Rearrangements of Tricyclo[5.3.1.0^{1,7}]undecatrienide Anion: Circumambulation and Cleavage of the Cyclopropane Ring

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Reaction of tricyclo[5.3.1.0^{1,7}]undeca-2,4,9-triene with butyllithium in tetrahydrofuran-hexamethylphosphoric triamide at −78 °C and subsequent quenching of the resulted dark red reaction mixture with water or methanol gave tricyclo[6.3.0.0^{1,3}]undeca-5,7,9-triene (**4**) as the sole isolable product. It was also found that quenching of the anion solution with deuterium oxide under the same conditions caused stereoselective incorporation of deuterium atom. On the other hand, quenching of the anion solution with water after it was warmed to 0 °C gave a mixture of dihydromethylazulenes. The cycloadduct of the rearranged hydrocarbon **4** with 4-phenyl-3*H*-1,2,4-triazoline-3,5(4*H*)-dione was obtained and its structure was confirmed by X-ray crystallographic analysis. A driving force of the circumambulation was thought to be the creation of conjugation between the cycloheptadienide part and the five-membered ring olefin in the product on the basis of the facts that a circumambulatory rearrangement in the opposite direction, which would lead to a different product via a less conjugated tricyclic anion, was not observed, and that the anion generated from tricyclo[5.3.1.0^{1,7}]undeca-2,4-diene was reluctant to undergo the rearrangement.

A circumambulatory rearrangement was defined as "*a molecular rearrangement in which an atom or group of atoms migrates around a ring in such a way that during a series of such reactions the atom or group of atoms can become bonded to any of the ring carbons*" by Childs in his review.[1] There are an enormous number of molecular rearrangements that can be classified as circumambulatory rearrangements. Among them, rearrangements in which a cyclopropane ring circumambulates on the periphery of a cyclic polyene or a polyenylium ion have been reported.[2,3] According to symmetry conservation considerations,[4] such a cyclopropane ring migration can thermally proceed regardless of the number of total electrons concerned in the process. However, stereochemical behavior of the migrating group differs depending on the number; the migrating group should invert its configuration in processes involving (4*n*+2) electrons and retain it in those involving 4*n* electrons. It has been recognized that in general, circumambulation occurs much more easily in the latter electron system, which displays an antiaromatic character and is destabilized relative to its transition state, than in the former electron system.[5] Although many experimental and theoretical studies[2,3,5] on circumambulatory rearrangements of polyenyl and cationic species have been documented, neither thermal nor photochemical migration of a cyclopropane ring in anionic species has been disclosed yet.[6] For example, two bicyclo[5.1.0]-octadienide anions, **1** and **2**, which are likely to be suitable for detecting a cyclopropane ring migration, have appeared in the literature.[7,8] However, Kloosterziel et al. concluded that the degenerate circumambulation does not thermally occur in bicyclo[5.1.0]octadienide anion (**1**), based on its temperature-independent ^{1}H NMR spectra.[7] Additionally irradiation of solutions of **1** and **2** proved that disrotatory ring opening and closing at the 1 and 7 positions are the only processes observed under the photochemical conditions (Chart 1).[8,9] In this paper we describe generation and thermal rearrangements of tricyclic undecatrienyl anions, derived from tricyclo[5.3.1.0^{1,7}]undeca-2,4,9-triene (**3**),[10,11] indicating chemical evidence supporting such cyclopropane ring circumambulation of anionic spieces[12] and also subsequent cleavage of the cyclopropane ring.

Results and Discussion

Rearrangement at Low Temperature. While treatment of **3** with butyllithium (*n*-BuLi) in tetrahydrofuran (THF) at −78 °C did not give any coloration of the solution, addition

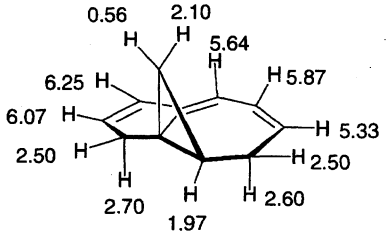
R = H **1**
= CH_3 **2**

3

Y = H **4**
= D **4-d$_1$**

Chart 1.

