Azulene-annulated tricyclo[4.3.1.0^{1,6}]deca-2,4,7-triene derivatives and their anions. A novel cycloheptatriene-norcaradiene valence isomerization in the azulene-annulated tricyclo[4.3.1.0^{1,6}]deca-2,4,7-triene ring system

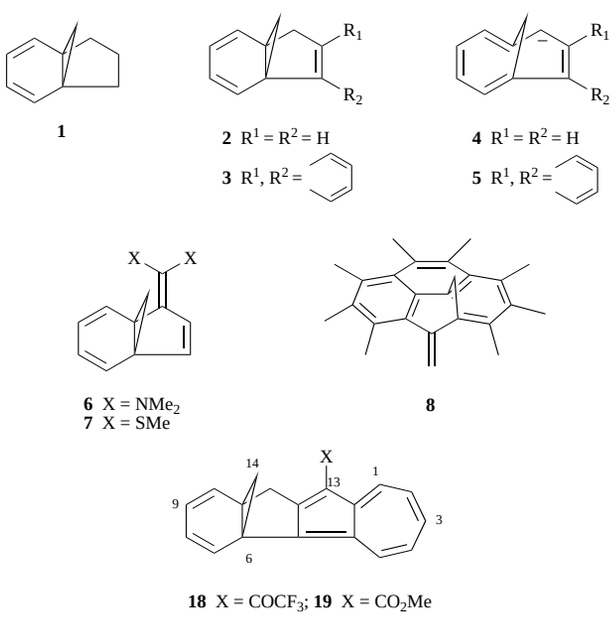
Makoto Nitta * and Tohru Takayasu

Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 169-8555, Japan

10-Trifluoroacetyl-11,11a-dihydro-4a*H*-4a,11a-methanoindeno[1,2-*a*]azulene 18 and methyl {11,11a-dihydro-4a*H*-4a,11a-methanoindeno[1,2-*a*]azulen-10-yl}carboxylate 19 are synthesized starting from the azulene-annulation reaction of 2*H*-cyclohepta[*b*]furan-2-one with the pyrrolidine enamine derived from tricyclo[4.3.1.0^{1,6}]dec-3-en-8-one. The ^{13}C NMR spectra at various temperatures reveal that compound 18 exists in a norcaradiene structure, while compound 19 is in equilibrium between norcaradiene and cycloheptatriene structures. The latter compound is the first example of a cycloheptatriene, which experiences a forced shortening of the C6–C11 distance by a three carbon chain.† The facile valence isomerization of compound 19 is ascribed to the interaction of the lowest unoccupied molecular orbital (LUMO) of the Walsh orbital of cyclopropane and the highest occupied molecular orbital (HOMO) of the methoxycarbonylazulene, and the interaction occurs effectively as to weaken the basal C6–C11 bond of the cyclopropane ring, as compared to that in compound 18 involving an azulene nucleus bearing the more electron-withdrawing trifluoroacetyl group. The hydrogen–deuterium exchange reaction of compounds 18 and 19 in MeONa–MeOD occurs stereospecifically to give 12-*exo*-deuterated products (*exo* to the bridge methylene), respectively. Marked spectroscopic differences between the anions 30 and 31, which are derived from compounds 18 and 19 by treatment with [$^2H_5$]dimsyl sodium in [$^2H_6$]DMSO, respectively, are also observed: the anionic charge in the former is not delocalized over the trifluoroacetylazulene nucleus, while that in the latter is delocalized over the methoxycarbonylazulene nucleus. The thermal rearrangement of the anion generated from compound 19 is also observed to result in the formation of 11-methoxycarbonylazuleno[1,2-*a*]azulene. Furthermore, the Diels–Alder reaction of the tricyclo[4.3.1.0^{1,6}]deca-2,4,7-triene (methanoindeno[1,2-*a*]azulene) ring system in compounds 18 and 19 has been studied as well.

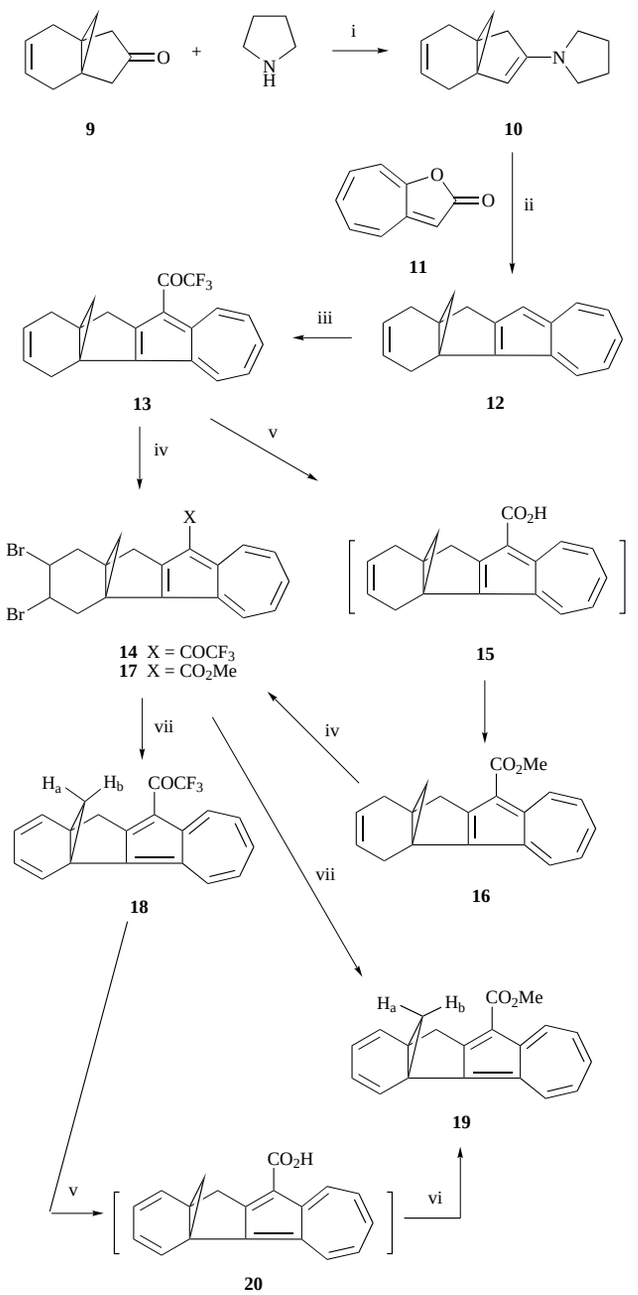
Introduction

Cycloheptatriene (CHT)–norcaradiene (NCD) tautomerism has received much attention from both the theoretical and synthetic point of view. Although the equilibrium lies in general on the side of the CHT, a variety of compounds have been known to prefer the NCD structure.[1] Four factors implicated in the stabilization of the NCD structure have been proposed as follows: (i) the placement of electron-accepting substituent(s) such as a cyano group at the C7-position,[2] (ii) the extension of conjugation at appropriate positions in the NCD form,[3] (iii) the non-bonding interaction between the C7-substituent and proximal π-bonds or substituents,[4] (iv) the forced shortening of the C1–C6 distance by a three-carbon chain as in compounds **1**,[5] **2**,[6,7] and **3**[8]. Regarding [6,5] close compounds **2** and **3**, they react with [$^2H_5$]dimsyl sodium in [$^2H_6$]DMSO to produce aromatic systems **4**[6,7] and **5**.[8] The introduction of a negative charge to form **4** and **5** favor the [6,5] open structures. Although the exomethylene-derivatives **6** and **7** have been shown to exist as the [6,5] close NCD structure rather than the [6,5] open nonafulvene,[9] an example of the [6,5] open neutral structure **8** has been found in the chemistry of fulleroid.[10,11] In relation to these facts as well as our previous studies concerning the synthesis and spectroscopic properties of azuleno- and 1-azaazuleno-annulated 1,6-methano[10] annulenes,[12a,b] we have embarked on the synthesis of 10-trifluoroacetyl-11,11a-dihydro-4a*H*-4a,11a-methanoindeno[1,2-*a*]azulene and methyl {11,11a-dihydro-4a*H*-4a,11a-methanoindeno[1,2-*a*]azulen-10-yl}carboxylate derivatives **18** and **19** and their anions. Since theoretical calculations[13] and the large dipole moment[14] of azulene have



1 **2** $R^1 = R^2 = H$ **3** $R^1, R^2 =$ **4** $R^1 = R^2 = H$ **5** $R^1, R^2 =$ **6** X = NMe_2 **7** X = SMe **8** **18** X = $COCF_3$; **19** X = CO_2Me

† The numbering system used throughout the Introduction and Discussion sections and for describing ^{1}H and ^{13}C NMR spectral data is shown on the representative compounds **18**, **19** shown above. However for the purposes of nomenclature in the Experimental section the IUPAC numbering system has been used.



