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Lewis Acid Mediated Synthesis of 2-Alkenenitriles Using *C*,*N*-Bis(trimethylsilyl)ketenimine and Carbonyl Compounds

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2-Substituted 2-alkenenitriles are obtained in the condensation reaction of carbonyl compounds with *C*,*N*-bis(trimethylsilyl)ketenimine in the presence of Lewis acid. The combination of tris(trimethylsilyl)ketenimine and aldehydes results in the high *E*-selective formation of 2-trimethylsilyl-2-alkenenitriles. Among some Lewis acids, magnesium bromide gives the best *E*-selectivity in the formation of 2-trimethylsilyl-2-undecenenitrile. Stereospecific protodesilylation of 2-trimethylsilyl-2-alkenenitriles in an aqueous methanol solution of potassium fluoride accomplishes a new route to (*Z*)-2-alkenenitriles from aldehydes.

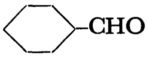
2-Alkenenitriles have been prepared by the carbonyl olefination with various cyanated reagents under the basic conditions.[1—15] Of these reactions, the silicon methods suffers from the lack of the stereoselectivity in spite of the higher reactivity.[13,14] Introduction of bulky substituents on the silicon atom and exchange of counter cation, lithium to magnesium, are reported in order to circumvent the deficiency.[15] On the other hand, we reported a stereoselective synthesis of methyl 2-alkenoate in the reaction of *C*,*O*-bis(trimethylsilyl)ketene acetal with aldehydes under the acidic conditions.[16] The bulky trimethylsilyl group on the carbon atom plays an important role to control the stereochemical course in that reaction.

Although it is widely accepted that trimethylsilyl enol ethers behave as an effective C nucleophile in the presence of Lewis acid,[17] there are very few examples[18] of *N*-trimethylsilylketenimine derivatives as an equivalent of *α*-cyano carbanions. Therefore, it is interesting to reveal a C nucleophilic character of *N*-trimethylsilylketenimine derivatives and to explore the stereoselective route to **3** by use of the trimethylsilyl group as a key stereocontrolling factor. A recent report[18] prompts us to publish our results of the carbonyl olefination using *C*,*N*-bis(trimethylsilyl)ketenimine (**1**) and Lewis acid, in which 2-substituted 2-alkenenitriles (**4**, **5**, and **6**) are produced in one-pot reactions and 2-alkenenitriles (**3**) are formed *Z*-selectively by the subsequent protodesilylation of **4**.

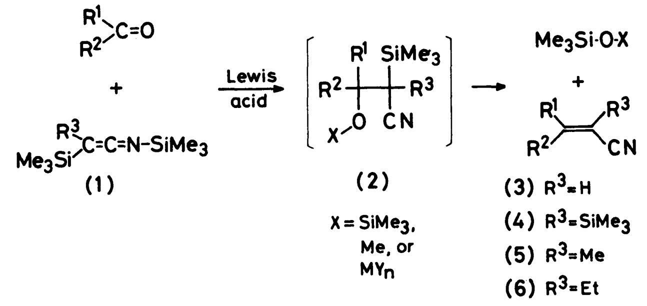
Results and Discussion

Tris(trimethylsilyl)ketenimine (**1a**) reacted with an equivalent of aldehydes, acetals, and 2-octanone in the presence of an equivalent of $BF_3 \cdot Et_2O$ to give 2-trimethylsilyl-2-alkenenitriles (**4**) in good yields as shown in Table 1. The discrimination of both geometrical isomers in **4** was based on the chemical shift of the vinyl proton in the ^1H NMR spectra[19] and the ratio of the both isomers was determined by HPLC analyses. The reaction is susceptible to the steric environment around the electrophilic carbon, because **1a** is relatively hindered as a nucleophile. Acetal showed lower *E*-selectivity than the corresponding aldehydes (entries 5 and 6 in Table 1) and 2-octanone gave poor result in the yield and the stereoselectivity (entry 7 in Table 1). On the contrary, bis(trimethylsilyl)acetonitrile anion (**7**) derived from bis(trimethylsilyl)acetonitrile could not react with benzaldehyde to give **4c**. Therefore, **1a** is important as a synthon of **7**.

