Reduction of 6,6-Disubstituted Fulvenes and 1,2-Benzoheptafulvene by Naphthalene Radical Anion

Akira Oku,* Mitsuhiro Yoshida, and Kenkichi Matsumoto
Department of Chemistry, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606

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Structural effects of fulvenes in the electron transfer reaction were examined by using naphthalene radical anion (**1**) as a homogeneous electron source in aprotic media. The reduction of 6,6-diphenylfulvene (**2**) with **1** in THF at −78 °C gave 3-benzhydrylcyclopentadiene (34%) and its 2-isomer (13%). The structures were determined by hydrogenation and by the reaction with *N*-phenylmaleimide. The reaction of 6,6-dimethylfulvene (**3**) with **1** gave bi(2-isopropylidene-3-cyclopentenyl) as the major product (39%) besides bi(2-isopropyl-1,3-cyclopentadienyl) (5%). The reaction of 3,3′,4′,5,5′,6,6′-heptamethyl-1,2-benzoheptafulvene (**4**) with **1** gave 3,3′,4,4′,5,5′,6′,7-octamethyl-1,2-benzo-1,3,6-cycloheptatriene (32%) and 3,3′,4′,5,5′,6,6′,7-octamethyl-1,2-benzo-1,3,5-cycloheptatriene (18%). These product structures as well as the CH_3I- and D_2O-quenching of the reduction intermediates indicate that **2** is reduced by the EEC-mechanism and **3** by the ECC-mechanism, whereas the results are rather complicated in the case of **4** to distinguish between EEC and ECC mechanism.

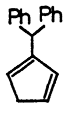
In the study of chemical reactions *via* electron transfer mechanism, it often turns out necessary to clarify the specificity of the reaction and correlate it with electrochemical processes. In the reduction of olefins by means of Birch-type reductions[1] and stable aromatic hydrocarbon radical anions[2] which proceeds quite rapidly under homogeneous and aprotic conditions,[3] the following mechanisms have hitherto been accepted: (i) two succeeding electron transfer steps followed by a chemical reaction (EEC mechanism), and (ii) an electron transfer step followed by two chemical reactions (ECC mechanism).[4] The ECE mechanism (two electron transfer steps intercepted by protonation) generally involved in electrolytic reductions is negligible in the case of reductions by aromatic radical anions. Nevertheless, radical anion $R^{\cdot-}$ is the initially formed common chemical species in all these routes, but its behavior thereafter varies depending upon the reaction conditions[5] and the structure of substrates.

$$R \xrightarrow{e} R^{\cdot-} \left\{ \begin{array}{l} \xrightarrow{e} [R]^{2-} \xrightarrow{2H^+} RH_2 \cdots\cdots\cdots\cdots\cdots\cdots \mathrm{EEC} \\ \xrightarrow{H\cdot} [RH]^- \xrightarrow{H^+} RH_2 \cdots\cdots\cdots\cdots\cdots\cdots \mathrm{ECC} \\ \xrightarrow{H^+} [RH]\cdot \xrightarrow{e} [RH]^- \xrightarrow{H^+} RH_2 \cdots \mathrm{ECE} \\ \xrightarrow{e} [R]^{2-} \xrightarrow{R} [R\text{-}R]^{2-} \\ \qquad\qquad\qquad \xrightarrow{2H^+} RH\text{-}RH \cdots\cdots \mathrm{EECC} \\ \xrightarrow{\text{coupling}} [R\text{-}R]^{2-} \xrightarrow{2H^+} RH\text{-}RH \cdots\cdots \mathrm{ECC} \end{array} \right.$$

In order to ascertain the structural effects that control the reaction paths and product structures, the authors chose some fulvenes as one type of olefin models, *i.e.*, 6,6-diphenylfulvene (**2**), 6,6-dimethylfulvene (**3**), and 1,2-benzoheptafulvene (**4**), and examined their behavior in chemical electron transfer reactions in aprotic media. Sodium naphthalene (**1**) in tetrahydrofuran (THF) was employed as a homogeneous electron source and was used with the reactant ratio of [reductant]/[fulvene]=2 in all reactions.

