *N,N*-dimethylhydrazones reacted with alkyl halides accompanied by double bond migration to give α-alkylated β,γ-unsaturated aldehyde *N,N*-dimethylhydrazones in satisfactory yields. This reaction was found to be caused at the first step by deprotonation from a γ-carbon atom by lithium diisopropylamide. In the case of hydrazones with two kinds of γ-protons, deprotonation from the less hindered γ-carbon occurred selectively. Using this reaction, a novel sesquiterpene, 2,5,9-trimethyl-2-vinyl-4,8-decadienal, which has a vinyl group at the α-position, was synthesized in a good yield.

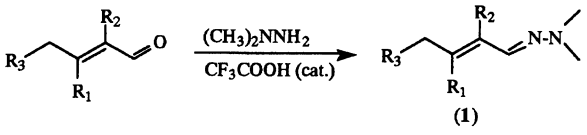
Alkylation of aldehydes or ketones via the carbanion (enolate anion) is one of the most important reactions in organic synthesis, but there are some limitations using free aldehydes or ketones for this purpose. For example, the direct alkylation of ketones with more than one α-hydrogens is complicated by the formation of dialkylated or polyalkylated products. With unsymmetrical ketones having α-hydrogens on both sides, the alkylation is further complicated by a need for selectivity toward a particular side. Although aldehydes have only one enolate site, their higher tendency to undergo aldol condensations limits their use in other carbanion reactions. In order to resolve these problems, the derivatives such as β-carbanions of imines, α-carbanions of aldehyde hydrazones, or enamines have been widely used.[2)]

In the course of our study using ketone or aldehyde *N,N*-dimethylhydrazones,[3,4)] we already have reported the alkylation reaction of hydrazones of unsymmetrical ketones[5—8)] and α,β-unsaturated cyclic enones.[9)] In this paper, we with to report the regioselective α-alkylation of α,β-unsaturated aldehyde *N,N*-dimethylhydrazones **1** accompanied with the double bond migration to β,γ. The preliminary communication was published elsewhere.[10)]

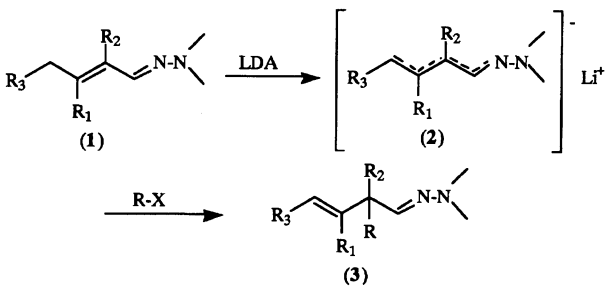
Results and Discussion

α,β-Unsaturated aldehyde *N,N*-dimethylhydrazones **1** were conveniently prepared from the corresponding aldehydes and *N,N*-dimethylhydrazine using trifluoroacetic acid as a catalyst (Scheme 1). The results of the syntheses of **1** are listed in Table 1.

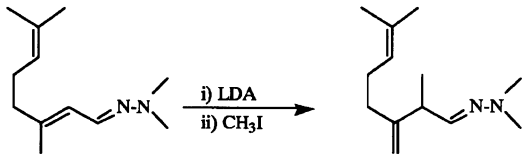
Lithiated α,β-unsaturated aldehyde *N,N*-dimethylhydrazones **2**, prepared in situ by the reaction of **1** with lithium diisopropylamide (LDA) in tetrahydrofuran, reacted with a variety of alkyl halides accompanied by double bond migration to afford α-alkylated β,γ-unsaturated aldehyde *N,N*-dimethylhydrazones **3** (Scheme 2). The results of the alkylation of hydrazones **1** are listed



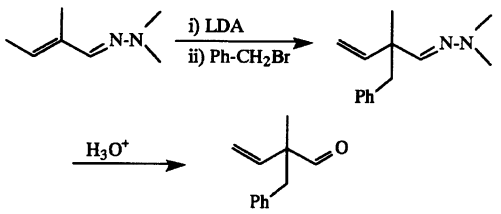
Scheme 1.



