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Bicyclo[6.3.0]undeca-1(11),2,4,6,8-pentaen-10-ylidene: An aromatic carbene having ambiphilic properties

Hiroyuki Ishikawa[a], Jun-ichi Nishida[a], John W. Jones, Jr.[b], Lawrence T. Scott[b,c]*, and Takeshi Kawase[a]*

Dedication ((optional))

Abstract: The title carbene (**4**) was generated as a highly reactive species in solutions by photoirradiation of 10-diazobicyclo[6.3.0]-undecapentaene (**5**) using a high pressure mercury lamp. The carbene **4** reacts with benzene to afford two isomeric adducts, 10-phenylbicyclo[6.3.0]undecapentaene (**10**) and tricyclo[9.3.0^{3,10}.0]heptadeca-1,3(10),4,6,8,12,14,16-octaene (**11**). The reactivity toward benzene is a characteristic of an electrophilic aromatic carbene analogous to cyclopentadienylidene **1**. On the other hand, the reaction of **4** with methanol produces 7-methoxybicyclo[6.3.0]undeca-1,3,5,8,10-pentaene (**15**). When methanol-d$_1$ was employed as a reactant, the 10-dueterated analogue was formed. The results clearly indicate the formation of bicyclo[6.3.0]undecapentaenyl cation (**7**) as a novel 10π-electronic compound by protonation of **4**. Theoretical calculations indicate that the 2 and 7 positions of the cation have the largest positive charge in the cation. Moreover, the carbene was generated in the presence of *t*-butyl hydroperoxide in aqueous THF to afford azulene via oxidation of **7**, followed by decarbonylation. The nucleophilic property of the carbene **3** is similar to that of cycloheptatrienylidene **2**. Thus, **4** can be regarded as a novel ambiphilic aromatic carbene.

Introduction

Aromatic carbenes constitute an interesting class of reactive chemical species. In general, they are divided into two categories, nucleophilic and electrophilic carbenes, on the basis of their structural and electronic features. Cyclopentadienylidene (**1**) and cycloheptatrienylidene (**2**) are typical aromatic carbenes (Fig. 1). ESR analysis reveals that **1** is a ground state triplet **1B**.[1] On the other hand, **1** can be regarded as an electrophilic carbene on the basis of the resonance contribution **1A**, which is consistent with the one-step insertion mechanism for alcoholic O-H bond.[2] In resonance contribution **1A**, the filled p orbital of the carbene is conjugated with the two π bonds, forming a cyclopentadienyl anion, which is aromatic in character. On the other hand, cycloheptatrienylidene (**2**) displays nucleophilic character consistent with the resonance contribution **2C**.[3] In this resonance contributor, the empty p orbital is conjugated with three π bonds, completing a six-electron seven-center cyclic system like the tropylium cation. The filled HOMO orbital of the carbene remains localized and imparts nucleophilic character. Thus, carbene **2** reacts readily with electrophilic alkenes but not with benzene.[3] Recent theoretical studies on **2** reveal that the energy minimum for this C_7H_6 species is not the carbene **2**, but cyclohepta-1,2,4,6-tetraene **3** possessing a highly strained allene moiety.[4]

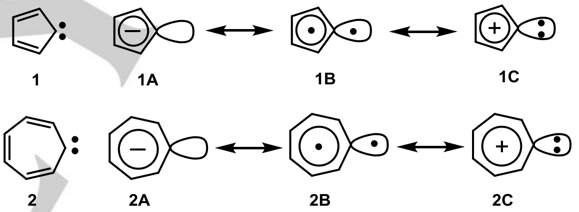
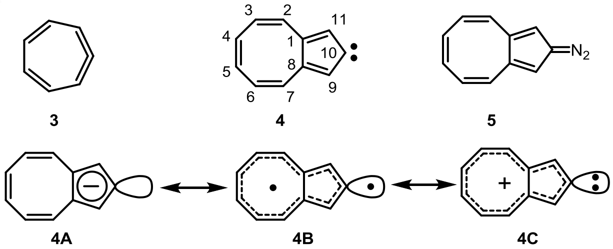


Fig. 1 Aromatic carbenes **1** and **2**, and their resonance contributions



Scheme 1 Molecular structure of **3**–**5**, and resonance contributions of **4**