Scheme 1 *Reagents and conditions:* i, PhH, heat; ii, BuOH, heat; iii, $(CF_3CO)_2O$, Et_3N, CH_2Cl_2, 0 °C; iv, $PyHBr_3$, CH_2Cl_2, −78 °C; v, 1 M KOH, MeOH–THF–H_2O, heat; vi, CH_2N_2, Et_2O, 0 °C; vii, DBU, THF, heat

been clearly reflected in the extremely stabilized azulene(s)-substituted carbocations,[15] our interest was especially focused on how the annulation of azulene affects the cyclopropane ring of the tricyclo[4.3.1.$0^{1,6}$]deca-2,4,7-triene system. We found that compound **18** exists in the NCD form, while compound **19** is in equilibrium between the NCD and CHT forms. Anions **30** and **31**, obtained by base treatment of compounds **18** and **19**, exist in the [6,5] open form. The quenching of anions **30** and **31** with D_2O as well as the proton–deuterium exchange reaction of compounds **18** and **19** in MeOD–MeONa afforded 12-*exo*-deuterated products **18-D** and **19-D** stereospecifically. The Diels–Alder reaction of compounds **18** and **19** was studied as well. We describe herein the results in detail.

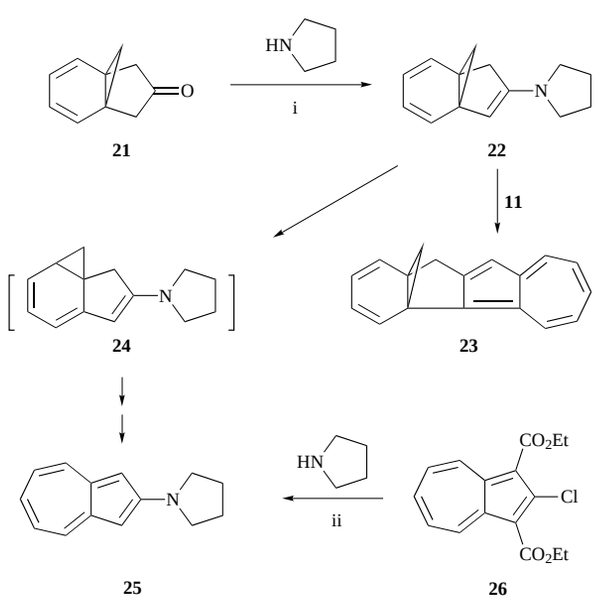
Results and discussion

Synthesis of the azulene-annulated tricyclo[4.3.1.$0^{1,6}$]deca-2,4,7-triene **18** was performed using the so-called enamine method explored by Takase and co-workers.[16,17] Tricyclo-[4.3.1.$0^{1,6}$]dec-3-en-8-one **9**[18] reacted with pyrrolidine to give enamine **10** *in situ*, which subsequently reacted with 2*H*-cyclohepta[*b*]furan-2-one **11** to give compound **12** (Scheme 1). For protection against electrophilic attack on the azulene nucleus, compound **12** was converted to trifluoroacetyl derivative **13** by treatment with $(CF_3CO)_2O$ at 0 °C.[19] Treatment of compound **13** with pyridinium tribromide in CH_2Cl_2 at −78 °C then afforded the crude dibromide **14**. On the other hand, hydrolysis of **13** leading to the carboxylic acid **15** followed by treatment with CH_2N_2 gave the methoxycarbonyl derivative **16** in 85% yield.[12b] Subsequent bromination of compound **16** afforded the crude dibromide **17**.

Structural assignment for new compounds **12**, **13**, **14** and **16**, were based on their ^{1}H NMR and mass spectra, and HRMS and/or elemental analyses. Compound **17** seemed to be labile and HRMS and analytical data could not be obtained. In the ^{1}H NMR spectra of these compounds, the chemical shifts and coupling patterns are in good agreement with the proposed structures of **12**–**14**, **16** and **17**.

Since dibromides **14** and **17** are not so stable, they were subsequently treated with excess 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to undergo bisdehydrobromination leading to the desired 10-trifluoroacetyl- and 10-methoxycarbonyl-azulene-annulated tricyclo[4.3.1.$0^{1,6}$]deca-2,4,7-trienes **18** and **19**. Compound **19** was also obtained *via* an alternative pathway: hydrolysis of the trifluoroacetyl group in compound **18** leading to the carboxylic acid **20**, followed by methylation with CH_2N_2 afforded compound **19** in good yield. The structures of **18** and **19** were supported by their ^{1}H and ^{13}C NMR spectra, which were assigned using H–H and C–H COSY spectroscopy, mass spectroscopy and elemental analysis. Interestingly, marked differences were observed in the ^{1}H and ^{13}C NMR spectra between compounds **18** and **19** (*vide infra*).

From the synthetic point of view, one may consider that the reaction of enamine **22** with furanone **11** directly gives unsubstituted azulene-annulated tricyclo[4.3.1.$0^{1,6}$]deca-2,4,7-triene **23** (Scheme 2). However, the attempted reaction of ketone **21**[7]

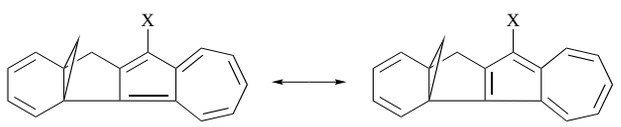


Scheme 2 *Reagents and conditions:* i, toluene, heat; ii, EtOH, heat

with pyrrolidine did not give the anticipated enamine **22**, and 2-(pyrrolidin-1-yl)azulene **25** was obtained instead. Compound **25** probably arose from a Berson–Willcott type rearrangement[20] of the anticipated enamine **22**, in which cleavage of the C–C bond at the diallylic position (C1) occurs to give intermediate **24**. The intermediate **24** would undergo norcaradiene–cycloheptatriene valence isomerization and in the ensuing

aromatization, eliminates hydrogen under the reaction conditions and/or work-up conditions. The structure of compound **25** was confirmed on the basis of mass and ^{1}H NMR spectral data, and elemental analyses as well as an independent synthesis of **25** according to the literature procedure using diethyl 2-chloroazulene-1,3-dicarboxylate **26** and pyrrolidine.[21] Thus the preparation of **23** had not been accomplished at this stage.

The ^{1}H and ^{13}C NMR spectral data of compounds **18** and **19** in $CDCl_3$ and [$^2H_6$]DMSO are summarized in Table 1. The chemical shifts and coupling patterns in the ^{1}H NMR spectra suggest structural differences between compounds **18** and **19**. The average chemical shifts of the seven-membered ring moiety of compounds **18** (δ_{av} 8.24) and **19** (δ_{av} 7.99) are shifted to high-field as compared with those of 1-trifluoroacetylazulene **27**[22] (δ_{av} 8.38) and 1-methoxycarbonylazulene **28**[23] (δ_{av} 8.17) (see Experimental), respectively, reflecting electron donation due to the annulation of the methanoindene ring system as well as the stronger electron-withdrawing ability of the $-COCF_3$ group than the $-CO_2Me$ group. The vicinal coupling constants of the seven-membered ring moieties suggest that bond-length alternation is small for both compounds **18** ($J_{4,5}$ 9.9 > $J_{2,3}$ 9.8 > $J_{1,2}$ 9.7 > $J_{3,4}$ 9.6) and **19** ($J_{2,3}$ 10.3 > $J_{1,2}$ ~ $J_{4,5}$ 9.7 > $J_{3,4}$ 9.2), and that the canonical structures, **18A** and **19A**, of the azulene moiety are slightly more important compared to structures **18B** and **19B**, respectively (Scheme 3). A noteworthy point is the geminal

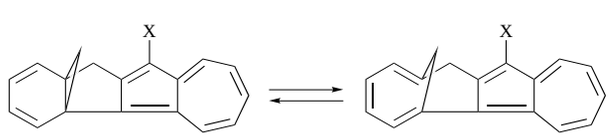


18A X = $COCF_3$
19A X = CO_2Me

18B
19B

Scheme 3

coupling constant of the methylene protons at C14: the value of J 4.1 for compound **18** is close to those for compound **2** (J 3.5)[6] and its benzo-analogue **3** (J 3.6).[8] On the other hand, the corresponding coupling constant for compound **19** (J 6.0) is too large for the [6,5] close NCD structure, while it is fairly close to that for the [6,5] open structure **4** (J 7.5)[6] and **5** (J 7.3).[8] Furthermore, the ^{13}C NMR signals of C6 and C11 for compound **18** appearing at δ_C 45.7 and 51.5 (Table 1) are close to the corresponding signals for compounds **2** (δ_C 40.1 and 48.1) and **3** (δ_C 39.6 and 45.6).[24] The signals of C6 and C11 for compound **19** appear at δ_C 81.3 and 90.0 (Table 1), and are largely shifted to lower field as compared with those of compounds **2**, **3** and **18**, but are higher than those of the corresponding values for the [6,5] open anions (δ_C 113.7 for **4** and 101.3 and 119.2 for **5**).[24] Thus, the ^{1}H and ^{13}C NMR spectra suggest that compound **18** exists as the [6,5] close NCD isomer **18N**, but compound **19** exists in equilibrium between two isomers **19N** and **19C** (Scheme 4). In addition, the average chemical shift of the



18N X = $COCF_3$
19N X = CO_2Me

19C X = CO_2Me

Scheme 4

C7–C8–C9–C10 moiety of compound **19** (δ_{av} 6.49 in $CDCl_3$) is lower than the corresponding value of compound **18** (δ_{av} 6.39) and the vicinal coupling constants in compound **19** ($J_{7,8}$ 8.4, $J_{9,10}$ 7.5) are smaller than those for compound **18** ($J_{7,8}$ 9.1, $J_{9,10}$ 9.0). This fact could be ascribed to the extension of conjugation of C7–C8–C9–C10 with the azulene moiety by participation of the equilibrium between the two isomers **19N** and **19C**. The

