

On the reaction of prop-2-enylidetriphenylphosphorane derivatives. Novel synthesis of 4,9-methanocyclopentacycloundecene derivatives and their spectroscopic and chemical properties

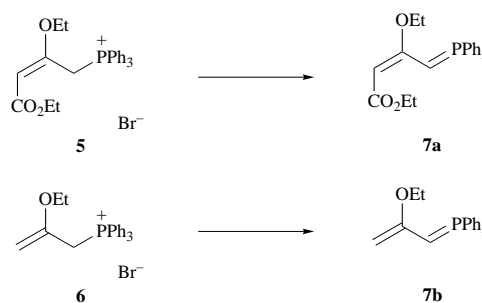
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Novel 3-ethoxycarbonyl-2-ethoxy- and 2-ethoxy-4,9-methanocyclopentacycloundecenes **12** and **13** are synthesized by the reaction of 9-chloro-1,6-methano[11]annulen-8-one **8**, a 10π -electron vinylogue of 2-chlorotropone, with 2-ethoxy-3-(ethoxycarbonyl)prop-2-enylidene- and 2-ethoxyprop-2-enylidene-triphenylphosphorane, **7a** and **7b**, respectively. The reaction pathways involve a Michael-type addition of phosphoranes **7a,b** onto ketone **8**, subsequent proton migration regenerating the phosphorane moiety, which undergoes intramolecular Wittig reaction, and aromatization, eliminating HCl. The ^1H NMR spectra show that compounds **12** and **13** are aromatic molecules having a diatropic 14-electron cyclic π system. The UV-visible absorption spectra of compounds **12** and **13** exhibit extended cyclic conjugation of the aromatic perimeter according to a bathochromic shift of the longest absorption maxima as compared to those of the related azulene derivatives having the same substituents. In addition, the first example of an aromatic substitution reaction of the methanocyclopentacycloundecene ring system has been studied, and shows that the compounds **12** and **13**, like azulene, undergo trifluoroacetylation under exceptionally mild conditions and exhibit the same site-selectivity as does azulene. The electrochemical properties of compounds **12** and **13** as well as the related azulene derivatives are also analyzed and discussed on the basis of MNDO calculations.

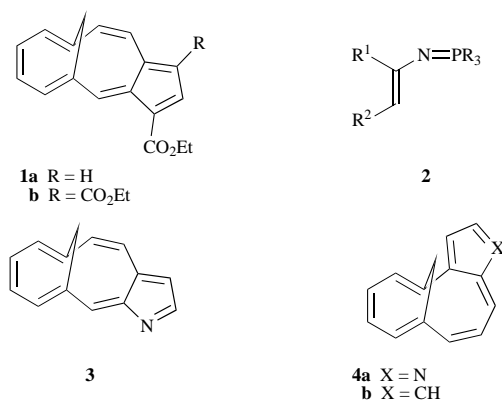
Introduction

The chemistry of bridged aromatics with nonplanar cyclic conjugation is still of interest to organic chemists particularly in consideration of the relationship between molecular strain and aromaticity in these molecules. As for methano-bridged aromatics having a 14π -electron system, Prinzbach *et al.*, have reported on a series of 5,10-methanocyclopentacycloundecenes **1** as vinylogous compounds of azulene and showed that compound **1** has spectroscopic properties similar to those of azulene.¹ We have also reported the synthesis of derivatives of 6,11- and 4,9-methanocycloundeca[b]pyrroles **3** and **4a**, which is a nitrogen analogue of the unknown 4,9-methanocyclopentacycloundecene **4b**, by utilizing the reaction of (vinylimino)phosphoranes of general structure **2** with



Scheme 1

enylidetriphenylphosphoranes such as **7a,b**,⁷ which are derived from **5** and **6**, respectively, and are hydrocarbon analogues of compound **2**, they have reacted with compounds containing two electrophilic centres, e.g. α -halogeno ketones and aldehydes and α,β -unsaturated ketones to give cyclopentadienes and cyclohexadienes,^{8,9} respectively. We have also studied the synthesis of the azulene ring system by utilizing the reaction of dienes **7a** and **7b** with activated tropones.¹⁰ In this context, we planned to explore the methodology for convenient synthesis of the 4,9-methanocyclopentacycloundecene ring system. Herein we report on a convenient preparation for, and spectroscopic properties of, novel 3-ethoxycarbonyl-2-ethoxy- and 2-ethoxy-4,9-methanocyclopentacycloundecene **12** and **13** by utilizing the reaction of compounds **7a,b** with 9-chloro-1,6-methano[11]annulen-8-one **8**. In order to gain insight into mechanistic aspects, the reaction of simple methylenetriphenylphosphorane **16** with compound **8** was also studied. In addition, electrophilic aromatic substitution of the methanocyclopentacycloundecene ring system was studied, and we confirmed that compounds **12** and **13**, like azulene, undergo trifluoroacetylation under extremely mild conditions and exhibit the same site-selectivity as azulene. Furthermore, the reduction and oxidation potentials of compounds **12** and **13** as well as the related azulene derivatives bearing the same substituents¹⁰ were