Bicyclo[6.3.0]undeca-1(11),2,4,6,8-pentaen-10-ylidene (**4**) is a derivative of cyclopentadienylidene **1**, fused with cyclooctatetraene (COT). From the view point of its reactivity as an aromatic carbene, **4** might be expected to exhibit electrophilic properties, as suggested by a partial cyclopentadienylidene moiety **4A** in Scheme 1, or nucleophilic properties, as suggested by the 10π electronic periphery in **4C**. Characterization of **4** generated by photoirradiation of 10-diazobicyclo[6.3.0]undeca-1(11),2,4,6,8-pentaene (**5**) in 2-methyltetrahydrofuran matrix at 17 K has been published previously.[5] The ESR spectrum of **4** exhibits intense signals characteristic of a triplet species, the zero-

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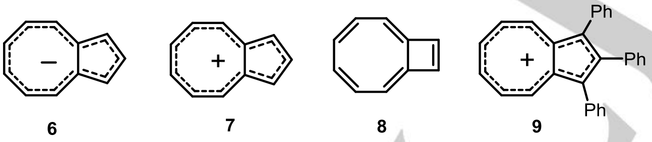
field splitting parameters of which were evaluated to be D = 0.2401 cm^{-1} and E = 0.0044 cm^{-1}. The spectroscopic properties of **4**, namely the red shift of the maximum in the UV-vis spectrum and the much smaller D value in the ESR spectrum compared to **1** (D = 0.4089 cm^{-1} and E = 0.0120 cm^{-1})[1a], imply a large degree of biradical character (**4B**) in the electronic structures of **4** (Scheme 1). However, the reactivity of **4** has not been well explored thus far.

Recently, we reported the synthesis, reactivity and magnetic properties of bicyclo[6.3.0]undecapentaenyl anion **6**.[6] The anion shows large chemical shift changes in its ^{1}H-NMR spectra that can be ascribed to ion-pairing effects. The ^{1}H-NMR analysis reveals that relatively small conformational changes of the COT ring appear to cause large changes in the paratropic properties. The counterbalance between the aromatic character of the five-membered ring and the antiaromatic character of the 12-electron periphery determines the overall electronic and magnetic properties of **6**.

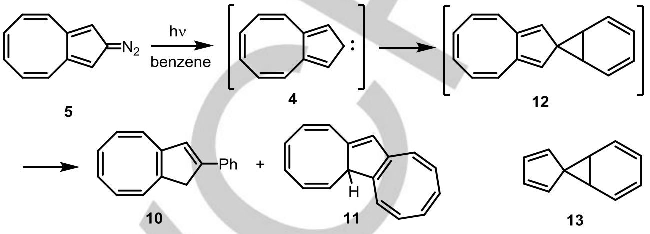
Analogous to **6**, the electronic property of carbene **4** should be highly susceptible to external stimuli. Therefore, we have investigated the reactivity of **4** under several conditions, and have found that **4** possesses ambiphilic properties: both electrophilic and nucleophilic properties in the same molecule. More specifically, the reactions of **4** in hydroxylic solvents give products via bicyclo[6.3.0]undecapentaenyl cation **7** as another reactive intermediate. Cation **7** can be regarded as a novel [4n]annuleno[4n]annulene,[7] isoelectronic with bicyclo[6.2.0]decapentaene **8**.[8] Although the formation of triphenyl derivative **9** was reported in a paper by Dürr and Scheppers,[9] neither the electronic nor the chemical properties of **9** were mentioned. Moreover, the parent cation **7** has been heretofore elusive. Herein, we describe and discuss the generation and reactions of aromatic carbene **4** and cation **7**.



Scheme 2 Molecular structures of **6–9**.