Results and Discussion

Reduction of 6,6-Diphenylfulvene (2) by Sodium Naphthalene. The reaction of diphenylfulvene (**2**)[6] with sodium naphthalene (**1**)[7] in THF at −78 °C gave a viscous oil as the major product (47%). Its mass spectrum showed the parent ion peak at $m/e=232$ which is equivalent to a hydrogenated structure, **2**+2H. The NMR spectrum indicated that the product molecule involves two allylic methylene hydrogen and has an unsymmetrical geometry. Therefore, among five possible [**2**+2H]-structures **5**—**9**, only **5** and **6** satisfy the NMR observations. In addition, VPC as well as NMR analysis indicated that the product consisted of two components with the ratio of *ca.* 3/1. Their separation was unsuccessful and the product was treated as a mixture in elucidating their structures in the following chemical transformations.



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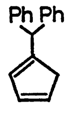

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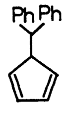

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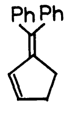

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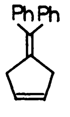

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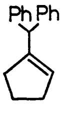
In catalytic hydrogenation (Pd/C), the mixture absorbed exactly 1 mol hydrogen per the molecular weight 232, giving the hydrogenated product **10** as the sole product. This supports that the structures of products are **5** and **6**, though the question of choosing the major isomer still remains unsolved. To know this answer, the mixture was treated with *N*-phenylmaleimide (**11**). The structure of the obtained adduct (isolated yield 40%) was ascribed to **12** with the support of mass spectrum ($M^+=405$) and NMR (the number of olefinic hydrogen per molecule was one), and consequently the major isomer was proved to be **5**, but not **6**. This structure agrees with the one previously proposed for the single reduction product isolated in the reaction of **2** with sodium metal in diethyl ether.[8]



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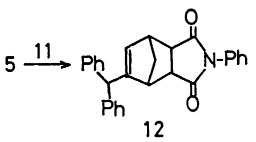

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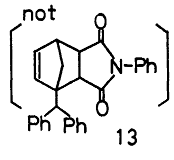

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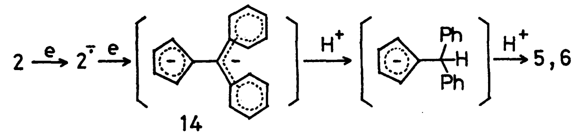
The D_2O-quenching technique in this reaction system seems inadequate to elucidate the carbanion intermediates, because cyclopentadiene hydrogens are so susceptible to the H/D exchange that excessive amount of deuterium incorporated in **5** and **6** (d_8 28%, d_4 18%).[9] Instead, the reaction was quenched by methyl iodide (which was added until the reaction mixture was decolorized) to give methylated products, which consisted of dimethylated (**2**+2Me), and monomethylated (**2**+Me+H) products with the ratio of 88: 12 (isolated total yield was 42% after repeated column chromatography). In contrast, no methyl group was introduced into the H_2O-quenched products in the treatment with methyl iodide under basic conditions. These results support that the trapped intermediate is a dianion. Additionally, the product structures **5** and **6** are indicative of the formation of dianion **14** as their precursor in which negative charges are separated so that the repulsive force can be minimized and both benzhydryl and cyclopentadienyl systems are contributing to stabilizing the separated charge (Scheme 1). The intermediacy of **14** is also compatible with the polarographic data of **2** ($^1E_{1/2}=-1.30$, $^2E_{1/2}=-1.78$ V *vs.* SCE; *cf.* naphthalene −2.6 V),[10] although the structures of the electrolytic reduction products have not been reported yet.

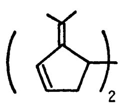


Scheme 1.

Reduction of 6,6-Dimethylfulvene (3) by Sodium Naphthalene. When 6,6-dimethylfulvene (**3**)[11] was treated under the same conditions as in the case of **2** (−78 °C in THF), only one product was detectable by VPC analysis (isolated yield 39%, air-sensitive) in addition to the formation of resinous solids. The mass spectrum showed M⁺ peak at $m/e=214$, which is equivalent to the formula, 2×**3**+2H. In the NMR spectrum, the proton spin coupling pairs are: i) allylic methyl protons at 1.80 with olefinic proton at 5.90, ii) methylene protons at 2.20 with both olefinic protons at 5.90 and 6.26.[12] However, no coupling was observed between methine proton at 3.1 and olefinic proton at 6.26. Therefore, among several possible structures, **16** seems to be most explainable of the above-mentioned NMR observation.

Before isolating products, the crude reaction mixture was mixed with maleimide **11** at −50 °C and the mixture was warmed up to ambient tempeature. A solid product was isolated (5%), M⁺ was 560. In its NMR spectrum, the absorption at 0.97 is ascribable to isopropyl methyl protons which couple with the methine proton ($J=7.5$ Hz) concealed in other protons around 2.0; this methine proton also couples with the olefinic proton at 5.90; a pair of doublet (AB-Type) appears at 1.45—2.10 which is ascribable to the apical methylene protons; the integrated intensity of the olefinic proton relative to the methyl is 1/6. These spectral data support the adduct structure **18**, thus proving the presence of another product **17** as a minor component.

