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Reactions of Azepine, Diazepine, Tropone, and Cyclopentadienone Derivatives with Some Chlorosilane Derivatives in the Presence of Magnesium

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The reaction of 1-ethoxycarbonyl-1*H*-azepine with chlorosilane derivatives in HMPA in the presence of magnesium afforded the silanol derivatives, which upon heating gave the corresponding siloxane derivatives. In the same manner, tropone and 2,5-dimethyl-3,4-diphenylcyclopentadienone afforded the reduced dimers of them. However, tetraphenylcyclopentadienone and 2,5-dimethoxy-3,4-diphenylcyclopentadienone were reduced to the corresponding cyclopentenones under the reaction conditions. These reactions are considered to proceed *via* the corresponding radical anions which are formed by electron transfer from magnesium.

Chlorosilane derivatives are known to add to olefins in the presence of magnesium in hexamethylphosphoric triamide (HMPA).[1] However, the reactions to heterocyclic compounds have not been investigated well, although much attention has been paid to the cycloaddition reactions of heterocyclic compounds.[2] Similarly, much effort has been devoted to the study of the Grignard reactions of troponoid compounds, but no report has been published concerning the reactions of chlorosilanes with these types of compounds.[3] We wish to report the results of reactions of some chlorosilanes to azepine, diazepine, tropone, and cyclopentadienone derivatives.

The reaction of 1-ethoxycarbonyl-1*H*-azepine (**1**) with diphenyldichlorosilane in HMPA in the presence of magnesium at room temperature, followed by quenching with water, afforded **7** and **8** in yields of 40 and 23%, respectively. Similarly, **1** was reacted with dimethyldichlorosilane and trimethylchlorosilane to afford **9** and **11** in yields of 35 and 40%, respectively. Upon standing at room temperature as a chloroform solution, **9** was converted to **10** in nearly quantitative yield. On the other hand, **7** afforded **8** almost quantitatively by heating at 120 °C in toluene.

It is clear from the elemental analyses and mass spectrometry that these products are derived from the 1:2 adducts of **1** and the chlorosilanes. The IR spectra indicate that **7** and **9** are silanol derivatives in which the chlorine atoms bonded to the silicon atoms are replaced with hydroxyl groups. The products **8** and **10** were determined to be siloxane derivatives which are derived from the dehydration of **7** and **9**, respectively, on the basis of the spectral data and of the experiments mentioned above. The fact that there are only three signals of the ring protons in their NMR spectra and that each of these three signals corresponds to two ring protons indicate that these adducts have symmetric structures, suggesting that 2,7-addition, 3,6-addition, or 4,5-addition have occurred. The 3,6-addition is rejected by the facts that the NMR spectra showed no three-membered ring proton resonances and that it is impossible for chlorosilanes to add to the 3 and 6 positions without forming an aziridine ring in the azepine nucleus.

In the low temperature NMR spectra (−30 to −50 °C), the signals of H_a and H_b showed no change, but the doublet signal of H_c was split into two doublets at slightly different chemical shifts. Similar behavior was observed with H_α of the compound **12**.[4] The observed splitting at low temperature is a result of a

