Reactions of 1,8-Dehydronaphthalene with Cyclic Polyenes

Masahiko KATO, Shigeru TAKAOKA, and Toshio MIWA
Faculty of Science, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka 558
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The reactivities of 1,8-dehydronaphthalene (**1**) to cyclic polyenes, *i.e.*, cycloheptatriene, cyclopentadiene, 6,6-dimethylfulvene, furan, and norbornadiene, were examined. It was found that the C–H insertion reaction at the end of the conjugated systems, a new type of reaction of **1**, as well as the 1,2-cycloaddition reaction occurs in every conjugated cyclic polyene. A stepwise mechanism for the formation of the C–H insertion product was proposed.

According to the MO calculations,[1] the peri-electrons of 1,8-dehydronaphthalene (**1**), one of the arynes, occupy an antisymmetric combination of 1,8-dehydro-orbital in the ground state, whereas the *ortho*-electrons of 1,2-dehydrobenzene (**2**) do a symmetric one. Accordingly these two species must show different reactivities towards olefinic compounds, and these were in line with the experimental results by Rees and Storr[2] Thus the reaction of **1** afforded acenaphthene derivatives in a stereospecific manner, whereas the reaction of **2** afforded benzocyclobutene derivatives in a non-stereospecific fashion.[3] As for cyclic polyenes, only the reaction of **1** with cyclopentadiene was reported.[4]

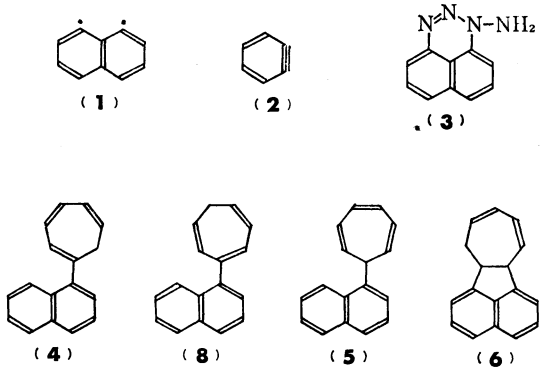
Present authors were interested in the reactivities of **1** to cyclic polyenes compared with those of **2**,[5] because the opposite character of the electronic ground states might be reflected in the difference between the reactivities of these species. By using cycloheptatriene, dimethylfulvene, furan, norbornadiene, and also cyclopentadiene as cyclic polyenes, we found that the insertion of **1** to a C–H bond of a conjugated polyene was also an important pathway as well as the cycloaddition reaction. A kind of such reaction was seen in the reaction of **1** with benzene to give α-phenylnaphthalene.[2]

Reaction Conditions and the Structures of the Products. Compound **1** was generated from 1-aminonaphtho-[1,8-*d*,*e*]triazine (**3**) by oxidation with lead tetraacetate in dichloromethane[2] in the presence of excess substrate under −20 °C or dry ice–acetone temperature, because the substrates were assumed to be susceptible to oxidation near room temperature.[6]

Reaction with Cycloheptatriene: Besides naphthalene, three products, (**4**), (**5**), and (**6**) [**4**: (**5**+**6**)=8: 10] (total yield 5.3%) were characterized as follows after partial separation by column chromatography of the reaction mixture.

The compound **5** was not formed when the separation was carried out in the dark. Catalytic hydrogenation (10% Pd–C) of the oily product **4** (mass spectrum, M^+ *m*/*e* 218) gave 1-cycloheptylnaphthalene which was identical with the authentic sample.[7] The structure **4** was selected among possible structures by consulting the NMR integral ratio of the olefinic proton signals to the aliphatic proton signals and the multiplicity of methylene proton signal. The structure was finally confirmed by the independent synthesis through **5**.

Owing to the difficulty of separation of the compound **6** from **4**, the mixture, enriched in **6** by chromatography in the dark, was subjected to the reaction.