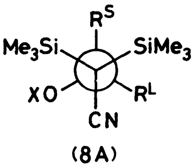
Table 1. Carbonyl olefination of **1a** by the assist of $BF_3 \cdot Et_2O$

Entry	Carbonyl compound	4 Yield/% a)	4 *E*/*Z* b)
1	Nonanal	79	96/4
2	Heptanal	67	96/4
3	PhCHO	99	100/0 c)
4		64	95/5
5	$CH_3(CH_2)_7CH(OMe)_2$	90	81/19
6	$PhCH(OMe)_2$	89	98/2 c)
7	2-Octanone	45	66/34

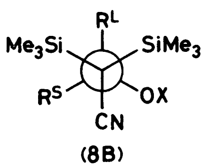
a) Isolated yields. b) Determined by HPLC (UV 233 nm, porous silica, hexane/*i*-PrOH=150/1). c) Determined by HPLC (UV 254 nm, porous silica, hexane/*i*-PrOH=150/1).



Scheme. 1



(8A)



(8B)

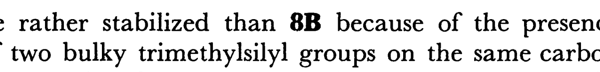
The present condensation proceeds through an intermediate such as aldol type adduct **2**, which is transformed to product **4** by the subsequent *β*-elimination of Me_3SiOX. The formation of both isomers (*E*)- and (*Z*)-**4** should be attributed to staggered conformers **8A** and **8B** because the *anti* elimination of *β*-hydroxy trimethylsilyl derivatives is well established[16,20] and the interconversion between *E* and *Z* isomers is not observed under the reaction conditions. Conformer **8A** would

Table 2. The effect of lewis acid in the condensation of **1a** with nonanal

Lewis acid	Solvent	Condition	**4a** Yield/%[a]	**4a** E/Z[b]
$BF_3 \cdot Et_2O$	CH_2Cl_2	−78 °C, 0.5 h ⟶ r.t. 3 h	79	96/4
$ZnCl_2$	$C_6H_6/Et_2O = 5/8$	r.t. 14 h	73	98/2
$MgBr_2$	$C_6H_6/Et_2O = 5/12$	r.t. 2 h ⟶ reflux 2.5 h	83	99/1
$TiCl_4$	CH_2Cl_2	−78 °C, 1 h ⟶ r.t. 2 h	47	99/1
$SnCl_4$	CH_2Cl_2	−78 °C, 2 h ⟶ r.t. 24 h	0	—
$MgCl_2$	$C_6H_6/Et_2O = 5/12$	r.t. 24 h	0	—

a) Isolated yields. b) Determined by HPLC (UV 233 nm, porous silica, hexane/*i*-PrOH=150/1).

be rather stabilized than **8B** because of the presence of two bulky trimethylsilyl groups on the same carbon atom. Therefore, the observed stereoselectivity can be attributed to the predominant presence of **8A** or much faster *β*-elimination in **8A** than in **8B**. Regardless of the manner (*syn* or *anti*) of Me_3SiOX elimination, respective conformer **8A** and **8B** corresponds specifically to (*E*)-**4** and (*Z*)-**4**. The thermodynamically controlled process would result in the greater stereochemical selectivity. Thus, several kinds of Lewis acid were compared in order to improve the stereoselectivity in the condensation of **1a** with nonanal. The results are summarized in Table 2. Excellent *E*-selectivity ($E/Z=99/1$) was attained by the assist of magnesium bromide. The fruitful result obtained by magnesium bromide makes possible the application of this type condensation to more unstable aldehydes. For example, a reaction of 2-acetoxydecanal with **1a** gives **9** in 60% yield by the assist of magnesium bromide (Eq. 1). The structure of **9** might be convertible to furan and 2-buten-4-olide derivatives.



(9)

Protodesilylation of (*E*)-**4** in an aqueous methanol solution of potassium fluoride gave (*Z*)-**3** selectively. Interconversion of (*Z*)-**3** to (*E*)-**3** was not detected at all in the reaction conditions. The stereospecificity of the reaction is well explained by Koenig and Webers' mechanism.[21] Although a similar protodesilylation of vinylsilane was carried out by hydroiodic acid,[22] iodine and water,[22] or dry hydrogen chloride,[23] potassium fluoride is suitable for stereospecific protodesilylation of **4**. Since it is difficult to form (*Z*)-**3** selectively by Peterson type olefination of aldehydes with trimethylsilylacetonitrile anion,[14,15] the present two-steps method composed of **1a** and aldehydes provides a facile *Z*-selective route to 2-alkenenitriles (**3**).