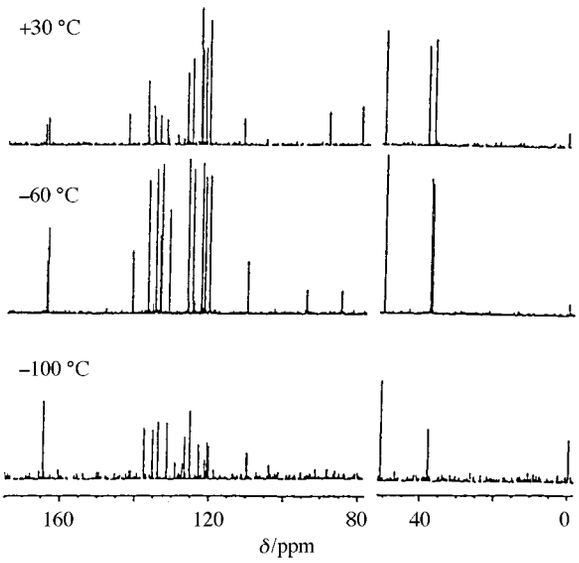


Fig. 1 ^{13}C NMR spectra of **19** in CD_2Cl_2 at various temperatures

electronic spectrum of compound **19** is largely shifted to longer wavelength as compared to that of compound **18**, suggesting not only the weaker electron-withdrawing ability of the $-CO_2Me$ group as compared with the $-COCF_3$ group but also the conjugation of C7–C8–C9–C10 with the azulene moiety by participation of the equilibrium between two structures **19N** and **19C**.[22,23]

Although the ^{1}H NMR (600 MHz, CD_2Cl_2) spectral studies were conducted at various temperatures, no clear change was observed for compounds **18** and **19** at temperatures ranging from 30 to −100 °C. In addition, the ^{13}C NMR spectrum (150.8 MHz) of compound **18** was not changed at temperatures ranging from 30 to −100 °C in CD_2Cl_2. This fact would also support the absence of the [6,5] open CHT structure for compound **18**. On the other hand, the ^{13}C NMR spectra of compound **19** do change at various temperatures as depicted in Fig. 1. At −60 °C, the signals appearing at δ 79.2 and 88.2 (C6 and C11) at room temperature (room temp.) are shifted to lower field (δ 85.1 and 94.5), and both signals disappear at −100 °C. The temperature dependency was also observed in the aromatic and olefinic carbons as well as the C12 and C14 carbons, which became overlapping peaks at −100 °C. In addition, the signals of C6 and C11 at δ 79.2 and 88.2 in [$^2H_6$]DMSO shifted to a higher field of δ 77.1 and 85.7 at 120 °C. These features clearly indicate that compound **19** exists in two different isomeric forms, **19N** and **19C**, at room temp. (Scheme 4) and the equilibrium between them is frozen at low temperature. Furthermore, on the basis of these temperature-dependent spectra, it would seem that the ratio of isomer **19C** increases at low temperature relative to **19N** while it decreases at high temperature. Thus, the [6,5] open isomer **19C** seems to be more stable than the [6,5] close isomer **19N**. Unfortunately, we could not conduct ^{13}C NMR spectroscopy below −100 °C, thus further detailed dynamic behavior of isomers **19N** and **19C** could not be clarified at this stage.

The difference in dynamic behavior between compounds **18** and **19** is rationalized on the basis of the interaction between the Walsh orbital of cyclopropane with the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) of a π-system.[25] The highly polarized azulene[13–15] would donate a π-electron to the cyclopropane ring as depicted in structure **29** (Fig. 2), which represents the interaction between the LUMO of the Walsh orbital of a cyclopropane and the HOMO of the azulenes. The calculated energy levels and HOMO coefficients for 1-trifluoroacetylazulene **27** and 1-methoxycarbonylazulene **28** are depicted in Fig. 2.[26] Regarding the azulene **28**, the energy level of the HOMO is

Table 1 ^{1}H (400 MHz) and ^{13}C NMR (100.6 MHz) spectral data of compounds **18** and **19** and anions **30** and **31**†

Compd.		C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C14	Remaining signals
18	δ_H [a]	9.60	7.77	7.57	7.60	8.65	—	6.88	6.04	6.14	6.45	—	3.82(*endo*) 3.84(*exo*)	0.44(a) [d] 1.95(b) [d]	
	J [c]	9.7	9.8	9.6	9.9			9.1	6.4	9.0			19.0 [e]	4.1 [e]	
	δ_H [b]	9.50	7.72	7.80	8.12	8.93	—	7.08	6.56	6.14	6.06	—	3.34(*endo*) 3.72(*exo*)	0.44 1.95	
	J [c]	9.5	9.6	9.5	9.7			8.1	5.7	9.0			19.1 [e]	4.1 [e]	
	δ_C [a]	138.4	139.2	129.1	131.1	134.9	45.7 or 51.5	124.9	121.0	119.3	127.8	45.7 or 51.5	38.8	29.2	112.8, 115.5, 118.4, 136.5, 141.3, 148.3, 159.8 (C=O)
19	δ_H [a]	9.33	7.36	7.48	7.31	8.49	—	6.73	6.48	6.32	6.44	—	3.31(*endo*) 4.03(*exo*)	0.53(a) [d] 2.76(b) [d]	3.84 (Me)
	J [c]	9.7	10.3	9.2	9.7			8.4	8.1	7.5			19.1 [e]	5.9 [e]	
	δ_H [b]	9.32	7.54	7.84	7.52	8.71	—	6.85	6.47	6.32	6.49	—	3.34(*endo*) 3.97(*exo*)	0.48(a) [d] 2.83(b) [d]	3.48 (Me)
	J [c]	9.8	10.0	9.7	9.9			7.6	7.7	7.8			19.1 [e]	6.0 [d]	
	δ_C [a]	136.4	127.3	137.8	125.8	134.4	81.3 or 90.0	122.3	123.6	123.4	121.4	81.3 or 90.0	39.0	37.5	50.9 (Me), 111.8, 132.9, 136.0, 143.0, 164.6, 165.5 (C=O)
30	δ_H [b]	9.97	7.29	7.61	7.38	8.66	—	6.92	6.24	5.86	7.01	—	5.78	0.14(a) [f] 3.02(b) [f]	
	J [c]	9.9	9.9	9.9	9.6			11.1	8.0	10.7				6.2 [e]	
31	δ_H [b]	7.59	6.43	5.90	6.46	7.14	—	6.88	6.48	6.40	6.41	—	5.77	−0.15(a) [f] (2.5)(b) [f]	3.61 (Me)
	J [c]	9.8	12.1	9.8	10.4			6.1	9.4	8.5				6.7 [e]	
	δ_C [b]	114.4	121.5	126.5	129.3	117.7	112.4 or 121.5	121.6	123.8	130.8	116.9	112.4	102.9 or 121.5	43.2	49.0 (Me), 128.3, 130.8, 134.1, 148.3, 158.5, 165.6 (C=O)

[a] Recorded in $CDCl_3$. [b] Recorded in [$^{2}H_6$]DMSO. [c] Vicinal coupling constant in Hz. [d] *cf.* Scheme 1. [e] Geminal coupling constant in Hz. [f] *cf.* Scheme 5.

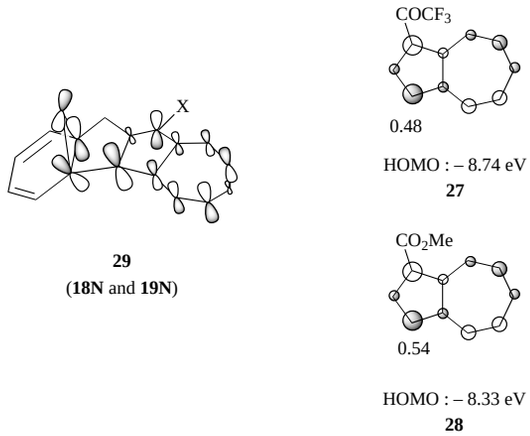
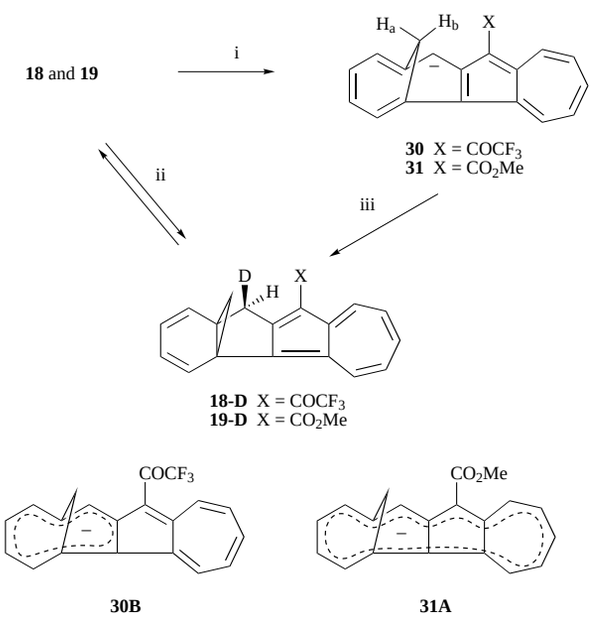


Fig. 2

higher, and the coefficient at C3 larger, than the corresponding values of azulene **27**. Thus, the LUMO (cyclopropane)–HOMO **28** interaction (overlapping of the lobes at C5b and C6) would occur so effectively as to weaken the basal C6–C11 bond in structure **29** in the case of isomer **19N** as compared with the LUMO (cyclopropane)–HOMO **27** interaction in the case of isomer **18N**. Thus, the relative stability of isomer **19C** is increased and the valence isomerization between isomers **19N** and **19C** occurs easily as compared to that of isomer **18N**.