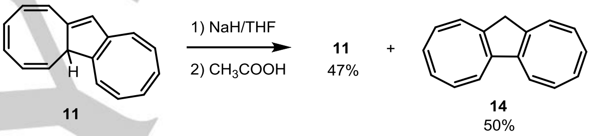
Results and Discussion

Irradiation of **5** with a high pressure mercury lamp (HPML) promotes the extrusion of N_2, generating the carbene **4**. The reaction was carried out in benzene at room temperature to afford 10-phenylbicyclo[6.3.0]undecapentaene (**10**) and tricyclic compound **11** in 27 and 29% yields, respectively (Scheme 3). The structures were confirmed by ^{1}H-NMR spectral and elemental analyses. The reaction providing these products is analogous to the reaction of triphenylcyclopentadienylidene with benzene.[9,10] Spiro compound **12** is likely formed as the initial product, because the reaction of cyclopentadienylidene **1** with benzene produces spiro compound **13** as an isolable product.[11] Compound **12**, however, cannot be isolated under the conditions, owing to its thermal lability. A subsequent C—C bond cleavage of the three membered ring of **12** and a proton transfer lead to the compound **10**, whereas thermal sigmatropic shift of **12** affords **11**. Cycloheptatrienylidene **2**, a nucleophilic carbene, does not react with benzene. These results indicate that carbene **4** acts as an electrophilic carbene analogous to **1**.



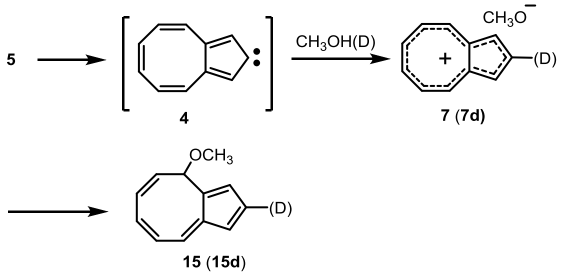
Scheme 3 Photoreaction of **5** in benzene, and molecular structure of **13**.

Treatment of **11** with sodium hydride in THF and quenching the generated anion with acetic acid furnishes a mixture of **11** and a new hydrocarbon **14** as an eight-membered ring vinylogue of fluorene in 47 and 50% yields, respectively (Scheme 4).



Scheme 4 Basic treatment and subsequent acidic quenching of **11**

To our surprise, when the photoreaction of **5** was performed in methanol (CH_3OH), we obtained 7-methoxybicyclo[6.3.0]undeca-1,3,5,8,10-pentaene (**15**) in 64% yield as the sole isolated product (Scheme 5). When deuterated methanol (CH_3OD) was employed for this reaction, the 10-deuterio derivative **15d** was obtained. The ^{1}H-NMR spectra reveal that the deuteration occurred at the 10-position of **15** (Fig. 2). The results clearly indicated the formation of cation **7** as another reactive intermediate, generated by nucleophilic proton abstraction from the hydroxyl group of methanol by **4**.[2] The optimized structure and the LUMO of **7** have been calculated by the PM3 method.[12,13] The cation has a twisted structure (Fig. 3a and 3b). The 9- and 11-carbons have the largest



Scheme 5 Photoreaction of **5** in methanol and methanol-d_1.

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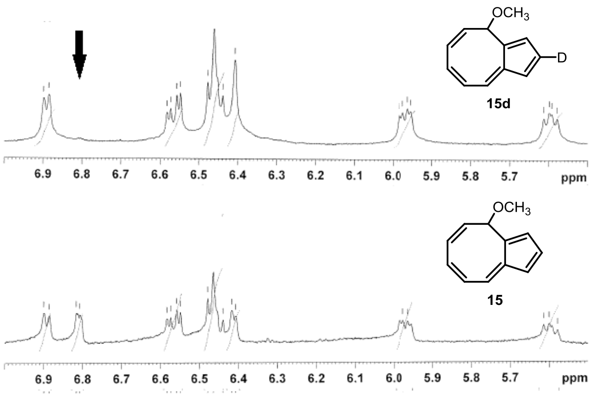


Fig. 2 ^{1}H-NMR spectra of **15** (down) and **15d** (upper) in $CDCl_3$.