A similar C-nucleophilicity of **1b** (R^3=Me) and **1c** (R^3=Et) was observed in the condensation with aldehydes. The reaction proceeded smoothly to give trisubstituted olefins **5** or **6** as a mixture of two geometrical isomers at room temperature in the presence of magnesium bromide. Even enolizable aldehydes such as nonanal and cyclohexanecarbaldehyde gave good results under the present conditions. Since *C*,*N*-bis(trimethylsilyl)ketenimines are easily prepared from *α*-unsubstituted nitriles,[24] this method could exploit a new general route to 2-substituted alkenenitriles. Experimental simplicity and mildness of conditions make the present method highly advantageous for the direct synthesis of 2-alkenenitriles **5** and **6** from aldehydes. In contrast, the reported methods include the reactions under strong basic conditions.[1—15] Although the stereochemistry could not be controlled in the formation of **5** and **6**, this problem might be solved by the kinetic control in the formation of the posturated intermediate **2**.

Experimental

All reactions were carried out under an atmosphere of argon. The IR spectra in carbon tetrachloride were recorded on a JASCO IR-403G. A JEOL C-60HL instrument was used to record the ^1H NMR spectra in carbon tetrachloride using tetramethylsilane as the internal standard. HPLC analyses were done on a JASCO TWINKLE equipped with a Model VL-611 injector and UVIDEC-100-II spectrophotometer. GLC analyses were performed on a Shimadzu GC-4BPT with TCD and a 2 m×3 mm i.d. column of 10% PEG-2M on Uniport B. Preparative TLC was carried out on precoated silica gel F-254 plates. Ketenimines, **1a**,[25] **1b**,[24] and **1c**[24] were prepared according to the literature. Magnesium bromide was prepared from 1,2-dibromoethane and magnesium in ether.

Condensation of **1a** *with Carbonyl Compounds in the Presence of* $BF_3 \cdot Et_2O$. *2-Trimethylsilyl-2-undecenenitrile* (**4a**): A solution of **1a** (1.92 g, 7.47 mmol) in 15 ml of CH_2Cl_2 was added to a solution of nonanal (0.59 g, 4.16 mmol) and $BF_3 \cdot Et_2O$ (0.87 g, 6.20 mmol) in 20 ml of dry CH_2Cl_2 at −78 °C. The mixture was stirred for 30 min at −78 °C, gradually warmed to 20 °C, and stirred at the same temperature for 3 h. After quenching the mixture with saturated aqueous Na_2CO_3 (10 ml), the phases were separated and the aqueous layer was extracted with ethyl acetate (20 ml×4). The combined organic portions were washed with saturated brine (20 ml×2), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual oil was purified by column chromatography on silica gel using a mixed solvent (hexane/ethyl acetate=7/1) as an eluent and Kugelrohr distillation (65—70 °C/0.2 mmHg) [1 mmHg=133.322 Pa] to give 0.79 g (79%) of **4a** (E/Z=96/4) as a colorless liquid. Found: C, 70.58; H, 11.66; N, 5.95%. Calcd for $C_{14}H_{27}NSi$: C, 70.80; H, 11.46; N, 5.90%. Both isomers of **4a** were isolated, respectively, by a preparative TLC with hexane/etyl acetate (15/1).

(*E*)-**4a**: IR 2200 ($\nu_{C\equiv N}$), 1595 ($\nu_{C=C}$), and 1252 cm^{-1}

($\delta_{\mathrm{S\ Si-C}}$). ^{1}H NMR δ 0.20 (s, 9H, $\mathrm{Si{-}C\underline{H}_3}$), 0.85 (t, J=4.7 Hz, 3H, $\mathrm{CH_2C\underline{H}_3}$), 1.1—1.5 (broad m, 12H), 2.39 (q, J=7.0 Hz, 2H, $\mathrm{C{=}C{-}C\underline{H}_2}$), and 6.35 (t, J=6.8 Hz, 1H, $\mathrm{C{=}C\underline{H}}$).

(*Z*)-**4a**: IR 2200 ($\nu_{\mathrm{C\equiv N}}$), 1592 ($\nu_{\mathrm{C=C}}$), and 1253 cm^{-1} ($\delta_{\mathrm{S\ Si-C}}$). ^{1}H NMR δ 0.30 (s, 9H, $\mathrm{Si{-}C\underline{H}_3}$), 0.90 (t, J=4.7 Hz, 3H, $\mathrm{CH_2C\underline{H}_3}$), 1.1—1.7 (broad m, 12H), 2.26 (q, J=7.3 Hz, 2H, $\mathrm{C{=}C{-}C\underline{H}_2}$), and 6.99 (t, J=7.8 Hz, 1H, $\mathrm{C{=}C\underline{H}}$).