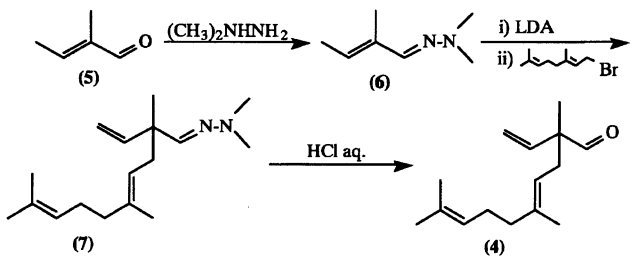
Scheme 2.



Scheme 3.

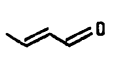
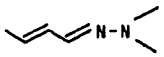
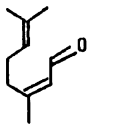
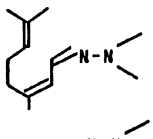
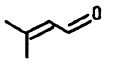
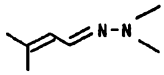
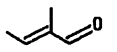
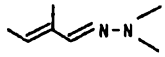
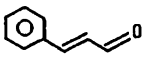
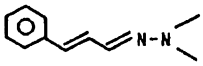
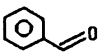
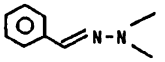


Scheme 4.



Scheme 5.

Table 1. Synthesis of α,β-Unsaturated Aldehyde Dimethylhydrazones

Run	Aldehyde	Hydrazone	Yield/%[a)]
1			69
2			91
3			86
4			81
5			96
6			84

a) Isolated yield.

in Table 2. For example, crotonaldehyde dimethylhydrazone reacted with allyl bromide, benzyl bromide, or hexyl bromide regioselectively at the α-position accompanied by double bond migration to afford the dimethylhydrazones of 2-vinyl-4-pentenal, 2-benzyl-3-butenal, and 2-hexyl-3-butenal in 53, 63, and 69% isolated yields, respectively. It is noteworthy that, in the reaction of the hydrazone of citral (Runs 4—7), the α,β-double bond rearranged to the methyl carbon to give a methylene exclusively, as shown in Scheme 3. And when 2-methyl-2-butenal *N,N*-dimethylhydrazone, which has no α-hydrogen, was also α-benzylated to give 2-benzyl-2-methyl-3-butenal (Scheme 4). This means that this reaction occurs at first by the abstraction of a γ-hydrogen as a proton to give the anion **2** as shown in Scheme 2. Probably, a proton was abstracted from the less hindered carbon, i.e. the methyl group of the citral hydrazone. Attempts to alkylate the *N,N*-dimethylhydrazone of cinnamaldehyde or benzaldehyde which has no γ-hydrogen gave no identifiable product and the starting material was recovered as expected. In contrast to this, the hydrazones which have γ-hydrogen but no α-hydrogen such as 2-methyl-2-butenal dimethylhydrazone gave the corresponding α-alkylated compounds (Runs 11,12).

These results show that the presence of a γ-hydrogen in α,β-unsaturated aldehyde dimethylhydrazones **1** is a requisite in these reactions. Therefore, in the alkylation reaction of **1**, deprotonation at the γ-position by LDA gave lithium salt **2**, which reacted with alkyl halides at the α-position regioselectively.