The bridged anions **30** and **31** were prepared by deprotonation of compounds **18** (**18N**) and **19** (**19N** and **19C**) with [$^2H_5$]dimsyl sodium in [$^2H_6$]DMSO by using the procedure described by Hunadi[8] at room temp. (Scheme 5). Although

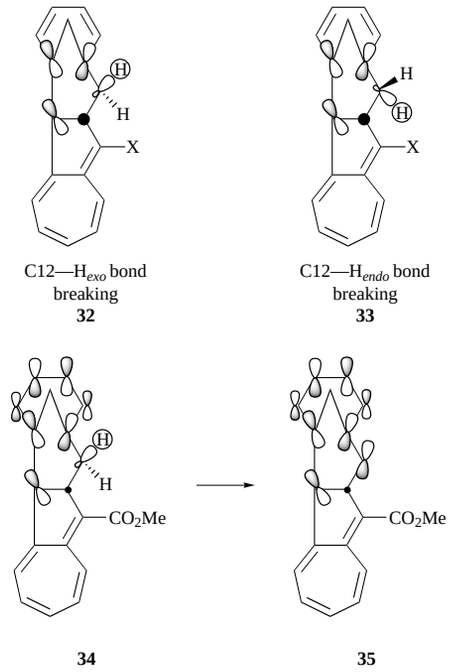


Scheme 5 *Reagents and conditions:* i, CD_3SOCD_2Na, [$^2H_6$]DMSO; ii, MeONa, MeOD, 0 °C; iii, D_2O

anion **30** is unstable and its ^{13}C NMR spectrum was not recorded, ^1H NMR of anions **30** and **31** and ^{13}C NMR spectra of anion **31** were recorded and are summarized in Table 1.

Concerning the ^1H NMR data for anion **30**, the average proton chemical shift (δ_{av} 8.18) of the seven-membered ring moiety is slightly higher than that (δ_{av} 8.24 in $CDCl_3$ and 8.41 in [$^2H_6$]DMSO) of compound **18**, suggesting a slight delocalization of anionic charge over the azulene moiety. The diatropic nature of anion **30** is suggested by the slightly higher chemical shifts of H_a-14 (δ 0.14) than that (δ 0.44) of compound **18**. The chemical shift of H_b-14 appearing at δ 3.02 is lower than that (δ 1.95) of compound **18**. This fact could be ascribed to the anisotropic effect of the C=O group, which is not co-planar with the azulene nucleus, and the fact that the oxygen is located in close proximity to H_b-14 (based on AM1 calculations).[26] Unlike in the case of anion **30**, the average proton chemical shift (δ 6.70) of the seven-membered ring moiety of anion **31** is largely shifted to high field as compared with that (δ_{av} 7.99 in $CDCl_3$ and 8.19 in [$^2H_6$]DMSO) of compound **19**. This feature indicates that an anionic charge is delocalized over the azulene moiety. The increased diatropicity of anion **31** as compared with that of anion **30** is suggested by the higher chemical shifts of H_a-14 (δ −0.15) and H_b-14 (δ 2.5: overlapping with DMSO) as compared with those (δ 0.48 and 2.83) of anion **30**. The weaker electron-withdrawing ability of the $-CO_2Me$ group as compared with that of the $-COCF_3$ group induces a large delocalization of anionic charge over the 18-electron cyclic π system of anion **31**. Thus the canonical structure **30B** seems to be more important for anion **30**, while the canonical structure **31A** is more important for anion **31** (Scheme 5).

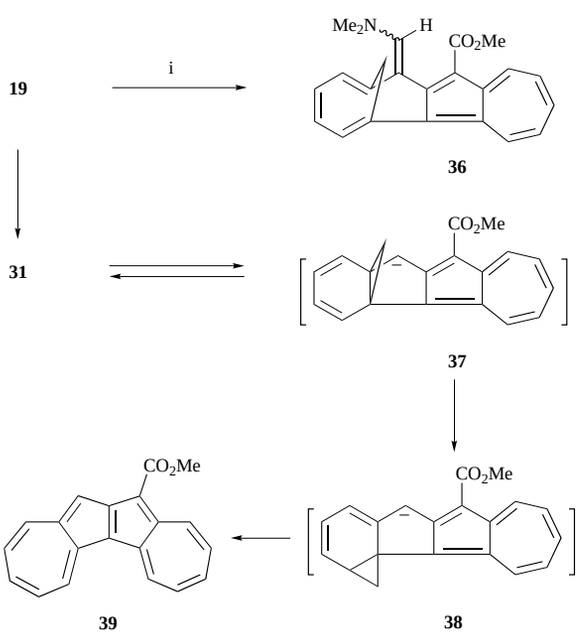
Treatment of anions **30** and **31** with D_2O afforded compounds **18-D** (**18N-D**) and **19-D** (**19N-D** and **19C-D**), in nearly quantitative yields, respectively (Scheme 5). As in Takahashi's observation,[27] deprotonation of methanoindene **2** and subsequent anion quenching are highly *exo* (to bridge-methylene) stereospecific processes. The results are absolutely opposite to the consideration by Radlick and Rosen,[18] on the basis of which it was long understood that the *endo* side was preferred for electrophilic attack from anion **5**.[8] They assigned the signal at δ 2.71 to H-9$_{exo}$ and the one at δ 2.47 to H-9$_{endo}$ in compound **2**. This assignment was corrected by Takahashi.[27] Considering the methylene protons at C11 of compounds **18-D** and **19-D**, the signal appearing at lower field at δ 3.84 for compound **18** and the one at δ 4.03 for compound **19** has disappeared, respectively. Thus, we deduce that deuterium is incorporated stereospecifically at the *syn*-position (*exo*) to the bridge-methylene. The hydrogen–deuterium exchange reaction of compounds **18** (**18N**) and **19** (**19N** and **19C**) in MeOD–MeONa occurred also stereospecifically to give compounds **18-D** and **19-D** (**19N-D** and **19C-D**) in quantitative yields, respectively. In the deprotonation of isomers **18N** and **19N**, the C12–H$_{exo}$ bond is in parallel arrangement with the C11 orbital participating in the cyclopropane basal bond, resulting in good overlap of these lobes, while the C12–H$_{endo}$ bond is envisaged at a perpendicular orientation with the cyclopropane basal bond C11 as indicated in structures **32** and **33** (Scheme 5). If the protonation (deuteration) of anions **30** and **31** and deprotonation (dedeuteration) of isomers **18N** and **19N** proceed *via* an identical transition state, such a mechanism as depicted in structure **32** could rationalize the *exo*-selectivity in the hydrogen–deuterium exchange reaction of compounds **18** (**18N**) and **19** (**19N** and then **19C**). Furthermore, in the case of compound **19** (**19N** and **19C**), direct deprotonation of the isomer **19C** would also be possible to give anion **31** leading to compounds **19D** (**19C-D** and then **19N-D**). Since the allylic moiety of the π HOMO orbital of C5b–C12a–C12 in structure **34**, as is clarified on the molecular model, should cant inwards at the *endo*-face and outwards at the *exo*-face to overlap well with lobes of C6 and C11 in the LUMO of the cycloheptatriene moiety, as seen in structure **35** (Scheme 6), this is where the diatropicity (aromaticity) can originate from. The difference in such a geometrical orientation of modified p orbitals between the *exo*- and *endo*-faces can be expected to influence the transition state of deprotonation–protonation (dedeuteration–deuteration) of compound **19C**: in the deprotonation (dedeuteration) of compound **19C**, the C12–H$_{exo}$ bond is in parallel arrangement with the lobe at C11 as depicted in structure **35**. The π orbitals in C12 and C5b are antisymmetric, and the relative signs of the terminal AO coefficients are inverted. Therefore the proton can approach the *exo*-lobe of C12 with less significant interference from the antibonding interaction because the *exo*-lobe of C5b is located away from the *exo*-lobe of C12. On the other hand,



Scheme 6

approach of the proton from the *endo* side suffers more significant antibonding interference because the antisymmetric p lobes are situated in close proximity at the *endo*-side. Thus *exo*-side approach giving isomer **19C-D** (and then **19N-D**) would result in a decrease of transition energy compared with the *endo*-side approach. Thus, on referring to the *exo*-deuteration of compound **19** (**19N** and **19C**) cyclopropyl participation does not necessarily contribute to the stereochemistry of the hydrogen–deuterium exchange reaction.

