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Octachloroazulene

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Received August 27, 2001

Abstract: The title compound, the first perhaloazulene, has been synthesized from hexachlorobutadiene and cyclopentadiene. Further chlorination of 1,3,4,5,6,7-hexachloroazulene results in addition, not substitution, under electrophilic as well as free radical conditions. Radical chlorination of the hexachloroazulene affords in good yield a single decachlorotetrahydroazulene. Treatment of this Cl_{10} compound with one equiv of a phosphazene base gives a nonachlorodihydroazulene, but the addition of a second equiv results in dechlorination to 1,2,3,4,5,6,7-heptachloroazulene as well as dehydrochlorination to octachloroazulene. The former azulene is obtained cleanly from the Cl_9 compound with acid catalysis or by reduction with mercury. In the presence of calcium carbonate, however, the Cl_9 intermediate yields the dark green octachloroazulene. Although octachloronaphthalene is readily converted into its octafluoro counterpart, the isomeric octachloroazulene is far too sensitive to undergo the analogous transformation.

Introduction

The aromatic hydrocarbon azulene (**1**) is a remarkable compound.[1] Though isomeric with the colorless naphthalene (**2**), its color is a beautiful deep blue. It is a significantly polar hydrocarbon ($\mu = 1.0$ D), again in contrast to the nonpolar naphthalene. These and other characteristics follow from the nonalternant nature of azulene, which is apparent in its frontier orbitals. Although the frontier orbitals of an alternant hydrocarbon such as naphthalene are mirror-related (except for the *signs* of the atomic orbital coefficients),[2] azulene's have a very different spatial distribution (Figure 1).

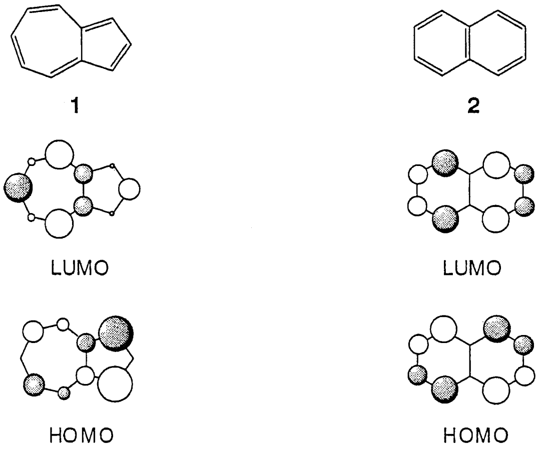
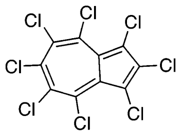


Figure 1. Frontier orbitals of azulene and naphthalene.

The striking contrasts that exist between azulene and benzenoid aromatic hydrocarbons in properties and chemistry presage large differences between perhaloazulenes and their benzenoid counterparts. This consideration made the synthesis of octachloroazulene (**3**), the first perhaloazulene, a worthwhile undertaking. In light of the dramatic contrasts one finds between hydrocarbons and fluorocarbons, octafluoroazulene (**4**) is an especially attractive synthetic target, and we regarded **3** at the outset as a promising precursor for this compound.



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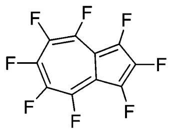

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Naphthalene is fully chlorinated in a single step by chlorine and antimony pentachloride,[3] and treatment with potassium fluoride in sulfolane transforms octachloronaphthalene into its octafluoro counterpart.[4] We began with the readily synthesized 5,6-dichloroazulene,[5] but quickly found that the aromatic system is destroyed under electrophilic chlorination conditions long before substitution of chlorine for hydrogen is finished. It became clear that several chlorines should already be in place in the seven-membered ring when the azulene skeleton is assembled if complete chlorination is to be achieved.

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* To whom correspondence should be addressed. E-mail: david.m.lemal@dartmouth.edu.

(1) Zeller, K.-P. Azulene. In *Houben-Weyl, Methoden der Organischen Chemie*, 4th ed.; Vol. 5, Part 2C, p 127. Lemal, D. M.; Goldman, G. D. *J. Chem. Educ.* **1988**, *65*, 923 and references therein.

(2) Yates, K. *Hückel Molecular Orbital Theory*; Academic Press: New York, 1978; pp 78−84.