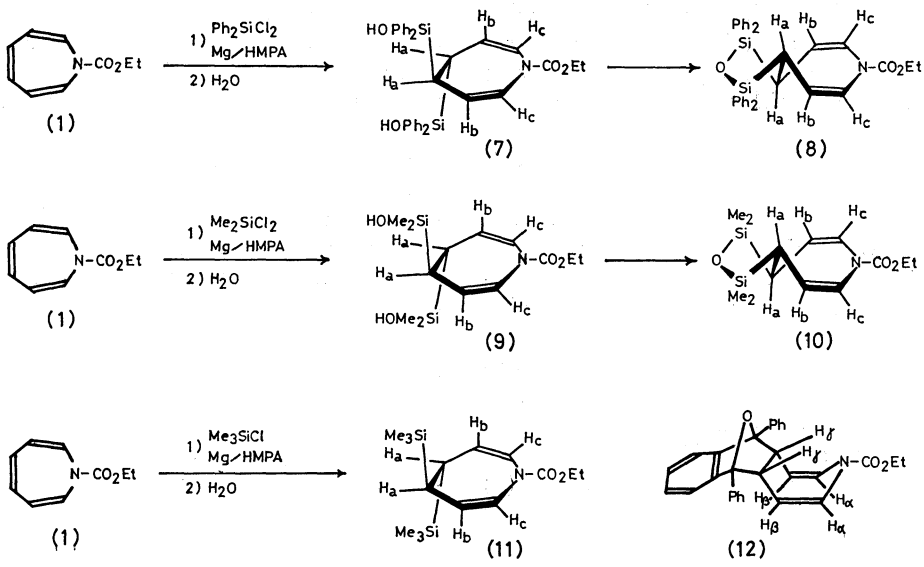

Fig. 1.

different anisotropic effect of the carbonyl group on the two H_c protons, which are revealed to be olefinic protons by the chemical shifts in the NMR spectra. This difference in the anisotropic effect is caused by freezing the free rotation of the ester group.[2b,5] A structure which has olefinic protons adjacent to the nitrogen atom can only be the result of the 4,5-addition. The 4,5-addition is further supported by the similarity of the NMR spectra of the adducts to the spectrum of the structurally analogous compound **12**.

The stereochemistry of the adducts was deduced from the coupling constants between the methine proton H_a and the olefinic proton H_b. The Dreiding models reveal that, for *cis*-addition, the dihedral angle between H_a and H_b is approximately 100°, which corresponds to the coupling constant of about 2 Hz according to the Karplus equation.[6] This value for the coupling constant is in accord with the observed value between H_γ and H_β of the authentic *cis*-adduct **12**. On the other hand, for *trans*-addition, the silyl groups would be expected to be arranged in a diaxial position in order to avoid the steric repulsion between them. In this case, the dihedral angle between the equatorial methine proton H_a and the olefinic proton H_b should be approximately 10°, which corresponds to a coupling constant of approximately 11 Hz. The observed coupling constants of **7**, **9**, and **11** are in accord with the expected value for the *trans*-addition. When the siloxane rings are formed, the silyl groups should be required to approach each other, resulting in the equatorial arrangement of the silyl groups and the axial arrangement of the methine protons. In this conformation, the dihedral angle between the axial methine proton and the olefinic proton is approximately 100°, which corresponds to a coupling constant of about 2 Hz and is in good agreement with the observed values for **8** and **10**. On the basis of these arguments, the structures of these adducts are determined as shown in Fig. 1.

In the same way, tropone (**2**) was reacted with trimethylchlorosilane in HMPA in the presence of magnesium. After quenching with water, **13** was obtained in 27% yield. The similar reactions of **2** with diphenyldichlorosilane or dimethyldichlorosilane resulted in almost the same consequences as above; however, in the absence of chlorosilanes, no reaction occurred.

The elemental analysis and the molecular ion peak in the mass spectrum reveal that **13** is the reduced dimer of **2**. The IR spectrum indicates that the carbonyl group is not conjugated with any double bond.[3b] The NMR spectral data employing the double resonance technique made it clear that **13** contains a 2,4-hexadiene moiety which has geminal protons at one end and a proton at the other end. The coupling constants are reasonably assigned on this carbon arrangement. On the basis of these facts, the structure of **13** is determined as shown in Fig. 2.

The reaction of tetraphenylcyclopentadienone (**3**) with trimethylchlorosilane in HMPA in the presence of magnesium, followed by quenching with water, produced a known cyclopentenone derivative **14**[7] in 74% yield. Similarly, 2,5-bis(methoxycarbonyl)-3,4-