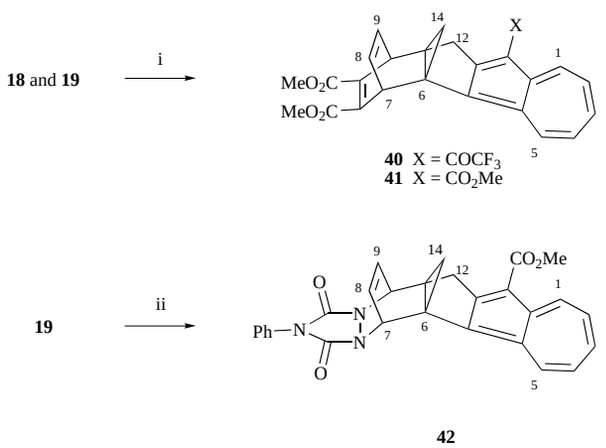
As an example of the perturbed electronic system of anion **31**, the preparation of the fulvene **36**, which is similar to compound **6** was carried out. According to the procedure synthesizing azulene-annulated 6-dimethylaminofulvene,[17] compound **19** reacted with *N*,*N*-dimethylformamide dimethylacetal in DMF at 100 °C to give 11-methoxycarbonylazuleno[1,2-*a*]azulene **39** in 34% yield, instead of anticipated compound **36** (Scheme 7). The structure of compound **39** was confirmed on



Scheme 7 *Reagents and conditions:* i, $(MeO)_2CHNMe_2$, DMF, 100 °C, 15 h

the basis of a comparison of its physical data with those of the authentic specimen.[28] The compound **39** would arise from anion **31**, which has a possibility to exist in equilibrium with a minor amount of anion **37** at high temperature. Anion **37** would undergo the Berson–Willcott type rearrangement to give anion **38**, which is subsequently oxidized under the reaction conditions. Thermal reaction of compound **19** in refluxing tetrachloroethylene, however, led to the starting material **19** being recovered. Thus the rearrangement would be facilitated *via* anionic **31** (and then **37**). As a novel example of cyclopropane ring circumambulation in an anion, the generation and thermal rearrangement of tricyclic undecatrienyl anions, derived from tricyclo[5.3.1.0]undeca-2,4,9-triene, have been reported recently.[29]

The chemical reactivity of neutral compounds **18** (**18N**) and **19** (**19N** and **19C**) was also investigated. The Diels–Alder reaction of compounds **18** and **19** with dimethyl acetylenedicarboxylate (DMAD) in refluxing PhH gave adducts **40** and **41** in 49 and 100% yields, respectively. Similarly the reaction of compound **19** with 3,5-dihydro-4-phenyltriazoline-3,5-dione (PTAD) in PhH at 0 °C gave adduct **42** (Scheme 7). The structures of the products **40**–**42** were assigned on the basis of their ^{1}H and ^{13}C NMR and mass spectra, as well as HRMS or analytical data. The numbering of compounds **40**–**42** in a convenient way is also shown in Scheme 8. The assigned ^{1}H NMR



Scheme 8 *Reagents and conditions:* i, DMAD, PhH, heat; ii, PTAD, PhH, 0 °C

spectra of **40**–**42** showed that the methanoindene skeleton had been lost and suggested also the existence of a cyclopropane ring, which causes a small coupling constant to the methylene protons. ^{13}C NMR spectra also suggested the existence of a cyclopropane ring. Although there is no spectroscopic evidence for the stereochemical identity of **42**, it is assumed that PTAD would undergo addition to **19** to give *endo*-adduct **42** in the usual manner of a Diels–Alder reaction. The results disclosed that both compounds **18** (**18N**) and **19** (**19N** and **19C**) react with dienophiles *via* the norcaradiene structure **18N** and **19N**, respectively, and have a reactivity similar to 1,6-methano[10]-annulene,[30] benzene-,[31] and pyridine-annulated[32] 1,6-methano-[10]annulenes.

Experimental

IR spectra were recorded on Shimadzu IR-400 and Perkin-Elmer 1640 spectrometers. Mass spectra and high resolution mass spectra were run on JEOL Automass 150, Shimadzu GCMS-QP 1000, and JEOL DX-300 spectrometers. Unless otherwise specified, ^{1}H NMR spectra at 90, 400 and 500 MHz and ^{13}C NMR spectra at 22.5, 100.6 and 125 MHz were recorded on Hitachi R-90, JNM-GSX400, and GE-OMEGA500 spectrometers in $CDCl_3$ and the chemical shifts are given relative to internal $SiMe_4$ standard. *J* Values are

given in Hz. ^{1}H (600 MHz) and ^{13}C NMR (150.8 MHz) spectral studies at various temperatures were conducted on a JNM-α-600 spectrometer in CD_2Cl_2. Microanalyses were performed at the Material Characterization Central Laboratory, Waseda University. Mps were recorded on a Yamato MP-21 apparatus and are uncorrected.

Preparation of 4,4a,11,11a-tetrahydro-1*H*-4a,11a-methanoindeno[1,2-*a*]azulene 12

A solution of **12** (731 mg, 5 mmol), pyrrolidine (5 cm^3) and TsOH ((38 mg) in benzene (10 cm^3) was placed in a 50 cm^3 round-bottomed flask fitted with a Dean–Stark apparatus, and heated under reflux for 17 h. After the solvent and excess pyrrolidine were removed *in vacuo*, the residual yellow oil of **10** and 2*H*-cyclohepta[*b*]furan-2-one **11** (1.44 g, 10 mmol) was dissolved in BuOH (10 cm^3) and heated at 110 °C for 24 h. After the BuOH was evaporated *in vacuo*, the resulting residue was chromatographed on silica gel (hexane) to give **12** (573 mg, 50%), blue plates, mp 65–66 °C (from EtOH); δ_H(90 MHz) 0.51 (1H, d, *J* 3.7, H-14), 1.34 (1H, d, *J* 3.7, H-14), 2.37–3.24 (6H, m, H-7, H-10 and 12), 5.56–5.69 (2H, m, H-8 and 9), 6.84 (1H, s, H-13), 7.00–7.50 (3H, m, H-2, 3 and 4), 8.02 (1H, d, *J* 9.2, H-5), 8.32 (1H, d, *J* 9.7, H-1); δ_C(22.5 MHz) 25.9, 27.2, 28.2, 30.9, 32.1, 38.6, 110.6, 120.8, 122.0, 123.3, 123.6, 129.3, 132.5, 134.1, 135.4, 143.3, 145.5 and 158.1; ν_{max}($CHCl_3$)/cm^{-1} 3012, 1493, 1410 and 909; *m*/*z* (rel. int.) 232 (M$^+$, 100%) (Found: C, 93.0; H, 7.0. $C_{18}H_{16}$ requires C, 93.06; H, 6.94%).

Preparation of 10-trifluoroacetyl-4,4a,11,11a-tetrahydro-1*H*-4a,11a-methanoindeno[1,2-*a*]azulene 13

To a stirred solution of **12** (573 mg, 2.5 mmol) and NEt_3 (1.25 g, 12 mmol) in CH_2Cl_2 (5 cm^3) was added $(CF_3CO)_2O$ (1.05 g, 5.0 mmol) dropwise at 0 °C and the mixture was stirred for 30 min. To the reaction mixture was added water, the mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4. After the solvent was evaporated *in vacuo*, the residue was chromatographed on silica gel (hexane–AcOEt, 5:1) to give the product **13** (810 mg, 100%), brown prisms, mp 127–129 °C (from EtOH); δ_H(90 MHz) 0.53 (1H, d, *J* 4.0, H-14), 1.34 (1H, d, *J* 4.0, H-14), 2.38–3.74 (6H, m, H-7, 10 and 12), 5.63–5.66 (2H, m, H-8 and 9), 7.44 (1H, dd, *J* 9.3 and 9.9, H-3), 7.69 (1H, dd, *J* 9.1 and 9.3, H-2), 7.76 (1H, dd, *J* 9.2 and 9.9, H-4), 8.38 (1H, d, *J* 9.2, H-5) and 9.58 (1H, d, *J* 9.1, H-1); ν_{max}($CHCl_3$)/cm^{-1} 1698 and 1621; *m*/*z* (rel. int.) 328 (M$^+$, 100%) (Found: M$^+$, 328.1082; C, 73.3; H, 4.5%. $C_{20}H_{15}OF_3$ requires *M*, 328.1075; C, 73.16; H, 4.60%).

Preparation of 10-trifluoroacetyl-2,3-dibromo-2,3,4,4a,11,11a-hexahydro-1*H*-4a,11a-methanoindeno[1,2-*a*]azulene 14

A solution of **13** (96 mg, 0.29 mmol) in CH_2Cl_2 (5 cm^3) was cooled to −78 °C. To this solution was added pyridinium tribromide (96 mg, 0.30 mmol), and the mixture was stirred at −78 °C for 24 h. The reaction mixture was then extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4. After the solvent was removed *in vacuo*, the residue was chromatographed on silica gel (hexane–AcOEt, 5:1) to give the product **14** (135 mg, 95%), mp 172–173 °C (from EtOH); δ_H(90 MHz) 0.70 (1H, d, *J* 5.3, H-14), 1.71 (1H, d, *J* 5.3, H-14), 2.72–3.62 (6H, m, H-7, 10 and 12), 4.41–4.64 (2H, m, H-8 and 9), 7.54 (1H, dd, *J* 9.7 and 10.3, H-3), 7.64 (1H, dd, *J* 9.7 and 9.9, H-4), 7.78 (1H, dd, *J* 10.3 and 11.0, H-2), 8.38 (1H, d, *J* 9.9, H-5) and 9.34 (1H, d, *J* 11.0, H-1); ν_{max}($CHCl_3$)/cm^{-1} 1698 and 1621; *m*/*z* (rel. int.) 328 (M$^+$, 100%) (Found: C, 49.5; H, 2.9. $C_{20}H_{15}OF_3Br_2$ requires C, 49.21; H, 3.10%).