of hexamethylphosporic triamide (HMPA) as a co-solvent to this mixture resulted in a dark red solution, suggesting generation of anionic species. Quenching of this reaction solution with either water or methanol after 20 min at −78 °C gave the rearranged hydrocarbon as a single product in 31 or 49% yield, respectively. Though this product was an air-sensitive oil, the gross structural features of **4** was deduced by a combination of ^{1}H and ^{13}C NMR spectra and two-dimensional experiments (H–H COSY, C–H COSY, and HMBC). Assignment of all carbon signals were unambiguously decided by the latter two-dimensional spectra. The coupling modes and constants made assignment of all proton signals possible except the two methylene protons at the C_{11} position. Definite assignment of these proton signals, as shown in Fig. 1, was done through the aid of the NOE experiments of the deuterated compound (vide infra). As seen in the ^{1}H NMR spectral data, it is a notable structural feature of **4** that the vicinal coupling between one of the methylene protons at the C_4 position with anti configuration to the cyclopropane ring and the methine proton at the C_5 position is almost negligible. The computed structure of **4** by the MM2 method[13] showed that the dihedral angle between these two hydrogen atoms through the C_4–C_5 axis is 71.5° in fairly good agreement with the spectral observation. Further structural confirmation of **4** was done by X-ray crystallographic analysis of its stable crystalline derivative; i.e. the cycloadduct **5** was obtained in reaction of **4** with 4-phenyl-3*H*-1,2,4-triazoline-3,5(4*H*)-dione in chloroform (Scheme 1). The connectivity of two components in this cycloadduct was deduced as the [4+2] adduct by analysis of ^{1}H and ^{13}C NMR spectroscopy. It is noteworthy that although the apparent



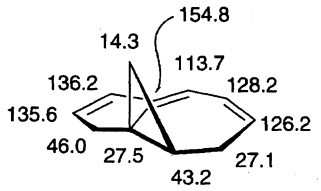
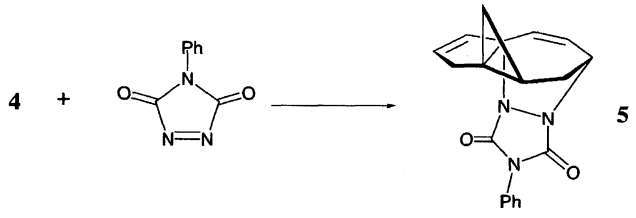


Fig. 1. NMR assignment for **4** (δ ppm).



Scheme 1.

vicinal coupling constants of some protons in the ^{1}H NMR spectrum of **5** are not always consistent with those of the coupled protons due to the high ordered spin–spin coupling, the H–H COSY spectrum clearly confirms the coupling relations. Correlations between the protons of the hydrocarbon moiety in the H–H COSY spectrum of this adduct are shown in Fig. 2. However, the stereochemical relationship between the cyclopropane ring and the triazole ring was not identified by spectroscopy and, thus, was dependent on the crystallographic analysis. As seen in Fig. 3, the triazole ring has the anti configuration to the cyclopropane ring in the adduct.

Quenching of the reaction solution with either D_2O or CH_3OD under the same reaction conditions afforded the hydrocarbon containing one deuterium atom. The incorporation of deuterium atom was found to be stereoselective by comparison of the ^{1}H NMR spectrum of the deuterated product with that of the undeuterated **4**, as shown partially in Fig. 4. That is, the incorporation occurs selectively at the C-4 carbon of **4** with an anti configuration against the cyclopropane ring. The ^{13}C NMR spectrum of **4-d$_1$** clearly shows the

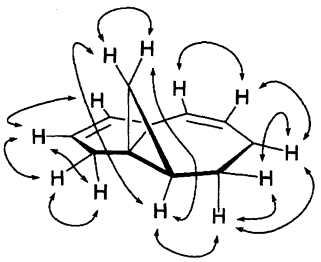


Fig. 2. Correlations of the hydrocarbon moiety in the H–H COSY spectrum of the adduct **5**.

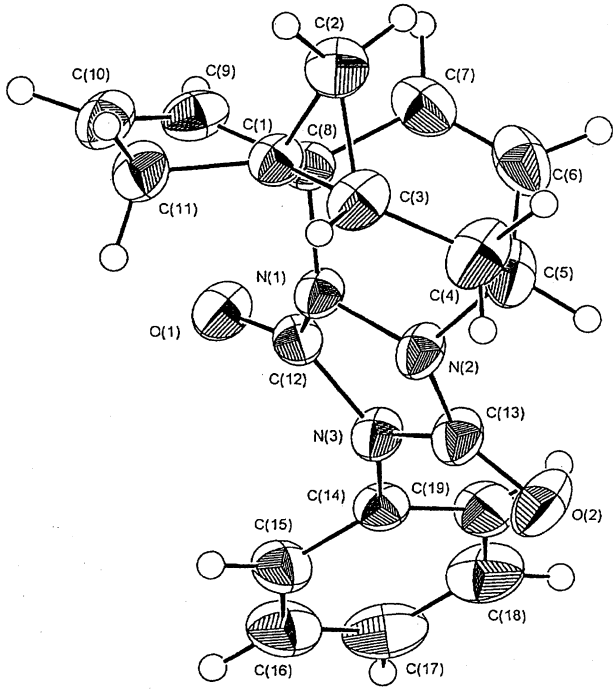


Fig. 3. ORTEP drawing of one of enantiomers present in the crystal of the adduct **5** showing our numbering system.