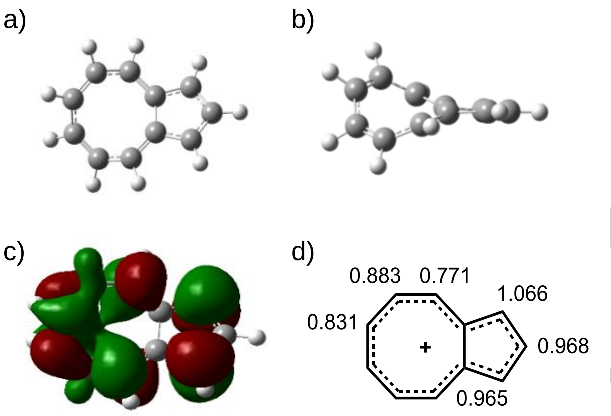
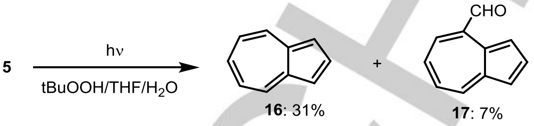


Fig. 3 Optimized structures of the cation **7** with PM3 calculations; a) top and b) side views, and c) the LUMO coefficients of **7**. d) Electron density of **7** obtained by HMO calculation.

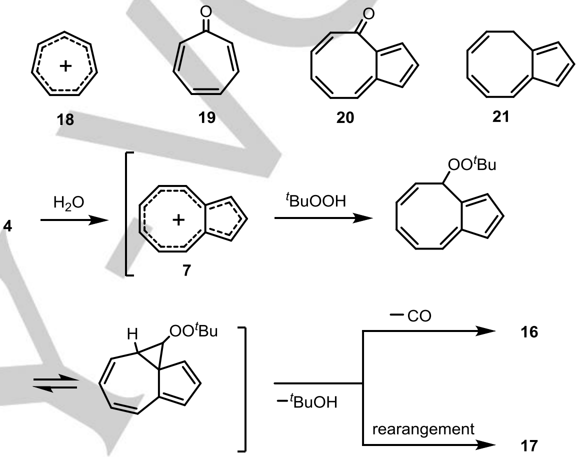
LUMO coefficients; however, the reaction took place at the 2(7)-position. A Hückel molecular orbital (HMO) calculation predicts the lowest electron density at the 2- and 7-carbons of **7** (Fig. 3d). The selective formation of **15** strongly supports the formation of **7**.

Further evidence for the generation of **7** was provided by the reaction of **5** with hydroperoxides (R-OOH), such as *t*-butyl hydroperoxide (^{t}BuOOH), hydrogen peroxide (HOOH), and *m*-chloroperbenzoic acid (mCPBA), affording azulene **16**. When the photoreaction of **5** was carried out in the presence of *t*-butyl hydroperoxide in aqueous THF [THF:H_2O:^{t}BuOOH (70 wt.% in H_2O) = 15:5:5], azulene **16** and 4-formylazulene **17**[14] were produced in 31 and 7% yields, respectively (Scheme 6). The reactions of **5** with HOOH or mCPBA in aqueous THF also afforded **16**, albeit in lower yields (~15%). On the other hand, the reaction of **5** and mCPBA in dry THF afforded no azulenic compounds. Therefore, the presence of both the hydroperoxides and water is critical for the formation of azulenes. The results strongly suggest the formation of the cation **7** as an intermediate.

It has been known that oxidation of tropylium cation **18** with hydrogen peroxides afforded benzene and/or benzaldehyde, but not tropone **19** (Scheme 7).[15] Consequently, formation of ketone **20** as a tropone vinylogue would not be anticipated in the reaction. A proposed reaction mechanism is outlined in Scheme 7.



Scheme 6 The reaction of **5** in the presence of *t*-butyl hydroperoxide in aqueous THF affording azulene **16** and 4-formylazulene **17**



Scheme 7 Molecular structures of **18**–**21**, and a proposed reaction mechanism of the reaction of **4** with ^{t}BuOOH in aqueous THF affording azulene **16** and 4-formylazulene **17** via cation **7**.

Carbinols derived from stable carbenium ions are normally quite labile,[16] because disproportionation of the carbinols to the corresponding ketone and hydrocarbon occur in protic media. For example, quenching of tropylium cation **18** with water affords tropone **19** and cycloheptatriene.[16a] Unfortunately, the reaction of **5** in aqueous THF led to a complex mixture, and neither **20** nor **21** could be detected. Because **21** is an isolable material,[17] the results indicate relatively low stability of cation **7**.