Preparation of 10-trifluoroacetyl-11,11a-dihydro-4a*H*-4a,11a-methanoindeno[1,2-*a*]azulene 18

A solution of **14** (60 mg, 0.12 mmol) and DBU (39 mg, 0.26 mmol) in THF (5 cm^3) was heated under reflux for 6 h. To this reaction mixture was added water, the mixture was extracted with diethyl ether, and the ethereal extract dried over $MgSO_4$. After the solvent was removed *in vacuo*, the residue was purified by TLC on silica gel (hexane–AcOEt, 5:1) to give the product **18**, brown plates, mp 151–152 °C (from EtOH); ν_{max}($CHCl_3$)/cm^{-1} 1645; λ_{max}(EtOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 200 (4.29), 231 (4.39), 283 (4.37), 327 (4.34), 414 (3.77), 432 (3.78), 532 (2.94) and 657 (sh. 1.82); *m*/*z* (rel. int.) 326 (M$^+$, 100%) (Found: M$^+$, 326.0870; C, 73.3; H, 4.5%. $C_{20}H_{13}OF_3$ requires *M*, 326.0918; C, 73.16; H, 4.60%). ^{1}H and ^{13}C NMR spectral data are summarized in Table 1.

Preparation of methyl {4,4a,11,11a-tetrahydro-1*H*-4a,11a-methanoindeno[1,2-*a*]azulen-10-yl}acetate 16

To a stirred solution of KOH (1.35 g) in a mixture of THF (15 cm^3), MeOH (6 cm^3), and H_2O (3 cm^3) was added compound **13** (366 mg, 1.1 mmol), and the mixture was heated at 60 °C for 9 h. Then the reaction mixture was neutralized with 1 M HCl and extracted with diethyl ether. The ether extract was washed with aqueous $NaHCO_3$ and then brine and dried over $MgSO_4$. After the solvent was removed *in vacuo*, the residual solid of **15** was dissolved in diethyl ether (70 cm^3) containing diazomethane (22 mmol) and the mixture was stirred for 5 h at 0 °C. After the diethyl ether was evaporated, the residue was purified by TLC on silica gel (hexane–AcOEt, 5:1) to give the product **16** (275 mg, 85%), purple prisms, mp 117–118 °C (decomp.) (from MeOH); δ_H(90 MHz) 0.51 (1H, d, *J* 4.2, H-14), 1.33 (1H, d, *J* 4.2, H-14), 3.91 (3H, s, Me), 2.59–3.67 (6H, m, H-7, 10 and 12), 5.61–5.65 (2H, m, H-8 and 9), 7.38 (1H, m, H-3), 7.47 (1H, m, H-2), 7.64 (1H, dd, *J* 9.2 and 9.8, H-4), 8.30 (1H, d, *J* 9.2, H-5) and 9.34 (1H, d, *J* 9.5, H-1); ν_{max}($CHCl_3$)/cm^{-1} 2941, 1695, 1445 and 1162; *m*/*z* (rel. int.) 290 (M$^+$, 100%) (Found: C, 82.7; H, 6.2. $C_{20}H_{18}O_2$ requires C, 82.73; H, 6.25%).

Preparation of methyl {2,3-dibromo-2,3,4,4a,11,11a-hexahydro-1*H*-4a,11a-methanoindeno[1,2-*a*]azulen-10-yl}acetate 17

A stirred solution of compound **16** (290 mg, 1.0 mmol) in CH_2Cl_2 (5 cm^3) was cooled to −78 °C. To this solution was added pyridinium tribromide (319 mg, 1.0 mmol) and the mixture was stirred for 24 h at −78 °C. To the reaction mixture was added water, the mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4. After the solvent was removed *in vacuo*, the resulting residue was chromatographed on silica gel (hexane–AcOEt, 5:1) to give the product **17** (182 mg, 63%), purple viscous oil; δ_H(90 MHz) 0.65 (1H, d, *J* 4.8, H-14), 1.28 (1H, d, *J* 4.8, H-14), 2.54–3.85 (6H, m, H-7, 10 and 12), 3.91 (3H, s, Me), 4.40–4.63 (2H, m, H-8 and 9), 7.26–7.74 (1H, m, overlapping, H-3), 7.47 (1H, m, H-4), 7.67 (1H, m, H-2), 8.25 (1H, d, *J* 9.7, H-5) and 9.38 (1H, d, *J* 9.5, H-1); ν_{max}($CHCl_3$)/cm^{-1} 1684; *m*/*z* (rel. int.) 452 (M$^+$, 23%), 450 (M$^+$, 46), 448 (M$^+$, 22) and 290 (100).

Bisdehydrobromination of compound 17 to give methyl {11,11a-dihydro-4a*H*-4a,11a-methanoindeno[1,2-*a*]- azulen-10-yl}-carboxylate 19

A solution of compound **17** (158 mg, 0.35 mmol) and DBU (274 mg, 1.8 mmol) in THF (7 cm^3) was heated under reflux for 10 h. To this reaction mixture was added water, the mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4. After the solvent was removed *in vacuo*, the residue was purified by TLC on silica gel (hexane–AcOEt, 5:1) to give the product **19**, purple prisms, mp 94–95 °C (decomp.) (from MeOH); ν_{max}($CHCl_3$)/cm^{-1} 1678; λ_{max}(EtOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 200 (4.61), 212 (4.65), 239 (4.62), 310 (4.80), 378 (3.97), 396 (4.00), 556 (2.94), 580 (2.89), 712 (1.76) and 721 (1.47); *m*/*z* (rel. int.) 288 (M$^+$, 82%) and 229 (100) (Found: M$^+$, 288.1172; C, 83.4; H, 5.6%. $C_{20}H_{16}O_2$ requires *M*, 228.1150; C, 83.31; H, 5.59%). ^{1}H and ^{13}C NMR spectral data are summarized in Table 1.

Conversion of compound 18 to 19

To a solution of KOH (1.64 g) in THF (25 cm^3), MeOH (10 cm^3) and H_2O (5 cm^3), was added compound **18** (49 mg, 0.15 mol) and the mixture was stirred at 60 °C for 1 h. The reaction mixture was neutralized with 1 M HCl solution, extracted with diethyl ether, and the ethereal extract was washed with aqueous $NaHCO_3$ and brine and dried over $MgSO_4$. After the solvent was removed *in vacuo*, the residual solid **20** was dissolved in MeOH (1 cm^3) and diethyl ether (5 cm^3). To this solution was added a solution of an excess amount of CH_2N_2 in diethyl ether, and the mixture was stirred at 0 °C overnight. After solvent removal *in vacuo*, the resulting residue was chromatographed on silica gel (hexane–AcOEt, 5:1) to give the product **19** (36 mg, 83%) which was identical with the authentic specimen.

Reaction of compound 21 with pyrrolidine to give 2-(pyrrolidin-1-yl)azulene 25

A solution of compound **21** (140 mg, 1 mmol), pyrrolidine (1 cm^3) and TsOH (10 mg) in toluene (3 cm^3) was placed in a round-bottomed flask fitted with a Dean–Stark apparatus and heated under reflux for 4.5 h. After the solvent and excess pyrrolidine were evaporated, the resulting residue was chromatographed on silica gel (hexane–AcOEt, 10:1) to give the product **25** (25 mg, 13%), mp 114–115 °C (from PhH); δ_H(90 MHz) 1.98–2.13 (4H, m), 3.42–3.51 (4H, m), 6.53 (2H, s), 7.00–7.22 (3H, m) and 7.76–7.88 (2H, m); *m/z* (rel. int.) 197 (M^+, 100%) (Found: M^+, 197.1156; C, 85.0; H, 7.8; N, 7.0%. $C_{14}H_{15}N$ requires *M*, 197.1204; C, 85.24; H, 7.66; N, 7.10%).

Independent preparation of compound 25

A solution of compound **26** (500 mg, 2 mmol) and pyrrolidine (1.4 g, 40 mmol) in dry EtOH (10 cm^3) was heated under reflux for 3 h. The reaction mixture was extracted with benzene, and the ethereal extract was washed with H_2O and dried over Na_2SO_4. After the solvent was evaporated *in vacuo*, the residue was chromatographed on alumina using PhH as eluent to give the product **25** (312 mg, 79%), the spectral data of which were identical with those of the authentic specimen.

Spectral data of 1-trifluoroacetylazulene 27 and 1-methoxycarbonylazulene 28

1-Trifluoroacetylazulene **27**[21] and 1-methoxycarbonylazulene **28**[22] were prepared according to the procedure described in the literature[21,22] and the following spectral data were obtained.

For 1-trifluoroacetylazulene **27**; $\nu_{max}(CHCl_3)/cm^{-1}$ 1645; δ_H(400 MHz) 7.32 (1H, d, *J* 4.6, H-3), 7.67 (1H, dd, *J* 9.5 and 9.7, H-7), 7.78 (1H, dd, *J* 9.9 and 9.9, H-5), 7.96 (1H, dd, *J* 9.5 and 9.9, H-6), 8.33–8.37 (1H, m, H-2), 8.55 (1H, d, *J* 9.9, H-4), 9.9 (1H, d, *J* 9.7); δ_C(100.6 MHz), 113.0 (C1), 117.3 (CF_3), 119.6 (C3), 130.1 (C7), 131.6 (C5), 139.1 (C4), 139.6 (C8), 140.6 (C6), 143.9 and 147.3 (C3a and C8a) and 175.9 (C=O).