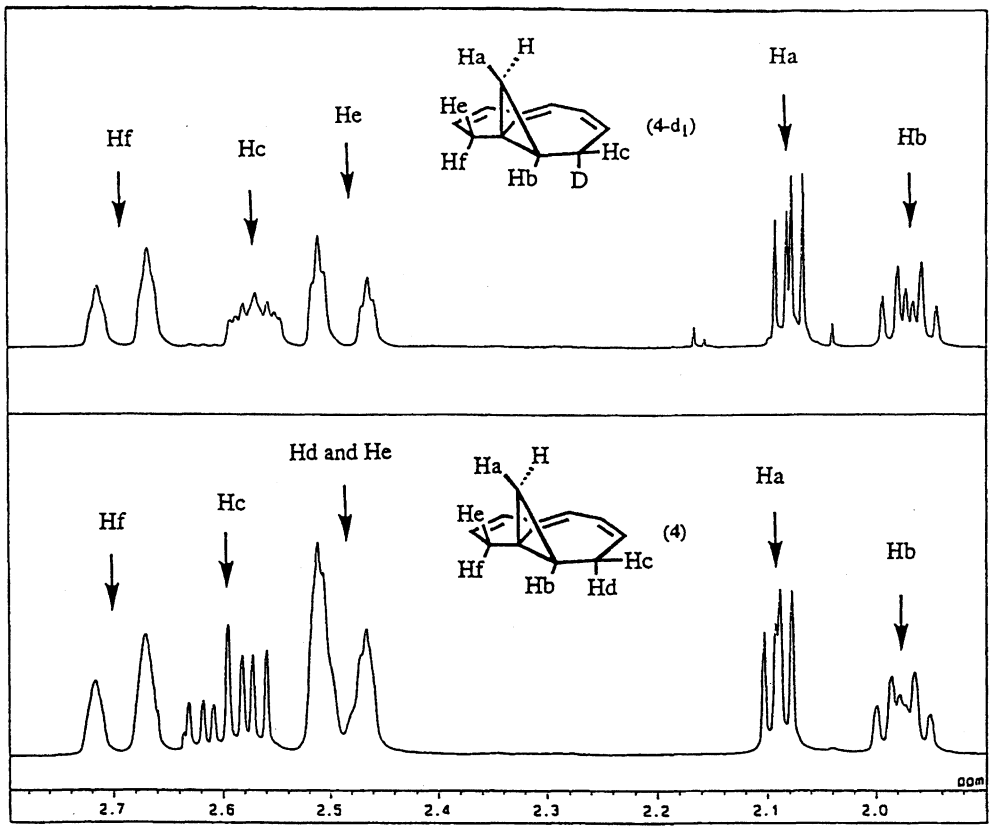


Fig. 4. ^{1}H NMR Spectra (400 MHz) in $CDCl_3$ solution of **4-d$_1$** (top) and **4** (bottom) (360 MHz sweep width).

carbon position attached by a deuterium atom; i.e. signals for the C_4 carbon appeared as a triplet with a C–D coupling constant of 19 Hz. It is worth noting that a deuterium isotope effect on chemical shifts of the carbons around the C_4 position was observed in a 0.7 M (1 M = 1 mol dm^{-3}) $CDCl_3$ solution. The differences between carbon shifts in **4** and **4-d$_1$** are shown in Fig. 5, some of which are unusually shifted to the lower field.[14] Extensive NOE measurements in **4-d$_1$**

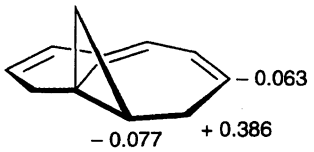


Fig. 5. Differences of carbon chemical shifts between **4** and **4-d$_1$** ($\Delta\delta = \delta_{4\text{-}d_1} - \delta_4$ in ppm). $\Delta\delta$ values below ±0.05 were neglected.

