HETEROCYCLES, Vol. 60, No. 2, 2003, pp. 365 - 372
Received, 19th November, 2002, Accepted, 18th December, 2002, Published online, 24th December, 2002

NOVEL [12 + 2] CYCLOADDITION OF 2*H*-4,9-METHANOCYCLO-UNDECA[*b*]FURAN-2-ONES WITH ENAMINES: SYNTHESIS AND PROPERTIES OF 4,9-METHANOCYCLOPENTACYCLOUNDECENES AND A BENZO-ANNULATED DERIVATIVE

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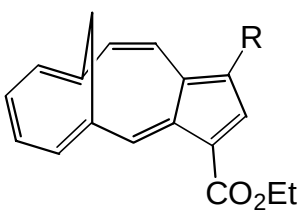
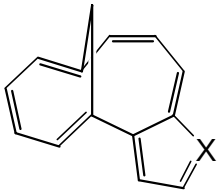
Abstract-Novel cycloaddition reactions of 2*H*-4,9-methanocycloundeca[*b*]furan-2-one and 3-chloro-substituted derivative with enamines underwent novel [12 + 2] cycloaddition reaction followed by decarboxylation and elimination of amine to give 4,9-methanocyclopentacycloundecene derivatives in modest yields. Upon treatment of DDQ, cyclohexane-annulated 5-chloro-4,9-methanocyclopentacyclo-undecene was dehydrogenated easily to give the first example of a benzo-annulated 4,9-methanocyclopentacycloundecene ring system. Chemical as well as spectroscopic properties of them were studied, and it was clarified that benzo-annulation causes an appreciable degree of bond alternation and reduced ring current.

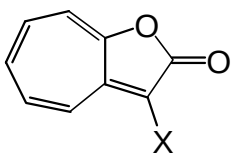
The chemistry of bridged annulenes with nonplanar cyclic conjugation has caused chemists to consider the relationship between molecular strain and aromaticity in these compounds. As for methano-bridged aromatics having 14π-electron system, Prinzbach *et al*. have reported a series of 5,10-methanocyclopentacycloundecenes (**1**) as vinylogous compounds of azulene and showed compounds (**1a,b**) have spectroscopic properties similar to those of azulene.[1] We have also reported the synthesis and spectroscopic properties of 6,11-methanocycloundeca[*b*]pyrrole and an isomer (**2a**),[2] by utilizing the reaction of (vinylimino)phosphoranes[3] with methano[11]annulenones.[4] In a similar manner, the synthesis, spectroscopic and chemical properties of a novel 14π-electron system of 4,9-methano-