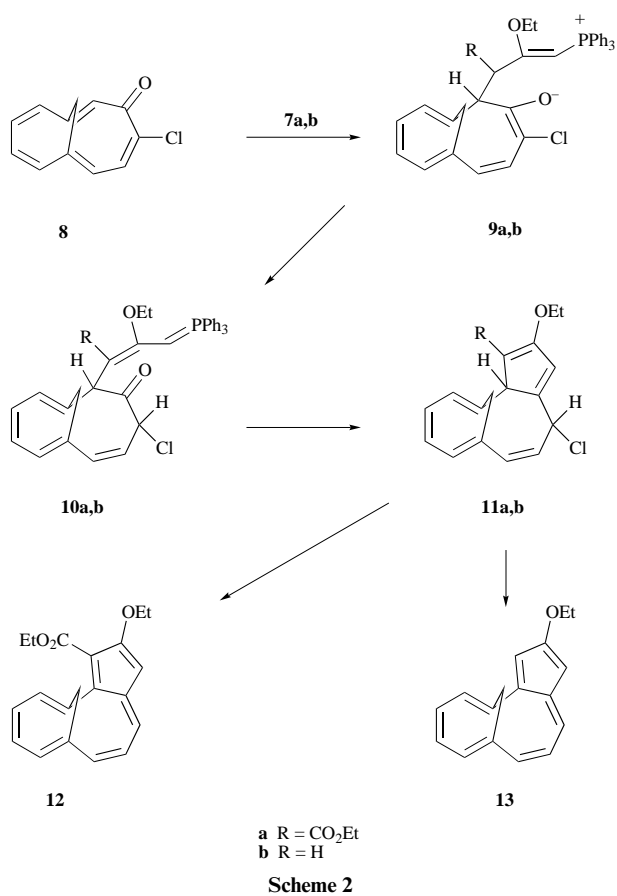


methano[11]annulenones.² The synthetic utility of (vinylimino)phosphoranes for the preparation of various kinds of heterocycles has been demonstrated.³ (Vinylimino)phosphorane reacts with α -bromo ketones, α,β -unsaturated ketones and aldehydes, and tropone derivatives to give pyrroles,⁴ pyridines,⁵ and the 1-azaazulene ring system.⁶ Regarding prop-2-

studied in order to clarify the electrochemical properties of the two ring systems, and the results are discussed on the basis of minimal neglect of differential overlap (MNDO) calculations.

Results and discussion

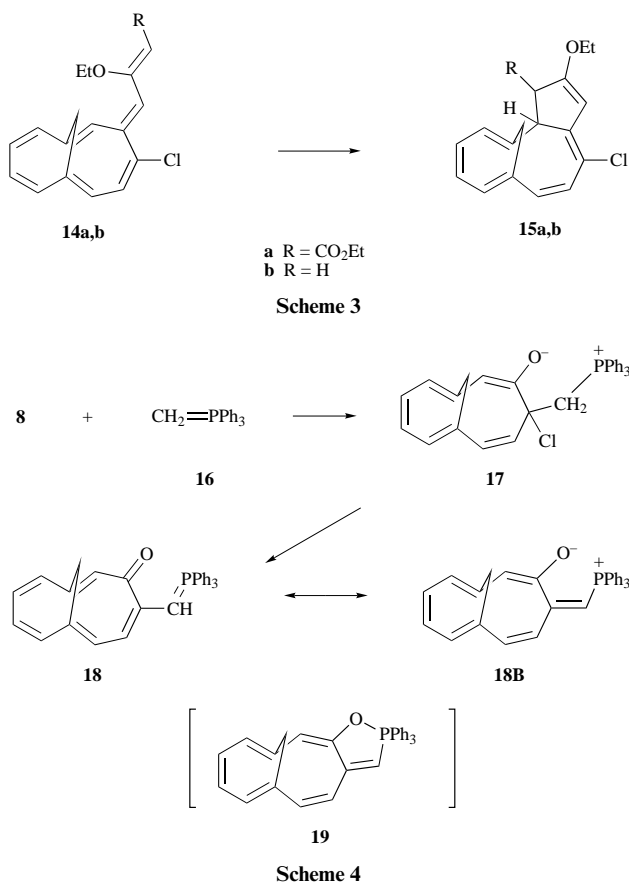
Our synthetic strategy for the preparation of the 4,9-methanocyclopentacycloundecene ring system involved the reaction of 9-chloro-1,6-methano[11]annulen-8-one **8**¹¹ with isolated 2-ethoxy-3-(ethoxycarbonyl)prop-2-enylidetriphenylphosphorane **7a**^{7a} and 2-ethoxyprop-2-enylidetriphenylphosphorane **7b**^{7b} prepared *in situ* (see Scheme 1). Preparation of annulenone **8** was accomplished by the modified method² of the original procedure explored by Vogel.^{11,12} The reaction of ketone **8** with 4 mol equiv. of **7a** in the presence of K₂CO₃ was carried out under heating at 80 °C for 12 h to give 2-ethoxy-3-ethoxycarbonyl-4,9-methanocyclopentacycloundecene **12** (86% yield). On the other hand, the phosphorane **7b**, which has no electron-withdrawing CO₂Et group, and was prepared *in situ* by base treatment of compound **6**, reacted with ketone **8** under mild conditions at room temp. to give 2-ethoxy-4,9-methanocyclopentacycloundecene **13** (12% yield) (Scheme 2). Com-