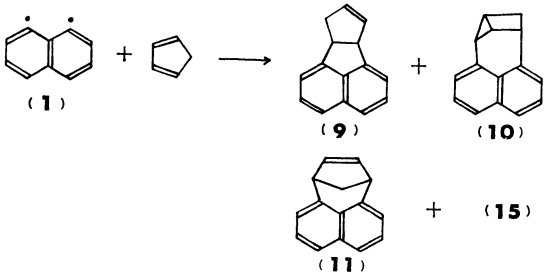
Scheme 1.

Catalytic reduction of the mixture gave, besides 1-cycloheptylnaphthalene originated from **4**, *cis*-1,2-pentamethyleneacenaphthene (**7**), which was identified by comparison with a sample prepared from cycloheptene and **1** and had to be formed from **6**. The NMR spectrum of **6** [δ ppm (CCl_4) 2.20—2.60 (2H, m), 4.21 (2H, m), 5.80—6.04 (2H, m), 6.12—6.20 (2H, m), 7.0—8.0 (6H, m)], obtained by a subtraction of the spectrum of **4** from that of the mixture, is consistent with the unsymmetrical structure rather than the other possible symmetrical ones.

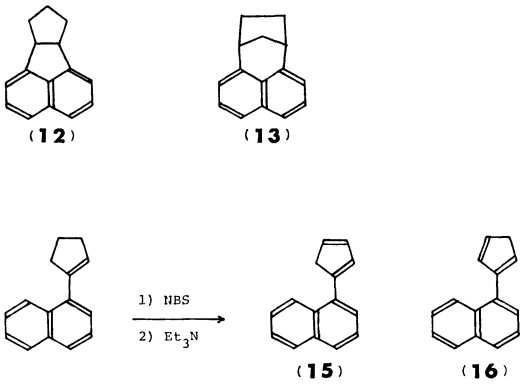
When a mixture of **4** and **6** in carbon tetrachloride was irradiated for a short peirod with a high-pressure mercury lamp through Pyrex filter, it was revealed by NMR spectrum that **4** was transformed almost completely to **5** while **6** remained unaltered. The structure **5**, an isomer of **4**, was obtained directly from consideration of the NMR spectrum and this was confirmed by its synthesis from tropylium fluoroborate[7] and α-naphthylmagnesium bromide. When heated for 15 hr at 125 °C, **5** gave a new compound **8** by 1,5-hydrogen shift, but when the temperature was raised to 160 °C, it gave mainly **4** by two series of 1,5-hydrogen shifts.[9] Irradiation[10] of **4** in carbon tetrachloride using a low pressure mercury lamp for 62 hr gave a mixture of **4** and **5** (4.6: 1).

Reaction with Cyclopentadiene: Meinwald and Gruber reported three kinds of cycloaddition products **9**—**11** from the reaction of **1** with cyclopentadiene.[4] The present authors expected the formation of an insertion product in the reaction as in the case of cycloheptatriene and reexamined the reaction. The resulting hydrocarbon fraction, separated by silicic acid chromatography, was hydrogenated catalytically. Thus, in addition to the products **12** and **13**,[4] 1-cyclopentylnaph-

thalene (**14**)[11] was obtained in almost equal quantity to the total amount of the other products. Although an insertion product (**15**), the precursor of **14**, could not be separated by solution chromatography (tlc or column) and by preparative glc, it was possible by comparing the NMR spectrum of the product mixture with those of **9** and **10** to obtain the spectral data of a new compound **15**. The structure was confirmed by obtaining **15** as a minor product, along with a main product (**16**), (1:3) from 1-(1-cyclopentenyl)naphthalene[11] by treatment with NBS in carbon tetrachloride followed by dehydrobromination with triethylamine in ether.



Scheme 2.