Conclusions

The title carbine **4** was generated by photoreaction of the corresponding diazo compound **5**. The reaction of **4** with benzene produces two compounds **10** and **11** via the spiro adduct **12**. On the other hand, the reaction of **4** in methanol affords adduct **15** via the bicyclo[6.3.0]undecapentaenyl cation **7** as another reactive intermediate. These results indicate that the carbene **4** acts as an electrophilic carbene in benzene, analogous to cyclopentadienylidene **1**, and as a nucleophilic carbene in methanol, analogous to cycloheptatrienylidene **2**. Thus, **4** can be regarded as a novel ambiphilic carbene, whose reactivity is highly susceptible to external stimuli. Moreover, the reaction of **4** was performed in the presence of ^{t}BuOOH in aqueous THF to afford the azulenes **16** and **17**. The azulenes are most likely formed by oxidation of **7** at the 2- or 7-position with hydroperoxides. The results are well consistent with the theoretical prediction.

Experimental Section

General: All reactions of air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen. Air- and moisture-sensitive liquids and solutions were transferred *via* syringe. Analytical thin-layer chromatography was performed using glass plates pre-coated with Merck Art. 7730 Kiesel-gel 60 GF-254. Thin layer chromatography plates were visualized by exposure to UV light. Organic solutions were concentrated by using rotary evaporation at *ca.* 15 Torr obtained with a diaphragm pump. Column chromatography was performed with Merck Kiesel-gel 60. All reagents were commercially available and used without further purification unless otherwise noted. THF was purchased from Wako Chemical Co. and distilled from lithium aluminum hydride at 760 Torr under a nitrogen atmosphere before use.

Melting points were recorded on a Yanaco MP–S3 apparatus and are reported uncorrected. Mass spectral analyses (EI) were performed on a JEOL JMS-O1SG-2 instrument. FAB- and HR-mass spectra were recorded with a JEOL JMS-700. FAB-mass spectrometer in a positive mode with 3-nitrobenzyl alcohol (NBA) as the matrix. Elemental analyses were obtained from Yanaco MT5 CHN corder. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker–Biospin DRX-500, spectrometer, and measured at 20 ˚C. IR spectra were obtained using a Shimadzu FTIR-8400 spectrometer. Electronic (UV-vis) and fluorescence spectra in solution were recorded with a JASCO V650. DFT calculations for **7** were carried out by using the B3LYP/6-31G(d) method with the Gaussian 09 program package.[12]

Synthesis: 10-Diazobicyclo[6.3.0]undeca-1(11),2,4,6,8-pentaene (**5**) was prepared by the reported procedure.[6]