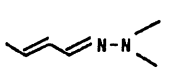
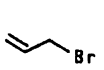
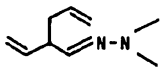
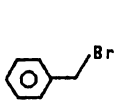
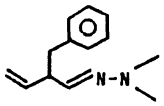
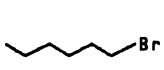
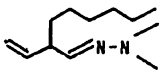
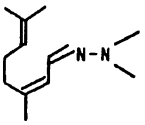
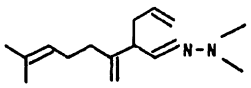
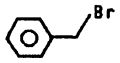
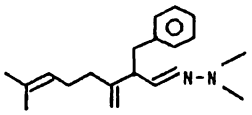
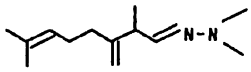
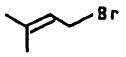
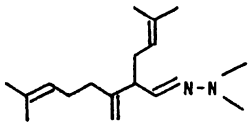
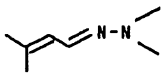
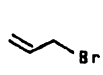
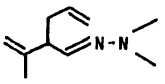
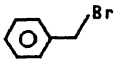
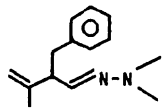
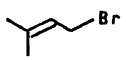
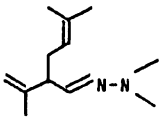
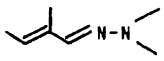
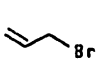
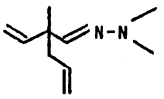
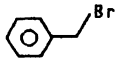
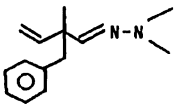
Using this reaction, the synthesis of 2,5,9-trimethyl-2-vinyl-4,8-decadienal (**4**), which has been found as a component of an essential oil of a beefsteak plant, was conducted (Scheme 5). 2-Methyl-2-butenal (**5**) reacted with *N,N*-dimethylhydrazine to give the hydrazone **6** in 81% yield. To the THF solution of LDA at −5 °C, was added an equimolar amount of the hydrazone **6**, followed by 1-bromo-3,7-dimethyl-2,6-octadiene to provide the corresponding hydrazone **7** in 52% yield, which was readily converted to the desired aldehyde **4** after hydrolysis in 72% yield.

In conclusion, it is noted that α,β-unsaturated aldehyde dimethylhydrazones **1** was found to be alkylated regioselectively at the α-position by various alkyl halides accompanied by double bond migration to give α-alkyl-β,γ-unsaturated aldehyde dimethylhydrazones **3** in good yields. This reaction was found to occur by deprotonation from a less hindered γ-carbon exclusively by a base.

Experimental

General. Infrared spectra (IR) were recorded on a Hitachi 260-10 Infrared Spectrophotometer as thin films and the frequencies are given in reciprocal centimeters. ^{1}H NMR spectra were determined on a Hitachi R-600 FT-NMR Spectrometer (60 MHz) or on a JEOL GX-400 FT-NMR Spectrometer (400 MHz). NMR spectra were taken in $CDCl_3$ and recorded in parts per million (ppm, δ) downfield from internal tetramethylsilane. Coupling constants are in Hz and splitting pattern abbreviations are s, singlet; d, doublet; t, triplet; q, quartet; m, unresolved multiplet; br, broad. Analytical gas chromatography (GC) was performed on a Yanagimoto G-8 instrument using a stainless column (3 mm i.d. ×2 m) packed with silicone gum SE-30 (3% on chromosorb W) and a Shimadzu GC-14A instrument equipped with a Shimadzu capillary column (CBP1-W12-100, 0.53 mm i.d. ×12 m). Mass spectra (MS) were measured on a Hitachi RM-50 GC-MS instrument or on a Hitachi M-80B GC-MS instrument, and are reported as *m/z* (relative intensity). Column chromatography was performed on Merck silica gel 60 (230—400 mesh) and thin-layer chro-

Table 2. Reaction of α,β-Unsaturated Aldehyde Dimethylhydrazones with Alkyl Halides

Run	Hydrazone	Alkyl Halide	Product[a)]	Yield/%[b)]
1				53
2				63
3				69
4				46
5				40
6		MeI		46
7				43
8				64
9				68
10				65
11				56
12				66

a) All compounds were identified by their IR, ^{1}H NMR, ^{13}C NMR, and mass spectra.
b) Isolated yield.

matography (TLC) was performed on Merck silica gel 60 plate F_{254}, eluting with various portion of hexane–ethyl acetate mixture.

Materials. Tetrahydrofuran (THF) was dried and deoxygenated by distillation from potassium-benzophenone under argon atmosphere just before use. Diethyl ether was also freshly distilled just before use. Benzene was purified by distillation over $CaCl_2$. Diisopropylamine was dried by distillation from potassium hydroxide. Butyllithium in hexane was purchased from Nacalai Tesque as a ca. 1.6 M (1 M=1

mol dm^{-3}) hexane solution and was titrated with 2-butanol using *o*-phenanthroline as an indicator just before use. The following organic compounds were commercial products of the highest available purity; crotonaldehyde, citral, 3-methyl-2-butenal, 2-methyl-2-butenal, cinnamaldehyde, benzaldehyde, *N*,*N*-dimethylhydrazine, trifluoroacetic acid, iodomethane, 3-bromo-1-propene, benzyl bromide, and 1-bromohexane. 1-Bromo-3-methyl-2-butene was purified by distillation. 1-Bromo-3,7-dimethyl-2,6-octadiene was prepared from geraniol according to the method in the literature.[12]