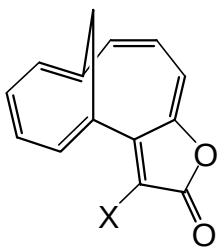
1a: R = H
b: R = CO_2Et



2a: X = N
b: X = CH



3a: X = H
b: X = Cl

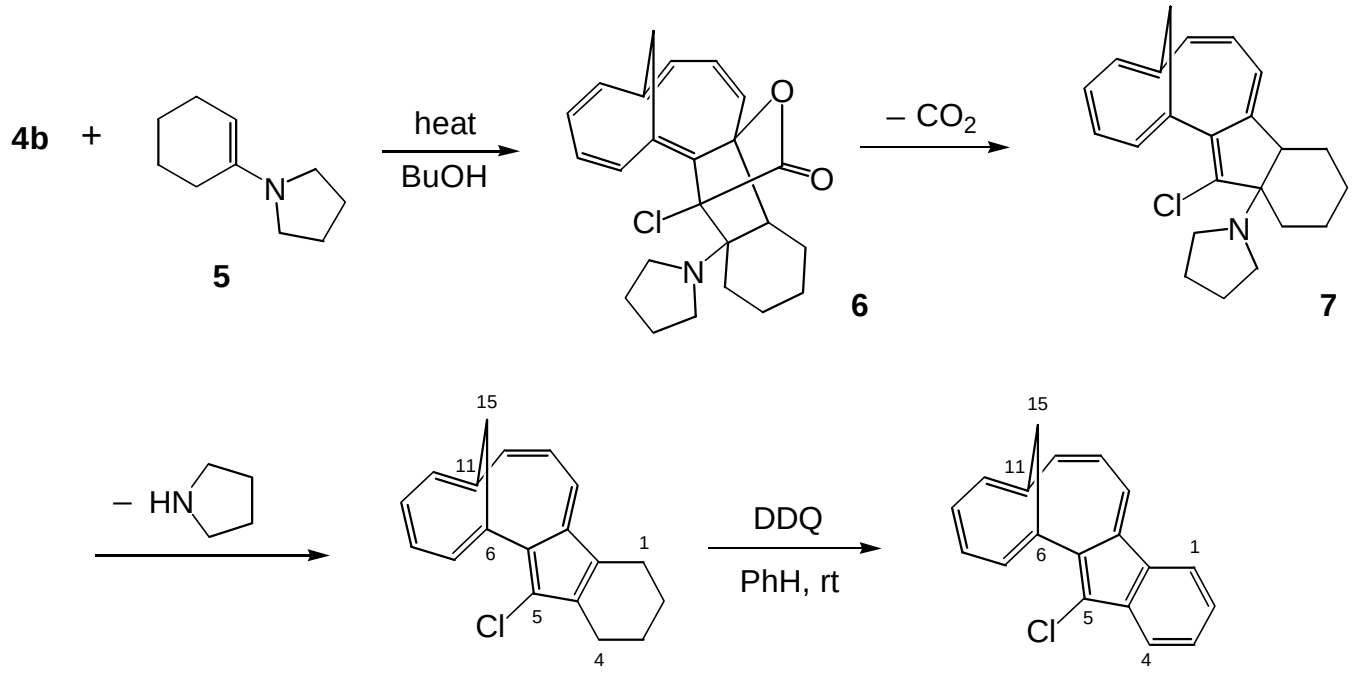


4a: X= H
b: X = Cl

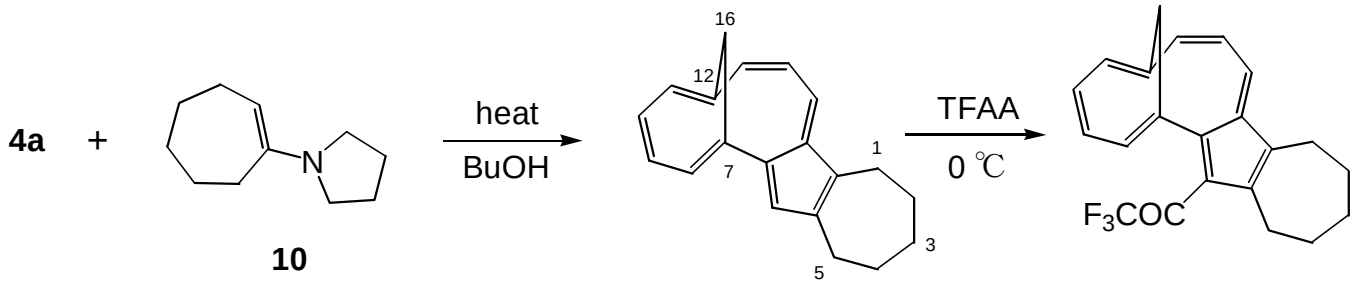
Scheme 1.

cyclopentacycloundecene (**2b**)[5] have also been studied by utilizing prop-2-enylidene-triphenylphosphorane derivatives.[6] 2*H*-Cyclohepta[*b*]furan-2-ones (**3a**) and **(3b**) are conveniently prepared starting from the reaction of activated tropones with active methylene compounds[7] and from the cycloaddition reaction of tropone with dichloroketene.[8] On the other hand, we have previously prepared 2*H*-4,9-methanocycloundeca[*b*]furan-2-ones (**4a,b)** through the cycloaddition of 3,8-methano[11]annulenone with dichloroketene.[9] Compounds (**3a,b)** have been used for the preparation of versatile azulenoid compounds by the formal [8 + 2] cycloaddition reaction with enamines,[10] vinyl ethers[11] and analogues,[12] ketene acetals,[13] and furans,[14] although the consideration based on the MO calculations predicts the preferential [4 + 2] cycloaddition reaction.[15] Thus, compounds (**4a,b**), which are vinylogous compounds of **3a,b**, are also expected to become precursors of a 4,9-methanocyclopentacycloundecene skeleton such as **2**, although the MO calculations predict [4 + 2] cycloaddition reaction.[16] We have now investigated the cycloaddition reaction of **4a,b** to explore the methodology for synthesizing the 4,9-methanocyclopentacycloundecene ring system and the first example of a benzo-annulated derivative of **2b**. We describe herein the results in detail.