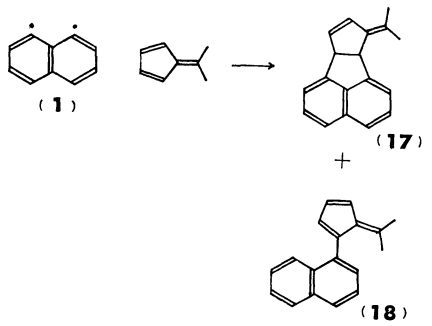


Scheme 3.

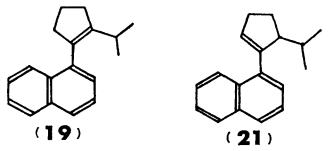
Reaction with 6,6-Dimethylfulvene: The reaction afforded compound **17** and **18** (1:2) (total yield 3%), which were separated by glc (3% Silicone OV-17, 1/4 in×6 ft, 170 °C). These compounds showed the same molecular ion peak at *m/e* 232 in their mass spectra (1:1 adducts of dimethylfulvene and **1**). The proton signal ratio (Ar–H: olefinic–H: benzylic–H: methyl–H=6:2:2:6) and the unsymmetrical feature of the NMR spectrum of **17** supported the structure.

A yellow solid **18**, mp 110—113 °C, showed an NMR spectrum [δ ppm (CCl_4) methyl proton signals at 1.36 (3H, s), 2.18 (3H, s), olefinic at 6.24—6.46 (3H, m) and aromatic at 7.2—7.44 (7H, m)] characteristic to the ring-substituted dimethylfulvene. The position of α-naphthyl group on dimethylfulvene was confirmed by the catalytic hydrogenation to a tetrahydro derivative [M^+ *m/e* 236; δ ppm (CCl_4) 0.90 (6H, d, J= 6 Hz), 1.8—2.9 (7H, m), 7.0—7.8 (7H, m)], which was identical with 1-(α-naphthyl)-2-isopropylcyclopentene (**19**) prepared by dehydration of 1-(α-naphthyl)-2-isopropylcyclopentan-1-ol (**20**).[13]

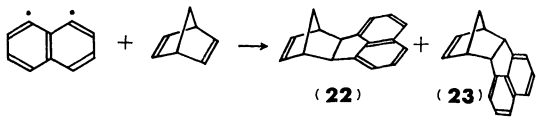
Reaction with Furan: The reaction was carried out in a usual way, and 2-(α-naphthyl)-furan[14] was obtained in 3% yield as a sole isolable product.



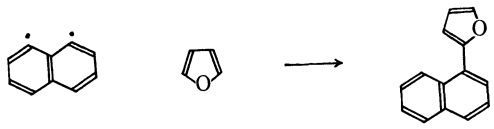
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

Reaction with Norbornadiene: It is known that norbornadiene sometimes reacts with other reagents as a homoconjugated diene owing to the interaction between two double bonds.[5f] Silicic acid chromatography of the reaction mixture gave two products **22** and **23** (total yield 7%), which were reported earlier by Baker and Mason.[15]

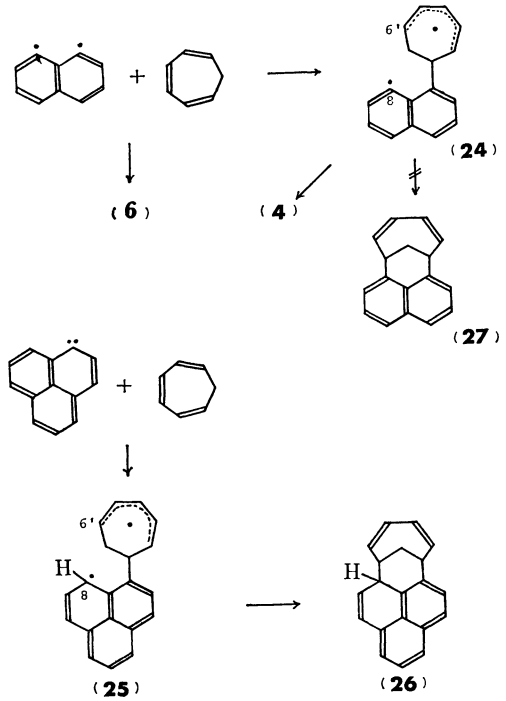
Discussion

Since the reactive intermediates like *o*-benzyne or 1,8-dehydronaphthalene are short-lived and react irreversively with other reagents, it may safely assumed that the reactivities are directly reflected to the yields of the products.[16]