General Procedure for the Preparation of α,β-Unsaturated Aldehyde Dimethylhydrazones 1. In a flask equipped with a trap to remove water, the mixture of aldehyde (50 mmol), *N*,*N*-dimethylhydrazine (6 ml, 80 mmol), trifluoroacetic acid (0.05 ml) and benzene 20 ml was added. The mixture was heated under reflux for 4 h, and then cooled to room temperature. The solution was extracted with diethyl ether (3×20 ml), and the organic layer was washed with saturated brine, dried ($MgSO_4$) and filtered. The filtrate was concentrated with a rotary evaporator. The residue was purified by distillation under reduced pressure.

Crotonaldehyde Dimethylhydrazone. ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.81 (3H, d, J=6.7 Hz, CH_3), 2.81 (6H, s, $N(CH_3)_2$), 5.82 (1H, dq, J=15.3 and 6.7 Hz, CH_3CH=), 6.20 (1H, dd, J=9.2 and 15.3 Hz, =CH–), 7.01 (1H, d, J=9.2 Hz, –CH=N); IR (neat): 2850, 1560, 1470, 1440, 1265, 1135, 1020, 965, 820 cm^{-1}; MS m/z 112 (M^+); bp 162 °C/760 Torr (1 Torr=133.322 Pa). Anal. ($C_6H_{12}N_2$) C, H, N.

Citral Dimethylhydrazone. ^{1}H NMR ($CDCl_3$) δ= 1.62 (3H, s, CH_3), 1.70 (3H, s, CH_3), 1.83 (3H, d, J=0.6 Hz, CH_3), 2.08—2.34 (4H, m, CH_2×2), 2.86 (6H, s, $N(CH_3)_2$), 5.16 (1H, m, =CH–), 6.02 (1H, d, J=10 Hz, =CH–), 7.25 (1H, d, J=10 Hz, –CH=N); MS m/z 194 (M^+); bp 94 °C/1 Torr. Anal. ($C_{12}H_{22}N_2$) C, H, N.

3-Methyl-2-butenal Dimethylhydrazone. ^{1}H NMR ($CDCl_3$) δ=1.82 (3H, s, CH_3), 1.85 (3H, s, CH_3), 2.85 (6H, s, $N(CH_3)_2$), 6.02 (1H, d, J=9.5 Hz, =CH–), 7.26 (1H, d, J=9.5 Hz, –CH=N); MS m/z 126 (M^+); bp 94 °C/30 Torr. Anal. ($C_7H_{14}N_2$) C, H, N.

2-Methyl-2-butenal Dimethylhydrazone (6). ^{1}H NMR ($CDCl_3$) δ=1.78 (3H, s, CH_3), 1.85 (3H, s, CH_3), 2.80 (6H, s, $N(CH_3)_2$), 5.67 (1H, m, =CH–), 7.07 (1H, s, –CH=N); IR (neat) 2860, 1585, 1480, 1455, 1270, 1145, 1025, 905, 815 cm^{-1}; MS m/z 126 (M^+). Anal. ($C_7H_{14}N_2$) C, H, N.

(*E*)-Cinnamaldehyde Dimethylhydrazone. ^{1}H NMR ($CDCl_3$) δ=2.93 (6H, s, $N(CH_3)_2$), 6.57 (1H, dd, J=9.2 and 13.0 Hz, =CH–), 6.85 (1H, d, J=13.0 Hz, –CH=), 7.05—7.50 (6H, m, C_6H_5 and –CH=N); IR (neat) 2870, 1550, 1465, 1360, 1270, 1130, 1025, 960, 745, 690 cm^{-1}; MS m/z 174 (M^+); bp 125 °C/24 Torr. Anal. ($C_{11}H_{14}N_2$) C, H, N.

