A Cyclopropane Sliding Reaction of Δ^3-Africen-10-yl Cation

Kiyoharu HAYANO, Haruhisa SHIRAHAMA,*,† and Takeshi MATSUMOTO††
Chemical Laboratory, Sapporo College, Hokkaido University of Education, Sapporo 002
†Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060
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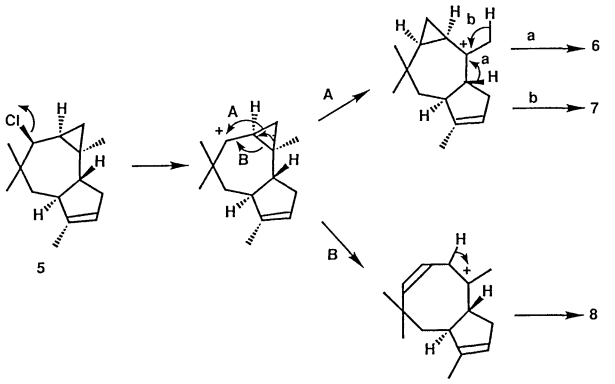
Synopsis. Rearrangement of Δ^3-africen-10-yl cation, generated by the treatment of 10β-chloro-Δ^3-africene with silica gel, accompanied cyclopropane sliding.

Previously we reported[1,2] biogenetic like conversion of humulene (**1**) into $\Delta^{8(13)}$-capnellene and dactylol. A characteristic feature of these syntheses was cyclopropane sliding reactions accompanying an apparent 1,2-shift of a methyl group. These cyclopropane sliding reactions occurred by generation of a carbocation at α-position of the cyclopropane ring. In connection with our project directed toward biogenetic like synthesis of cyclohumulanoids, we investigated the rearrangement of Δ^3-africen-10-yl cation, generated from 10β-chloro-Δ^3-africene (**5**) with an aim to establish the generality of cyclopropane sliding reaction of tricyclo[6.3.0.0^{2,4}]undecane skeleton. In this report, we wish to describe a rearrangement of **5**, which resulted in cyclopropane sliding (Scheme 1).

10β-Chloro-Δ^3-africene (**5**) was synthesized from Δ^3-africen-10α-ol, which had been previously prepared[3] from **1**, via Δ^3-africen-10β-ol (**4**) by the following sequence of reactions: 1) Collin's oxidation, 2) stereoselective reduction of Δ^3-africen-10-one (**3**) (90%, from **2**), and 3) treatment of **3** with phosphorous pentachloride. Without any purification, unstable **5** was directly absorbed on silica-gel column. After 1 h, elution with hexane gave a mixture of three olefins (**6**—**8**). These compounds were separated by a column chromatography using silica gel impregnated with 10% $AgNO_3$ to give **6**, **7**, and **8** in 26, 1.8, and 27% yields from **3**, respectively (Fig. 1). The high resolution mass spectra of these products showed the same molecular formula $C_{15}H_{22}$. For the purpose of elucidating its structure, **6** was converted to epoxy alcohol **9**. Oxidation of **6** with *m*-chloroperbenzoic acid afforded a mixture of diastereomeric diepoxides. This mixture was separated by a silica-gel column chromatography to yield major diepoxide (40%) and minor one (27%). Reduction of the minor diepoxide with lithium aluminum hydride gave rise to **9** as a single product. ^{1}H NMR studies on **9** including extensive decoupling experiments in the presence of a shift reagent [Eu(fod)$_3$] revealed the existence of partial structures depicted in Fig. 2. Consideration of the possible combination of these fragments, probable reaction course and lanthanide induced shift values[4] of several protons (Fig. 2) suggested that structure of the epoxy alcohol was represented by **9**. Therefore, structure of the diene was figured as formula **6**. ^{1}H NMR spectrum of **7** was so similar to that of **6** except for olefinic methyl proton (3H) in **6** and exomethylene (2H) in **7**. Thus, **6** and **7** were implied to be isomers about position of double bond. From the results the molecule should be depicted as formula **7**. Furthermore, examination of ^{1}H NMR spectrum of **8** and the corresponding diepoxide **10**, which was obtained from **8** by epoxidation with *m*-



Scheme 1.

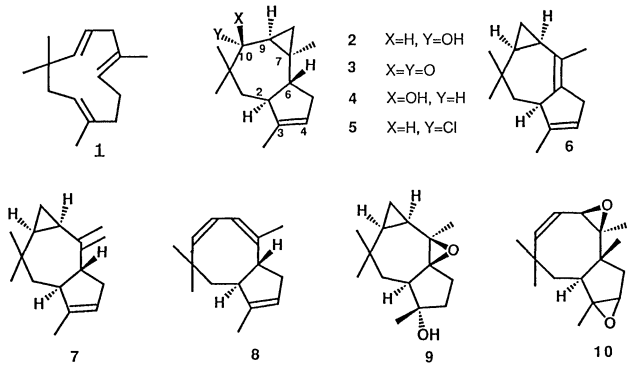


Fig. 1.