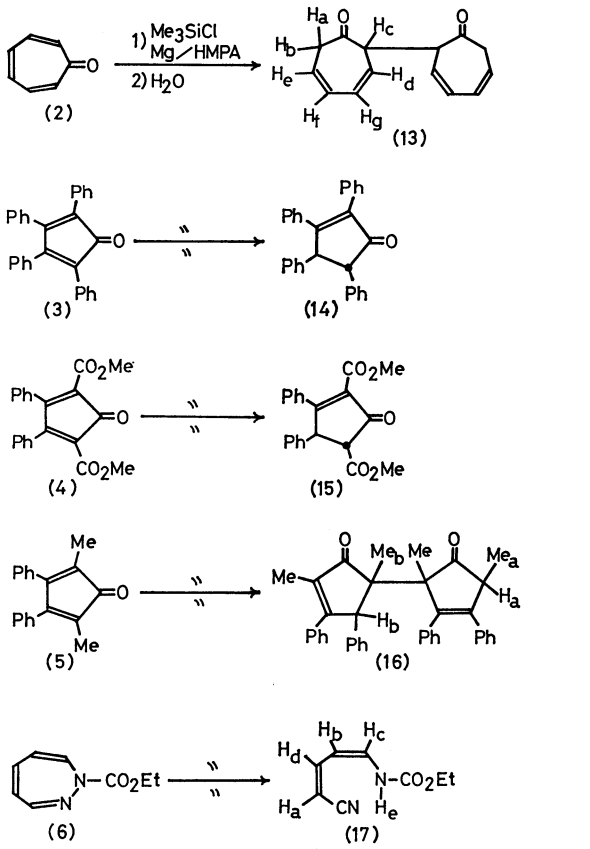

Fig. 2.

diphenylcyclopentadienone (**4**) and 2,5-dimethyl-3,4-diphenylcyclopentadienone (**5**) were reacted with trimethylchlorosilane to yield **15** and **16** in yields of 25 and 18%, respectively. The reactions of **3**, **4**, and **5** with diphenyldichlorosilane or dimethyldichlorosilane gave approximately the same results as above; however, in the absence of chlorosilane derivatives, no reaction proceeded.

The IR spectrum of **15** suggests that this product is a cyclopentenone derivative, which is also supported by the elemental analysis and the molecular ion peak in the mass spectrum. The stereochemistry of **15** was determined on the basis of the coupling constant between the ring protons. The elemental analysis and the molecular ion peak in the mass spectrum reveal that **16** is a reduced dimer of **5**. The IR spectrum indicates the existence of a conjugated and an unconjugated carbonyl group. The NMR spectrum shows that there are two ring protons: one proton (H_a) interacts with a methyl group (Me_a) with a coupling constant of 8 Hz and the other proton (H_b) has a long range coupling of 2 Hz with the other methyl group (Me_b). On the basis of these facts, the structures of **15** and **16** are determined as shown in Fig. 2.

1-Ethoxycarbonyl-1*H*-1,2-diazepine (**6**) was reacted with trimethylchlorosilane in HMPA in the presence of magnesium. After quenching with water, **17** was obtained in 25% yield. However, **17** was also obtained from the reaction of **6** with magnesium in HMPA in the absence of chlorosilanes.

The structure of **17** was determined as shown in

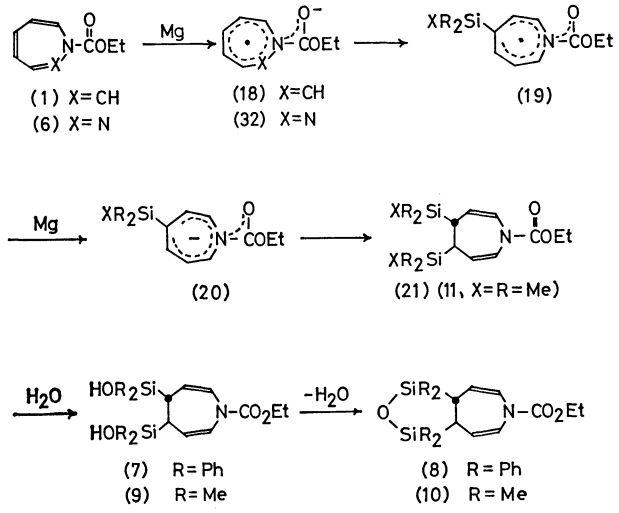

Fig. 3.

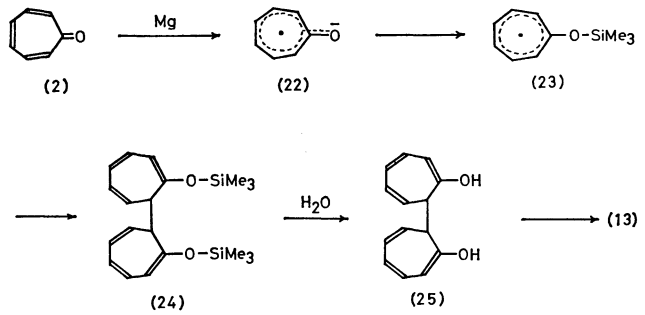

Fig. 4.