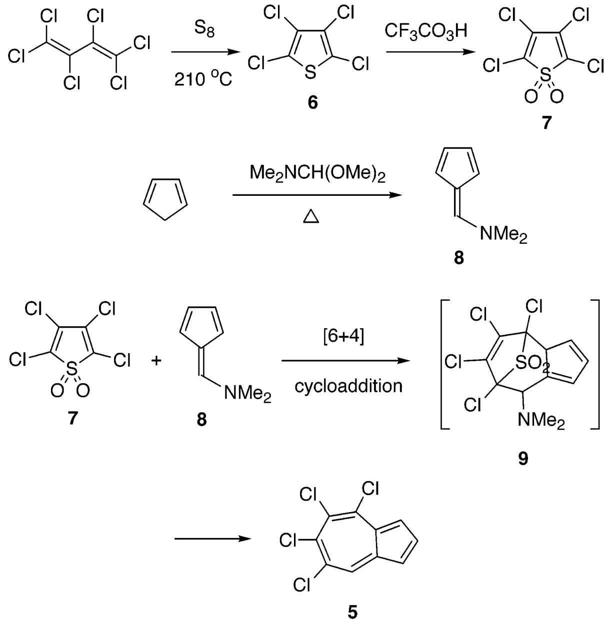
(3) Stroh, R. In *Houben-Weyl Methoden der Organischen Chemie*, 4th ed.; Vol. 5/3, p 670.

(4) Fuller, G. *J. Chem. Soc.* **1965**, 6264. See also: Maynard, J. T. *J. Org. Chem.* **1962**, *28*, 112.

(5) Reiter, S. E.; Dunn, L. C.; Houk, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 4199. Copland, D.; Leaver, D.; Menzies, W. B. *Tetrahedron Lett.* **1977**, 639.

10.1021/ja012051h CCC: $22.00 © 2002 American Chemical Society

Scheme 1



Results and Discussion

Accordingly, we synthesized 4,5,6,7-tetrachloroazulene (**5**) as shown in Scheme 1. Tetrachlorothiophene (**6**) was prepared from hexachlorobutadiene according to Raasch,[6] who oxidized it to the sulfone **7** in 50% yield using using *m*-chloroperbenzoic acid. We have found that the oxidation is essentially quantitative when the more powerful peroxytrifluoroacetic acid is employed. The yield of 6-dimethylaminofulvene (**8**) from cyclopentadiene and dimethylformamide dimethyl acetal has also been improved from 32[7] to 77% simply by adding excess diene during the reaction until the acetal is completely consumed. Unfortunately, the key [6 + 4] cycloaddition leading via **9** to 4,5,6,7-tetrachloroazulene (**5**) is reported to give only a 10% yield of the azulene, the principal reaction product being the 2:1 Diels−Alder adduct of **7** to the ring bonds of the fulvene.[8,9]

The order of addition is critical, as the yield drops to 3−5% if **7** is added to **8** instead of vice versa. Amine released in the condensation slowly attacks the azulene; we found that the yield could be increased to 16% by limiting the reaction time.[10]

If the behavior of azulene **5** paralleled that of naphthalene, electrophilic chlorination could lead directly to the octachloro derivative **3**.[3,11] However, treatment of **5** with chlorine and aluminum chloride in sulfuryl chloride as solvent resulted in a rapid fading of the intense blue color of chloroazulenes to a pale yellow, reminiscent of what happened with 5,6-dichloroazulene. This was clear evidence that the aromatic system was gone. NMR and GC/MS revealed a complex mixture of products, and it was found that sulfuryl chloride alone in the dark produced a similar result. When a solution of **5** in that solvent was irradiated with visible light the color again faded, but now spectra revealed a single dominant product, $C_{10}H_2Cl_{10}$, that was isolated by chromatography as white crystals in ~70% yield.

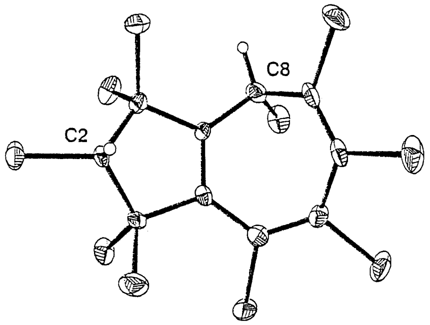
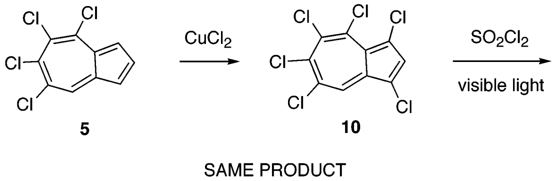
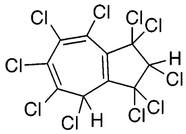


Figure 2. ORTEP drawing of decachlorotetrahydroazulene **11**.