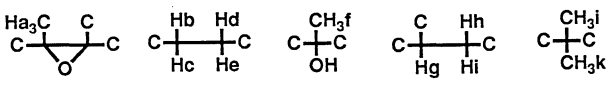


Fig. 2. The following partial structure of **9** was revealed by ^{1}H NMR spectra in the presence of Eu(fod)$_3$ (Eu/**9**=0.37).

Lanthanide induced shift values [$\Delta\delta$/([Eu]/[**9**])]
a=4.8, b=9.7, c=10.4, d=9.7, e=15.4, f=5.0, g=31.1, h=8.3, i=7.2, j=1.6, k=3.9.

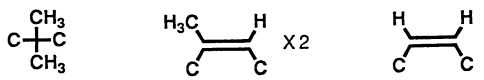


Fig. 3. Partial structures in the molecule of **8**.

†† Present address: Department of Bioscience and Technology, School of Engineering, Hokkaido Tokai University, Minaminosawa Minamiku, Sapporo 005.

chloroperbenzoic acid (72%) as a sole product, revealed that the absence of cyclopropane and the presence of partial structures depicted in Fig. 3 in the molecule of **8**. Considering the above results and possible reaction process, the structure of the triene was presumed to be expressed by the formula **8**.

As described above, it was found that cyclopropane sliding was also took place in acidic rearrangement of 10β-chloro-Δ^3-africene (**5**). These results combined with the previous one could suggest that carbocations generated at C-1 or C-5 position of tricyclo[6.3.0.0^{2,4}]undecane skeleton (α-carbon of the cyclopropane ring) rearranged through cyclopropane sliding in general.

Experimental

^{1}H NMR and ^{13}C NMR spectra were recorded on a HITACHI R20B (60 MHz) and a JEOL JNM FX-100 (25 MHz) instrument using TMS as an internal standard, respectively. High-resolution mass spectra were measured on a JEOL JMS D-300 mass spectrometer. All reactions were carried out under argon atmosphere and stirring.

***t*-2,6,6,9-Tetramethyl-*trans*-1-*transoid*-1,2-*cis*-2-tricyclo[6.3.0.0^{2,4}]undec-9-en-*r*-5-ol (4). (10-Hydroxyafricene).** To a suspension of Collin's reagent (630 mg, 2.4 mmol) and dry Celite (1.0 g) in dry CH_2Cl_2 (10 ml) was added a solution of **2** (150 mg, 0.55 mmol) in CH_2Cl_2 (2 ml) at room temperature. After stirring for 0.5 h at room temperature, the reaction mixture was diluted with Et_2O (20 ml) and filtered through Celite bed. After the filtrate was concentrated in vacuo, the crude oil was dissolved in THF (5.0 ml) and $LiAlH_4$ (20 mg, 0.53 mmol) was added to the solution at room temperature. After stirring at room temperature for 1 h, the solution was cooled to 0 °C, diluted with Et_2O, quenched by the addition of ice, and dried over Na_2SO_4. After filtration, the solvent was removed in vacuo and the residue was chromatographed on silica-gel column (4% EtOAc-C_6H_6) to yield a pure product **4** (135 mg, 90%): ^{1}H NMR ($CDCl_3$) δ=1.01 (3H, s), 1.05 (6H, s), 1.60 (3H, bs), 3.84 (1H, d, J=6 Hz), 5.24 (1H, bs); IR (neat) 3600—3200 cm^{-1}. Found: m/z 220.3537. Calcd for $C_{15}H_{24}O$: M, 220.3540.