*Photoreaction of **5** in benzene:*

A solution of **5** (280 mg, 1.7 mmol) in benzene (150 mL) was irradiated using a HPML through a Pyrex filter at RT for 30 min. The reaction mixture was concentrated under reduced pressure. The residue was charged on silica gel and purified by column chromatography to afford **10** as an orange solid (88 mg, 29%), **11** as a yellow oil (81 mg, 27%) and recovered **5** (46 mg) from subsequent three hexane elusions. 10-phenylbicyclo[6.3.0]undeca-1(8),2,4,6,10-pentaene **10**: mp 121.0—121.5 ºC; MS (EI) *m/z* (%) = 218 (100) [M^{+}], 217 (85) [M–1]${}^{+}$; IR (KBr): ν = 2995 (m), 1490 (m), 1450 (m), 1370 (m), 755 (s), 696 (s) cm^{-1}; UV/Vis (cyclohexane): λ_{max} (log ε) = 225 (4.23), 298 (4.10), 350 (3.71); ^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.40 (br. s, 2H), 5.63–5.69 (m, 2H), 5.82 (dd, *J* = 11.3, 3.0 Hz, 1H), 5.90 (dd, *J* = 11.5, 3.5 Hz, 1H), 5.99 (d, *J* = 11.7 Hz, 1H), 6.03 (d, *J* = 11.7 Hz, 1H), 6.57 (s, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 2H) ppm;^{13}C NMR (125 MHz, CDCl$_3$) δ = 44.7, 124.8, 126.9, 128.6, 129.6, 130.2, 130.8, 132.1, 132.6, 133.1, 133.6, 135.8, 142.7, 144.1, 147.5 ppm; Anal. Found C 93.37; H 6.45%; Calcd. For C$_{17}$H$_{14}$: C 93.54; H 6.46%; HRMS (FAB, NBA) *m/z*: calcd. for [C$_{17}$H$_{14}$]: 218.1096; found: 218.1092. Tricyclo[9.3.0^{3,10}.0]heptadeca-1,3(10),4,6,8,12,14,16-octaene **11**: MS (EI) *m/z* (%) = 218 (100) [M]${}^{+}$, 217 (95) [M–1]${}^{+}$; IR (KBr): ν = 2995 (s), 1403 (m), 1339 (m), 850 (m), 655 (s), 639 (s) cm^{-1}; UV/Vis (cyclohexane): λ_{max} (log ε) = 265 sh (4.01), 297 (3.74), 378 (3.68); ^{1}H NMR (500 MHz, CDCl$_3$) δ = 3.47 (s, 3H), 4.18 (dd, *J* = 6.8, 1.4 Hz, 1H), 5.59 (dd, *J* = 10.9, 6.8 Hz, 1H), 5.95 (ddt, *J* = 10.9, 6.8, 1.4 Hz, 1H), 6.39 (dd, *J* = 5.1, 1.7 Hz, 1H), 6.44 (dd, *J* = 12.5, 6.9 Hz, 1H), 6.46 (dd, *J* = 2.3, 1.4 Hz, 1H), 6.55 (dd, *J* = 12.5, 4.7 Hz, 1H), 6.79 (dd, *J* = 5.1, 2.3 Hz, 1H), 6.87 (d, *J* = 6.9 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$) δ = 57.2, 78.3, 122.6, 123.22, 124.4, 127.6, 131.2, 132.1, 133.5, 134.5, 137.1, 147.5 ppm; HRMS (FAB, NBA) *m/z*: calcd. for [C$_{17}$H$_{14}$]: 218.1096; found: 218.1097.

*Isomerization of **11**.*

A solution of **11** (70 mg) in THF (2 mL) was added to a suspension of sodium hydride (100 mg) in THF (5 mL), and the mixture was stirred at 0 ˚C for 30 min under N$_2$. The purple anion solution was cooled to –50 ˚C, and quenched with acetic acid (1 mL). The solution was stirred at that temperature for 5 min, and then allowed to warm at RT. The reaction mixture was diluted with water and extracted with hexane. The organic layer was washed with water and brine, and dried over anhydrous Na$_2$SO$_4$. The solvent was evaporated under reduced pressure. The residue was charged on silica gel and purified by column chromatography to give **11** (32 mg, 46%) from the first fraction and **14** (35 mg, 50%) as a pale yellow oil from the second fraction of hexane elutions. Tricyclo[9.3.0^{3,10}.0]heptadeca-1(11),3(10),4,6,8,12,14,16-octaene **14**: MS (EI) *m/z* (%) = 218 (100) [M]${}^{+}$, 217 (42) [M–1]${}^{+}$; UV/Vis (cyclohexane) : λ_{max} (log ε) = 261 (3.97), 374 (3.35); IR (KBr): ν = 3000 (s), 2920 (s), 1380 (m), 708 (s), 650 (s) cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ = 2.94 (s, 2H), 5.61–5.68 (m, 4H), 5.74–5.81 (m, 4H), 5.85–5.89 (m, 2H), 5.94 (d, *J* = 11.5 Hz, 2H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$) δ = 46.8, 129.2, 130.7, 132.0, 132.8, 133.1, 134.0, 144.0, 144.6 ppm; HRMS (FAB NBA) *m/z*: calcd. for [C$_{17}$H$_{14}$]: 218.1096; found: 218.1096.