Fig. 2 on the basis of its spectral data and the resemblance of its NMR spectrum to that of the analogous compounds.[10]

Discussion

The reaction mechanism of **1** with chlorosilane derivatives can be explained as follows.[1] The first step of the reaction is considered to be one electron transfer from magnesium to **1** in the strongly basic solvent HMPA to form the anion radical **18**, which reacts with chlorosilanes to give the radical **19**, as shown in Fig. 3. One more electron transfer to **19**, followed by the reaction with chlorosilane, gives the disilyl compounds **21** (**11**, X=R=CH_3) *via* the anion **20**. When the reaction mixture is quenched with water, **21** is hydrolyzed to form the silanols. Dehydration of the silanols **7** and **9** to the siloxanes **8** and **10** is a well-documented reaction.[8]

The reaction mechanism of tropone (**2**) is thought to proceed *via* the initial formation of the radical anion **22**, which further reacts with chlorosilanes to yield the silyl ether radical **23**[9] as shown in Fig. 4. Dimerization of **23** affords **24**, which subsequently gives the reduced dimer **13** by the hydrolysis *via* the enol intermediate **25**.

The silyl ether radical **27** is also considered to be formed in the reactions of cyclopentadienones, as shown in Fig. 5. In the case of **5**, which has methyl groups at the 2 and 5 positions, **27** dimerizes to form **28** which

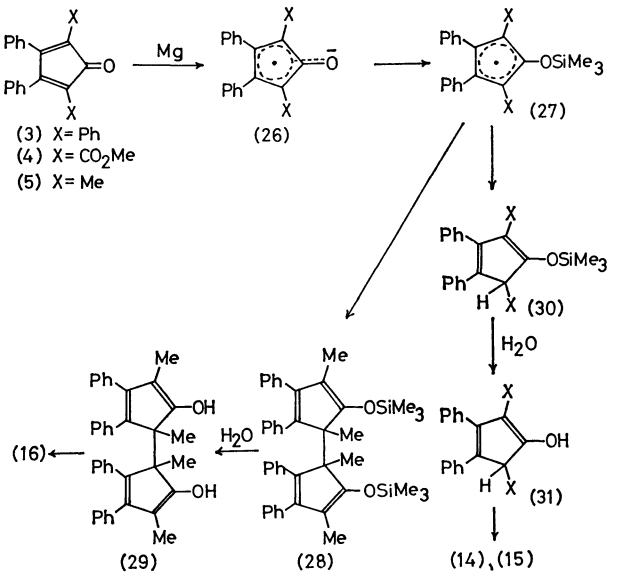

Fig. 5.

affords the reduced dimer **16** by hydrolysis. However, the bulky substituents, phenyl and methoxycarbonyl groups, located at the 2 and 5 positions in **3** and **4**, inhibit the dimerization of **27**. Thus, **27** abstracts a hydrogen from the solvent to yield the silyl ether **30**, which subsequently affords the cyclopentenones **14** and **15** after hydrolysis.

Nitrile compounds similar to **17** are known to be formed in the reaction of diazepine derivatives with strong bases.[10] The reaction products are thought to be formed *via* the N–N bond fission of the radical **32** shown in Fig. 3.

Experimental

All the melting points were uncorrected. IR spectra were measured in carbon tetrachloride solutions or potassium bromide disks and UV spectra in methanol solutions. NMR spectra were measured with Hitachi R-20B or Varian HA-100 spectrometer with deuteriochloroform or carbon tetrachloride as solvent and tetramethylsilane as internal standard. Wakogel C-200 and activated alumina of Wako Pure Chemicals Industries LTD were used for column chromatography.