ound **13** seems to be labile, it decomposes gradually even at room temp., and satisfactory analytical data have not been obtained; however, HRMS data are satisfactory. The low yield of product **13** may be ascribed to its instability. The structures of compounds **12** and **13** were supported by their ¹H and ¹³C NMR spectra (*vide infra*), analytical data, and/or high-resolution mass spectrometry (HRMS) data. In analogy with the reaction of prop-2-enylidene phosphoranes with compounds having two electrophilic centres,^{7,8} as well as the reaction of (vinylimino)phosphoranes such as **2** with methano[11]annulenone,² we propose the pathways for the formation of products **12** and **13** as outlined also in Scheme 2. A Michael-type addition of the phosphoranes **7a** and **7b** to C-7 of compound **8** gives the intermediates **9a,b**, respectively. Hydro-

gen migration in intermediates **9a,b** regenerates the phosphorane moieties in tautomers **10a,b**. The phosphoranes then undergo an intramolecular Wittig reaction giving tricycles **11a,b**, which undergo aromatization eliminating HCl to give products **12** and **13**, respectively.

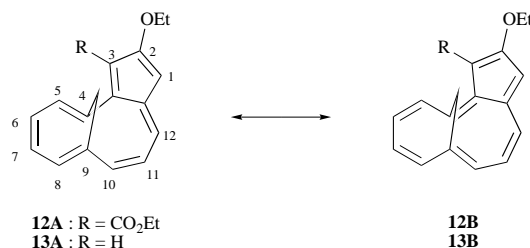
One may propose alternative pathways, which involve the Wittig reaction of compounds **7a,b** with the ketone **8** at first to give the intermediates **14a,b**. Regioselective electrocyclicization of compounds **14a,b** to give tricycles **15a,b** and subsequent dehydrochlorination would give compounds **12** and **13**, respectively. In order to gain insight into this possibility, the reaction of methylenetriphenylphosphorane **16** with ketone **8** was studied (Scheme 4). However, compound **16** did not undergo a Wittig reaction with ketone **8**, but instead a substitution occurs at C-9 to give compound **18** *via* zwitterion **17**. Structural assignment of compound **18** was accomplished by spectral analysis and satisfactory analytical data. In the ¹H NMR spectrum of compound **18**, the vinyl proton of 2-H appears at δ 6.36 as a singlet. The vinyl protons of 9-H and 10-H appear at δ 6.75 and δ 6.90, both of which are coupled to each other. Thus it is clear that the triphenylphosphoranylidene methyl group is introduced at C-9. Furthermore, a ³¹P NMR spectrum showed that the signal appears at high field of δ_p -36.3, indicating that the triphenylphosphine moiety is not bonded to an oxygen atom such as the structural formula **19**, in which the δ_p value is expected to be large and positive.¹³ Thus compound **18** is considered to exist as a resonance hybrid of structures **18** and **18B**. In this relation, the Wittig reaction of compounds **7a,b** with ketone **8** leading to products **14a,b** seems to be unlikely. In addition, we have no explanation for the regioselective electrocyclicization of compounds **14a,b** leading to tricycles **15a,b** (Scheme 3), and thus we prefer the pathways outlined in



Scheme 2. At this stage, there is no reasonable explanation for the different site-selectivity between phosphoranes **7a,b** and **16** toward ketone **8**.

The ¹H NMR spectra of 4,9-methanocyclopentacycloundecene derivatives **12** and **13** are noteworthy since the

chemical shifts of bridge-annulene systems are quite useful in determining such structural properties as diatropicity and bond alternation. The chemical shifts of the methylene protons of compounds **12** and **13** were found in the deshielding region (δ -0.26 to 0.37), and the peripheral protons appear in the aromatic region (δ 6.55–8.40). The large geminal coupling constants of the methylene protons (J 11.7 and 11.1) support the absence of a norcaradiene structure for compounds **12** and **13**. The chemical shifts of the methylene protons reflect the degree of ring current in methano-bridged aromatics.^{1,14} The average values for compounds **12** ($\delta_{av} = -0.22$) and **13** ($\delta_{av} = 0.17$) suggest that the degree of diatropic ring current decreases in the order **12** > **13**. This feature is similar to that of bridge tricycles **1b** ($\delta_{av} = -0.18$) and **1a** ($\delta_{av} = 0.33$). Furthermore, the mean chemical shifts of the methanoannulene moieties (δ_{av} 7.67 for **12**; δ_{av} ~7.4 for **13**) compare well with those of compounds **1b** ($\delta_{av} = 8.01$) and **1a** ($\delta_{av} = 7.57$).¹ The higher diatropicity and large values of mean chemical shifts for compound **12**, as compared with those of compound **13**, is ascribed to the additional electron-withdrawing CO₂Et group, which causes an increase in the polar nature of the ring system and a large electron delocalization in the 14-electron cyclic π -system. Vicinal coupling constants of aromatic perimeter protons suggest bond alternation in compounds **12** [$J_{10,11}$ 9.7 > $J_{11,12}$ 8.3] and **13** [$J_{10,11}$ 9.4 > $J_{11,12}$ 8.6]. There is a well known tendency for double-bond localization in methano[11]annulene systems to favour cycloheptatriene moieties predominantly and to avoid giving 1,6-dimethylenecyclohepta-2,4-diene moieties.^{11,12,15} According to their ¹H NMR spectra, the canonical structures **12A** and **13A** containing a cycloheptatriene element seem to be more preferable to the canonical structures **12B** and **13B** having a dimethylenecycloheptadiene element, respectively (Scheme 5). Despite a plausible distortion from planarity, 4,9-