Cycloaddition Reactions: It is well known that **2** reacts with cyclic diene to give Diels-Alder reaction products.[5] On the contrary, it is found that **1** gives [$\pi 2_s + \pi 2_s$] cycloaddition product instead of [$\pi 2_s + \pi 4_s$] product as described above.

Cycloheptatriene reacted with **2** rather abnormally to give a 1,2-cycloaddition product and an ene reaction product.[5g,5h,17] With **1**, it reacted to give a 1,2-cycloaddition product (**6**) and an insertion product (**4**). If the products were formed by a stepwise mechanism, the intermediate will be formulated as **24**,

which is stereochemically very similar to the proposed intermediate (**25**) for the reaction of cycloheptatriene and phenalenylidene.[18] The latter forms exclusively a [$_\pi$2+$_\pi$6] product (**26**). From the examination of the molecular model, successive overlap between the electrons on C-6′ of the cycloheptatrienyl and on C-8 of the naphthalene ring is thought to be slightly easier in **24** than in **25**. Nevertheless, the product (**27**), corresponding to **26**, was not detected in the products of **1** with cycloheptatriene. Thus the formation of **6** might occur through another pathway without forming **27**, *via* concerted process rather than the stepwise one. The principal formation of **6**, among 1,2-cycloaddition products, may be explained by the two-fold statistical advantage for the addition to C_1–C_2 compared with that to C_3–C_4 bond in cycloheptatriene and by the thermodynamical stability of **6** over the symmetrical one.



Scheme 8.

Dimethylfulvene with **1** gave a 1,2-cycloaddition product (**17**) and a C–H insertion product (**18**). The exclusive addition to C_1–C_2 double bond rather than the C_5–C_6 double bond is explained also by the same reason discussed above in the case of the formation of **6**, in addition to the steric hindrance to disturb approaching to the tetrasubstituted C_5–C_6 double bond.

With norboranadiene, a homoconjugated diene, **1** reacted exclusively in a manner of [$_\pi$2+$_\pi$2] cycloaddition. Because the rearranged products, as in the case of a radical reaction to substituted norbornadienes,[19] were not detected, the intermediacy of a diradical with a considerable life time cannot be anticipated.

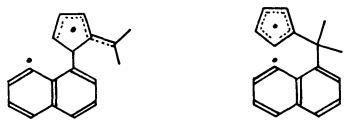
Furthermore, from the steric consideration of the reaction, there is no reason to assume that an *endo*-cycloaddition to 1,2-bond surpasses over a homoconjugate addition to C_1 and C_5 of norbornadiene under a stepwise mechanism. In the concerted mechanism, the orbital symmetry consideration may well conclude the symmetry allowed process for the former and the forbidden process for the latter. The exclusive formation **22** and **23** strongly supports that the reaction might be a concerted one. The abundant formation of **22** over **23** may be recognized by the steric reason, that is, easier approach from the *exo* side than from the *endo* side.

The C–H Insertion Reaction: To clarify whether **1** reacts directly with C_1 carbon atom of cycloheptatriene to form the C–H insertion product or not, its reaction with cycloheptatriene-7-d_1 was carried out and **4**-d_1 was isolated. Investigation of the NMR spectrum revealed that the deuterium in **4**-d_1 was found at a sole position C_7 of the cycloheptatriene ring.