Mild chlorination of **5** with cupric chloride yielded 1,3,4,5,6,7-hexachloroazulene (**10**),[12] which was transformed into the same unknown product when irradiated in sulfuryl chloride. By suggesting the location of six chlorines in the new molecule, this finding facilitated its structure determination. Analysis of the ^{13}C NMR and DEPT spectra led to the structure **11** for the chlorination product, and in confirming that assignment the X-ray crystal structure further revealed that its configuration is cis (ORTEP, Figure 2).





11

When the chlorination of **5** is performed under electrophilic conditions, i.e., in the dark or with aluminum chloride catalyst, the first two chlorines are introduced at the 1 and 3 positions, yielding **10**, both because the HOMO coefficients are very large there and because the substituted tropylium cations formed as intermediates are especially stable. When **10** is attacked again at the 1 and/or 3 position for the same reasons, instead of at an unsubstituted position, no proton is there to be lost. Thus, addition of chloride follows and the aromatic system is destroyed. Because the reaction conditions that give the best yield of decachloro compound **11** clearly generate chlorine atoms, part if not all of the chlorination sequence presumably occurs via a radical chain process. Given the high electron

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(6) Raasch, M. S. *J. Org. Chem.* **1980**, *45*, 856.

(7) Meerwein, H.; Florian, W.; Schön, N.; Stopp, G. *Liebigs Ann. Chem.* **1961**, *641*, 1.

(8) Kanematsu, K.; Kazunobu, H.; Dantsuji, H. *Heterocycles* **1981**, *16*, 1145.

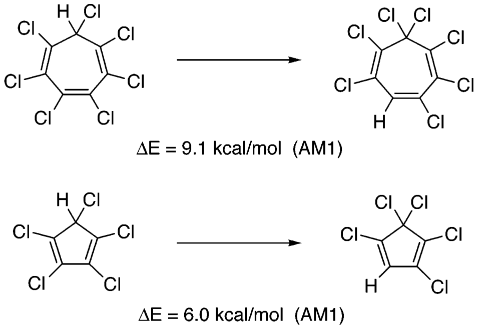
(9) For other [6+4] cycloadditions of fulvenes, see Dunn, L. C.; Chang, Y.-M.; Houk, K. N. *J. Am. Chem. Soc.* **1976**, *98*, 7095. Mukherjee, D.; Dunn, L. C.; Houk, K. N. *J. Am. Chem. Soc.* **1978**, *101*, 251. Dunn, L. C.; Houk, K. N. *Tetrahedron Lett.* **1978**, 3411; and ref 5.

(10) To disfavor Diels−Alder addition relative to the desired [6+4] pathway with the help of steric hindrance, we substituted the 1,3-dichloro- and 1,2,3-trichloro-6-(dimethylamino)fulvenes (Hafner, K.; Schmidt, F. *Tetrahedron Lett.* **1973**, 5101) for **8** in the reaction with **7**. Azulene yields remained poor, however, probably because of the instability of these fulvenes.

(11) Perchlorination of benzenoid hydrocarbons commonly proceeds *beyond* complete substitution, as additional chlorines relieve steric repulsions by rehybridizing sp^2 carbons. Ballester, M. Perchloro-organic Chemistry: Structure, Spectroscopy and Reaction Pathways. In *Adv. Phys. Org. Chem.*; Bethell, D., Ed.; Academic Press: London, 1989; Vol. 25, p 267.

(12) Bolton, R.; Hamilton, D. G.; Sandall, J. P. B. *J. Chem. Soc., Perkin Trans. 2* **1991**, 431. These authors carried out the chlorination of **7** with *N*-chlorosuccinimide.