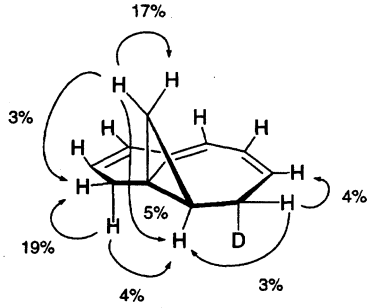


Fig. 6. Results of differential NOE measurements of **4-d$_1$**.

clearly distinguished two methylene protons at the C_{11} position. The intensity of the signal of one of two methylene protons at the C_{11} position was increased on irradiating outward proton of the cyclopropane ring methylene, appeared at 2.09 ppm (Fig. 6).

From the fact of the deuterium incorporation, it is evident that the rearrangement of **3** to **4** proceeds through an anionic intermediate. Therefore, the formation of **4** might best be explained by the mechanism depicted in Scheme 2; deprotonation of **3** with *n*-BuLi gives the anion **6**, which then undergoes the circumambulatory rearrangement to give the anion **7**, followed by protonation to lead to **4** as a final product. Judging from the optimized structure of the anion

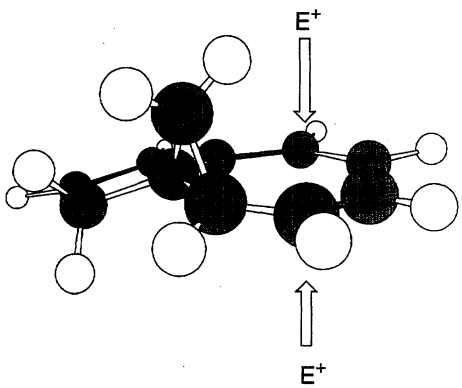
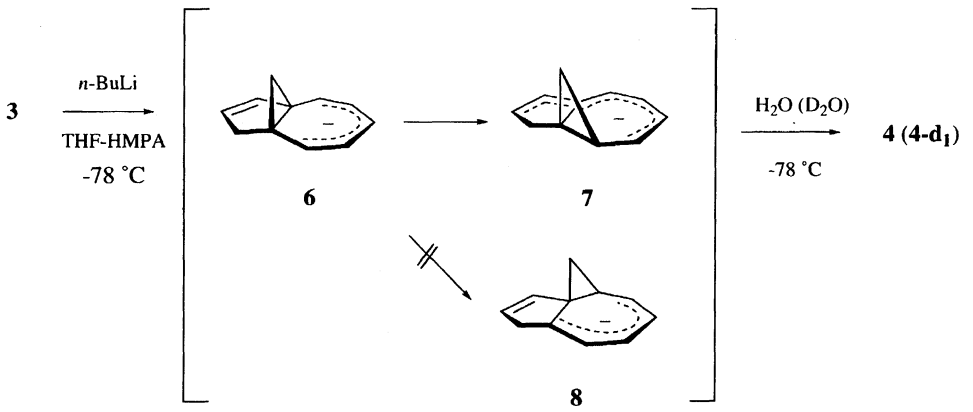


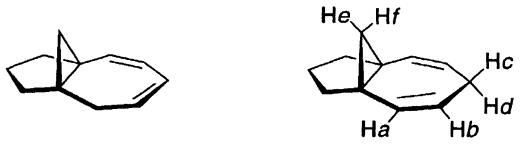
Fig. 7. The optimized structure (Chem 3D output) of the anion **7** by the PM3 method.



Scheme 2.

7 obtained by semiempirical molecular orbital calculations (PM3 method),[15] the anti face of **7** is sterically less crowded for an electrophilic attack (Fig. 7).[16] Therefore, the reason for the stereoselectivity observed in the deuteration reaction can be attributed to steric hindrance between deuteron and one of the methylene protons on the cyclopropane ring, at least as one of it. A circumambulatory rearrangement of the intermediary anion **6** in the opposite direction, which would lead to a different product via a less conjugated tricyclic anion **8**, was not observed (Scheme 2). Thus a major part of the driving force of the rearrangement seems to be the creation of the more conjugated anion. Calculated heats of formation (ΔH_f) by the AM1[17] and PM3 methods predict that the observed process is favorable; the differences of them ($\Delta\Delta H_f$) for conversion of **6** into **7** are greater than that of **6** to **8** (Table 1). Since quenching with deuterium oxide even after a short reaction period of 5 min at −78 °C gave **4-d$_1$** and **3** without any detection of the dueterated **3** or its double bond position isomers, the circumambulatory rearrangement appears to be a quite easy process.