Benzaldehyde Dimethylhydrazone. ^{1}H NMR ($CDCl_3$) δ=2.96 (6H, s, $N(CH_3)_2$), 7.24 (1H, s, =CH–), 7.18—7.72 (5H, m, C_6H_5); IR (neat) 2880, 1600, 1575, 1480, 1455, 1045, 760, 700 cm^{-1}; MS m/z 148 (M^+); bp 129 °C/18 Torr. Anal. ($C_9H_{12}N_2$) C, H, N.

General Procedure for the Alkylation of α,β-Unsaturated Aldehyde Dimethylhydrazones 1. To a THF (10 ml) solution of diisopropylamine (7.3 mmol, 1.0 ml) in a dried reaction flask was added dropwise with stirring butyllithium in hexane (7.1 mmol) at −5 °C under argon atmosphere. After standing for 0.5 h, the hydrazone **1** (6.9 mmol) was added at −5 °C. After 1 h, an alkyl halide (7.1 mmol) was added at −5 °C and the mixture was stirred for 15 h at room temperature. The reaction mixture was extracted with ethyl acetate (3×20 ml) and the organic layer was washed with saturated brine, dried ($MgSO_4$) and filtered. The filtrate was concentrated with a rotary evaporator. The residue was purified by silica-gel column chromatography.

2-Vinyl-4-pentenal Dimethylhydrazone. ^{1}H NMR ($CDCl_3$) δ=2.33 (2H, t, J=3.5 Hz, CH_2), 2.74 (6H, s, $N(CH_3)_2$), 3.00 (1H, m, CH), 4.83—5.26 (4H, m, $=CH_2$×2), 5.96—6.20 (2H, m, –CH=×2), 6.49 (1H, d, J=6.2 Hz, –CH=N); IR (neat) 3075, 2840, 1635, 1465, 1440, 1250, 1135, 1030, 990, 910 cm^{-1}; MS m/z 152 (M^+). Anal. ($C_9H_{16}N_2$) C, H, N.

2-Benzyl-3-butenal Dimethylhydrazone. ^{1}H NMR ($CDCl_3$) δ=2.72 (6H, s, $N(H_3)_2$), 2.90 (2H, m, CH_2), 3.30 (1H, m, CH), 4.80—5.20 (2H, m, $=CH_2$), 5.57—6.18 (1H, m, –CH=), 6.53 (1H, d, J=6.0 Hz, –CH=N), 7.21 (5H, s, C_6H_5); IR (neat) 3040, 1645, 1610, 1475, 1260, 1140, 1035, 1000, 910, 750, 700 cm^{-1}; MS m/z 202 (M^+). Anal. ($C_{13}H_{18}N_2$) C, H, N.

2-Hexyl-3-butenal Dimethylhydrazone. ^{1}H NMR ($CDCl_3$) δ=0.88 (3H, t, J=4.3 Hz, CH_3), 1.09—1.70 (10H, m, CH_2×5), 2.74 (6H, s, $N(CH_3)_2$), 2.95 (1H, m, CH), 4.88—5.28 (2H, m, $=CH_2$), 5.63—6.15 (1H, m, –CH=), 6.50 (1H, d, J=6.2 Hz, –CH=N); IR (neat) 3090, 2850, 1640, 1465, 1260, 1140, 1015, 910 cm^{-1}; MS m/z 196 (M^+). Anal. ($C_{12}H_{24}N_2$) C, H, N.

2-Allyl-7-methyl-3-methylene-6-octenal Dimethylhydrazone. ^{1}H NMR ($CDCl_3$) δ=1.62 (3H, s, CH_3), 1.69 (3H, s, CH_3), 2.00—2.20 (4H, m, CH_2CH_2), 2.40 (2H, t, J=7.0 Hz, CH_2), 2.74 (6H, s, $N(CH_3)_2$), 2.94 (1H, m, CH), 4.80—5.30 (5H, m, $=CH_2$×2 and –CH=), 5.43—6.23 (1H, m, –C<u>H</u>=CH_2), 6.48 (1H, d, J=6.0 Hz, –CH=N); IR (neat) 3090, 2860, 1640, 1440, 1380, 1260, 1140, 1030, 910, 890 cm^{-1}; MS m/z 234 (M^+). Anal. ($C_{15}H_{26}N_2$) C, H, N.