In our previous study, the reaction of **4a** with 1-(1-pyrrolidinyl)cyclohexene (**5**) did not give 4,9-methanocyclopentacycloundecene except tarry materials. Even a [4 + 2] cycloadduct, which is expected as a kinetically controlled product based on the MO calculations, was not obtained.[16] On the other hand, an attempted reaction of **4b** with **5** afforded 4,9-methanocyclopentacycloundecene derivative (**8**) in 14% yield (Scheme 2). The six-membered ring of compound (**8**) was easily dehydrogenated by DDQ at room temperature to give the first example of benzo-annulated 4,9-methanocyclopentacyclo-undecene (**9**) albeit in modest yield. As in the cases of the enamine method of azulene synthesis,[10] compound (**8**) was probably derived from the initially formed [12 + 2] cycloadducts (**6)**, which underwent decarboxylation giving **7** and subsequent aromatization eliminating pyrrolidine. Unlike in



Scheme 2.



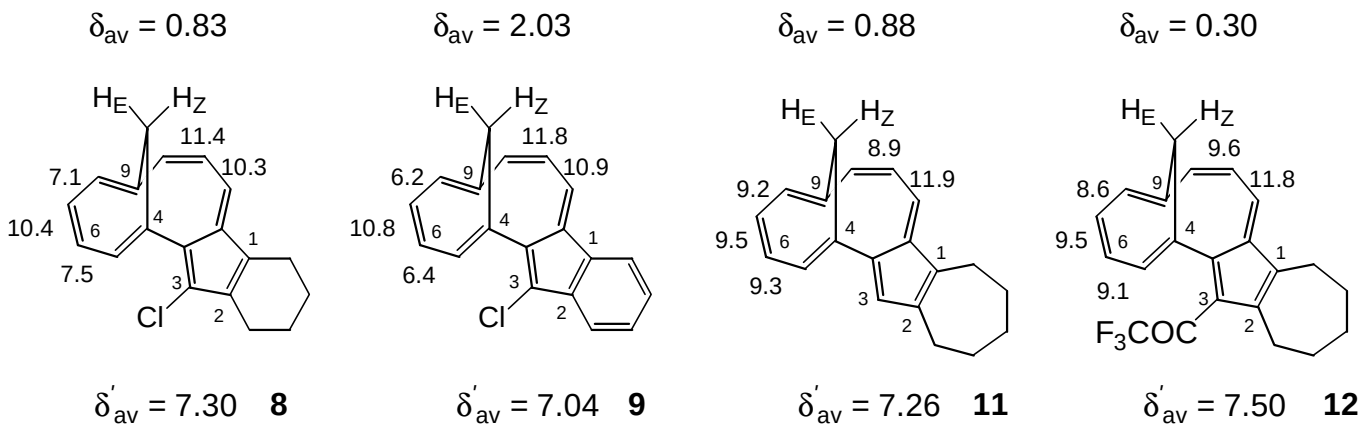
10 **11** **12**

Scheme 3.

the case of the reaction of **4a** with **5**, the reaction of **4a** with 1-(1-pyrrolidinyl)cycloheptene (**10**) in BuOH under reflux for 3 h afforded 4,9-methanocyclopentacycloundecene (**11**) in 38% yield (Scheme 3). It is interesting to compare the reactivity of **11** with that of azulene. Azulenes are known to undergo electrophilic aromatic substitution at the α-position of the five-membered ring under mild conditions.[17] This fact is fully consistent with theoretical predictions and with the known polarization of azulenes, which concentrate electron density in the five-membered ring. Thus, as expected,[6] compound (**11**) was quickly trifluoroacetylated upon treatment with TFAA at 0 ºC to give **12** albeit in modest yield. This fact clearly indicates similarity of the reactivity due to the electronic property of the 4,9-methanocyclopentacycloundecene skeleton and azulene.