For 1-methoxycarbonylazulene **28**; $\nu_{max}(CHCl_3)/cm^{-1}$ 1667; δ_H(400 MHz) 3.95 (3H, s, Me), 7.28 (1H, d, *J* 4.22, H-3), 7.43 (1H, dd, *J* 9.7 and 9.9, H-7), 7.54 (1H, dd, *J* 9.5 and 9.9, H-5), 7.79 (1H, dd, *J* 9.9 and 9.9, H-6), 8.36 (1H, d, *J* 4.2, H-2), 8.44 (1H, d, *J* 9.5, H-4), 9.64 (1H, d, *J* 9.7, H-8); δ_C(100.6 MHz) 51.5 (Me), 116.7 (C1), 117.6 (C3), 126.7 (C7), 127.6 (C5), 138.2 (C4), 137.7 (C8), 138.9 (C6), 140.1 (C2), 140.7 and 144.7 (C3a and C8a) and 165.8 (C=O).

Generation of anions 30 and 31 and their quenching with D_2O

To a thin-walled NMR tube (5 ϕ) covered with a septum was added compound **18** (10 mg, 0.03 mmol) in [$^2H_6$]DMSO (0.4 cm^3) under an argon atmosphere. [$^2H_5$]Dimsyl sodium was prepared by heating NaH (2 mg, 0.08 mmol) in [$^2H_6$]DMSO (0.5 cm^3) for 1 h at 70–75 °C under a nitrogen atmosphere. After the solution was cooled to room temp., it was transferred to the NMR tube *via* a syringe and kept under argon. Immediately a dark green color indicating formation of **30** was observed and the NMR tube was shaken a few times to ensure complete mixing. The ^1H NMR spectrum was recorded within 30 min. The anion **30** was not so stable at room temp., and decomposed gradually, thus a ^{13}C NMR spectrum could not be recorded. A dark blue colored solution of **31** was also prepared by using compound **19** (9 mg, 0.03 mmol) in the manner described above. This anion is stable at room temp., and ^1H and ^{13}C NMR spectra were recorded. The results are summarized in Table 1.

Solutions of anions **30** and **31** in [$^2H_6$]DMSO were prepared by using **18** (10 mg, 0.03 mmol) and **19** (9 mg, 0.03 mmol) in a manner described above. To the solutions were added D_2O, the mixtures were extracted with CH_2Cl_2, and the extracts were dried over Na_2SO_4, respectively. After solvent removal *in vacuo*, the products **18-D** and **19-D** were obtained in quantitative yield.

For **18-D**; δ_H(90 MHz) 0.44 (1H, d, *J* 4.1, H-14), 1.95 (1H, d, *J* 4.1, H-14), 3.82 (1H, br s, H-12), 6.04 (1H, dd, *J* 6.4 and 9.1, H-8), 6.14 (1H, dd, *J* 6.4 and 9.0, H-9), 6.45 (1H, d, *J* 9.0, H-10), 6.88 (1H, d, *J* 9.1, H-7), 7.57 (1H, dd, *J* 9.6 and 9.8, H-3), 7.60 (1H, dd, *J* 9.6 and 9.9, H-4), 7.77 (1H, dd, *J* 9.7 and 9.8, H-2), 8.65 (1H, d, *J* 9.9, H-5) and 9.60 (1H, d, *J* 9.7, H-1); *m/z* (rel. int.) 327 (M^+, 100%) (Found: M^+, 327.0960. $C_{20}H_{12}DO_2$ requires *M*, 327.0981).

For **19-D**; δ_H(90 MHz) 0.53 (1H, d, *J* 6.2, H-14), 2.76 (1H, d, *J* 6.2, H-14), 3.31 (1H, br s, H-12), 3.85 (3H, s, Me), 6.32 (1H, dd, *J* 7.5 and 8.1, H-9), 6.44 (1H, d, *J* 7.8, H-9), 6.48 (1H, dd, *J* 8.1 and 8.4, H-8), 6.73 (1H, d, *J* 8.4, H-7), 7.31 (1H, dd, *J* 9.2 and 10.1, H-4), 7.36 (1H, dd, *J* 9.7 and 10.3, H-2), 7.48 (1H, dd, *J* 9.2 and 10.3, H-3), 8.51 (1H, d, *J* 10.1, H-5) and 9.33 (1H, d, *J* 9.7, H-1); *m/z* (rel. int.) 289 (M^+, 45%), 288 (40) and 229 (100) (Found: M^+, 289.1180. $C_{20}H_{15}DO_2$ requires *M*, 289.1213).

Hydrogen–deuterium exchange reaction of compounds 18 and 19

A solution of compound **18** (10 mg, 0.03 mmol) or **19** (9 mg, 0.03 mmol) and MeONa (24 mg, 0.44 mmol) in MeOD (1 cm^3) was stirred at 0 °C for 5 h. To the reaction mixture was added D_2O (0.3 cm^3), the mixture was extracted with CD_2Cl_2, and the extract was dried over Na_2SO_4. After solvent removal *in vacuo*, the pure products **18-D** and **19-D** were obtained in quantitative yield. The physical data of the products were identical with the authentic specimen.

Reaction of 34 with dimethylformamide dimethylacetal to give 11-methoxycarbonylazuleno[1,2-*a*]azulene 39

A mixture of **34** (6 mg, 0.02 mmol), dimethylformamide dimethylacetal (0.5 cm^3), and DMF (10 mg) was heated at 100 °C for 1.5 h. The reaction mixture was concentrated under reduced pressure, and the resulting residue was purified by TLC on alumina (hexane–AcOEt, 10:1) to give 11-methoxycarbonylazuleno[1,2-*a*]azulene **39** (2 mg, 34%), dark brown prisms, mp 118–119 °C (lit.,[28] mp 118–119 °C).

Thermal reaction of 19

A solution of compound **19** (20 mg, 0.07 mmol) in tetrachloroethylene (0.4 cm^3) was heated under reflux for 22 h. After evaporation of the solvent *in vacuo*, the residue was purified by TLC on silica gel (hexane–AcOEt, 5:1) to give the starting material **19** (12 mg, 60%).

Diels–Alder reaction of compounds 18 and 19 with DMAD

A solution of compound **18** (5.0 mg, 1.5×10^{-2} mmol) or **19** (6.2 mg, 2.0×10^{-2} mmol) and DMAD (56 mg, 3.9×10^{-2} mmol) in PhH (2 cm^3) was heated under reflux for 12 h. After the solvent was removed *in vacuo*, the residue was purified by TLC on silica gel (hexane–AcOEt, 3:1) to give the product **40** (3.5 mg, 49%) or **41** (9.0 mg, 100%).

For **40**, brown plates, mp 163–164 °C (decomp.) (from MeOH); δ_H(500 MHz) 1.00 (1H, d, *J* 6.1, H-14), 2.16 (1H, d, *J* 6.1, H-14), 3.35 (3H, s, Me), 3.42 (1H, d, *J* 19.6, H-12), 3.53 (1H, d, *J* 19.6, H-12), 3.74 (3H, s, Me), 4.28 (1H, d, *J* 6.2, H-7 or 10), 4.90 (1H, d, *J* 6.2, H-10 or 7), 6.34 (1H, dd, *J* 6.2 and 8.7,

H-8 or 9), 6.40 (1H, dd, *J* 6.2 and 8.7, H-9 or 8), 7.60 (1H, dd, *J* 9.6 and 9.7, H-2), 7.61 (1H, dd, *J* 9.6 and 9.8, H-4), 7.77 (1H, dd, *J* 9.6 and 9.6, H-3), 8.52 (1H, d, *J* 9.8, H-5) and 9.60 (1H, d, *J* 9.7, H-1); δ_C(125 MHz) 33.5, 36.3, 37.3, 41.4, 42.4, 45.4, 51.8, 52.3, 111.9, 118.1, 129.1, 131.2, 132.6, 133.2, 134.8, 138.1, 139.0, 139.1, 139.8, 145.5, 148.8, 149.3, 165.0, 166.3 and 168.0; $\nu_{max}(CHCl_3)/cm^{-1}$ 1728, 1713 and 1645; *m*/*z* (rel. int.) 468 (M^+, 37%) and 252 (100) (Found: M^+, 468.1183. $C_{26}H_{19}O_5F_3$ requires *M*, 468.1184).

For **41**, violet viscous oil; δ_H(500 MHz) 0.91 (1H, d, *J* 6.1, H-14), 2.11 (1H, d, *J* 6.1, H-14), 3.31 (3H, s, Me), 3.36 (1H, d, *J* 19.7, H-12), 3.41 (1H, d, *J* 19.7, H-12), 3.71 (3H, s, Me), 3.87 (3H, s, Me), 4.30 (1H, d, *J* 6.1, H-7 or 10), 4.85 (1H, d, *J* 6.0, H-10 or 7), 6.31 (1H, dd, *J* 6.1 and 7.4, H-8 or 9), 6.38 (1H, dd, *J* 6.0 and 7.4, H-9 or 8), 7.32 (1H, dd, *J* 9.6 and 9.8, H-2), 7.36 (1H, dd, *J* 9.8 and 10.0, H-4), 7.61 (1H, dd, *J* 9.8 and 9.8, H-3), 8.38 (1H, d, *J* 10.0, H-5) and 9.34 (1H, d, *J* 9.6, H-1); δ_C(125 MHz) 33.5, 36.2, 37.6, 42.1, 42.2, 45.2, 50.9, 51.7, 52.3, 110.2, 125.6, 127.3, 132.8, 133.3, 133.8, 135.6, 135.7, 136.9, 137.3, 145.6, 147.2, 147.7, 165.6, 165.7, 167.5 and 167.8; $\nu_{max}(CHCl_3)/cm^{-1}$ 1709, 1687 and 1683; *m*/*z* (rel. int.) 430 (M^+, 60%) and 252 (100) (Found: M^+, 430.1403. $C_{26}H_{22}O_6$ requires *M*, 430.1416).