In every conjugated polyene case we examined, the C–H insertion products were formed in considerable amount and this reaction seemed to proceed by the attack of a radical of **1** to a position with the largest value of the free valence in the polyene system.[20]

In the reaction with cycloheptatriene, the intramolecular hydrogen abstraction by an aryl radical in **24**, giving **4**, might occur much faster than the cyclization to **27**. On the other hand, the ability of H-abstraction of allylic radical in **25** could be small owing to the delocalization of the radical electron over the phenalene ring.

In case of dimethylfulvene, two biradical intermediates **28** and **29** are possible, but any products through **29**, which can not be derived to any C–H insertion product, are not observed.



Scheme 9.

Experimental[21]

Reaction of 1,8-Dehydronaphthalene. Reaction with Cycloheptatriene: To a stirred CH_2Cl_2 (5 ml) solution of cycloheptatriene (3.37 g, 37 mmol) cooled externally with dry ice–acetone was added lead tetraacetate (1.5 g, 3.4 mmol) in one portion and followed by dropwise addition of **3** (564 mg, 3.1 mmol) in CH_2Cl_2 (20 ml) over 30 min. After the addition had been completed, the mixture was allowed to come to room temperature and filtered. The filtrate was washed successively with water and saturated salt solution and dried (anhyd. Na_2SO_4). The residue was chromatographed ($CHCl_3$) on silicic acid (60 g) in the dark: Fractions were collected in every 30 ml. Fractions 2—3 contained a liquid (218 mg), which was rechromatographed (*n*-hexane) on silicic acid (20 g) in the dark. Fractions were collected in every 10 ml: Fractions 7—10 contained compounds **4** and **6** (30 mg, 8: 10), which were further chromatographed (*n*-hexane) on neutral alumina (10 g). Fractions were collected in every 10 ml. Fractions 11—13 contained pure **4** (16 mg), which was identical with a sample of **4** described below.

Compound (**4**): NMR δ ppm (CCl_4) 2.76 (2H, d, J=8 Hz), 5.36 (1H, t-d, J=8, 6 Hz), 6.08—6.30 (2H, m), 6.52—6.64

(2H, m), 7—8 (7H, m); mass spectrum *m/e* (%) 218 (100), 217 (94), 215 (38), 203 (63), 202 (63), 152 (21); λ_{max}^{EtOH} nm (log ε) 225.5 (4.54), 295 (3.81).

Reaction with Cyclopentadiene: To a stirred CH_2Cl_2 (30 ml) solution of lead tetraacetate (3.8 g, 8.5 mmol) cooled externally with dry ice–acetone was added cyclopentadiene (5.1 g) in one portion and followed by dropwise addition of CH_2Cl_2 (50 ml) solution of **3** (1.3 g, 7.0 mmol) over 25 min. After stirring at the temperature for 30 min, the mixture was warmed up to 0 °C, treated with ice–water, and then filtered through Hyfrosupercel. The filtrate was washed successively with 5% aq. $NaHCO_3$, H_2O and brine. After drying (anhyd. Na_2SO_4) and concentrating the organic layer, the residue was chromatographed ($CHCl_3$) on silicic acid (40 g), fractions were collected in every 10 ml. Fractions 3—4 (536 mg) were rechromatographed (*n*-hexane) on silicic acid (30 g); fractions were collected in every 10 ml. Fractions 8—12 gave 220 mg of a mixture of **9**, **10** and **15** (1: 0.5: 2). This mixture was characterized by hydrogenation as described below.