*Photoreaction of **5** in methanol:*

A solution of **5** (280 mg, 1.7 mmol) in methanol (100 mL) was irradiated using a HPML through a Pyrex filter at 0 ˚C for 30 min. The reaction mixture was diluted with water and extracted with hexane. The organic layer was washed with water and brine, and dried over anhydrous Na$_2$SO$_4$. The solvent was evaporated under reduced pressure. The residue was charged on silica gel and purified by column chromatography to give the methoxy derivative **15** (182 mg, 64%) as a red oil from a hexane/ethyl acetate (95:5) elution. 7-Methoxybicyclo[6.3.0]undeca-1,3,5,8,10-pentaene **15**: MS (EI) *m/z* (%) = 172 (25) [M]${}^{+}$, 171 (17) [M–1]${}^{+}$, 141 (100) [M–OCH$_3$]${}^{+}$; IR (KBr): ν = 2931 (m), 2828 (m), 1684 (s), 1456 (m), 1198 (m), 1111 (s), 979 (m), 768 (m), 755 (m) cm^{-1}; UV/Vis (cyclohexane): λ_{max} (log ε) = 232 (4.10), 261 (3.95), 319 (3.81), 430 (2.45); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.47 (s, 3H), 4.18 (dd, J = 6.8, 1.4 Hz, 1H), 5.59 (dd, J = 10.9, 6.8 Hz, 1H), 5.95 (ddt, J = 10.9, 6.8, 1.4 Hz, 1H), 6.39 (dd, J = 5.1, 1.7 Hz, 1H), 6.44 (dd, J = 12.5, 6.9 Hz, 1H), 6.46 (dd, J = 2.3, 1.4 Hz, 1H), 6.55 (dd, J = 12.5, 4.7 Hz, 1H), 6.79 (dd, J = 5.1, 2.3 Hz, 1H), 6.87 (d, J = 6.9 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 57.2, 78.3, 122.6, 123.2, 124.4, 127.6, 131.2, 132.1, 133.5, 134.5, 137.1, 147.5 ppm; HRMS (FAB, NBA) *m/z*: calcd. for $[C_{12}H_{12}O]$: 172.0888; found:172.0887.

Photoreaction of ***5*** *with* ^{t}BuOOH *in aqueous THF:*

To a solution of **5** (255 mg, 1.5 mmol) in THF/H_2O (15 mL/5 mL) was added ^{t}BuOOH (70 wt.% in H_2O, 5 mL), and the mixture was irradiated using a HPML through a Pyrex filter at 0 ˚C for 1 hour. The reaction mixture was extracted with hexane. The organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure. The residue was charged on silica gel and purified by column chromatography to give azulene **16** (35 mg, 31%) as a blue solid and unreacted **5** (105 mg) from hexane elutions, and 4-formylazulene **17** (10 mg, 7%) as a dark blue solid from a hexane/diethyl ether (95:5) elution. 4-Formylazulene **17**[14]: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.39 (m, 1H), 7.53 (t, J = 5.4 Hz, 1H), 7.76–7.83 (m, 2H), 8.18 (t, J = 5.4 Hz, 1H), 8.27 (d, J = 5.4 Hz, 1H), 8.45 (d, J = 9.4 Hz, 1H), 10.91 (s, 1H) ppm.

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Keywords: aromatic carbenes • diazo compound • photoreaction • azulenes • carbocations

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[13] We also performed a theoretical calculation for the optimized structure of the cation by using DFT methods (MP2/6-31+G(d)revel) with Gaussian 09. The calculations predicted that the cation possessed a more flattened structure than the predicted one by the PM3 calculation.

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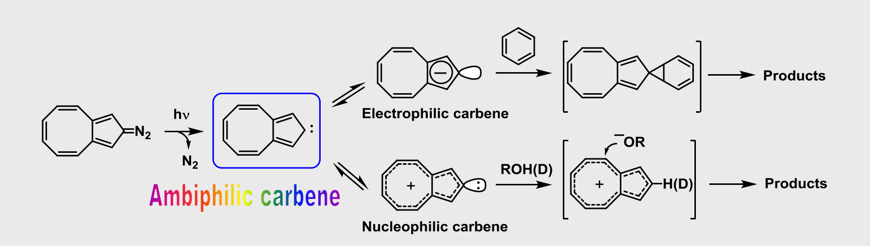

The title carbene was generated by photodecomposition of the corresponding diazo compound. The carbene reacts with benzene in an electrophilic manner and with methanol in a nucleophilic manner, respectively. The reaction with methanol generates a heretofore unknown cationic species as a reactive intermediate.

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Bicyclo[6.3.0]undeca-1(11),2,4,6,8-pentaen-10-ylidene: An aromatic carbene having ambiphilic properties