Diels–Alder reaction of compound 19 with PTAD

A solution of **19** (4 mg, 1.4×10^{-2} mmol) and PTAD (10 mg, 5.7×10^{-2} mmol) in PhH (5 cm^3) was stirred at 0 °C for 1 h. After the solvent was removed *in vacuo*, the resulting residue was purified by TLC on silica gel (hexane–AcOEt, 3 : 1) to give the product **42** (6.4 mg, 100%), violet plates, mp 184–185 °C (from MeOH); δ_H(500 MHz) 0.90 (1H, d, *J* 6.7, H-14), 1.63 (1H, d, *J* 6.7, H-14), 3.48 (1H, d, *J* 19.4, H-12), 3.80 (1H, d, *J* 19.4, H-12), 3.86 (3H, s, Me), 5.34 (1H, d, *J* 5.9, H-7 or 10), 5.82 (1H, d, *J* 5.9, H-10 or 7), 6.25 (1H, dd, *J* 5.9 and 8.1, H-8 or 9), 6.33 (1H, dd, *J* 5.9 and 8.1, H-9 or 8), 7.23–7.32 (5H, m, Ph), 7.35 (1H, dd, *J* 9.7 and 9.9, H-4), 7.41 (1H, dd, *J* 9.9 and 10.1, H-2), 7.65 (1H, t, *J* 9.9, H-3), 8.38 (1H, d, *J* 9.7, H-5) and 9.41 (1H, d, *J* 10.1, H-1); δ_C(125 MHz) 24.5, 26.5, 30.3, 33.7, 51.0, 55.6, 57.9, 110.2, 120.6, 125.6, 126.6, 127.2, 128.0, 128.2, 129.0, 129.2, 134.1, 136.1, 136.6, 138.1, 145.7, 156.7, 157.1, 164.9 and 165.4; $\nu_{max}(CHCl_3)/cm^{-1}$ 1770, 1714; *m*/*z* (rel. int.) 463 (M^+, 3%) and 228 (100) (Found: C, 72.3; H, 4.5; N, 8.9. $C_{28}H_{21}N_3O_4$ requires C, 72.56; H, 4.57; N, 9.07%).

Acknowledgements

Financial support from a Waseda University Grant for a Special Research Project is gratefully acknowledged. The authors thank Professor Tadashi Nakata, Dr Jun Uzawa and Dr Nobuhiro Kanomata of the Institute of Physical and Chemical Research (RIKEN) for the measurement of low temperature NMR spectra. The authors also thank Mr Hideki Horiuchi, for a part of the experimental work, and the Material Characterization Central Laboratory, Waseda University, for technical support of spectral data and elemental analyses.

References

1 J. F. Liebman and A. Greenberg, *Chem. Rev.*, 1989, **89**, 1225; W. H. Okamura and A. R. Delela, '*Comprehensive Organic Synthesis*', ed. B. M. Trost and I. Fleming, Pergamon, Oxford, 1991, vol. 5, pp. 699–750.
2 E. Ciganek, *J. Am. Chem. Soc.*, 1967, **89**, 1454; E. Ciganek, *J. Am. Chem. Soc.*, 1967, **89**, 1458; E. Hall and J. D. Roberts, *J. Am. Chem. Soc.*, 1971, **93**, 2203; E. Ciganek, *J. Am. Chem. Soc.*, 1971, **93**, 2207.
3 T. Mukai, H. Kubota and T. Toda, *Tetrahedron Lett.*, 1967, 3581; T. Toda, M. Nitta and T. Mukai, *Tetrahedron Lett.*, 1969, 4401.
4 H. Printzbach and U. Fischer, *Helv. Chim. Acta*, 1967, **50**, 1669; F.-G. Kläner, *Tetrahedron Lett.*, 1974, 19; H. Tsuruta, S. Mori and T. Mukai, *Chem. Lett.*, 1974, 1127; K. Takeuchi, M. Arima and K. Okamoto, *Tetrahedron Lett.*, 1981, **22**, 3081; K. Takeuchi, H. Fujimoto and K. Okamoto, *Tetrahedron Lett.*, 1981, **22**, 4981; K. Takahashi, K. Takase and H. Toda, *Chem. Lett.*, 1981, 979; K. Takeuchi, H. Fujimoto, T. Kitagawa, H. Fujii and K. Okamoto, *J. Chem. Soc.*, *Perkin Trans. 2*, 1984, 461.
5 E. Vogel, W. Wiedemann, H. Kiefer and W. F. Harrison, *Tetrahedron Lett.*, 1963, 673.
6 P. Radlick and W. Rosen, *J. Am. Chem. Soc.*, 1966, **88**, 3461.
7 W. Grimme and M. Kaufold, U. Dettmeier and E. Vogel, *Angew. Chem.*, 1966, **78**, 643.
8 R. J. Hunadi and G. K. Helmkamp, *J. Org. Chem.*, 1978, **43**, 1586.
9 I. Murata, K. Nakasuji and T. Moria, *Chem. Lett.*, 1974, 742.
10 F. Diederich and C. Thilgen, *Science*, 1996, **271**, 317; F. Diederich, L. Isaac and D. Philip, *Chem. Soc. Rev.*, 1994, 243.
11 A. B. Smith III, R. M. Strongin, L. Brard, G. T. Furst, W. J. Romanow, K. G. Owens, R. J. Goldschmidt and R. C. King, *J. Am. Chem. Soc.*, 1995, **117**, 5492; F. Diederich, L. Isaacs and D. Philp, *J. Chem. Soc.*, *Perkin Trans. 2*, 1994, 391; T. Suzuki, Q. Li, K. C. Khemani and F. Wudl, *J. Am. Chem. Soc.*, 1992, **114**, 7300.
12 M. Nitta, H. Kawaji and N. Kanomata, *Tetrahedron Lett.*, 1992, **33**, 251; K. Ito, H. Kawaji and M. Nitta, *Tetrahedron Lett.* 1994, **35**, 2561.
13 J. O. Morley, *J. Am. Chem. Soc.*, 1988, **110**, 7660.
14 A. J. Anderson, Jr. and B. M. Steckler, *J. Am. Chem. Soc.*, 1959, **81**, 4941.
15 S. Ito, N. Morita and T. Asao, *Tetrahedron Lett.*, 1991, **32**, 773; S. Ito, N. Morita and T. Asao, *Tetrahedron Lett.*, 1992, **33**, 3773.
16 P.-W. Yang, M. Yasunami and K. Takase, *Tetrahedron Lett.*, 1971, 4275; K. Takase and M. Yasunami, *J. Synth. Org. Chem.*, *Jpn*, 1981, **39**, 1172; M. Yasunami, S. Miyoshi, N. Kanegae and K. Takase, *Bull. Chem. Soc. Jpn*, 1993, **66**, 892.
17 M. Yasunami, T. Hioki, Y. Kitamori, I. Kikuchi and K. Takase, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 2273.
18 P. Radlick and W. Rosen, *J. Am. Chem. Soc.*, 1967, **89**, 5308.
19 L. J. Mathias and C. G. Overberger, *J. Org. Chem.*, 1980, **45**, 1701.
20 J. A. Berson and M. R. Willcott III, *J. Am. Chem. Soc.*, 1966, **98**, 2494.
21 T. Nozoe, S. Masumura, Y. Murase and S. Seto, *Chem. Ind.*, 1958, 1251.
22 A. G. Anderson, Jr. and R. G. Anderson, *J. Org. Chem.*, 1962, **27**, 3578.
23 A. G. Anderson, Jr. and J. J. Tazuma, *J. Am. Chem. Soc.*, ,1953, **75**, 4979.
24 R. J. Hunadi, *J. Org. Chem.*, 1982, **47**, 1940.
25 R. Hoffmann and W.-D. Stohrer, *J. Am. Chem. Soc.*, 1971, **93**, 6941; H. Gunther, *Tetrahedron Lett.*, 1970, 5173; W.-D. Stohrer and R. Hoffmann, *Angew. Chem.*, 1972, **84**, 820.
26 AM1 calculations: MOPAC Ver. 6.00, J. J. P. Stewart, *QCPE Bull.*, 1989, **9**, 10; revised as Ver 6.12 by D. Athansopoulos, *QCPM*, 1994, 137.
27 K. Takahashi, K. Takase and T. Kagawa, *J. Am. Chem. Soc.*, 1981, **103**, 1186.
28 M. Nitta, K. Nishimura and Y. Iino, *Tetrahedron Lett.*, 1993, **34**, 2157.
29 M. Oda, Y. Masaki, Y. Okazaki, T. Kajioka, M. Izawa, R. Miyatake, S. Kuroda and L. T. Scott, *Chem. Lett.*, 1997, 595.
30 E. Vogel, W. Grimme and S. Korte, *Tetrahedron Lett.*, 1965, 3625.
31 S. Tanimoto, R. Schafer, J. Ippen and E. Vogel, *Angew. Chem.*, *Int. Ed. Engl.*, 1976, **15**, 613.
32 N. Kanomata, H. Kawaji and M. Nitta, *J. Org. Chem.*, 1992, **57**, 618.

Paper 7/07163I
Received 3rd *October* 1997
Accepted 22nd *January* 1998