Reaction with 6,6-Dimethylfulvene: To a stirred CH_2Cl_2 (15 ml) solution of dimethylfulvene (5.3 g, 50 mmol) cooled at −20 °C was added dropwise alternately a CH_2Cl_2 (40 ml) solution of **3** (916 mg, 5.0 mmol) and a CH_2Cl_2 (15 ml) solution of lead tetraacetate (2.55 g, 5.6 mmol). After usual work-up, the residue was chromatographed (*n*-hexane) on silicic acid (100 g), fractions were collected in every 100 ml. Fractions 8—9 gave a mixture of **17** and **18** (23 mg, 1: 2.8), fraction 10 gave a pure **18** (10 mg). The glc separation of **17** and **18** was carried out using a column of 3% Silicone OV-17 (1/4 in × 5 ft, He 60 ml/min) at 200 °C. Retention time **17**, 8.0 min; **18**, 8.44 min. **17** mp 110—113 °C; mass spectrum *m/e* (%) 232 (86), 217 (100), 202 (46); NMR δ ppm (CCl_4) 1.36 (3H, s), 2.18 (3H, s), 6.24—6.46 (3H, m), 7.2—7.84 (7H, m); λ_{max}^{EtOH} nm (log ε) 222 (4.84), 273 (4.27). **18** mp 119—120 °C; mass spectrum *m/e* (%) 232 (100), 217 (84), 165 (32); NMR δ ppm (CCl_4) 1.84 (3H, s), 2.22 (3H, s), 4.82 (2H, bq), 5.94 and 6.24 (2H, broad AB type), 7.2—7.6 (6H, m).

Reaction with Furan: To a stirred CH_2Cl_2 (30 ml) solution of lead tetraacetate (4.87 g, 11 mmol) cooled externally with dry ice–acetone, was added furan (6.8 g, 100 mmol) in one portion and followed by a dropwise addition of **3** (1.84 g, 10 mmol) in CH_2Cl_2 (40 ml). After usual work-up and chromatography (*n*-hexane/silicic acid 30 g), 2-(α-naphthyl)-furan 56 mg (3.2%) was obtained and identified with an authentic sample;[14] NMR δ ppm (CCl_4) 6.48 (1H, d-d, J=2, 3.5 Hz), 6.64 (1H, d, J=3.5 Hz), 7.32—7.88 (7H, m), 8.28—8.44 (1H, m).

Reaction with Norbornadiene: To a CH_2Cl_2 (20 ml) solution of norbornadiene (5.0 g, 50 mmol) cooled at −20 °C was added dropwise, alternately a solution of **3** (923 mg, 5 mmol) in CH_2Cl_2 (50 ml) and a solution of lead tetraacetate (2.44 g, 5.5 mmol) in CH_2Cl_2 (25 ml) over 45 min. After usual work-up, the product was chromatographed (*n*-hexane) on silicic acid (100 g) to give **22**[15] (75 mg, 7.5%), and **23**[15] (10 mg, 1%).

Reaction with Cycloheptene: To a stirred CH_2Cl_2 (5 ml) solution of cycloheptene (443 mg, 4.5 mmol) cooled externally with dry ice–acetone was added lead tetraacetate (931 mg, 2.1 mmol) in one portion followedby a dropwise addition of CH_2Cl_2 (5 ml) solution of **3** (276 mg, 1.5 mmol) over 15 min. Usual work-up and chromatography (*n*-hexane) on neutral alumina (10 g) gave **7** (10 mg, 3%). [Mass spectrum, *m/e* (%) 222 (100), 179 (53), 166 (25), 165 (66), 153 (20); NMR spectrum, δ ppm (CCl_4) 1.1—2.4 (10H, m), 3.6—3.9 (2H, m), 7.0—7.6 (6H, ABC type); λ_{max}^{EtOH} nm (log ε) $223^{infl.}$ (4.72), 228 (4.84), 244 (3.21), 281 (3.75), 289 (3.80), 301 (3.50), 306 (3.49), 315.5 (3.04), 320 (3.11).

*Catalytic Hydrogenation of a Mixture of Compounds **4** and **6**.* A mixture of **4** and **6** (30 mg), obtained above, was hydrogenated in ethanol over 10% Pd–C (100 mg) at room temperature for 4.5 hr. The mixture was filtered and evaporated *in vacuo*. Repeated chromatography (*n*-hexane/neutral alumina) of the residue gave a mixture (1: 1, 15 mg) of 1-(1-cycloheptenyl)naphthalene[7] and 1-cycloheptylnaphthalene[7] and **7** (16 mg). These were characterized by direct comparison with the authentic samples synthesized independently.