***rel*-(3*R*,5*S*,8*R*)-2,6,6,9-Tetramethyltricyclo[6.3.0.0^{3,5}]undeca-1,9-diene (6), 6,6,9-Trimethyl-2-methylene-*trans*-1-*transoid*-1,3-*cis*-3-tricyclo[6.3.0.0^{3,5}]undec-9-ene (7), and *trans*-2,6,6,9-Tetramethylbicyclo[6.3.0]undeca-2,4,9-triene (8).** To a solution of PCl_5 (162 mg, 0.74 mmol) in a mixture of C_6H_6 (27 ml) and $C_6H_5CH_3$ (27 ml) was added 185 mg (0.89 mmol) of **4** at 0 °C and the mixture was stirred for 1 h at room temperature. The reaction mixture was quenched with saturated $NaHCO_3$ aqueous solution (25 ml), and extracted with C_6H_6 three times. The combined extracts were washed with water, dried over Na_2SO_4 and concentrated in vacuo to give a pasty mass which was absorbed on SiO_2 (WAKO silica gel, 8 g) with hexane. After 1 h, mixture of hydrocarbons was eluted with hexane. Separation of the mixture with $AgNO_3$ silica-gel column (0.5% EtOAc-hexane) afforded **6** (44 mg, 26%), **7** (3 mg, 1.8%), and **8** (45 mg, 27%). **6**: ^{1}H NMR ($CDCl_3$) δ=0.6—1.1 (4H, m), 1.0, 1.2 (each 3H, s), 1.65 (6H, bs), 5.29 (1H, bs). Found: m/z 202.3386. Calcd for $C_{15}H_{22}$: M, 202.3388. **7**: ^{1}H NMR ($CDCl_3$) δ=0.2—0.8 (3H, m), 0.93, 1.23 (each 3H, s), 1.63 (3H, bs), 4.73 (2H, bs), 5.29 (1H, m). Found: m/z 202.3384. Calcd for $C_{15}H_{22}$: M, 202.3388. **8**: ^{1}H NMR ($CDCl_3$) δ=1.08, 1.13 (each 3H, s), 1.65, 1.75 (each 3H, bs), 5.2, 5.9 (4H, m); ^{13}C NMR ($CDCl_3$) δ=14.8 (q), 19.7 (q), 23.6 (q), 33.4 (s and t, 2C), 34.8 (q), 40.8 (t), 45.4 (d), 46.8 (d), 123.0 (d), 123.3 (d), 125.4 (d), 139.5 (s), 140.1 (d), 141.3 (s). Found: m/z 202.3382. Calcd for $C_{15}H_{22}$: M, 202.3388.

***rel*-(1*S*,2*R*,3*R*,5*S*,8*R*,9*S*)-1,2-Epoxy-2,6,6,9-tetramethyltricyclo[6.3.0.0^{3,5}]undecan-9-ol (9).** To a solution of *m*-chloroperbenzoic acid (183 mg, 1.01 mmol) in CH_2Cl_2 (20 ml) at 0 °C was added 97 mg (0.48 mmol) of **6**. After stirring for 1 h at room temperature, usual workup followed by chromatographic separation with silica-gel column (2% EtOAc-hexane) afforded minor diepoxide (30 mg, 27.7%): ^{1}H NMR ($CDCl_3$) δ=0.0—0.9 (3H, m), 0.99, 1.11, 1.3, 1.4 (each 3H, s), 1.74 (1H, d, J=15 Hz), 2.22 (1H, dd, J=15 and 1.5 Hz), 3.3 (1H, bs), and major diepoxide (45 mg, 40%): ^{1}H NMR ($CDCl_3$) δ=0.1—1.0 (4H, m), 1.0, 1.1, 1.33, 1.4 (each 3H, s), 1.8 (1H, dd, J=16 and 2.5 Hz), 2.33 (1H, d, J=16 Hz), 3.3 (1H, d, J=2.5 Hz). A solution of the minor diepoxide (30 mg, 0.13 mmol) in THF (0.5 ml) was added to a well stirred slurry of $LiAlH_4$ (5.4 mg, 0.14 mmol) in THF (15 ml) at 0 °C. After stirring for 2 h at room temperature, the excess of reagent was decomposed by the addition of ice-water and the mixture was extracted with EtOAc three times. The combined extracts were dried over Na_2SO_4 and evaporated in vacuo to give paste, which was purified with chromatography on a silica-gel column (10% EtOAc-C_6H_6) to afford **9** (27 mg, 89%): IR (neat) 3600—3200 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.0—0.9 (3H, m), 0.99, 1.11, 1.18, 1.35 (each 3H, s). Found: m/z 236.3531. Calcd for $C_{15}H_{24}O_2$: M, 236.3534.

***rel*-(1*R*,2*S*,3*R*,8*S*)-2,3,9,10-Diepoxy-2,6,6,9-tetramethylbicyclo[6.3.0]undec-4-ene (10).** To a solution of *m*-chloroperbenzoic acid (56 mg, 0.33 mmol) in CH_2Cl_2 (12 ml) at 0 °C was added **8** (30 mg, 0.15 mmol) and the reaction mixture was stirred for 2 h at room temperature. Usual workup followed by chromatographic purification with silica-gel column (2% EtOAc-hexane) gave a pure diepoxide **10** (25 mg, 72%): ^{1}H NMR ($CDCl_3$) δ=1.1, 11.2, 1.3, 1.35 (each 3H, s), 3.26 (1H, bs), 3.3 (1H, s), 5.39 (1H, d, J=11 Hz), 5.51 (1H, d, J=11 Hz). Found: m/z 234.3374. Calcd for $C_{15}H_{22}O_2$: M, 234.3376.

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