On the other hand, when the tricyclic undecadiene **9**[18] was deprotonated under the same reaction conditions, no coloration in the reaction mixture was observed. Using *t*-BuLi, a stronger base, at higher temperature of −30 °C resulted in orange coloration, however quenching this mixture with water after the reaction time of 20 min at the same temperature gave an unseparable mixture of hydrocarbons, the ^{1}H NMR spectrum of which showed that it contained **9** and its double bond position isomer **10** (Chart 2). Particularly, the presence of the latter in the mixture can be deduced by some signals seen at both the olefinic and aliphatic proton regions; i.e. signals as a doublet of a doublet at 5.88 ppm (J = 11.5, 2.9 Hz) for H*a*, a multiplet at 5.52 ppm for H*b*, a doublet of a multiplet at 2.85 ppm (J = 19.2 Hz) for H*c*, a doublet of a triplet at 2.61 ppm (J = 19.2, 5.8 Hz) for H*d* (interchangeable with H*c*), a doublet at 1.60 ppm (J = 3.6 Hz) for H*e*, and a doublet at 0.46 ppm (J = 3.6 Hz) for H*f* (interchangeable with H*e*) were observed, besides signals of **9**. Although we could not fully characterize this mixture, the formation of the isomer **10** indicates that the anion derived from **9** is more reluctant to undergo circumambulatory rearrangement than the anion **6**. Thus, the conjugation of the cycloheptadienide moiety with an external olefinic part (a double bond at the five-membered ring) in the rearranged product appears to be essential to observed such a circumambulatory rearrangement at low temperature in this tricyclic system.



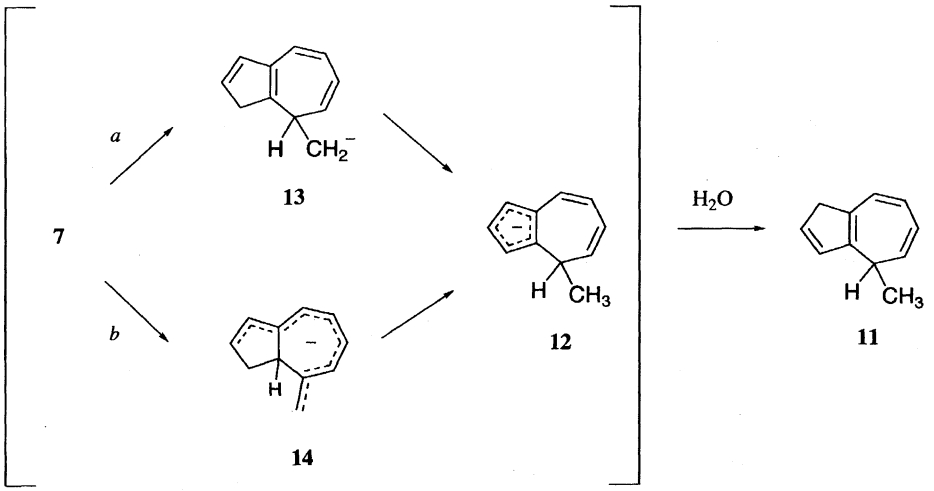
9 **10**

Chart 2.

Table 1. Calculated Heats of Formation of Anions and Differences between Them [kJ mol^{-1}]

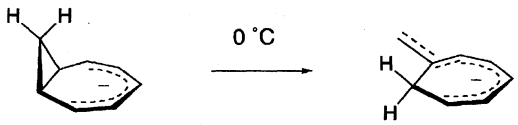
Anion	Calculated heats of formation (ΔH_f)	
	PM3	AM1
6	268.4	296.0
7	227.7	258.2
8	256.6	285.9
12	119.2	150.6
16	369.9	400.3
17	164.8	188.6
	$\Delta\Delta H_f$	
6→**7**	40.7	37.8
6→**8**	11.8	10.1
7→**13**	−142.2	−142.1
7→**14**	62.9	69.6
14→**12**	45.6	38.0

Rearrangement at Elevated Temperature. Quenching of the anion solution derived from **3** with water after the reaction mixture was warmed to 0 °C gave a mixture of dihydro-4-methylazulenes, which included 1,4-dihydro-4-methylazulene (**11**) as a major product, in 23% yield. This mixture of products was found to be entirely the same as the one obtained in the reaction of methyllithium and azulene,[19] indicating the formation of 4-methyl-1,4-dihydro-1-azulenide (**12**) as the latest intermediary carbanion for this second rearrangement. Although a variety of pathways, stepwise