Reaction of 1 with Diphenyldichlorosilane. A mixture of **1** (1.00 g, 6 mmol), magnesium (0.22 g, 9 mg atom), diphenyldichlorosilane (5.00 g, 20 mmol), and HMPA (30 mL) was stirred at room temperature for 20 h under a nitrogen stream. The reaction mixture was poured into ice water and extracted with ether. The organic layer was washed with water, brine, and dried over anhydrous sodium sulfate. After filtering, the solvent was evaporated on a rotary evaporator to yield a yellow oil (3.7 g). Silica gel chromatography of this oil gave pale yellow crystals **8** (0.85 g) by benzene–ether 50:1, and a pale yellow oil **7** (1.50 g) by benzene–ether 25:1. Recrystallization of **8** from cyclohexane gave colorless crystals (0.73 g, 23%), mp 174—175 °C. The oil **7** was further purified with silica gel chromatography to give a colorless oil (1.30 g, 40%). **7**: Found: C, 70.13; H, 6.11; N, 2.43%. Calcd for $C_{33}H_{33}NO_4Si_2$: C, 70.30; H, 5.90; N, 2.48%. UV_{max} 244 nm (log ε 4.37), 248 (4.39), 254 (4.29), 260 (4.23), 265 (4.01), 272 (3.83). IR (neat) 3420, 1710 cm^{-1}. NMR ($CDCl_3$) δ=1.13 (3H,

t), 2.73 (2H, H_a, d), 3.44 (2H, OH, bs), 4.02 (2H, q), 4.91 (2H, H_b, t), 6.44 (2H, H_c, d), 7.1—7.8 (20H, Ph); coupling constants in Hz $J_{ab}=9.0$, $J_{bc}=11.0$. MS, *m/e* (rel intensity), 545 (M^+-18, 3), 319 (81), 257 (64), 181 (100), 105 (86). **8**: Found: C, 72.88; H, 5.59; N, 2.62%. Calcd for $C_{33}H_{31}NO_3Si_2$: C, 72.62; H, 5.72; N, 2.57%. UV_{max} 244 nm (log ε 4.33), 254 (4.17), 260 (4.11), 265 (4.03), 272 (3.76). IR (KBr) 1720 cm^{-1}. NMR ($CDCl_3$) $\delta=1.22$ (3H, t), 2.73 (2H, H_a, nm), 4.08 (2H, q), 5.20 (2H, H_b, md), 6.62 (2H, H_c, md), 7.1—7.8 (20H, Ph); coupling constants in Hz $J_{ab}=2.0$, $J_{bc}=10.0$. MS, *m/e* (rel intensity) 545 (M^+, 23), 319 (100).

*Reaction of **1** with Dimethyldichlorosilane.* A mixture of **1** (1.65 g, 10 mmol), magnesium (0.36 g, 15 mg atom), dimethyldichlorosilane (4.00 g, 31 mmol), and HMPA (40 mL) was stirred at room temperature for 16 h under a nitrogen stream. The usual workup afforded a pale orange oil (2.55 g), which was chromatographed on silica gel to give pale yellow crystals **9** (1.25 g) by benzene–ether 7:3 and recovered starting material **1** (0.67 g) by benzene–ether 1:1. Recrystallization of **9** from cyclohexane gave colorless crystals (1.10 g, 35%), mp 99—100 °C. Found: C, 49.44; H, 7.96; N, 4.46%. Calcd for $C_{13}H_{25}NO_4Si_2$: C, 49.49; H, 7.99; N, 4.44%. UV_{max} 240 nm (log ε 4.09). IR (KBr) 3400, 1730 cm^{-1}. NMR ($CDCl_3$) $\delta=0.08$ (6H, s), 0.15 (6H, s), 1.41 (3H, t), 2.20 (2H, H_a, d), 3.38 (2H, OH, s), 4.33 (2H, q), 5.24 (2H, H_b, t), 6.68 (2H, H_c, d); coupling constants in Hz $J_{ab}=10.0$, $J_{bc}=10.0$. MS, *m/e* (rel intensity) 315 (M^+, 14), 149 (100).