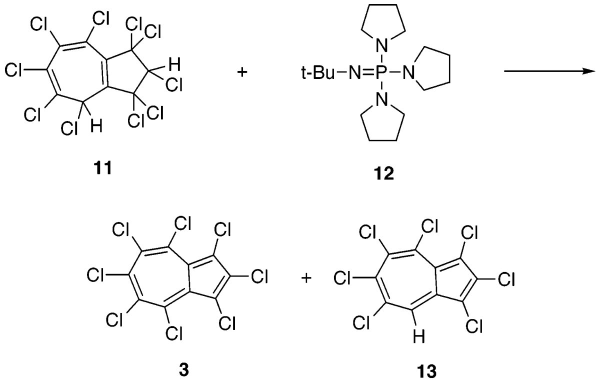
Scheme 2



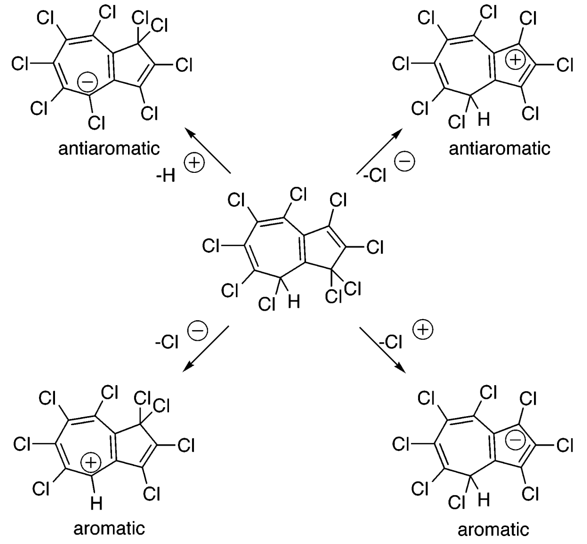
affinity of the chlorine atom,[13] however, repeated attack at the 1- and/or 3-position, as in electrophilic chlorination, is easily understood.

There are no fewer than 61 structures (not counting stereoisomers) that can arise by the addition of four chlorines to hexachloro compound **10**. Frontier orbital considerations do not explain why triene **11** is so heavily favored in the course of events following formation of **10**, but product stability considerations may. The energetics of the model isomerization reactions shown in Scheme 2 indicate that in both the seven- and five-membered rings chlorine geminal to hydrogen is favored strongly vis-à-vis chlorine geminal to chlorine. If one therefore assumes that the lowest energy decachloro isomers will have chlorines at the previously unsubstituted 2 and 8 positions, the choice is now limited to eight structures and a total of 20 stereoisomers. At the semiempirical AM1 level of theory[14] these isomers (in their lowest energy conformations) range in relative energy from 0.0 to 18.4 kcal/mol, and the lowest of all are the cis (0.0 kcal/mol) and trans (1.3 kcal/mol) isomers of **11** (see Supporting Information). Because the next-lowest energy isomer lies at 6.6 kcal/mol, it seems reasonable to conclude that the predominance of *cis*-**11** in the chlorination product is indeed largely a consequence of its thermodynamic stability. Steric hindrance probably also plays a role by favoring introduction of chlorine at the unsubstituted positions.

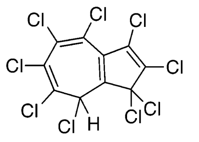
Twofold dehydrochlorination of **11** to give octachloroazulene (**3**) would appear to be straightforward. In fact, the several weak bases that were tried failed to react with **11** and all but one of the strong ones, even if bulky, were found to destroy it without yielding any of the desired **3**. Success was finally achieved with the fifteenth candidate, the potent, highly hindered Schwesinger base **12**[15] (in THF at −40 °C with warming to room temperature). However, octachloroazulene was accompanied in the product by 1,2,3,4,5,6,7-heptachloroazulene (**13**), in the ratio 2:1, respectively, showing that loss of 2Cl competed effectively with loss of a second molecule of HCl.

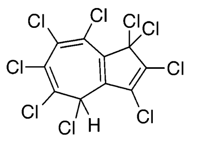

11 **12** **3** **13**

Scheme 3



Treatment of decachloro compound **11** with a single equivalent of the phosphazene base followed by “spontaneous” aromatization gave a striking result: the ratio of octa- to heptachloroazulene was now 4:1. Thus, *more* dehydrochlorination had occurred in the presence of *less* base. One equiv of the base transforms **11** into the nonachloro compound **14** or its double bond isomer **15**. Efforts to obtain this labile compound in pure form were unavailing. Because the ^{1}H NMR signal of the remaining proton (at C8) was shifted only slightly (0.07 ppm) from its position in **11**, we favor structure **14** over **15**, in which the proton’s environment is significantly altered. Structure **14** is assumed in the discussion to follow.