When **3** was treated with **1** at 0 °C, a new product **19** (65%) was obtained in addition to **16** (15%). This product (mp 156 °C) showed the M⁺ peak at 342 which is equivalent to [2×**3**+2H+naphthalene], but the structure is not elucidated yet. The same product was also formed when **3** was added into **1** at −78 °C (inverse dropping method).



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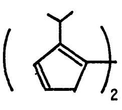

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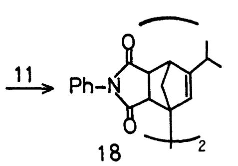

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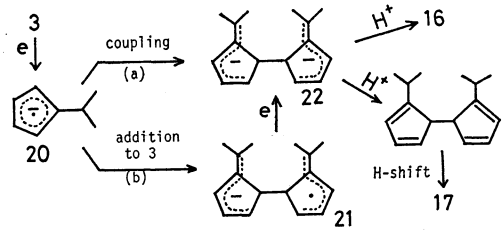
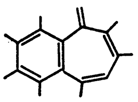
In contrast to the reaction of **2**, **3** is anticipated to show an entirely different behavior and give different product due to the methyl substituents at C-6 position. In fact, no possible monomeric product was formed, but dimeric products **16** and **17** were obtained. These structures are entirely different from the reported one in the reduction of **3** by sodium metal.[8] The formation of dimers can be most reasonably explained in terms of ECC mechanism (route *a*) or ECEC mechanism (route *b*)[4] (Scheme 2), although the averaged polarographic two-electron reduction potential of **3** was reported to be −1.90 V *vs.* SCE,[13] so far not low enough to rule out an EECC mechanism. In this Scheme, the C–C bond formation by either radical coupling (route *a*) or addition (route *b*) takes place more favorably between C-1 positions rather than between C-6 positions, because the latter position is sterically more crowded and the bonding at C-1 positions results in the formation of stable dienyl conjugation in **22** (or **21**). Another evidence against EEC mechanism was obtained in the reaction using an inverse dropping method (in which **3** was added into **1** at −78 °C); no monomeric product was obtained but **16**, **17**, and **19**. If any EEC mechanism had been involved, then a significant change in the products would have been observed. Scheme 2 postulates the derivation of **16** and **17** from an identical intermediate **22**; probably the protonation on the C-2 position of **22** takes place more favorably than on C-6 due to the difference in the stability between secondary and tertiary carbanions.



Scheme 2.

Reduction of 1,2-Benzoheptafulvene (4) by Sodium Naphthalene. Unsubstituted heptafulvene and its simple homologues are usually unstable and difficult to prepare.[14] In the present study, 3,3′,4′,5,5′,6,6′-heptamethyl-1,2-benzoheptafulvene (**4**)[15] was chosen as a model of seven-membered fulvene system, though not the most suitable, but because it is stable and has the unsymmetrically substituted structure easy to elucidate the reduction products.

The reduction of **4** with **1** was carried out at −40 °C and two isomeric products, 3,3′,4,4′,5,5′,6′,7-octamethyl-1,2-benzo-1,3,6-cycloheptatriene (**23**) and 3,3′,4′,5,5′,6,6′,7-octamethyl-1,2-benzo-1,3,5-cycloheptatriene (**24**), were isolated (total yield 50%, **23**/**24**=64/36). Both of them showed the identical M^+ peaks in their mass spectra (254, equivalent to **4**+2H) and their NMR spectra did not show the presence of exo methylene protons. Thus the exo double bond was preferably reduced. These isomers were able to be separated by VPC and their structures were determined independently by the NMR analysis (see the Experimental section). Consequently, the major product was ascribed to the structure **23** and the minor to **24**. The fact that the isomer ratio **23**/**24** stayed almost unchanged (63—66/37—34) throughout the reaction period (3 h at −40—0 °C) and that deuterium was not incorporated when a mixture of **23** and **24** was treated by NaOD in D_2O, rules out the possibility of base-induced isomerization between products.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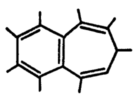
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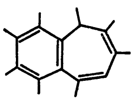
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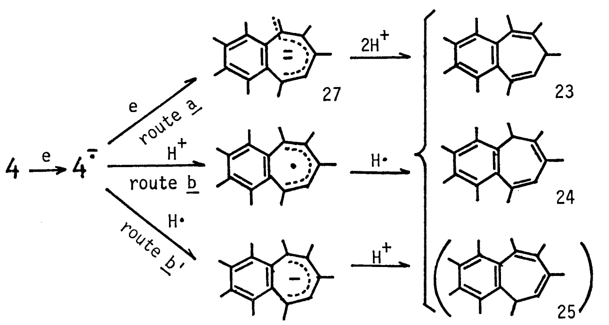
Table 1. *d*-Distribution in the D_2O-quenched products **23** and **24**