Scheme 5

methanocyclopentacycloundecenes **12** and **13**, just like 5,10-methanocyclopentacycloundecene derivatives, can therefore be regarded as aromatic on the basis of their ¹H NMR spectra. The ¹³C NMR spectra are also consistent with the presence of aromaticity in these systems. Additional support regarding structural assignments of compounds **12** and **13** is evident from their UV-visible absorption spectra. The UV-visible spectral data of compounds **12** and **13** as well as the related azulene derivatives **20**¹⁶ and **21**,¹⁷ which have the same substituents and were independently prepared by us previously,¹⁰ are listed in Table 1. Compared with azulenes **20** and **21**, compounds **12** and **13** exhibit a red-shifted absorption maxima for the longest-wavelength absorption. These bathochromic shifts are consistent with an extension of conjugation in compounds **12** and **13**. Furthermore, the substituent effects in compounds **12** and **13** are consistent with those of azulenes **20** and **21**:¹⁸ the absorption maxima of esters **12** and **20** exhibit shorter-wavelength absorption than those of the simpler ethers **13** and **21**, respectively.

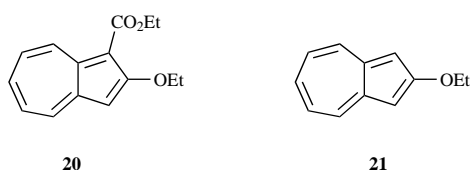
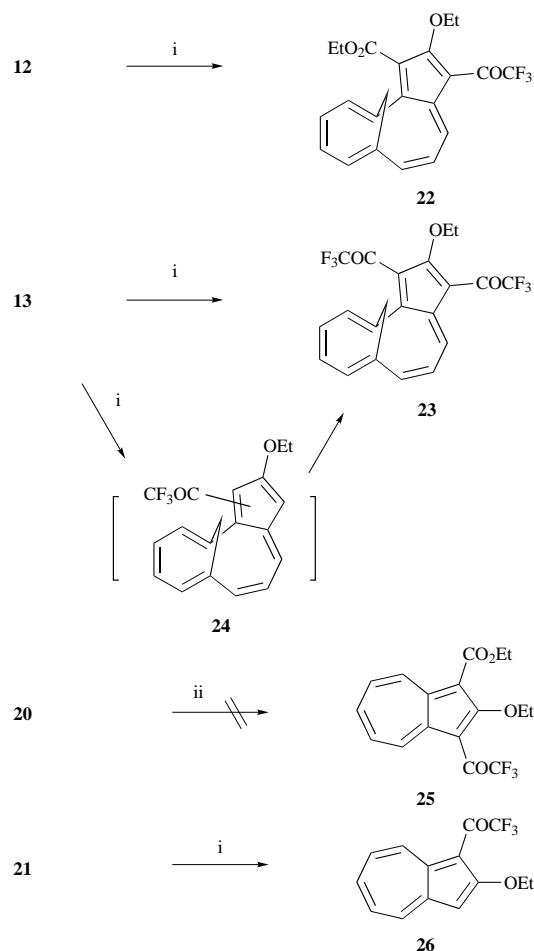


Table 1 UV-visible spectral data of compounds **12**, **13**, and the related azulenes **20** and **21**

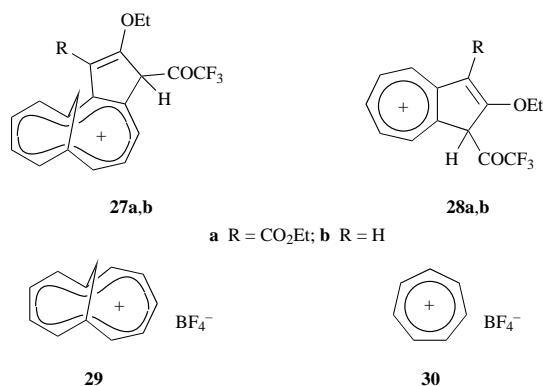
Compound	$\lambda_{max}(\text{EtOH})/\text{nm}$ ($\log \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)
12	240 (4.53), 312 (4.35), 369 (4.66), 445 (3.95), 644 (2.82)
13	223 (3.13), 364 (3.22), 485 (2.39), 617 (1.50), 719 (1.61)
20	277 (3.20), 286 (3.29), 316 (2.22), 340 (2.00), 356 (2.13), 373 (2.05), 400 (0.76), 449 (0.78), 476 (0.80), 489 (0.81), 508 (0.83), 542 (0.85), 562 (0.82), 574 (0.65)
21	264 (3.34), 317 (2.78), 340 (2.57), 357 (2.72), 373 (2.63), 518 (1.21), 558 (1.12), 602 (0.65)