14


15

Scheme 3 provides a plausible resolution of the paradox that “spontaneous” aromatization of **14** results in more dehydrochlorination than occurs with a second equiv of base. Loss of the C8 proton of **14** develops antiaromatic character in the seven-membered ring, whereas chloride loss from that position develops aromatic character in the transition state; and loss of chloride from the five-membered ring creates antiaromatic character, whereas loss of positive chlorine there creates aromatic character in the transition state. Regarding loss of chloride from C8, it is interesting that the C8−Cl bond in the crystal of **11**, which is nicely aligned with the adjacent π orbitals, is 0.06 Å longer than the C2−Cl bond (the other bond to a Cl geminal to hydrogen).

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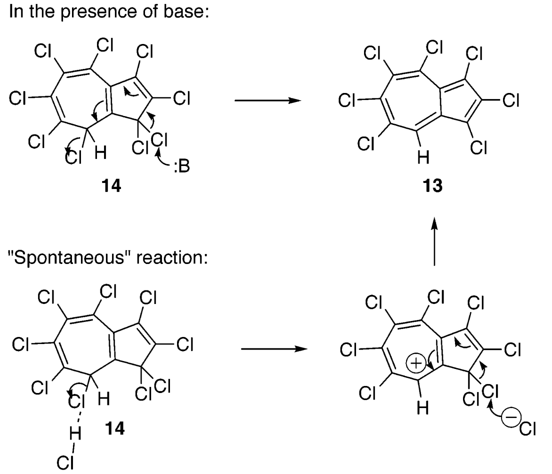
(13) The EA of the chlorine atom is 3.62 eV, higher even than that of the fluorine atom (3.40 eV). Trainham, R.; Fletcher, G. D.; Larson, D. J. *J. Phys. B: At. Mol. Phys.* **1987**, *20*, L777. Blondel, C.; Cacciani, P.; Delsart, C.; Trainham, R. *Phys. Rev. A* **1989**, *40*, 3698.

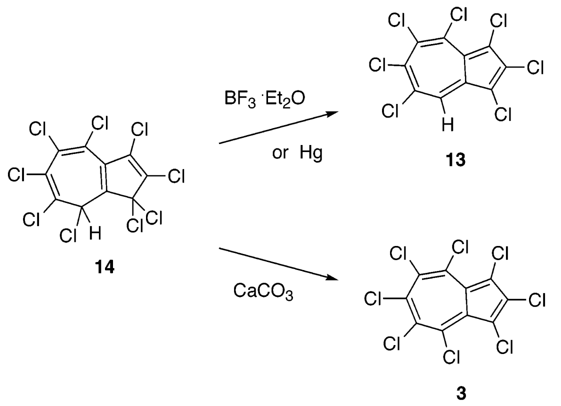
(14) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(15) Schwesinger, R.; Willaredt, J.; Schlemper, H.; Keller, M.; Schmitt, D.; Fritz, H. *Chem. Ber.* **1994**, *127*, 2435.

Scheme 4



These considerations suggest that base attack at chlorine in **14**, leading to heptachloroazulene (**13**), could compete effectively with deprotonation (Scheme 4). Under the conditions of "spontaneous" aromatization of **14**, hydrogen chloride is present from the pathway leading to octachloroazulene (**3**). We propose that HCl assists chloride loss from C8 by hydrogen bonding, again leading to **13**, though less efficiently than it is formed under the basic conditions (Scheme 4).[16] In accord with this surmise, treatment of nonachloro compound **14** with concentrated hydrochloric acid yielded **13** contaminated with <1% of **3**, albeit slowly and in very low yield. Treatment of **14** with Lewis acid boron trifluoride etherate gave **13** in 35% yield, again slowly but unaccompanied by **3**.



Also consistent with Scheme 4 was the observation that including a small amount of tetrabutylammonium chloride in the reaction of **14** with boron trifluoride etherate accelerated the aromatization considerably. Now the product was a 94:6 mixture of **13** and **3**, reflecting the ability of chloride ion to function as a base as well as to assist loss of "Cl^+". Mercury reduced **14** smoothly to **13**, free of **3**, at room temperature in 48% yield.