Run	Compound	Treatment	*d*-Distribution, % d_0	d_1	d_2
1	**23**	—[a)]	19	43.5	37.5
2	**24**	—[a)]	26	40	34
3	**23**	D/H[b)]	20.1	45.4	34.2
4	**23**	H/D[c)]	20.2	45.2	34.6

a) After D_2O quenching. b) The D_2O-quenched product was treated with 15% NaOD/D_2O at 25 °C for 10 h. c) The D_2O-quenched product was treated with 15% NaOH/H_2O at 25°C for 10 h.

The geometrical and electronic structure of benzoheptafulvene **4** is essentially different from pentafulvenes and its immediate comparison with **2** and **3** in the reduction behavior seems complicated. The D_2O quenching technique of the reaction of **4** incorporated 34—37% d_2 and 40—44% d_1 in both products **23** and **24** (see Table 1), whereas the standard experiment in which the mixture of **23** and **24** was treated with 15% NaOD/D_2O or NaOH/H_2O did not show any appreciable H/D exchange. In so far as the formation of these dideuterio compounds is concerned, a rational species to be protonated seems to be dianion intermediate **27** which can be formed by the EEC mechanism (route *a* in Scheme 3). However, the extent of the d_2-incorporation was not high enough to exclude the ECC (route *b* or *b′* in Scheme 3) or ECEC mechanism.



Scheme 3.

Experimental

General. The NMR spectra were measured by Varian T-60A and HA-100 spectrometers and chemical shifts were expressed in δ units. The mass spectra were measured by Hitachi RU-6L GC-MS spectrometer with the chamber voltage of 80 eV. Generally, the reductions were carried out by the method of dropping the reductant into fulvenes (normal dropping method) unless otherwise stated.

Sodium Naphthalene (1). Under the atmosphere of purified nitrogen, a THF solution of **1** was prepared from sodium metal and naphthalene, the latter recrystallized repeatedly from methanol before use. The amount of reagents which were charged initially for the preparation of **1** was kept constant at 0.5 g atom Na/0.5 mol naphthalene/liter THF throughout all experiments.[16)]

Pentafulvenes. 6,6-Diphenylfulvene (**2**) and 6,6-dimethylfulvene (**3**) were prepared from cyclopentadiene according to the reported methods.[6,11)]

3,3′,4′,5,5′,6,6′-Heptamethyl-1,2-benzoheptafulvene (4). Heptafulvene **4** was prepared by the reduction of the corresponding 4-Cl derivative (**4a**) which was obtained by the reaction of octamethylnaphthalene (OMN) with dichlorocarbene. The alternative 4-Br derivative (**4b**)[17)] can also be used though the reaction of OMN with CBr_2 yielded 6-Br isomer as a by-product.[15)]

Under a gentle stream of purified N_2, a THF solution of **1** (10 ml) was added dropwise to a cooled (−78 °C) solution of **4a** (1.28 g, 4.5 mmol) in THF (50 ml) over 10 min. After additional stirring for 20 min, the solution was decolorized by a mixture of H_2O and THF (2+10 ml). Solvent was removed and the residue, dissolved in Et_2O, was washed with aq NaCl and dried. Naphthalene was removed by sublimation and the residue was chromatographed through a silica gel column (pet. ether) to yield 0.55 g of **4** (49%); mp 104—105 °C, M^+ 252. ^{1}H-NMR (CCl_4) 1.66 and 1.92 (3H each, q, J=0.5 Hz, 5- and 6-Me), 2.06 (3H, d, J=1.4 Hz, 3-Me), 2.18 (3H, s), 2.20 (3H, s), 2.21 (3H, s), 2.29 (3H, s), 4.75 and 5.03 (1H each, dd, J=2.2 Hz, exo CH_2), 5.99 (1H, bs, J=1.4 Hz, 4-H).