4a: An analogous treatment of **1a** (0.502 g, 1.95 mmol) with 1,1-dimethoxynonane (0.198 g, 1.05 mmol) and $\mathrm{BF_3{\cdot}Et_2O}$ (0.220 g, 1.55 mmol) in $\mathrm{CH_2Cl_2}$ (10 ml) gave **4a** (0.225 g, 90%, *E*/*Z*=81/19).

2-Trimethylsilyl-2-nonenenitrile (4b): An analogous treatment of **1a** (0.932 g, 3.61 mmol) with heptanal (0.182 g, 1.60 mmol) and $\mathrm{BF_3{\cdot}Et_2O}$ (0.34 g, 2.40 mmol) in $\mathrm{CH_2Cl_2}$ (15 ml) gave **4b** as a colorless liquid (bp 53 °C/0.15 mmHg, 0.224 g, 67%, *E*/*Z*=96/4). Found: C, 68.70; H, 10.96; N, 6.70% Calcd for $\mathrm{C_{12}H_{23}NSi}$: C, 68.83; H, 11.07; N, 6.69%.

(*E*)-**4b**: IR 2200 ($\nu_{\mathrm{C\equiv N}}$), 1595 ($\nu_{\mathrm{C=C}}$), and 1253 cm^{-1} ($\delta_{\mathrm{S\ Si-C}}$). ^{1}H NMR δ 0.23 (s, 9H, $\mathrm{Si{-}C\underline{H}_3}$), 0.91 (t, J=5.3 Hz, 3H, $\mathrm{CH_2C\underline{H}_3}$), 1.1—1.4 (broad m, 8H), 2.44 (q, J=7.5 Hz, 2H, $\mathrm{C{=}C{-}C\underline{H}_2}$), and 6.45 (t, J=7.5 Hz, 1H, $\mathrm{C{=}C\underline{H}}$).

(*Z*)-**4b**: IR 2200 ($\nu_{\mathrm{C\equiv N}}$), 1592 ($\nu_{\mathrm{C=C}}$), and 1252 cm^{-1} ($\delta_{\mathrm{S\ Si-C}}$). ^{1}H NMR δ 0.29 (s, 9H, $\mathrm{Si{-}C\underline{H}_3}$), 0.92 (t, J=5.3 Hz, 3H, $\mathrm{CH_2C\underline{H}_3}$), 1.1—1.6 (broad m, 8H), 2.31 (q, J=7.4 Hz, 2H, $\mathrm{C{=}C{-}C\underline{H}_2}$), and 7.09 (t, J=7.4 Hz, 1H, $\mathrm{C{=}C\underline{H}}$).

3-Phenyl-2-trimethylsilylpropenenitrile (4c): An analogous treatment of **1a** (0.981 g, 3.80 mmol) with benzaldehyde (0.209 g, 1.97 mmol) and $\mathrm{BF_3{\cdot}Et_2O}$ (0.400 g, 2.83 mmol) in $\mathrm{CH_2Cl_2}$ (15 ml) gave **4c** as a colorless liquid (bp 88 °C/0.5 mmHg, 0.398 g, 99%, *E*/*Z*=100/0). Found: C, 71.64; H, 7.72; N, 7.05%. Calcd for $\mathrm{C_{12}H_{15}NSi}$: C, 71.58; H, 7.51; N. 6.96%.

(*E*)-**4c**: IR 2200 ($\nu_{\mathrm{C\equiv N}}$), 1590 ($\nu_{\mathrm{C=C}}$), and 1254 cm^{-1} ($\delta_{\mathrm{S\ Si-C}}$). ^{1}H NMR δ 0.32 (s, 9H, $\mathrm{Si{-}C\underline{H}_3}$), 7.02 (s, 1H, $\mathrm{C{=}C\underline{H}}$), and 7.2—8.0 (m, 5H, $\mathrm{C_6\underline{H}_5}$).

4c: An analogous treatment of **1a** (0.861 g, 3.34 mmol) with dimethoxyphenylmethane (0.326 g, 2.14 mmol) and $\mathrm{BF_3{\cdot}Et_2O}$ (0.390 g, 2.75 mmol) in $\mathrm{CH_2Cl_2}$ (17 ml) gave **4c** (0.382 g, 89%, *E*/*Z*=98/2).