Spectral data of compounds (**8**), (**9**), (**11**), and (**12**) are satisfactory for the proposed structures. Satisfactory analytical data of **12** are obtained, and HRMS data are obtained for a minute amount of **8** and **9** as well as an oily compound (**11**).

The ^{1}H NMR spectra of 4,9-methanocyclopentacycloundecene derivatives (**8**), (**9**), (**11**), and (**12**) are noteworthy since the chemical shifts of the bridged-annulene system are quite useful in determining such structural properties as diatropicity and bond alternation. The average chemical shifts of the bridge protons (δ_{av}) and the peripheral protons (δ'_{av}) of the methanoundecene moiety as well as selected coupling constants of the peripheral protons are listed in Scheme 4. The chemical shifts of the methylene protons of the compounds are found in the shielding region (δ = 0.30-0.88). Furthermore, the large geminal coupling constants of the methylene protons ($J_{E,Z}$ = 10.7-11.6) support the absence of a norcaradiene structure for the compounds. These findings indicate that **8**, **9**, **11**, and **12** all exist as diatropic molecules having the 14π-electron system. The chemical shifts of the bridge protons reflect the degree of ring current in methano-bridged aromatics.[18] Their average vlaues of **8** (δ_{av} = 0.83), **9** (δ_{av} = 2.03), **11** (δ_{av} = 0.88), and **12** (δ_{av} = 0.30) suggest that the degree of diatropic ring current decreases in the order of **8** > **9** and of **12** >**11**. The much lower diatropicity of **9** as compared with **8** would be ascribed to the reduced π-electron delocalization due to benzo-annulation. This feature is in good accordance with the average chemical shifts of peripheral protons for **8** (δ'_{av} =7.30) and **9** (δ'_{av} =7.04). The diatropicity of compound (**12**) is higher than that of **11**, probably due to the electron-withdrawing substituent (CF_3CO) on the five-membered ring. This feature agrees well with the average chemical shifts of **12** (δ'_{av} =7.50) and **11** (δ'_{av} =7.26). Vicinal coupling constants of aromatic perimeter protons (numbering of the carbon skeleton in a convenient way is shown in Scheme 4) suggest bond alternation in **8** [$J_{6,7}$ (10.4) > $J_{5,6}$ (7.5) > $J_{7,8}$ (7.1)] and **9** [$J_{6,7}$ (10.8) > $J_{5,6}$ (6.4) ≈ $J_{7,8}$ (6.2)]. A



Scheme 4. Numbering of the carbon skeleton is in a convenient way

remarkable point is the much enhanced bond alternation of **9** as compared with **8**. Thus, it is clarified for the first time, that benzo-annulation onto the 4,9-methanocyclopentacycloundecene system causes bond alternation as in the cases of azulenes annulated with benzene,[19] azulene,[20] 1-azaazulene,[21] and other heteroaromatic rings.[22] This feature is agreeable with the position of the signals for the bridge protons of compounds **9** (δ_{av} = 2.03), which reflect the much reduced diatropicity. Similarly, seven-membered ring-annulated systems (**11**) [$J_{6,7}$ (9.5) > $J_{5,6}$ (9.3) ≈ $J_{7,8}$ (9.2)] and (**12**) [$J_{6,7}$ (9.5) > $J_{5,6}$ (9.1) > $J_{7,8}$ (8.6)] also exhibit bond alternation, which seems to be smaller than those of **8** and **9**. This fact may suggest that the seven-membered ring of **11** and **12** is more flexible than the six-membered ring of **8**, indicating unsuccessful preparation of a chlorine-unsubstituted derivative of **8**.[16] Thus, compounds (**11**) and (**12**) seem to be highly conjugated molecules as compared with **8** and **9**. The coupling constant $J_{10,11}$ is smaller than $J_{11,12}$ for compounds (**11**) and (**12**). This feature is not rationalized at the present stage.