In light of the evidence that acid catalysis transforms the nonachloro intermediate **14** into heptachloroazulene, a solution of **14** was stirred with the acid scavenger calcium carbonate. The rewarding result was a 95:5 mixture of **3** and **13**, which gave upon recrystallization dark green octachloroazulene, mp 131−133 °C.[17]

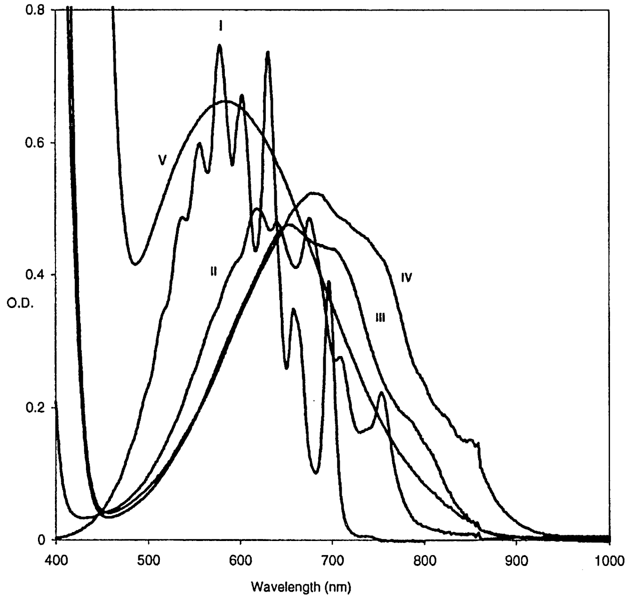


Figure 3. Visible/near infrared spectra of azulenes (1.1 × 10^{-3} M in cyclohexane). Curve I, azulene; II, 4,5,6,7-tetrachloroazulene; III, 1,3,4,5,6,7-hexachloroazulene; IV, 1,2,3,4,5,6,7-heptachloroazulene; V, octachloroazulene.

The electronic transition to S_2 in azulene lies in the UV, leaving a large gap between the S_1 and S_2 states and, thus, a "blue window" in the electronic spectrum. That gap explains azulene's anomalous fluorescence from the S_2 state.[18] In octachloroazulene, the $S_0 \rightarrow S_2$ transition extends well into the visible region, eliminating the "blue window" and thereby effectively adding a yellow component to the transmitted light (Figure 3). Though the maximum of the featureless $S_0 \rightarrow S_1$ band in **3** lies close to the parent molecule's, absorption extends far beyond that of azulene itself, nearly to 900 nm. Together with the absence of the "blue window", this accounts for the very dark green color of octachloroazulene. The UV spectra of the two azulenes reveal that, like the transition to S_2, higher energy transitions are also shifted bathochromically by perchlorination.

The mass spectrum of octachloroazulene, like that of its naphthalene counterpart, is striking, as it reveals the peeling off of chlorines all the way down to C_{10}^+. For comparison with azulene's dipole moment of 1.0 D, that of **3** calculated at the B3LYP/6-31G* level of theory is 0.83 D.[19]

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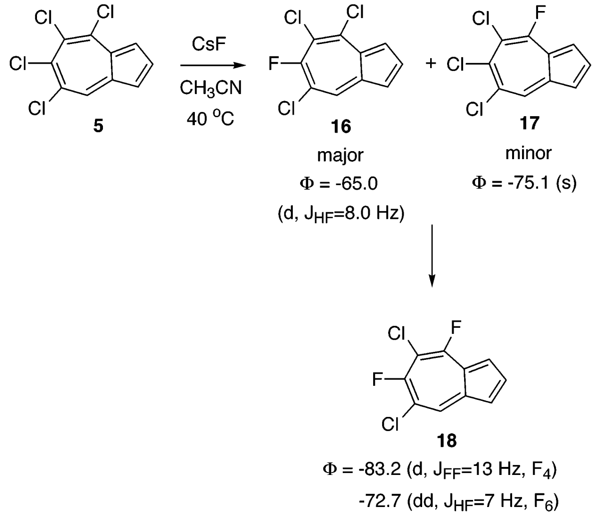
(16) "Spontaneous" aromatization was much slower in hexane than in THF.

(17) Early efforts to dehydrochlorinate decachloro compound **11** to obtain **3** included pyrolysis. Heating **11** at 250 °C gave a pale yellow mixture, so no azulenes were present. The major products were 1*H*-heptachloronaphthalene and, in smaller amount, octachloronaphthalene (see the Experimental Section). Because pyrolysis of hexachloroazulene **10** under the same conditions destroyed it without giving any identifiable compound, it is unlikely that azulenes were intermediates in the pyrolysis of **11**.