Scheme 3.

and concerted, can be envisioned for this conversion from **7** into **12**, we evaluated, on the basis of molecular orbital calculations, two plausible mechanisms involving intermediary carbanions which are speculated from some previous works.[7,20,21] One is the sequence in which the cleavage of a cyclopropane structure to generate the methanide **13** occurs (route *a* in Scheme 3) and subsequent intra- or intermolecular proton transfer provides **12**, because a few studies have suggested that cyclopropylmethanide may undergo ring opening to give 4-butenide.[20] The other is the pathway involving the anion **14** (route *b*) depicted in Scheme 3, which can be suggested by the facts that the anion **1** undergoes cleavage of the cyclopropane ring to the methylenecycloheptadienide (**15**) above 0 °C[7] (Scheme 4) and the cycloheptadienide in hexahydroazulene isomerizes to the more stable cyclopentadienide by a stepwise protonation–deprotonation mechanism (**16** to **17**, Scheme 5).[21] Since a process from **7** to **13** is predicted to be endothermic on the basis of calculated heats of formations and one from **7** to **14** to be exothermic (Table 1), the latter pathway seems to be more plausible at the present stage.



1 **15**

Scheme 4.

16 **17**

Scheme 5.

In summary, for the first time we have obtained chemical evidence that supports a cyclopropane ring migration on the periphery of a cyclic polyenide, though lacking direct detection of the anionic species, **6** and **7**. A driving force of the circumambulation was thought to be the creation of conjugation between the dienide part and the five-membered ring olefin in the product on the basis of the facts that a circumambulatory rearrangement in the opposite direction, which would lead to a different product via a less conjugated tricyclic anion **8**, was not observed, and that the anion generated from the tricyclic undecadiene **9** was reluctant to undergo the rearrangement. Concurrently we discovered some chemical behavior of the intermediary anion, such as the selective incorporation of an electrophile at low temperatures and the rearrangement to a stable anionic species at elevated temperatures.

Experimental

Melting points were measured on an Yanaco MP-3 and are uncorrected. IR spectra were recorded on a Hitachi IR-810 spectrometer. UV spectra were measured on a Shimadzu UV-256FS spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded in $CDCl_3$ solutions with tetramethylsilane as an internal standard on a JEOL α400. Mass spectra were measured on a JEOL JMS-D-300 mass spectrometer at an ionization energy of 70 eV. Column chromatography was done with Merk Kieselgel 60 Art 7743. The tricyclic undecatriene **3** was synthesized in three steps from 3,8-dihydro-1(2*H*)-azulenone[22] by the reported method.[11] Deuterium oxide (isotopic purity 99.8%) (Aldrich) and methanol-d_1 (99.5%) (Aldrich) were used for the deuterium labelling. A solution of *n*-BuLi in hexane was purchased from Kanto Chemical Co. and titrated before use. HMPA was purchased from Tokyo Kasei Co. and purified by distillation from calcium hydride. THF was purified just before use by distillation from sodium diphenylketyl under a nitrogen atmosphere. Semiempirical molecular orbital calculations were done on an IBM RS/6800-580 computer by using the MOPAC program (ver. 6.02) with full geometry optimization.

The Rearrangement of Tricyclo[5.3.1.0^{1,7}]undeca-2,4,9-triene (3) in the Presence of *n*-BuLi at Low Temperature; Tricyclo[6.3.0.0^{1,3}]undeca-5,7,9-triene (4) and [4-^{2}H$_1$]Tricyclo[6.3.0.0^{1,3}]undeca-5,7,9-triene (4-d$_1$): A solution of **3** (520 mg, 3.60 mmol) in a mixture of dried THF (20 ml) and HMPA (5 mL) was placed in a flame-dried flask with an inlet tube connected to a nitrogen source and a rubber septum. A butyllithium solution (1.0 M solution, 10.8 ml, 10.8 mM) was added dropwise via