Reduction of 6,6-Diphenylfulvene (2) by 1. **2** (4.7 g, 20.4 mmol) was dissolved in 50 ml of dry THF and the solution was bubbled through by N_2 for 10 min at ambient temperature. The solution was cooled to −72—−78 °C and a THF solution of **1** (40 mmol) was added dropwise over 30 min. After additional stirring (1 h at −78 °C) of the colored solution (dark crimson purple), a mixture of H_2O and THF (3+10 ml) was added and the solution was warmed up to ambient temperature. The solution was diluted by Et_2O (100 ml), washed with water repeatedly till the aq layer showed pH=7.0, and dried over anhyd $MgSO_4$. After removing solvents, the residue was chromatographed through a silica gel column (pet. ether). The first fraction consisted mainly of naphthalene and the second one contained reduction products 3-benzhydrylcyclopentadiene (**5**) and its 2-isomer (**6**) as a mixture. A resinous substance trapped in the column was incapable of being identified. The products **5** and **6** could not be separated satisfactorily by such attempted means as TLC and VPC. Yield of the mixture, 2.2 g (47%). Isomer ratio **5**/**6**=34/13 (by NMR). M$^+$, 232. NMR (CCl_4) 2.80—3.00 (2H, m+m′, coupling with H at 5.15 and 5.7—6.0), 5.15 (1H, m, coupling with H at 2.80—3.0 and 6.45), 5.70—6.00 (1H, m+m′, coupling with H at 2.80—3.0 and 6.2—6.45), 6.20—6.45 (2H, d+m′, coupling with H at 5.70—6.0 and 5.15), 7.20 (10H, bs).

*Reduction of **2** by **1**, D_2O-Quenching*: The procedure was essentially the same with that described above except that 99.9% D_2O was used as the quencher instead of H_2O. The product mixture showed an analogous VPC chromatogram to that of the H_2O-quenched products. The deuterium content of the products was determined by mass spectrometry: d_0 5.0, d_1 14.6, d_2 26.1, d_3 28.8, d_4 18.2%.

*Reduction of **2** by **1**, CH_3I-Quenching*: The solution of the reaction mixture of **2** (4.7 g, 20 mmol) and **1** (50 mmol) was quenched by methyl iodide (5.7 g, 40 mmol in 30 ml of THF) at −78 °C. After stirring for 40 min, the temperature was gradually raised to 0 °C and the mixture was worked-up with water and Et_2O. The organic residue was chromatographed three times through silica gel columns (pet. ether) to isolate methylated products, 2.9 g (42%). The VPC-mass spectral analysis showed that this consisted of dimethylated (88%) and monomethylated product (12%). The NMR showed methyl protons (6H at 1.8—2.0) relative to other aliphatic protons (2H at 2.6—2.8 and 2H at 5.5—6.5) and aromatic protons (10H at 7.15). The mass spectral analysis of the isolated dimethyl-product showed the M$^+$ peak at 260 (**2**+2Me) consistent with the dimethylated structure and that of the monomethylated product at 246 (**2**+Me+H), although the methylated positions were not elucidated.

*Catalytic Hydrogenation of the Mixture **5**+**6***: A mixture of **5** and **6** (0.64 g, 2.8 mmol) was hydrogenated over Pd/C (0.13 g) in EtOH (13 ml) at 25 °C. The solution absorbed 61.3 ml H_2 (calcd 61.6 ml for one double bond) over 6.5 h to afford 1-benzhydryl cyclopentene (**10**). IR (C=C) 1600 cm^{-1} (CCl_4). NMR (CCl_4) 1.5—2.3 (6H, m), 4.7 (1H, bs), 5.2 (1H, dd, J_1=4, J_2=2 Hz), 7.1 (10H, s). Only one eluting spot was shown by TLC.

*Reaction of the Mixture (**5**+**6**) with* N-Phenylmaleimide *(**11**)*: Under N_2 atmosphere, a solution of **11** (0.53 g, 3 mmol, in 5 ml of benzene) was mixed with a benzene solution of **5** and **6** (0.70 g, 3 mmol in 5 ml), (slightly exothermic). The mixture was heated in a sealed tube at 60 °C for 2 h to give colorless solids of adduct **12**. 0.49 g (40%), mp 247.0—248.5 °C. NMR (acetone-d_6) 1.60 and 2.00 (1H each, dd, J=9 Hz, apical CH_2), 3.23 (1H, m), 3.45—3.55 (3H, m, coupling with H at 1.60, 2.00, and 5.52, bridgehead), 4.60 (1H, d, J=2 Hz, coupling with H at 5.52, benzhydryl), 5.52 (1H, m, olefinic), 6.70—7.60 (15H, m, ArH). Found: C, 82.85; H, 5.64; N, 3.34%; M$^+$, 405. Calcd for $C_{28}H_{23}NO_2$: C, 82.94; H, 5.72; N, 3.45%; M, 405.