3-Cyclohexyl-2-trimethylsilylpropenenitrile (4d): An analogous treatment of **1a** (0.987 g, 3.80 mmol) with cyclohexanecarbaldehyde (0.204 g, 1.82 mmol) and $\mathrm{BF_3{\cdot}Et_2O}$ (0.390 g, 2.80 mmol) in $\mathrm{CH_2Cl_2}$ (14 ml) gave **4d** as a colorless liquid (bp 57 °C/0.2 mmHg, 0.241 g, 64%, *E*/*Z*=95/5). Found: C, 69.48; H, 10.26; N, 6.78%. Calcd for $\mathrm{C_{12}H_{21}NSi}$: C, 69.50; H, 10.21; N, 6.75%.

(*E*)-**4d**: mp 42—42.5 °C. IR 2200 ($\nu_{\mathrm{C\equiv N}}$), 1595 ($\nu_{\mathrm{C=C}}$), and 1250 cm^{-1} ($\delta_{\mathrm{S\ Si-C}}$). ^{1}H NMR δ 0.21 (s, 9H, $\mathrm{Si{-}C\underline{H}_3}$), 0.7—2.0 (m, 10H), 2.3—3.0 (m, 1H, $\mathrm{C{=}C{-}C\underline{H}}$), and 6.24 (d, J=9.1 Hz, 1H, $\mathrm{C{=}C\underline{H}}$).

(*Z*)-**4d**: IR 2200 ($\nu_{\mathrm{C\equiv N}}$), 1588 ($\nu_{\mathrm{C=C}}$), and 1252 cm^{-1} ($\delta_{\mathrm{S\ Si-C}}$). ^{1}H NMR δ 0.30 (s, 9H, $\mathrm{Si{-}C\underline{H}_3}$), 0.7—2.0 (m, 10H), 2.0—2.6 (m, 1H, $\mathrm{C{=}C{-}C\underline{H}}$), and 6.80 (d, J=10.5 Hz, 1H, $\mathrm{C{=}C\underline{H}}$).

3-Methyl-2-trimethylsilyl-2-nonenenitrile (4e): An analogous treatment of **1a** (0.977 g, 3.79 mmol) with 2-octanone (0.251 g, 1.96 mmol) and $\mathrm{BF_3{\cdot}Et_2O}$ (0.390 g, 2.75 mmol) in $\mathrm{CH_2Cl_2}$ (12 ml) gave **4e** as a colorless liquid (bp 80 °C/0.4 mmHg, 0.197 g, 45%, *E*/*Z*=66/34). Found: C, 69.72; H, 11.19; N, 6.10%. Calcd for $\mathrm{C_{13}H_{25}NSi}$: C, 69.88; H, 11.28; N, 6.27%.

(*E*)-**4e**: IR 2200 ($\nu_{\mathrm{C\equiv N}}$), 1595 ($\nu_{\mathrm{C=C}}$), and 1252 cm^{-1} ($\delta_{\mathrm{S\ Si-C}}$). ^{1}H NMR δ 0.28 (s, 9H, $\mathrm{Si{-}C\underline{H}_3}$), 0.90 (t, J=4.5 Hz, 3H, $\mathrm{CH_2C\underline{H}_3}$), 1.1—1.6 (broad m, 8H), 1.93 (s, 3H, $\mathrm{C{=}C{-}C\underline{H}_3}$), and 2.44 (broad t, J=6.9 Hz, 2H, $\mathrm{C{=}C{-}C\underline{H}_2}$).

(*Z*)-**4e**: IR 2200 ($\nu_{\mathrm{C\equiv N}}$), 1595 ($\nu_{\mathrm{C=C}}$), and 1252 cm^{-1} ($\delta_{\mathrm{S\ Si-C}}$). ^{1}H NMR δ 0.28 (s, 9H, $\mathrm{Si{-}C\underline{H}_3}$), 0.91 (t, J=4.5 Hz, 3H, $\mathrm{CH_2C\underline{H}_3}$), 1.1—1.6 (broad m, 8H), 2.13 (s, 3H, $\mathrm{C{=}C{-}C\underline{H}_3}$), and 2.24 (broad t, J=7 Hz, 2H, $\mathrm{C{=}C{-}C\underline{H}_2}$).

*Condensation of **1a** with Nonanal in the Presence of Various Lewis Acids.* Analogous reactions of **1a** with nonanal were carried out on a 3 mmol scale in the presence of $\mathrm{ZnCl_2}$, $\mathrm{MgBr_2}$, $\mathrm{TiCl_4}$, $\mathrm{SnCl_4}$, and $\mathrm{MgCl_2}$, respectively. Reaction conditions, yields of **4a**, and ratios of *E* and *Z* isomers are summarized in Table 2.