a syringe at −78 °C. The reaction solution immediately turned to red and then to dark red. The resulted mixture was stirred at the same temperature for 20 min and then was quenched with methanol (0.2 ml). This mixture was poured into water (100 ml) and was extracted with pentane (3×30 ml). The combined organic layer was washed with brine and dried with $MgSO_4$. After careful evaporation of the solvent at 5 °C, the residual pale yellow oil was purified by chromatography (SiO_2, pentane) to give 259 mg (49%) of **4** as an air-sensitive colorless oil. IR (film) ν = 3040w, 3000w, 2960m, 2940m, 2910s, 2835m, 1590w, 1430m, 1370w, 1320w, 1285w, 1235w, 1200w, 1063m, 1030w, 860m, 740m, 655m cm^{-1}; ^1H NMR δ = 0.56 (1H, dd, J = 8.4, 4.4 Hz), 1.97 (1H, dt, J = 8.4, 6.0 Hz), 2.10 (1H, dt, J = 6.0, 4.4 Hz), 2.50 (2H, dm, J = ca. 18 Hz), 2.60 (1H, ddd, J = 14.4, 8.8, 6.0 Hz), 2.70 (1H, dm, J = 18.4 Hz), 5.33 (1H, ddd, J = 11.2, 8.8, 4.2 Hz), 5.64 (1H, d, J = 6.0 Hz), 5.87 (1H, ddd, J = 11.2, 6.0, 3.2 Hz), 6.07 (1H, dt, J = 5.6, 2.8 Hz), 6.25 (1H, dt, J = 5.6, 2.0 Hz); ^{13}C NMR δ = 14.3, 27.1, 27.5, 43.2, 46.0, 113.7, 126.2, 128.2, 135.6, 136.2, 154.8. UV/vis (MeOH) λ_{max} 302 (log ε = 3.86) nm; EIMS m/z (rel intensity) 144 (M^+; 99), 143 (23), 130 (13), 129 (100), 128 (29), 117 (10), 116 (40), 78 (24), 66 (16), 59 (12), 43 (11). Found: m/z 144.0981. Calcd for $C_{11}H_{12}$: M, 144.0940. Quenching of the anion solution with water, deuterium oxide, or methanol-d_1 under the same condition gave **4** or **4-d$_1$** in 31, 29, or 23% yield, respectively.

4-d$_1$: An air-sensitive colorless oil. IR (film) ν = 2220w cm^{-1}; ^1H NMR δ = 0.56 (1H, dd, J = 8.7, 4.3 Hz), 1.97 (1H, dt, J = 8.4, 5.6 Hz), 2.09 (1H, dt, J = 5.9, 4.1 Hz), 2.52 (1H, dm, J = ca. 18 Hz), 2.58 (1H, m), 2.70 (1H, J = 18.4 Hz, dm), 5.32 (1H, t-like, J = 9.8 Hz), 5.64 (1H, d, J = 5.9 Hz), 5.87 (1H, ddd, J = 10.4, 5.6 Hz), 6.07 (1H, dt, J = 5.6, 2.7 Hz), 6.25 (1H, dt, J = 5.7, 2.1 Hz); ^{13}C NMR δ = 14.2, 26.7 (t, J_{C-D} = 19 Hz), 27.5, 43.1, 46.0, 113.7, 126.2, 128.3, 135.6, 136.1, 154.7. EIMS m/z (rel intensity) 145 (M^+; 91), 144 (33), 143 (8), 142 (14), 130 (96), 129 (100), 128 (54), 118 (13), 117 (22), 116 (45), 115 (24), 103 (14), 79 (10), 78 (30), 77 (10). Found: m/z 145.0974. Calcd for $C_{11}H_{11}D$: M, 145.0993. Results of elemental analysis of **4** and **4-d$_1$** were not satisfactory, probably because of their instability.