*Reduction of 6,6-Dimethylfulvene (**3**) by **1***. Under N_2 stream, **1** (51 mmol in 92 ml of THF) was added over 30 min to a freshly distilled **3** (2.70 g, 25.5 mmol, in 50 ml of THF) at −76 °C. The rate of decoloration of the radical anion was slow compared with that in the case of **2**. After additional stirring for 30 min, H_2O (0.9 ml in 25 ml of THF) was added and the solution was warmed up to ambient temperature. After working-up, the obtained mixture showed three TLC spots. The ethereal solution of the products, 210 ml, was divided into two parts, 160 and 50 ml, and the former was chromatographed first through a silica gel column (pet. ether) to remove polymeric products, and then by VPC (PEG 20M) to separate three fractions corresponding to the TLC spots. The first two fractions were di- and tetrahydronaphthalene, and the third fraction, liquid, was determined to be a dimeric product **16**, bi(2-isopropylidene-3-cyclopentenyl), 1.05 g (39%), by the following spectral data. NMR (CCl_4) 1.80 (6H, bs, allylic Me, slightly coupling with H at 5.90), 2.20 (2H, m, coupling with H at 3.10, 5.90, and 6.26), 3.10 (1H, m, coupling with H at 2.20), 5.90 (1H, m, coupling with H at 2.20, 6.26 by J=6 Hz, and slightly with 1.80), 6.26 (1H, a pair of t, coupling with H at 5.90 by J=6, with H at 2.20 by J=2 Hz). M$^+$ 214.

*Reaction of the Product Mixture Obtained from **3** with **11***: The latter of the divided solution (50 ml) prepared in the preceding experiment was mixed with **11** (0.65 g, 3.8 mmol) under N_2 at 0 °C and the mixture was stirred for 15 h. White solids of adduct **18** separated, 0.12 g (5.3%), mp 300 °C. NMR ($CDCl_3$) 0.97 (12H, splitted d, J=7.5 Hz, isopropyl Me), 1.62 and 1.93 (2H each, dd, J=8 Hz, apical), 1.45—2.10 (2H, concealed, coupling with Me), 3.46 (6H, m, coupling with H at 5.90, bridgehead), 5.90 (2H, m, olefinic, coupling with H at 1.45—2.10 and 3.46), 7.30 (10H, m, ArH). Found: C, 77.31; H, 6.59; N, 4.81%; M$^+$, 560. Calcd for $C_{18}H_{18}NO_2$: C, 77.12; H, 6.47; N, 5.00%; M, 560.

*Reduction of **4** by **1***. A solution of **4** (200 mg, 0.83 mmol) in dry THF (30 ml) was treated by a THF solution of **1** (1.8 mmol) at −40 °C for 1 h under N_2. The initially dark-green colored solution turned brown-red, which was then decolorized by a mixture of H_2O and THF (1+3 ml) at −30 °C. The mixture was extracted with Et_2O, washed with water and dried ($MgSO_4$). After removing naphthalene by sublimation, the residue was analyzed by VPC (PEG 20M, 2 m) to show two products. They could not be separated by TLC but by preparative VPC, where the first eluting fraction was **23** and the second was **24** (total yield 50%, **23**/**24**=64/36). **23**, liquid, M$^+$ 254. NMR (CCl_4) 1.10 (3H, d, J=12 Hz), 1.80 (6H, bs), 1.85 (3H, d, J=1.2 Hz), 2.1—2.25 (12H, m, plus concealed 1H coupling with Me at 1.10 as well as with H at 5.54), 5.54 (1H, dq, J=7.0 and 1.2 Hz). **24**, liquid, M$^+$ 254. NMR (CCl_4) 1.10 (3H, d, J=12 Hz), 1.63 (3H, bs), 1.79 (3H, bs), 2.04 (3H, d, J=1.5 Hz), 2.11 (3H, s), 2.17 (6H, s), 2.24 (3H, s), 3.75 (1H, q, J=12 Hz), 6.05 (1H, bs, coupling with Me at 2.04). The product ratio **23**/**24** stayed almost constant (63—66/37—34) during the reaction period.

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