Azulene undergoes electrophilic aromatic substitution at the α -position in the five-membered ring under mild conditions.^{18,19} Further substitution induces a second group more slowly at the α' -position in the same ring to give 1,3-disubstituted azulenes. The results are fully consistent with theoretical predictions and with the known polarization of azulenes, which concentrates electron density in the five-membered ring. We studied here the first example of a chemical reaction of the methanocyclopentacycloundecene ring system, and note that the parallels between methanocyclopentacycloundecene and azulene extend to the chemistry of the two systems. Treatment of compound **12** with (CF₃CO)₂O (TFAA) and NEt₃ in CH₂Cl₂ at 0 °C gave compound **22**, while that of the related azulene **20** in a similar fashion at 0 °C or under reflux did not give any expected product **25** except recovery of starting material. Compound **12** is more reactive than the azulene **20** which has the same substituents. Similarly, compound **13** having an ethoxy group at C-2 underwent trifluoroacetylation at 0 °C to give bistrifluoroacetylated product **23** in good yield. Since no monotrifluoroacetylated product **24** was isolated, the second trifluoroacetyl group is therefore also introduced to give final product **24** under mild conditions. On the other hand, reaction of the azulene **21** having an ethoxy group at C-2 under similar conditions to that of the reaction with compound **13** proceeded smoothly to give trifluoroacetylated product **26**. These reactions are summarized in Scheme 6. These facts clearly indicate that 4,9-methanocyclopentacycloundecenes such as **12** and **13** as well as the possible intermediate **24** are more reactive towards electrophilic substitution as compared with azulenes having the same substituents. Furthermore methanocyclopentacycloundecenes **12** and **13** seem to exhibit the same site-selectivity as does azulene. The high reactivity and site-selectivity of aromatic substitution of azulene is commonly explained by the exceptional stability of a Wheland intermediate which contains a tropylium ion.²⁰ Thus, it would be of interest to relate the reactivity of compounds **12** and **13** to that of azulenes **20** and **21** based on the stability of putative carbocations **27** and **28**. In the case of carbocations, the criterion of stability usually adopted is the pK_R -value, which is numerically equal to the pH required to establish a 1 : 1 equilibrium between a carbocation and the derived alcohol. The pK_R of simple cation **29** was found to be 6.2¹² as compared with pK_R 4.7²¹ for **30**. Exceeding the pK_R -value of even tropylium ion **30**, cation **29** is therefore more stable than cation **30**. Thus the intermediates **27a,b** are expected to be more stable than the respective related intermediates **28a,b** having the same substituent(s). The assumption predicts that compounds **12** and **13** are able to react with weaker electrophiles and/or under milder conditions as compared with those needed for azulenes **20** and **21**, and thus our results above are rationalized.

Both compounds **22** and **23** are slightly unstable and decompose gradually, and structures of the new compounds **22**, **23** and **26** were unequivocally assigned on the basis of their ¹H NMR, IR, HRMS or analytical data. The characteristics of ¹H NMR spectra of tricycles **22** and **23**, as compared with those of their non-trifluoroacetylated precursors **12** and **13**, are as follows. The very low chemical shifts of H-12 (δ 9.61) for **22** and H-5 (δ 8.00) and H-12 (δ 8.76) for **23** suggest the existence of the



Scheme 6 Reagents and conditions: i, TFAA, Et₃N, CH₂Cl₂, 0 °C; ii, TFAA, Et₃N, CH₂Cl₂, 0 °C to reflux



CF₃CO group(s) at C-1 for compound **22** and C-1 and C-3 for compound **23**, respectively. Although the mean chemical shifts of the methanoannulene moieties (bridged eleven-membered ring) for compounds **22** ($\delta_{av} \sim 8.0$) and **23** ($\delta_{av} 8.00$) are much shifted to low field as compared with those of precursors **12** and **13**, the average chemical shifts of the bridge-methylene systems for compounds **22** ($\delta_{av} -0.28$) and **23** ($\delta_{av} -0.64$) are shifted to higher field as compared with those of compounds **12** and **13**. This feature suggests an enhanced diatropicity and increased electron delocalization including some polar nature for the ring system in compounds **22** and **23**. The feature is remarkable for compound **23**, because of the introduction of two CF₃CO groups. Vicinal coupling constants of peripheral protons in compound **23** ($J_{10,11} 10.3 \sim J_{11,12} 10.4$) suggest decreased bond alternation, while those of compound **22** ($J_{10,11} 10.5 < J_{11,12} 11.5$) suggest the existence of bond alternation retaining a dimethylenecycloheptadiene element. In the case of the azulene **26**, the chemical shifts and coupling patterns of the ¹H NMR

Table 2 Reduction and oxidation potentials and calculated energy levels of LUMO and HOMO of compounds **12** and **13**, and the related azulenes **20** and **21**

Compound	E^{Red}/V	LUMO/eV	E^{Ox}/V	HOMO/eV
12	-1.47	-1.42	0.64	-8.25
13	-1.64	-1.06	~ 0.4	-8.13
20	-1.50	-1.18	1.02	-8.44
21	-1.92	-0.81	0.93	-8.12

spectrum and the low chemical shift of H-8 (δ 9.4–9.6) suggests the introduction of a CF₃CO group at C-1 of the azulene **21**; thus the structure of compound **26** was also assessed. As an indication of the electronic properties of compounds **22**, **23** and **26**, it should be noted that the carbonyl stretching (CF₃CO) bands in the IR spectra appear at 1628 cm⁻¹ (**22**) and 1648 cm⁻¹ (**23**), and 1645 cm⁻¹ (**26**), which are comparable with that of 1-(trifluoroacetyl)azulene (1645 cm⁻¹).