2-Benzyl-7-methyl-3-methylene-6-octenal Dimethylhydrazone. ^{1}H NMR ($CDCl_3$) δ=1.62 (3H, s, CH_3), 1.68 (3H, s, CH_3), 1.98—2.22 (4H, m, CH_2CH_2), 2.68 (6H, s, $N(CH_3)_2$), 2.94 (2H, d, J=8.9 Hz, CH_2), 3.20 (1H, m, CH), 4.88 (2H, s, $=CH_2$), 5.08 (1H, m, =CH–), 6.52 (1H, d, J=6.0 Hz, –CH=N), 7.20 (5H, s, C_6H_5); IR (neat) 2930, 1645, 1450, 1380, 1260, 1145, 1040, 890, 825, 700 cm^{-1}; MS m/z 284 (M^+). Anal. ($C_{19}H_{28}N_2$) C, H, N.

2,7-Dimethyl-3-methylene-6-octenal Dimethylhydrazone. ^{1}H NMR ($CDCl_3$) δ=1.21 (3H, d, J=7.0 Hz, $CHC\underline{H}_3$), 1.63 (3H, s, CH_3), 1.70 (3H, s, CH_3), 2.00—2.28 (4H, m, CH_2CH_2), 2.74 (6H, s, $N(CH_3)_2$), 3.05 (1H, m, CH), 4.87 (2H, s, $=CH_2$), 5.14 (1H, m, =CH–), 6.48 (1H, d, –CH=N); MS m/z 208 (M^+). Anal. ($C_{13}H_{24}N_2$) C, H, N.

2-(3-Methyl-2-butenyl)-7-methyl-3-methylene-6-octenal Dimethylhydrazone. ^{1}H NMR ($CDCl_3$) δ=1.62 (6H, s, CH_3×2), 1.68 (6H, s, CH_3×2), 2.00—2.24 (4H, m, CH_2CH_2), 2.32 (2H, t, J=7.0 Hz, CH_2), 2.72 (6H, s, $N(CH_3)_2$), 2.86 (1H, m, CH), 4.86 (2H, s, $=CH_2$), 4.94—5.31 (2H, m, =CH–×2), 6.48 (1H, d, J=6.0 Hz, –CH=N); MS m/z 262 (M^+). Anal. ($C_{17}H_{30}N_2$) C, H, N.

2-Isopropenyl-4-pentenal Dimethylhydrazone. ^{1}H NMR ($CDCl_3$) δ=1.75 (3H, s, CH_3), 2.40 (2H, t, J=7.0 Hz, CH_2), 2.75 (6H, s, $N(CH_3)_2$), 3.01 (1H, m, CH), 4.77—5.27

(4H, m, $=CH_2\times2$), 5.45—6.17 (1H, m, =CH–), 6.51 (1H, d, J=6.0 Hz, –CH=N); IR (neat) 3090, 2920, 1645, 1475, 1445, 1375, 1250, 1140, 1030, 890 cm^{-1}; MS m/z 166 (M^+). Anal. ($C_{10}H_{18}N_2$) C, H, N.

2-Benzyl-3-methyl-3-butenal Dimethylhydrazone. ^1H NMR ($CDCl_3$) δ=1.73 (3H, s, CH_3), 2.70 (6H, s, $N(CH_3)_2$), 2.80—3.40 (3H, m, CH and CH_2), 4.78 (2H, s, $=CH_2$), 6.55 (1H, d, J=6.0 Hz, –CH=N), 7.20 (5H, s, C_6H_5); IR (neat) 2950, 1645, 1450, 1250, 1140, 1030, 890, 695 cm^{-1}; MS m/z 216 (M^+). Anal. ($C_{14}H_{20}N_2$) C, H, N.

2-Isopropenyl-5-methyl-4-hexenal Dimethylhydrazone. ^1H NMR ($CDCl_3$) δ=1.58—1.83 (9H, m, $CH_3\times3$), 2.32 (2H, t, J=7.0 Hz, CH_2), 2.73 (6H, s, $N(CH_3)_2$), 2.92 (1H, m, CH), 4.81 (2H, s, $=CH_2$), 4.95—5.30 (1H, m, –CH=), 6.51 (1H, d, J=6.0 Hz, –CH=N); MS m/z 194 (M^+). Anal. ($C_{12}H_{22}N_2$) C, H, N.