Regarding the electronic spectra of the methanocyclopentacycloundecene ring system, compounds (**8**) and (**9**) exhibit the longest absorption maxima at around 643 nm 522 nm, respectively (Figure 1). The benzo-annulated system **9** is observed by blue shift (121 nm) as compared with that of **8**. This feature suggests that the benzo-annulation onto the 4,9-methanocyclopentacycloundecene ring system caused

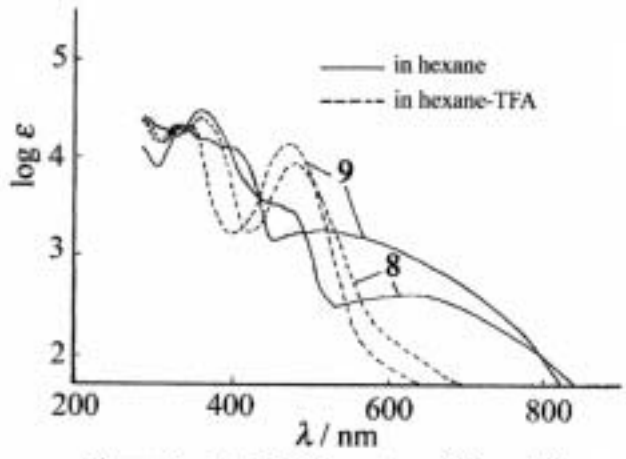


Figure 1. UV-VIS spectra of **8** and **9**

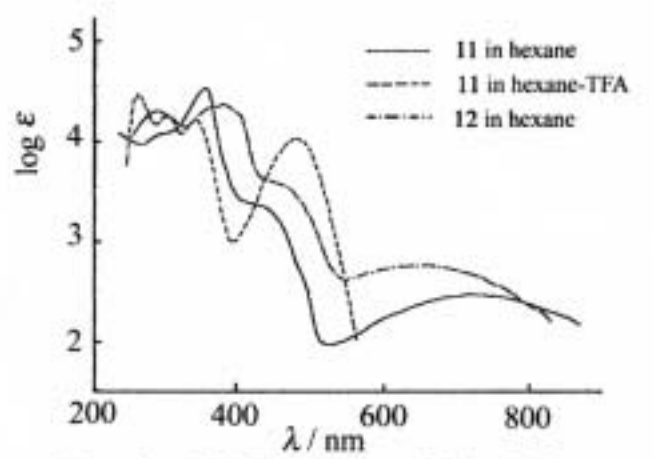


Figure 2. UV-VIS spectra of **11** and **12**

enlargement of the HOMO-LUMO energy gap due to the fixation of the original π-conjugation by the benzene ring. The longest absorption maxima of **8** and **9** disappeared by addition of TFA and new absorption appeared

at 482 nm and 475 nm, respectively, which probably correspond to the absorption of the methano[11]annulenylium cation[24] generated by protonation. Similarly, compounds (**11**) and (**12**) exhibit characteristic absorption maxima at 720 nm and 644 nm, respectively (Figure 2). The longest absorption maximum of **12**, which has an electron-withdrawing substituent of the CF_3CO group at the five-membered ring (corresponding to C1 and C3 position of the azulene), exhibits a blue shift as compared with **11**, as observed in the chemistry of azulene.[23] The longest absorption maximum of **11** disappeared also by adding TFA, and strong absorption maximum appeared around 485 nm due to the formation of the methano[11]annulenylium cation.[24]

In summary, it is clarified that 2*H*-4,9-methanocycloundeca[*b*]furan-2-one undergoes [12 + 2] cycloaddition reactions with enamines to result in the formation of the 4,9-methanocyclopenata-cycloundecene ring system. The six-membered ring-annulated 4,9-meathanocyclopentacycloundecene is easily dehydrogenated to give the first example of benzo-annulated 4,9-methanocyclopentacycloundecene. It is clarified also that the benzo-annulation causes much reduced diatropicity and an appreciable degree of bond alternation in the 4,9-methanocyclopentacycloundecene ring system.

EXPERIMENTAL

IR spectra were recorded on a Horiba FT-710 spectrometer. UV-VIS spectra were recorded on a Shimadzu UV-3101PC spectrophotometer. MS spectra and high-resolution mass spectra were run on JEOL JMS-AUTOMASS150 and JMS-SX102A spectrometers. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a JNM-GSX400 spectrometer using $CDCl_3$ as a solvent, and the chemical shifts are given relative to internal $SiMe_4$ standard; *J*-values are given in Hz. Mps were recorded on a Yamato MP-21 apparatus and are uncorrected. All reactions were carried out under anhydrous conditions and dry nitrogen atmosphere.