Cyclic voltammetry of compounds **12** and **13** as well as of azulenes **20** and **21** in MeCN gave irreversible reduction and oxidation waves, and each of the half-height potentials was measured independently. The results and the calculated energies of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) predicted by MNDO calculations²² are listed in Table 2. In the series **12** and **13**, the E^{Red} of compound **12** exhibits a smaller negative value as compared to that of compound **13**, while the E^{Ox} of compound **12** is larger than that of compound **13**. This feature is clearly reflected in the lower (*i.e.*, more negative) calculated LUMO and HOMO values for compound **12**, which has an electron-withdrawing CO₂Et group, as compared with those of compound **13**. These features are similar to the values for the series of azulenes **20** and **21**.

In summary, the reaction utilizing prop-2-enylidene-triphenylphosphorane derivatives and 9-chloro-1,6-methano-[11]annulen-8-one provide considerable advantage for the preparation of 4,9-methanocyclopentacycloundecene derivatives. The spectral and electrochemical properties as well as the electrophilic aromatic substitution reactions of products **12** and **13** indicate that they are vinylogous aromatic compounds of the azulenes **20** and **21**, respectively.

Experimental

IR spectra were recorded on a Shimadzu IR-400 spectrometer. UV-Visible absorption spectra were recorded on a Shimadzu UV-3101PC spectrophotometer. Mass spectra and high-resolution mass spectra were run on a JEOL Automass 150 and a DX-300 spectrometer. Unless otherwise specified, ¹H NMR (400 MHz) and ¹³C NMR (100.6 MHz) spectra were recorded on a JNM-GSX-400 spectrometer all for solutions in CDCl₃; and the chemical shifts are given relative to internal SiMe₄ standard. J -Values are given in Hz. ³¹P NMR (109.3 MHz) spectra were recorded on a JNM-EX-270 spectrometer and the chemical shift is given relative to an external standard of 85% aq. H₃PO₄. Mps were recorded on a Yamato MP-21 apparatus and are uncorrected. All the reactions were carried out under anhydrous conditions and a dry nitrogen atmosphere.

Preparation of the 4,9-methanocyclopentacycloundecene **12**

To a stirred solution of K₂CO₃ (138 mg, 1 mmol) and the phosphorane **7a** (427 mg, 1 mmol) in anhydrous dimethylformamide (DMF) (1 cm³) was added a solution of ketone **8** (50 mg, 0.25 mmol) in anhydrous DMF (1 cm³) at room temp., and the mixture was heated at 80 °C for 12 h. After the reaction was complete, the solvent was removed *in vacuo*, and the residue was purified by TLC on alumina (hexane–AcOEt, 10:1) to give *title compound* **12** (65 mg, 86%) as dark green plates, mp 58–61 °C (from EtOH); δ_H -0.26 (1 H, d, J 11.7, H-13), -0.17 (1 H, d, J 11.7, H-13), 1.46 (3 H, t, J 7.1, Me), 1.53 (3 H, t, J 7.1, Me), 4.17

(2 H, q, J 7.1, CH₂), 4.28 (2 H, q, J 7.1, CH₂), 6.55 (1 H, s, H-1), 7.05 (1 H, dd, J 9.1 and 10.2, H-6), 7.42 (1 H, dd, J 8.3 and 9.7 H-11), 7.53 (1 H, d, J 9.1, H-5), 7.55 (1 H, d, J 9.7, H-10), 7.59 (1 H, dd, J 8.3 and 10.2, H-7), 8.13 (1 H, d, J 8.3, H-8) and 8.40 (1 H, d, J 8.3, H-12); δ_C 13.2, 13.3, 30.8, 58.7, 62.9, 94.2, 99.3, 119.8, 125.5, 125.6, 125.7, 127.7, 128.5, 130.3, 131.3, 131.8, 137.7, 137.8, 164.0 and 166.0; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1700; m/z (rel. int.) 308 (M⁺, 46%) and 177 (100) (Found: M⁺, 308.1401; C, 77.7; H, 6.3. C₂₀H₂₀O₃ requires M , 308.1422; C, 77.90; H, 6.54%).