*Protodesilylation of **4** with Potassium Fluoride.* *2-Undecenenitrile (3a)*: To a solution of (*E*)-**4a** (0.263 g, 1.11 mmol) in methanol (8 ml) was added potassium fluoride (0.460 g, 7.92 mmol) and water (0.7 ml). The clear homogenized solution was stirred for 12 h at room temperature and concentrated under reduced pressure. The residue contained water was diluted with ethyl acetate (70 ml). The solution was washed with water (20 ml×2), dried ($\mathrm{MgSO_4}$), and concentrated under reduced pressure. The residual oil was purified by Kugelrohr distillation to give **3a** as a colorless liquid (bp 70 °C/0.2 mmHg,[26] 0.178 g, 97%, *E*/*Z*=0/100). Found: C, 79.86; H, 11.71; N, 8.31%. Calcd for $\mathrm{C_{11}H_{19}N}$: C, 79.94; H, 11.59; N, 8.48%. IR 2240 ($\nu_{\mathrm{C\equiv N}}$) and 1622 cm^{-1} ($\nu_{\mathrm{C=C}}$). ^{1}H NMR δ 0.89 (t, J=4.5 Hz, 3H, $\mathrm{CH_2C\underline{H}_3}$), 1.1—1.6 (broad m, 12H), 2.42 (d of t, J=7.5 and 7.5 Hz, 2H, $\mathrm{C{=}C{-}C\underline{H}_2}$), 5.21 (t of d, J=1.5 and 10.8 Hz, 1H, $\mathrm{C{=}C{<}^{\underline{H}}_{CN}}$), and 6.36 (t of d, J=7.5 and 10.8 Hz, 1H, $\mathrm{{}_{NC}{>}C{=}C{<}^{\underline{H}}}$).

A crude product obtained by a condensation reaction of **1a** (0.969 g, 3.76 mmol), nonanal (0.452 g, 3.18 mmol), and $\mathrm{MgBr_2}$ (0.759 g, 4.12 mmol) in a mixed solvent of benzene (15 ml) and diethyl ether (5 ml) was treated with potassium fluoride (1.865 g, 32.1 mmol) in methanol (20 ml) and water (1.5 ml). After an analogous treatment to (*E*)-**4a**, pure **3a** (0.457 g, 87% based on nonanal, *E*/*Z*=1/99) was obtained.

Cinnamonitrile (3c): An analogous protodesilylation of (*E*)-**4c** (0.260 g, 1.29 mmol) gave **3c**[14] (0.159 g, 95%, *E*/*Z*=0/100).

3-Cyclohexylpropenenitrile (3d): An analogous protodesilylation of (*E*)-**4d** (0.138 g, 0.665 mmol) gave **3d** as a colorless liquid (bp 110 °C/7 mmHg, 0.086 g, 96%, *E*/*Z*=0/100). Found: C, 79.82; H, 9.51; N, 10.42%. Calcd for $\mathrm{C_9H_{13}N}$: C, 79.95; H, 9.69; N, 10.36%. IR 2230 ($\nu_{\mathrm{C\equiv N}}$) and 1622 cm^{-1} ($\nu_{\mathrm{C=C}}$). ^{1}H NMR δ 0.9—2.0 (m, 10H), 2.4—2.8 (broad m, 1H, $\mathrm{C{=}C{-}C\underline{H}}$), 5.12 (d, J=11.3 Hz, 1H, $\mathrm{C{=}C{<}^{\underline{H}}_{CN}}$), and 6.18 (d of d, J=9.5 and 11.3 Hz, 1H, $\mathrm{{}_{NC}{>}C{=}C{<}^{\underline{H}}}$).