Preparation of compound (8). A solution of **4b** (210 mg, 0.86 mmol) and **5** (980 mg, 0.5 mmol) in BuOH (10 mL) was heated under reflux for 3 h. After evaporation of the solvent and excess enamine, the resulting residue was separated by TLC on Al_2O_3 (hexane-AcOH/ 30:1) to give **8** (11 mg, 4.6%) and **4b** (30 mg, 14%).

For 5-chloro-6,11-methano-1,2,3,4-tetrahydroindeno[2,1-*g*]cycloundecene (**8**): greenish prisms; mp 102-103 ºC (MeOH); ^{1}H NMR δ 0.21 (1H, d, *J* = 11.4, H_E-15), 1.44 (1H, d, *J* = 11.4, H_Z-15), 1.84-1.94 (4H, m, H-2 and H-3), 2.75-2.84 (4H, m, H-1 and H-4), 6.56 (1H, dd, *J* = 11.4, 10.3, H-13), 7.07 (1H, d, *J* = 7.1, H-10), 7.15 (1H, dd, *J* = 10.4, 7.1, H-9), 7.33 (1H, d, .*J* = 11.4, H-12),7.43 (1H, dd, *J* = 10.4, 7.5, H-8), 7.56 (1H, d, *J* = 10.3, H-14), 7.99 (1H, d, *J* = 7.5, H-7); ^{13}C NMR δ 22.7, 23.l, 23.3, 23.7, 33.8, 119.4, 122.8, 123.7, 125.6, 126.6, 127.1, 127.6, 127.7, 128.1, 129.4, 133.0, 138.0, 139.0, 141.0; IR ($CHC1_3$) 3008, 2936, 2860, 2837, 1559, 1516, 1448, 1438, 1418 cm^{-1}; MS (m/z) 283 (M^++3, 28), 282 (M^++2, 29),

281 (M^++1, 24), 280 (M^+, 91), 203 (100). HRMS Calculated for $C_{19}H_{17}Cl$: 280.1019. Found: 280.1031.

Preparation of compound (9). A solution of **8** (11 mg, 0.04 mmol) and DDQ (27 mg, 0.12 mmol) in PhH (2 mL) was stirred at rt for 12 h. After evaporation of the PhH, the residue was purified by TLC on Al_2O_3 (hexane-AcOEt/ 30:1) to give **9** (4 mg, 36%).

For 5-chloro-6,11-methanoindeno[2,1-*g*]cycloundecene (**9**): dark violet prisms; 114-115. ºC (MeOH); ^{1}H NMR δ 1.11 (1H, d, *J* =11.6, H_E-15), 2.94 (1H, d, *J* = 11.6, H_Z-15), 6.30 (1H, dd, *J* = 11.8, 10.0, H-13), 6.68 (1H, d, *J* = 6.2, H-10), 7.01 (1H, d, *J* = 11.8, H-12), 7.03 (1H, dd, *J* = 10.8, 6.2, H-9), 7.19 (1H, dd. *J* = 10.8, 6.4, H-8), 7.40 (1H, dd, *J* = 7.5, 7.3, H-2), 7.46 (1H, d, *J* = 6.4, H-7), 7.52 (1H, dd, *J* = 7.6, 7.3, H-3), 7.59 (1H, d, *J* = 10.0, H-14), 7.64 (1H, d, *J* = 7.5, H-1), 7.91 (1H, d, *J* = 7.6, H-4); ^{13}C NMR δ 34.7, 118.0, 118.3, 120.8, 124.0, 124.3, 124.5, 126.4, 126.6, 127.5, 127.7, 129.2, 132.1, 134.0, 135.3, 135.8, 137.6, 139.8 (one carbon overlapping); IR ($CHC1_3$) 3060, 3016, 1602, 1532, 1452 cm^{-1}; MS (m/z) 279 (M^++3, 5), 278 (M^++2, 26), 277 (M^++1, 18), 276 (M^+, 75), 239 (100). HRMS Calculated for $C_{19}H_{17}Cl$: 276.0706. Found: 276.0682.

Preparation of compound (11). A solution of **4a** (300 mg, 1.43 mmol) and **10** (2,36 g, 3 mmol) in BuOH (20 mL) was heated under reflux for 2 h. After evaporation of the solvent and excess enamine, the resulting residue was separated by TLC on Al_2O_3 (hexane) to give **11** (141 mg, 38%).