Preparation of the 4,9-methanocyclopentacycloundecene 13

To a stirred solution of Bu^tOK (112 mg, 1 mmol) in anhydrous dimethyl sulfoxide (DMSO) (1 cm³) was added a solution of (2-ethoxyprop-2-enyl)triphenylphosphonium bromide **6** (418 mg, 1 mmol) in anhydrous DMSO (1 cm³), and the mixture was stirred at room temp. for 30 min. To this mixture was added a solution of ketone **8** (102 mg, 0.5 mmol) in anhydrous DMSO (1 cm³) and the mixture was stirred at room temp. for a further 6 h. After the reaction was complete, the mixture was extracted with hexane–AcOEt (5:1), and the extract was washed with water, and dried over Na₂SO₄. After evaporation of the solvent, the resulting residue was purified through TLC on alumina (hexane–AcOEt, 5:1) to give *compound 13* (14 mg, 12%) as a dark green, viscous oil; δ_H –0.03 (1 H, d, J 11.1, H-13), 0.37 (1 H, d, J 11.1, H-13), 1.50 (3 H, t, J 7.1, Me), 4.49 (2 H, q, J 7.1, CH₂), 6.55 (1 H, d, J 1.6, H-1 or -3), 6.84 (1 H, dd, J 8.6 and 9.4, H-11), 7.23 (1 H, d, J 1.6, H-3 or -1), 7.32–7.39 (3 H, m, H-5, -6 and -7), 7.37 (1 H, d, J 9.4, H-10), 7.86 (1 H, d, J 8.6, H-12) and 7.92 (1 H, d, J 11.2, H-8); δ_C 14.8, 32.1, 65.7, 101.0, 106.3, 120.0, 125.3, 125.4, 126.8, 127.3, 129.4, 131.4, 131.5, 136.1, 138.5, 139.3 and 163.8; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3006, 1521, 1210 and 1043; m/z (rel. int.) 236 (M⁺, 42%) and 131 (100) (Found: M⁺, 236.1222. C₁₇H₁₆O requires M , 236.1202).

Reaction of ketone 8 with methylenetriphenylphosphorane 16

To a stirred solution of KN(SiMe₃)₂[†] (2 cm³ of 0.5 M solution in toluene; 1 mmol) was added a solution of methyltriphenylphosphonium bromide (357 mg, 1 mmol) in dry DMSO (1 cm³) at room temp. To the mixture was added a solution of ketone **8** (102 mg, 0.5 mmol) in anhydrous DMSO (2 cm³). Then the mixture was stirred at room temp. for another 12 h. After the reaction was complete, the solvent was removed *in vacuo*, and the residue was purified by TLC on alumina (hexane–AcOEt, 1:1) to give the *product 18* (62 mg, 28%) as brown crystals, mp 78–81 °C (from PhH–hexane, 1:1); δ_H 0.44 (1 H, d, J 10.4, H-12), 2.14 (1 H, d, J 10.4, H-12), 5.50 (1 H, br d, J 39.6, CHPPPh₃), 6.36 (1 H, s, H-2), 6.58 (1 H, d, J 7.5, H-4 or -7), 6.75 (1 H, d, J 11.8, H-9 or -10), 6.82 (1 H, d, J 7.0, H-7 or -4), 6.89 (1 H, dd, J 9.7 and 7.0, H-5 or -6), 6.90 (1 H, d, J 11.8, H-9 or -10), 7.01 (1 H, J 9.7 and 7.5, H-6 or -5) and 7.33–7.50 (15 H, m, Ph); δ_C 38.3, 110.9 (J_{CP} 143.1), 112.3 and 121.3 (J_{CCCP} 26.4), 122.0, 122.9, 127.1 (J_{CP} 35.2), 128.2 (J_{CCCP} 11.7), 128.8 (m), 129.1 (m), 131.9, 132.2, 134.0, 134.2, 135.5, 159.1 (J_{CCCP} 8.8) and 160.9 (J_{CCCP} 3.7); δ_P –36.3; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2857, 1490, 1391, 1291, 1160, 1087 and 847; m/z (rel. int.) 444 (M⁺, 23%) and 277 (100) (FAB-MS. Found: [M + 1]⁺, 445.1720; C, 83.7; H, 5.8%. C₃₁H₂₅OP requires M + 1, 445.1723. C, 83.76; H, 5.67%).

Trifluoroacetylation of compounds 12 and 13

To a stirred solution of a substrate **12** (61 mg, 0.2 mmol) or **13** (46 mg, 0.2 mmol) and NEt₃ (202 mg, 2 mmol) in CH₂Cl₂ (3 cm³) at 0 °C was added a solution of TFAA (210 mg, 1 mmol) in CH₂Cl₂ (1 cm³) and the mixture was stirred at 0 °C for a further 1 h. The reaction mixture was extracted with CH₂Cl₂ and the extract was dried over Na₂SO₄. Evaporation of the mixture and