*Condensation of **1a** with 2-Acetoxydecanal in the Presence of $\mathit{MgBr_2}$.* To a solution of $\mathrm{MgBr_2}$ prepared from Mg (0.035 g, 1.44 mgatm) and 1,2-dibromoethane (0.336 g, 1.79 mmol) in benzene (3.5 ml) and diethyl ether (3.5 ml) were added 2-acetoxydecanal (0.200 g, 0.93 mmol) and **1a** (0.467 g, 1.81 mmol) successively at room temperature. The mixture was stirred for 3 h at room temperature, refluxed for 1 h, and poured into ethyl acetate (80 ml). The solution was washed with water (20 ml×2), dried ($\mathrm{MgSO_4}$), and concentrated under reduced pressure. The residual oil was treated analogously to the case of **4a** to give pure (*E*)-**9** as a colorless liquid (bp 100 °C/0.9 mmHg, 0.172 g, 60%). Found: C, 65.93; H, 10.35; N, 4.52%. Calcd for $\mathrm{C_{17}H_{31}NO_2Si}$: C, 65.97; H, 10.10; N, 4.53%. IR 2200 ($\nu_{\mathrm{C\equiv N}}$), 1750 ($\nu_{\mathrm{C=O}}$), and 1254 cm^{-1} ($\delta_{\mathrm{S\ Si-C}}$). ^{1}H NMR δ 0.26 (s, 9H, $\mathrm{Si{-}C\underline{H}_3}$), 0.90 (t, J=5.1 Hz, 3H, $\mathrm{CH_2C\underline{H}_3}$), 1.1—1.8 (m, 17H), 2.07 (s, 3H, $\mathrm{C({=}O){-}C\underline{H}_3}$), 5.46 (q, J=6.6 Hz, 1H, $\mathrm{O{-}C\underline{H}}$), and 6.31 (d, J=6.6 Hz, 1H, $\mathrm{C{=}C\underline{H}}$).

*Condensation of **1b** with Aldehydes in the Presence of $\mathit{MgBr_2}$.* *2-Methyl-2-undecenenitrile (5a)*:[27] Nonanal (0.159 g, 1.12 mmol) and **1b** (0.549 g, 2.76 mmol) were added successively into a solution of $MgBr_2$ (0.315 g, 1.70 mmol) in benzene (4 ml) and diethyl ether (9 ml) at room temperature. The mixture was stirred for 4h at the same temperature and poured into ethyl acetate (70 ml). The solution was washed with water (20 ml×2), dried ($MgSO_4$), and concentrated under reduced pressure. The residual oil was dissolved in methanol (7 ml). Acidic ammonium fluoride (0.223 g, 5.87 mmol) was added into the solution. The homogeneous solution obtained by the addition of water (0.8 ml) was stirred for 10 min at room temperature and concentrated under reduced pressure. The residue was poured into ethyl acetate (80 ml). The solution was washed with water (15 ml×2), dried ($MgSO_4$), and concentrated under reduced pressure. The residual oil was purified by column chromatography through short pad of silica gel (eluent; hexane/ethyl acetate, 5/1) and Kugelrohr distillation to give **5a** as a colorless liquid (bp 85 °C/2 mmHg, 0.196 g, 98%, $E/Z=69/31$).

(*E*)-**5a**: IR 2210 ($\nu_{C\equiv N}$) and 1640 cm^{-1} ($\nu_{C=C}$). ^{1}H NMR δ 0.88 (t, $J=5.1$ Hz, 3H, $CH_2C\underline{H}_3$), 1.0—1.5 (m, 12H), 1.83 (d, $J=1.8$ Hz, 3H, $C{=}C{-}C\underline{H}_3$), 1.9—2.4 (m, 2H, $C{=}C{-}C\underline{H}_2$), and 6.15 (q of t, $J=1.8$ and 7.5 Hz, 1H, $C{=}C\underline{H}$).

(*Z*)-**5a**: IR 2210 ($\nu_{C\equiv N}$) and 1640 cm^{-1} ($\nu_{C=C}$). ^{1}H NMR δ 0.88 (t, $J=5.1$ Hz, 3H, $CH_2C\underline{H}_3$), 1.0—1.5 (m, 12H), 1.91 (d, $J=1.8$ Hz, 3H, $C{=}C{-}C\underline{H}_3$), 2.0—2.6 (m, 2H, $C{=}C{-}C\underline{H}_2$), and 5.93 (q of t, $J=1.8$ and 7.8 Hz, 1H, $C{=}C\underline{H}$).

2-Methyl-3-phenylpropenenitrile (5c):[6,28,29] An analogous treatment of **1b** (0.861 g, 4.33 mmol) with benzaldehyde (0.136 g, 1.28 mmol) gave **5c** as a colorless liquid (0.150 g, 82%, $E/Z=38/62$).

3-Cyclohexyl-2-methylpropenenitrile (5d):[27] An analogous treatment of **1b** (0.517 g, 2.60 mmol) with cyclohexanecarbaldehyde (0.165 g, 1.47 mmol) gave **5d** as a colorless liquid (bp 135 °C/22 mmHg, 0.187 g, 86%, $E/Z=55/45$).