For 7,11-methano-1,2,3,4,5-pentahydroazuleno[2,1-*g*]cycloundecene **(11)**: greenish oil; ^{1}H NMR δ 0.82 (1H, d, *J* = 10.7, H_E-16), 0.93 (1H, dt, *J* = 10.7, 1.5, H_Z-16), 1.62-1.74 (2H, m, H-3), 1.75-1.87 (2H, m, H-2 or H-4, 1.90-1.99 (2H, m, H-2 or H-4), 2.91-2.97 (1H, m, H-1 or H-5), 3.04-3.13 (3H, m, H-1 or H-5), 6.70 (1H, dd, *J* = 11.9. 8.9, H-14), 6.81 (1H, t, *J* = 9.3, H-10), 7.08 (1H, dd, *J* = 9.5, 9.3, H-9), 7.10 (1H, d, *J* = 8.9, H-13), 7.22 (1H, d, *J* = 9.2, H-11), 7.40 (1H, s, H-6), 7.94 (1H, d, *J* = 9 3, H-8), 7.97 (1H, d, *J* = 11.9, H-15); ^{13}C NMR δ 27.2, 28.8, 28.8, 32.2, 32.9, 33.7, 116.2, 118.1, 125.3, 127.0, 127.9, 129.2, 13l.2, 132.8. 133.5, 134.0, 136.1, 136.1, 140.2, 149.4; IR ($CHC1_3$) 2996, 2917, 2849, 1502,1443, 1382, 1275, 958 cm^{-1}; MS (m/z) 260 (M^+, 100). HRMS Calculated for $C_{20}H_{20}$: 260.1565. Found: 260.1548.

Trifluoroacetylation of 11. To a stirred solution of **11** (92 mg, 0.36 mmol) and Et_3N (359 mg, 3.6 mmol) in CH_2Cl_2 (10 mL) was added $(CF_3CO)_2O$ (373 mg, 1.8 mmol) in CH_2Cl_2 (2 mL) at 0 ºC and the mixture was stirred for 5 min. To this mixture was added aq NH_4Cl solution and the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and the CH_2Cl_2 was evaporated. The resulting residue was separated by TLC on SiO_2 to give **12** (74 mg, 59%).

For 6-trifluoroacetyl-7,11-methano-1,2,3,4,5-pentahydroazuleno[2,1-*g*]cycloundecene (**12**): purple prisms; mp 100-102 ºC (MeOH) ; ^{1}H NMR δ 0.28 (1H, dt, *J* = 11.3, 1.3, H_Z-16), 0.3l (1H. d, *J* = 11.3, H_E-16), 1.63-1.73 (2H, m, H-2 or H-4), 1.75-1.86 (2H, m, H-2 or H-4), 1.89-1.99 (2H, m, H-3), 2.91-3.03 (2H, m, H-1 or H-5), 3.04-3.15 (2H, m, H-1 or H-5), 7.07 (1H, dd, *J* = 11.8, 9.6, H-14), 7.21 (1H, dd, *J* = 9.5, 8.6, H-10), 7.37 (1H, dd, *J* = 9.5, 9.1, H-9), 7.49 (1H, d, *J* = 8.6, H-11), 7.53 (1H, d, *J* = 9.6, H-13),

1.59 (1H, d, *J* = 9.1, H-8), 8.23 (1H, d, *J* = 11.8, H-15) ; ^{13}C NMR δ 26.5, 27.5, 27.8, 28.6, 32.4, 32.7, 115.0, 117.9, 120.5, 123.1, 128.1, 128.8, 129.3, 131.0, 131.9, 133.5, 134.4, 136.1, 140.2, 149.3, 186.4; IR ($CHC1_3$) 2927, 2857, 1671, 1446, 1397. 1150, 946 cm^{-1}; MS (m/z) 356 (M^+, 94), 287 (100). Anal. Calcd for $C_{22}H_{19}OF_3$: C, 74.14; H, 5.31. Found: C, 74.05; H,5.35.

ACKNOWLEDGEMENT

Financial support from a Waseda University Grant for Special Research Project is gratefully acknowledged. We thank the Materials Characterization Central Laboratory, Waseda University, for technical assistance with the spectral data and elemental analyses.

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