Reaction of the Rearranged Hydrocarbon 4 with 4-Phenyl-3*H*-1,2,4-triazoline-3,5(4*H*)-dione; (±)-(1*R, 5*S**, 7*R**, 9*R**)-11,13-Dioxo-12-phenyl-10,12,14-triazapentacyclo-[7.5.2.0^{1,5}.0^{5,7}.0^{10,14}]hexadeca-2,15-diene (5):** To a solution of **4** (259 mg, 1.80 mM) in chloroform (20 ml) was added 4-phenyl-3*H*-1,2,4-triazoline-3,5(4*H*)-dione (315 mg, 1.80 mM) in one portion. This mixture was stirred at room temp for 1 h and then was concentrated under reduced pressure. The residual solids was purified by chromatography (SiO_2, ethyl acetate/chloroform = 15/85) to give 323 mg (57%) of **5** as colorless prisms. An analytical sample was obtained by recrystallization from a mixture of hexane and dichloromethane. Mp 178—180 °C. IR (film) ν = 2910w, 1760m, 1700s, 1650w, 1590w, 1490w, 1400s, 1255m, 1140m, 1085m, 1065w, 975w, 750w, 640w cm^{-1}; ^1H NMR δ = 0.57 (1H, dd, J = 10.0, 4.9 Hz), 0.98 (1H, dd, J = 5.9, 5.1 Hz), 1.37 (1H, td, J = 9.2, 6.3 Hz), 1.99 (1H, dd, J = 16.4, 2.4 Hz), 2.12 (2H, dd, J = 14.8, 2.3 Hz), 2.44 (1H, ddd, J = 14.7, 8.6, 4.6 Hz), 3.10 (1H, dt, J = 16.1, 3.3 Hz), 4.81 (1H, m), 6.15 (1H, d, J = 9.0 Hz), 6.29—6.31 (1H, m), 6.30 (1H, dd, J = 9.0, 6.8 Hz), 6.39 (1H, ddd, J = 5.7, 3.3, 2.0 Hz), 7.33 (1H, tt, J = 7.2, 1.6 Hz), 7.41 (2H, t-like, J = 7.6 Hz), 7.48 (2H, dm, J = 8.0 Hz); ^{13}C NMR δ = 16.0, 21.7, 29.3, 32.8, 41.1, 51.5, 72.4, 125.8, 127.9, 128.9, 129.4, 130.3, 131.8, 132.2, 137.5, 151.1, 152.0. EIMS m/z (rel intensity) 319 (M^+; 2), 177 (7), 143 (37), 142 (51), 141 (100), 128 (27), 119 (9), 115 (43), 63 (10), 51 (6), 39 (8). Found: C, 71.47; H, 5.51; N, 13.20%. Calcd for $C_{19}H_{17}N_3O_2$: C, 71.46; H, 5.37; N, 13.16%.

X-Ray Structure Analysis of the Cycloadduct 5: A colorless, single prism was obtained by recrystallization from a mixture of hexane and dichloromethane. Reflactions were measured on a MacScience DIP2000 diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.7107 Å). The structure was solved by the direct method and refined by the full-matrix least-squares method. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms isotopically. $C_{19}H_{17}N_3O_2$ (319.36), triclinic, $P\bar{1}$, a = 6.742(1), b = 8.869(1), c = 13.338(2) Å, α = 97.358(6)°, β = 98.517(7)°, γ = 102.072(6)°, V = 760.80(1) Å, Z = 2, D_{cald} = 1.394 g cm^{-3}, 3101 independent fractions ($1.36 \leq 2\Theta \leq 54.28°$) on a crystal (0.3×0.25×0.18 mm), 2359 fractions [$I_0 > 3.00\sigma(I_0)$] used, 285 parameters, R = 0.050, R_w = 0.053.[23]

The Rearrangement of Tricyclo[5.3.1.0^{1,7}]undeca-2,4,9-triene (3) in the Presence of *n*-BuLi at Elevated Temperature; a Mixture of Dihydro-4-methylazulenes: A solution of **3**, (30 mg, 0.21 mmol) in a mixture of dried THF (4 ml) and HMPA (1 ml) was placed in a flame-dried flask with an inlet tube connected to a nitrogen source and a rubber septum. A buthyllithium solution (1.2 M solution, 0.53 ml, 0.66 mM) was added dropwise via syringe at −78 °C. The resulting mixture was stirred at the same temperature for 10 min and then the cooling was changed from a dry-ice/2-propanol one to an ice/water one. After being stirred at 0 °C for 20 min, this mixture was poured into water (30 ml) and was extracted with pentane (3×30 ml). The combined organic layer was washed with brine and dried with $MgSO_4$. After careful evaporation of the solvent at 5 °C, the residual pale yellow oil was purified by chromatography (SiO_2, pentane) to give 7.0 mg (23%) of a mixture of dihydro-4-methylazulene as an air-sensitive pale yellow oil, the spectral data of which were identical to those of a reaction mixture from azulene and methyllithium.[19] The following ^1H NMR data are for a major component, 1,4-dihydro-4-methylazulene, picked up from the spectrum of the product mixture. ^1H NMR δ = 1.30 (3H, d, J = 7.2 Hz), 2.67 (1H, qd, J = 7.2, 6.0 Hz), 3.15 (2H, dd, J = 5.8, 1.0 Hz), 5.25 (1H, dd, J = 10.0, 6.0 Hz), 6.05 (1H, dd, J = 10.0, 6.0 Hz), 6.33 (1H, dd, J = 11.2, 6.0 Hz), 6.47 (1H, d, J = 5.2 Hz), 6.55 (1H, d, J = 5.2 Hz), 6.47 (1H, d, J = 10.8 Hz).

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