*7-(α-Naphthyl)cycloheptatriene (**5**).* To a stirred suspension of tropylium fluoroborate (2.1 g, 12 mmol) in anhyd. THF (10 ml) was added dropwise α-naphthylmagnesium bromide in ether (8 ml), prepared from α-bromonaphthalene (2.88 g, 11 mmol) and Mg (245 mg, 10 mgatom) at room temperature. Insoluble material was filtered and the filtrate was concentrated *in vacuo* The residue (2.4 g) was chromatographed (*n*-hexane) on silicic acid (70 g), fractions were collected in every 50 ml; fractions 10—18 gave **5** (904 mg, 30%). [Found: C, 93.46; H, 6.54%. Calcd for $C_{17}H_{14}$: C, 93.53; H, 6.47%: Mass spectrum; *m/e* (%) 218 (100), 217 (76), 215 (32), 203 (61), 202 (61): NMR spectrum, δ ppm (CCl_4) 3.36 (1H, t, J=5 Hz), 5.47 (2H, d-d, J=9, 5 Hz), 6.08—6.32 (2H, m), 6.52—6.76 (2H, m), 7.2—8.0 (7H, m): λ_{max}^{EtOH} nm (log ε) 224.5 (4.97), $263^{infl.}$ (3.91), 272 (4.01), 282 (4.06), $292^{infl.}$ (3.91).

*Thermal Rearrangement of 7-(α-Naphthyl)cycloheptatriene (**5**).* When **5** (30 mg) dissolved in DMSO-d_6 (0.4 ml) in an NMR tube was heated at 125 °C for 15 hr.[22] The NMR measurement revealed that **5** was transformed almsot completely to **8**, which was further transformed to **4** by heating it at 160 °C for 4 hr. **8** was isolated by chromatography (*n*-hexane) on neutral alumina (1 g); fractions were collected in every 1 ml. Fraction 5 gave almost pure **8**. Sublimation at 90 °C/1 mmHg. **8** Found: C, 93.35; H, 6.56%. Calcd for $C_{17}H_{14}$: C, 93.53; H, 6.47%. Mass spectrum; *m/e* (%) 219 (19), 218 (100), 217 (71), 215 (33), 203 (54), 202 (56). NMR spectrum; δ ppm (CCl_4) 2.46 (2H, t, J=6 Hz), 5.2—5.6 (2H, m), 6.1—6.4 (2H, m), 6.63 (1H, d, J=5 Hz), 7.2—7.8 (7H, m).

*Photochemical Interconversion of Compounds **4** and **5**.* The CCl_4 solution (0.4 ml) of **5** in a quartz NMR tube was irradiated with a low pressure mercury lamp at room temperature and the reaction was followed by NMR method. The ratios of **4** and **5** in the mixture were observed in the course of the irradiation time as follows; **5**: **4**=16: 1 (18 hr), 5: 1 (38 hr), 4.6: 1 (62 hr).

When a CCl_4 (0.4 ml) solution of **4** (30 mg) was irradiated with a high pressure mercury lamp (UM-452) through Pyrex filter for 30 min, **4** was transformed to **5**, giving a ratio of 23: 1 (**5** to **4**).

*Catalytic Reduction of a Mixture of **9**, **10** and **15**.* A mixture of **9**, **10** and **15** (199 mg, 1: 0.5: 2) dissolved in 95% EtOH (15 ml) was hydrogenated over 10% Pd–C (46 mg) for 2 hr. The glc separation (10% Apiezone L, 1/4 in × 5 ft, 185 °C) of the residue gave almost equal amounts of a mixture of **12** and **13**[4] (4: 3) and **14**, which was identified with the authentic sample[11] [NMR δ ppm (CCl_4) 1.72 (6H, m), 2.0—2.3 (2H, m), 3.5—3.8 (1H, m), 7.12—7.72 (6H, m), 7.8—8.0 (1H, m); λ_{max}^{EtOH} nm (log ε) 225.5 (4.88), 272 (3.79), 283 (3.87), 293 (3.70)].