2-Methyl-2-vinyl-4-pentenal Dimethylhydrazone. ^1H NMR ($CDCl_3$) δ=1.16 (3H, s, CH_3), 2.32 (2H, d, J= 7.2 Hz, CH_2), 2.72 (6H, s, $N(CH_3)_2$), 4.80—5.25 (4H, m, $=CH_2\times2$), 5.45—6.10 (2H, m, $-CH_2\times2$), 6.51 (1H, s, –CH=N); IR (neat) 3960, 1645, 1475, 1450, 1260, 1145, 1010, 910, 840 cm^{-1}; MS m/z 166 (M^+). Anal. ($C_{10}H_{18}N_2$) C, H, N.

2-Benzyl-2-methyl-3-butenal Dimethylhydrazone. ^1H NMR ($CDCl_3$) δ=1.15 (3H, s, CH_3), 2.73 (6H, s, $N(CH_3)_2$), 2.86 (2H, s, CH_2), 4.75—6.20 (3H, m, $=CH_2$), 6.03 (1H, dd, J=11.0 and 17.0 Hz, –CH=), 6.53 (1H, s, –CH=N), 7.20 (5H, s, C_6H_5); IR (neat) 2960, 1640, 1605, 1470, 1450, 1250, 1140, 1010, 910, 700 cm^{-1}; MS m/z 216 (M^+). Anal. ($C_{14}H_{20}N_2$) C, H, N.

2,5,9-Trimethyl-2-vinyl-4,8-decadienal Dimethylhydrazone (7). ^1H NMR ($CDCl_3$) δ=1.15 (3H, s, CH_3), 1.61 (6H, s, $CH_3\times2$), 1.70 (3H, s, CH_3), 1.95—2.38 (6H, m, $CH_2\times3$), 2.71 (6H, s, $N(CH_3)_2$), 4.80—5.35 (4H, m, $=CH_2$ and –CH=×2), 5.99 (1H, dd, J=9.1 and 18.2 Hz, $-CH=CH_2$), 6.53 (1H, s, –CH=N); IR (neat) 2920, 1445, 1375, 1250, 1140, 1015, 910, 835 cm^{-1}; MS m/z 262 (M^+). Anal. ($C_{17}H_{30}N_2$) C, H, N.

2,5,9-Trimethyl-2-vinyl-4,8-decadienal (4). To a mixture of THF (16 ml) and 1 M (1 M=1 mol dm^{-3}) HCl aq (16 ml) was added the hydrazone **7** (0.863 g, 3.19 mmol), and the mixture was stirred for 10 h at room temperature. Then the reaction mixture was extracted with diethyl ether (3×10 ml). The organic layer was washed with 1 M NaOH aq and then saturated brine, dried ($MgSO_4$) and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (hexane : ethyl acetate=9 : 1) to give the aldehyde **4** (0.50 g, 72% yield): ^1H NMR ($CDCl_3$) δ=1.15 (3H, s, CH_3), 1.59 (3H, s, CH_3), 1.60 (3H, s, CH_3), 1.67 (3H, s, CH_3), 2.00—2.07 (4H, m, CH_2CH_2), 2.30 (1H, dd, J=7.3 and 14.0 Hz, CHH), 2.32 (1H, dd, J=7.3 and 14.0 Hz, CHH), 5.03—5.07 (2H, m, –CH=×2), 5.12 (1H, d, J=18.3 Hz, =CHH), 5.26 (1H, d, J=11.0 Hz, =CHH), 5.82 (1H, dd, J=11.0 and 18.3 Hz, CH_2=CH–), 9.42 (1H, s, CHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ=16.2, 17.69, 17.73, 25.7, 26.5, 34.0, 39.9, 53.3, 116.5, 118.3, 124.1, 131.5, 138.4, 138.7, 202.9; IR (neat) 2920, 1730, 1635, 1455, 1380, 1000, 920 cm^{-1}; MS m/z (rel intensity): 220 (M^+, 5), 81 (73), 69 (100). Anal. ($C_{15}H_{24}O$) C, H.

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