(*E*)-**5d**: IR 2210 ($\nu_{C\equiv N}$) and 1640 cm^{-1} ($\nu_{C=C}$). ^{1}H NMR δ 0.8—1.9 (m, 10H), 1.86 (d, $J=1.8$ Hz, 3H, $C{=}C{-}C\underline{H}_3$), 2.1—2.8 (m, 1H, $C{=}C{-}C\underline{H}$), and 6.02 (q of d, $J=1.8$ and 11.2 Hz, 1H, $C{=}C\underline{H}$).

(*Z*)-**5d**: IR 2210 ($\nu_{C\equiv N}$) and 1640 cm^{-1} ($\nu_{C=C}$). ^{1}H NMR δ 0.8—1.9 (m, 10H), 1.90 (d, $J=1.8$ Hz, 3H, $C{=}C{-}C\underline{H}_3$), 2.1—2.8 (m, 1H, $C{=}C{-}C\underline{H}$), and 5.83 (q of d, $J=1.8$ and 9.9 Hz, 1H, $C{=}C\underline{H}$).

*Condensation of **1c** with Aldehydes in the Presence of $MgBr_2$. 2-Ethyl-2-undecenenitrile (6a)*: A reaction of **1c** (0.736 g, 3.45 mmol) with nonanal (0.429 g, 3.01 mmol) in the presence of $MgBr_2$ (0.642 g, 3.39 mmol) gave **6a** as a colorless liquid analogously to the case of **5a** (bp 90 °C/0.75 mmHg, 0.358 g, 62%, $E/Z=43/57$). Found: C, 80.54; H, 12.13; N, 7.05%. Calcd for $C_{13}H_{23}N$: C, 80.76; H, 11.99; N, 7.24%. IR 2215 ($\nu_{C\equiv N}$) and 1630 cm^{-1} ($\nu_{C=C}$). ^{1}H NMR δ 0.91 (t, $J=6.0$ Hz, 3H, $CH_2C\underline{H}_3$), 1.16 (t, $J=7.5$ Hz, 3H, $CH_2C\underline{H}_3$), 1.0—1.5 (broad m, 12H), 2.23 (q, $J=7.5$ Hz, 4H, $2\times C\underline{H}_2CH_3$), 6.06 (t, $J=7.5$ Hz, $^{\underline{H}}{>}C{=}C{<}_{CN}$), and 6.21 (t, $J=7.5$ Hz, $_{\underline{H}}{>}C{=}C{<}_{CN}$).

2-Ethyl-3-phenylpropenenitrile (6c): An analogous treatment of **1c** (0.361 g, 1.69 mmol) with benzaldehyde (0.162 g, 1.53 mmol) gave **6c** as a pale yellow liquid (bp 90 °C/0.2 mmHg, 0.156 g, 65%, $E/Z=65/35$). Found: C, 83.86; H, 7.14; N, 8.69%. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91%. IR 2220 ($\nu_{C\equiv N}$) and 1620 cm^{-1} ($\nu_{C=C}$). ^{1}H NMR δ 1.26 (t, $J=7.8$ Hz, 3H, $CH_2C\underline{H}_3$), 2.41 (q, $J=7.8$ Hz, 2H, $C\underline{H}_2CH_3$), 6.79 (s, $^{\underline{H}}{>}C{=}C{<}_{CN}$), 7.02 ($_{\underline{H}}{>}C{=}C{<}_{CN}$), and 7.2—7.6 (m, $C_6\underline{H}_5$).

3-Cyclohexyl-2-ethylpropenenitrile (6d): An analogous treatment of **1c** (0.739 g, 3.46 mmol) with cyclohexanecarbaldehyde (0.326 g, 2.91 mmol) gave **6d** as a colorless liquid (bp 85 °C/0.2 mmHg, 0.276 g, 58%, $E/Z=32/68$). Found: C, 80.67; H, 10.62; N, 8.64%. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58%. IR 2210 ($\nu_{C\equiv N}$) and 1630 cm^{-1} ($\nu_{C=C}$). ^{1}H NMR δ 1.15 (t, $J=7.2$ Hz, 3H, $CH_2C\underline{H}_3$), 1.0—1.9 (m, 10H), 2.0—2.7 (m, 3H, $C{=}C{-}C\underline{H}_2$ and $C{=}C{-}C\underline{H}$), 5.84 (t of d, $J=1.2$ and 9.3 Hz, $^{\underline{H}}{>}C{=}C{<}_{CN}$) and 6.01 (t of d, $J=0.9$ and 9.0 Hz, $_{\underline{H}}{>}C{=}C{<}_{CN}$).

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