chromatography of the resulting residue on silica gel (hexane–AcOEt, 5:1) gave product **22** (41 mg, 56%) or **23** (53 mg, 82%), respectively. For *compound 22*: brownish oil; δ_H –0.40 (1 H, d, J 11.6, H-13), –0.16 (1 H, d, J 11.6, H-13), 1.48 (3 H, t, J 7.1, CH₃), 1.49 (3 H, t, J 7.0, CH₃), 4.39 (2 H, q, J 7.0, CH₂), 4.56 (2 H, q, J 7.1, CH₂), 7.34 (1 H, dd, J 11.5 and 10.5, H-11), 7.65–7.72 (3 H, m, H-5, -6 and -7), 7.85 (1 H, d, J 10.5, H-10), 8.03 (1 H, d, J 7.2, H-8) and 9.61 (1 H, d, J 11.5, H-12); δ_C 14.1, 15.0, 31.4, 62.0, 70.2, 107.5, 114.9, 115.7, 118.6, 124.0, 126.3, 128.8, 129.4, 131.3, 133.6, 136.0, 143.3, 146.4, 166.2, 168.2 and 176.1 (one carbon is overlapping); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1628; m/z (rel. int.) 405 (M⁺ + 1, 95%), 404 (M⁺, 72) and 262 (100) (Found: M⁺, 404.1262; C, 65.4; H, 4.8%. C₂₂H₁₉F₃O₄ requires M , 404.1235; C, 65.34; H, 4.78%).

For *compound 23*: brownish oil; δ_H –0.88 (1 H, d, J 10.5, H-13), –0.39 (1 H, d, J 10.5, H-13), 1.49 (3 H, t, J 6.9, CH₃), 4.24 (2 H, q, J 6.9, CH₂), 7.56 (1 H, dd, J 10.4 and 10.3, H-11), 7.76 (1 H, dd, J 9.3 and 9.2, H-6), 7.86 (1 H, dd, J 9.4 and 9.2, H-7), 7.96 (1 H, d, J 10.3, H-10), 8.00 (1 H, d, J 9.3, H-5), 8.11 (1 H, d, J 9.4, H-8) and 8.76 (1 H, d, J 10.4, H-12); δ_C 14.8, 31.7, 51.2, 110.2, 115.6, 124.6, 128.6, 131.0, 131.7, 133.2, 134.8, 135.3, 135.4, 136.0, 136.3, 138.4, 139.6, 145.0, 146.0, 154.9 and 166.3; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1648; m/z (rel. int.) 428 (M⁺, 69%) and 176 (100) (Found: M⁺, 428.0859. C₂₁H₁₄F₆O₃ requires M , 428.0847).

Attempted trifluoroacetylation of the azulene 20

To a stirred solution of compound **20** (31 mg, 0.13 mmol) and NEt₃ (128 mg, 1.3 mmol) in CH₂Cl₂ (3 cm³) at 0 °C was added a solution of TFAA (135 mg, 0.64 mmol) in CH₂Cl₂ (1 cm³) and the mixture was stirred for 0.5 h. The reaction was monitored by TLC. The mixture was then stirred at room temp. for 3 h, and refluxed for another 6 h. After evaporation of the solvent, the residue was purified through column chromatography on Al₂O₃ by using a mixture of hexane–AcOEt (10:1) to give compound **20** (30 mg, 100% recovery).

Trifluoroacetylation of the azulene 21

To a stirred solution of the azulene ether **21** (75 mg, 0.4 mmol) and NEt₃ (440 mg, 4.0 mmol) in CH₂Cl₂ (5 cm³) at 0 °C was added a solution of TFAA (460 mg, 2.2 mmol) in CH₂Cl₂ (2 cm³) and the mixture was stirred for 1 h. The reaction mixture was then extracted with CH₂Cl₂ and the extract was dried over Na₂SO₄. After evaporation of the mixture, the residue was purified by TLC on Al₂O₃ (hexane–AcOEt, 10:1) to give *compound 26* (88 mg, 75%) as orange plates, mp 104–105 °C (from hexane); δ_H (90 MHz) 1.60 (3 H, t, J 7.0, CH₃), 4.40 (2 H, q, J 7.0, CH₂), 6.66 (1 H, s, H-3), 7.33–7.76 (3 H, m, H-5, -6 and -7), 8.16 (1 H, d, J 8.0, H-4) and 9.43–9.55 (1 H, m, H-8); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1645; m/z (rel. int.) 268 (M⁺, 39%) and 171 (100) (Found: C, 62.4; H, 3.9. C₁₄H₁₁F₃O₂ requires C, 62.69; H, 4.13%).

Cyclic voltammetry of methanocyclopentacycloundecenes 12 and 13 and azulenes 20 and 21

Reduction and oxidation potentials of compounds **12**, **13**, **20** and **21** were determined by means of a CV-27 voltammetry controller (BAS Co.). A three-electrode cell was used consisting of Pt working and Pt counter electrodes and a reference Ag/AgNO₃ electrode. An acetonitrile solution (4 cm³) of the compounds (1 mmol dm^{–3}) and Bu₄NClO₄ (0.1 mol dm^{–3}) was deaerated by bubbling nitrogen through the solution for 30 min. The measurements were made at a scan rate of 0.1 V s^{–1}, and the voltammograms were recorded on a WX-1000-UM-010 (Graphtec Co.) X–Y recorder. Immediately after the measurements, ferrocene (0.1 mmol) ($E_2^+ = +0.083\text{V}$) was added as an internal standard, and the observed cathodic or anodic peak potential was corrected with reference to this standard. All the compounds exhibited no reversible reduction or oxidation waves; each of the potentials was measured through independent scan and they are summarized in Table 2.

[†] TMS = trimethylsilyl.

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