Dehydrogenation of 1-(1-Cyclopentenyl)naphthalene. 1-(1-Cyclopentenyl)naphthalene[11] (193 mg, 1 mmol), NBS (178 mg, 1 mmol) and benzoylperoxide (10 mg) in CCl_4 (3 ml) was refluxed for 2 hr. The cooled mixture was filtered and the residue dissolved in anhyd. ether (5 ml) was treated with Et_3N (3 ml). After refluxing the mixture for 2 hr and evaporation of the solvent, the residue (261 mg) was chromato-

graphed (*n*-hexane) on silicic acid (3 g); fractions were collected in every 3 ml. Fractions 4 and 5 gave a mixture of **15** and **16** (58 mg, 1:3) [NMR; charasteristic methylene signals at δ 3.38 (q, J=1.1 Hz) and 3.15 (q, J=1.1 Hz) ppm]. The spectral data of the former were identical with the sample obtained from the reaction of cyclopentadiene with **1**. Because of their instability, further purification of **15** was not effected. Catalytic hydrogenation (10% Pd-C/EtOH) of the mixture gave **14** as a sole product.

Catalytic Hydrogenation of 1-(α-Naphthyl)-6,6-dimethylfulvene (18). A solution of **18** (10 mg) in gracial acetic acid (10 ml) was hydrogenated over 5% Pd-C (50 mg) for 3 hr to give a tetrahydro derivative **19** (8 mg), which was identified with the authentic sample described below.

Synthesis of 1-Isopropyl-2-(α-Naphthyl)cyclopentene (19). A solution of **20** (2.3 g, 9.1 mmol)[13] in bromobenzene (20 ml) was heated at 180 °C in the presence of $KHSO_4$ (1.3 g) until the separation of water had ceased. After evaporation of bromobenzene, the residue was chromatographed (*n*-hexane) on silicic acid (25 g); fractions were collected in every 25 ml. Fractions 3—5 gave a mixture of products (1.17 g), which was further chromatographed (*n*-hexane) on neutral alumina (35 g); 20 ml-fractions were collected and fractions 2—5 (948 mg) contained **19** and **21**. The pure samples of **19** and **21** were obtained by glc (5% SE-30, 1/4 in×5 ft, 156 °C, He 40 ml/min). Retention time; **19** 7.2 min, **21** 11.5 min. [**19** Found: C, 91.34; H, 8.55%. Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53%. NMR spectrum: δ ppm (CCl_4); 0.90 (6H, d, J=6 Hz), 1.8—2.9 (7H, m), 7.0—7.8 (7H, m). Mass spectrum: *m/e* (%) 236 (62), 221 (100), 193 (41), 179 (30), 178 (24), 165 (37). λ_{max}^{EtOH} nm (log ε) 226 (4.82), 274$^{infl.}$ (3.77), 284 (3.86), 293$^{infl.}$ (3.79). **21** Found: C, 91.46, H, 8.26%. NMR spectrum: δ ppm (CCl_4); 0.67 (3H, d, J=7 Hz), 0.79 (3H, d, J=7 Hz), 1.6—2.7 (5H, m), 3.1—3.4 (1H, m), 5.82 (1H, bq, J=2 Hz), 7.1—7.42 (4H, m), 7.54—7.8 (2H, m), 7.9—8.16 (1H, m). Mass spectrum: *m/e* (%) 236 (34), 221 (9), 194 (18), 193 (100), 192 (9), 191 (9), 179 (9), 178 (32), 165 (19). λ_{max}^{EtOH} nm (log ε) 226 (4.73), 286 (3.87), 294 (3.86)].

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