*Reaction of **1** with Trimethylchlorosilane.* A mixture of **1** (1.00 g, 6 mmol), magnesium (0.22 g, 9 mg atom), trimethylchlorosilane (1.10 g, 10 mmol), and HMPA (20 mL) was stirred under a nitrogen stream for 18 h at room temperature. The usual workup afforded a pale orange oil (1.60 g), which was chromatographed on silica gel to give a colorless oil **11** (0.85 g) by petroleum ether–benzene 3:7 and recovered starting material **1** (0.19 g) by benzene–ether 9:1. The crude oil **11** was purified by chromatography on silica gel to yield a colorless oil (0.76 g, 40%). Found: C, 57.58; H, 9.16; N, 4.52%. Calcd for $C_{15}H_{29}NO_2Si_2$: C, 57.82; H, 9.38; N, 4.50%. UV_{max} 240 nm (log ε 4.16). IR (neat) 1730 cm^{-1}. NMR ($CDCl_3$) $\delta=0.08$ (12H, s), 1.32 (3H, t), 1.79 (2H, H_a, d), 4.11 (2H, q), 4.87 (2H, H_b, t), 6.63 (2H, H_c, d); coupling constants in Hz $J_{ab}=10.0$, $J_{bc}=12.0$. MS, *m/e* (rel intensity) 311 (M^+, 46), 120 (100).

*Reaction of **2** with Trimethylchlorosilane.* A mixture of **2** (2.00 g, 16 mmol), magnesium (0.38 g, 16 mg atom), trimethylchlorosilane (5.43 g, 50 mmol), and HMPA (30 mL) was allowed to react for 2 h at room temperature under a nitrogen stream. The usual workup gave a yellow oil (2.10 g), which was chromatographed on silica gel to give yellow crystals **13** (0.68 g) by benzene. Recrystallization of **13** from methanol gave pale yellow crystals (0.61 g, 27%), mp 91—92 °C. Found: C, 78.25; H, 6.48%. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59%. UV_{max} 241 nm (log ε 3.69). IR (KBr) 3010, 2960, 1710 cm^{-1}. NMR ($CDCl_3$) $\delta=3.01$ (2H, H_a, m), 3.53 (2H, H_b, m), 3.90 (2H, H_c, m), 5.65 (2H, H_d, m), 6.04 (2H, H_e, m), 6.35 (4H, H_f, H_g, m); coupling constants $J_{ab}=20.0$, $J_{ac}=1.5$, $J_{ae}=3.5$, $J_{af}=1.5$, $J_{be}=7.0$, $J_{cd}=3.0$, $J_{cg}=0.5$, $J_{dg}=10.5$, $J_{df}=1.5$, $J_{ef}=11.0$, $J_{eg}=1.5$. MS, *m/e* (rel intensity) 214 (M^+, 24), 107 (100).

*Reaction of **3** with Trimethylchlorosilane.* A mixture of **3** (2.50 g, 6.5 mmol), magnesium (0.16 g, 6.6 mg atom), trimethylchlorosilane (2.17 g, 20 mmol), and HMPA (20 mL) was stirred for 20 h at room temperature under a nitrogen stream. The usual workup gave a black mixture of crystalline starting material **3** and a tarry material (3.4 g). After removing the starting material **3** (0.28 g) by filtration, the tarry filtrate was chromatographed on alumina to yield additional starting material **3** (0.22 g) by petroleum ether–benzene 4:6 and colorless crystals **14** (2.03 g) by petroleum ether–benzene 1:9. Recrystallization from cyclohexane gave pure crystals of **14** (1.86 g, 74%), mp 162—163 °C, (lit,[7] 162—163 °C).

*Reaction of **4** with Trimethylchlorosilane.* A mixture of **4** (3.48 g, 10 mmol), magnesium (0.24 g, 10 mg atom), trimethylchlorosilane (4.30 g, 40 mmol), and HMPA (60 mL) was stirred for 2 h under a nitrogen stream at room temperature. The usual workup gave a brown oil (3.33 g) which was chromatographed on silica gel to yield yellow crystals **15** (0.98 g) by benzene–ether 20:1. Recrystallization of **15** from chloroform gave colorless crystals (0.89 g, 25%), mp 113—114 °C. Found: C, 71.92; H, 5.41%. Calcd for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18%. UV_{max} 287 nm (log ε 4.08). IR (KBr) 3030, 2940, 1730 (broad) cm^{-1}. NMR ($CDCl_3$) $\delta=3.58$ (1H, d, $J=3.5$ Hz), 3.80 (6H, s), 5.06 (1H, d, $J=3.5$ Hz), 7.2 (10H, Ph). MS, *m/e* (rel intensity) 350 (M^+, 14), 317 (100).

*Reaction of **5** with Trimethylchlorosilane.* A mixture of **5** (2.03 g, 4 mmol), magnesium (0.19 g, 8 mg atom), trimethylchlorosilane (3.48 g, 32 mmol), and HMPA (20 mL) was stirred at room temperature under a nitrogen stream for 2 h. The usual workup gave a brown oil (2.9 g), which was chromatographed on silica gel to yield yellow crystals **16** (0.41 g) by benzene–ether 20:1. Recrystallization of **16** from ethanol gave colorless crystals (0.36 g, 18%), mp 213—214 °C. Found: C, 87.55; H, 6.39%. Calcd for $C_{38}H_{34}O_2$: C, 87.32; H, 6.56%. UV_{max} 275 nm (log ε 4.26). IR (KBr) 3050, 2970, 1743, 1690 cm^{-1}. NMR ($CDCl_3$) $\delta=0.16$ (3H, Me_a, d, $J=8.0$ Hz), 1.30 (3H, Me_b, d, $J=2.0$ Hz), 1.94 (3H, s), 2.08 (3H, s), 3.06 (1H, H_a, q, $J=8.0$ Hz), 4.50 (1H, H_b, q, $J=2.0$ Hz), 7.2 (20H, Ph). MS, *m/e* (rel intensity) 261 ($M^+/2$, 53), 91 (100).

*Reaction of **6** with Trimethylchlorosilane.* A mixture of **6** (0.53 g, 3 mmol), magnesium (0.072 g, 3 mg atom), trimethylchlorosilane (1.08 g, 10 mmol), and HMPA (10 mL) was allowed to react for 2 h at room temperature under a nitrogen stream. The usual workup afforded a red oil (1.5 g), which was chromatographed on silica gel to yield yellow crystals **17** (0.16 g) by benzene–ether 4:1, and recovered starting material **6** (0.086 g) by benzene–ether 3:2. Recrystallization from benzene gave pale yellow crystals **17** (0.13 g, 25%), mp 141—142 °C. Found: C, 57.79; H, 6.23; N, 16.82%. Calcd for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86%. UV_{max} 303 nm (log ε 4.43). IR (KBr) 3330, 2210, 1710 cm^{-1}. NMR ($CDCl_3$) $\delta=1.32$ (3H, t), 4.32 (2H, q), 5.09 (1H, H_a, d), 5.73 (1H, H_b, dd), 6.86 (1H, H_c, dd), 7.09 (1H, H_d, dd), 7.75 (1H, H_e, broad); coupling constants in Hz $J_{ad}=10.5$, $J_{bc}=9.0$, $J_{bd}=12.0$, $J_{ce}=12.0$. MS, *m/e* (rel intensity) 166 (M^+, 33), 91 (100).

*Formation of **8** from **7**.* A solution of **7** (1.00 g) in toluene-d_8 (5 mL) was heated at 120 °C under a nitrogen stream for 3 h. The NMR spectrum of this reaction mixture indicated that **7** was converted to **8**. The yield of **8** was found to be nearly quantitative by comparison of the area of the absorption peak of H_c of **8** with the area of the peak of the ethyl group as the standard. The solvent was then evaporated to yield a colorless oil, which was crystallized from cyclohexane to give colorless crystals **8** (0.88 g, 91%).

*Formation of **10** from **9**.* A solution of **9** (0.50 g) in deuteriochloroform (2 mL) was stirred at room temperature under a nitrogen stream for 72 h. The NMR spectrum of this reaction mixture showed that **9** was converted to **10** almost quantitatively, using the absorption signal of H_c of

10 and the signal of the ethyl group as the standard. After evaporation of the solvent, the colorless residue was chromatographed on silica gel to yield a colorless oil **10** (0.14 g, 29%). Compound **10** was unstable and an analytically pure sample could not be obtained. UV_{max} 238 nm (log ε 4.37). IR (neat) 1730 cm^{-1}. NMR ($CDCl_3$) δ=0.16 (6H, s), 0.25 (6H, s), 1.42 (3H, t), 2.06 (2H, H_a, nm), 4.28 (2H, q), 5.13 (2H, H_b, md), 6.68 (2H, H_c, md); coupling constants in Hz J_{ab}=2.0, J_{bc}=10.0. MS, *m/e* (rel intensity) 297 (M^+, 14), 149 (100).

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