(18) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; pp 147−8.

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratman, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; and Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.; Pittsburgh, PA, 1998.

Scheme 5



For the transformation of **3** into octafluoroazulene (**4**), model reactions were first run with tetrachloroazulene **5**. Treatment of **5** with cesium fluoride in acetonitrile at 50 °C resulted in substitution of the C6 chlorine and somewhat more slowly the C4 chlorine with fluorine, giving **16** and**17**, respectively. The LUMO coefficients in **5** are largest at The 4-, 6-, and 8-positions, as are the (+) atomic charges. Eventually both positions bore fluorine atoms (**18**), but attempts to push the reaction farther led to wholesale destruction. Doublet splitting of the ^{19}F NMR resonance by the C8 proton distinguished **16** from **17**, and **18** displayed an additional larger splitting arising from the F−F coupling (Scheme 5). When fluorination of **5** was attempted with dried tetrabutylammonium fluoride, decomposition occurred immediately even at room temperature.

Similar results were found with hexachloroazulene **10** and octachloroazulene (**3**). In sharp contrast to octachloronaphthalene, which undergoes the halex reaction successfully at 235 °C,[4] **3** is a remarkably sensitive compound. It is now clear that octafluoroazulene must be approached in an entirely different manner: for example, by assembling the azulene skeleton with fluorines already in place.

Conclusion

Octachloroazulene (**3**), the first fully halogenated azulene, has been synthesized from hexachlorobutadiene and cyclopentadiene. Further chlorination of the intermediate 1,3,4,5,6,7-hexachloroazulene (**10**) results, not in substitution, but in addition under both electrophilic and free radical conditions. Radical chlorination of the hexachloroazulene gives in good yield a single decachlorotetrahydroazulene (**11**). Equimolar phosphazene base dehydrochlorinates this Cl_{10} compound to a nonachlorodihydroazulene (**14**), and a second equiv of the base both dechlorinates and dehydrochlorinates **14**, yielding a mixture of 1,2,3,4,5,6,7-heptachloroazulene (**13**) and octachloroazulene. Acids and mercury dechlorinate the Cl_9 intermediate **14** to give the heptachloroazulene, but in the presence of calcium carbonate **14** aromatizes to octachloroazulene. The surprising anomalies encountered in this investigation are attributable primarily to azulene's nonalternant nature and to the Hückel $4N + 2$ Rule. Fluorodechlorination reactions show that the sensitive octachloroazulene cannot be transformed into octafluoroazulene by this method.

Experimental Section

All NMR spectra were obtained on a Varian Unity Plus 300 MHz instrument. GC/MS was performed on a Hewlett-Packard 5890A gas chromatograph equipped with a 5971 series mass selective detector. IR spectra were run on a Perkin-Elmer 599 FTIR spectrometer. Electronic spectra were measured on Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer. Octachloroazulene and heptachloroazulene were separated on an Agilent 1100 series HPLC with a variable wavelength detector using an XDB-C8, 4.6 × 160 mm column (flow rate 0.5 mL/min, eluting solvent 90:10 methanol/water, detector wavelength 580 nm).

Tetrachlorothiophene (6).[6] A 2 L three-necked flask was equipped with a mechanical stirrer, thermometer, and a simple distillation setup. Hexachloro-1,3-butadiene (680 g, 2.6 mol) was added and heated to 160 °C. Then sulfur (250 g, 7.8 g at) was added, and the mixture was heated at 225 °C for 8 h with stirring. The mixture was kept at 210 °C for 3 d with stirring. Finally, S_2Cl_2 was distilled out at atmosphere pressure, followed by 380 g of product which was distilled at 45 °C (∼4 Torr) and collected as a pale yellow solid. Recrystallization from hexane gave white crystals of **6**: mp 29 °C (lit.[6] 29 °C). Yield: 320 g, 56%.

Tetrachlorothiophene Dioxide (7). In a 500 mL three-necked flask with a pressure-equalizing dropping funnel, 50 mL (518 mmol) 30% H_2O_2 was added and cooled to −10 °C in a NaCl/ice bath. Trifluoroacetic anhydride (117 mL, 530 mmol) was added dropwise during 1.5 h, and the reaction mixture was stirred for an additional 0.5 h. Concentrated H_2SO_4 (94 mL) was added dropwise over 0.5 h, and stirring was continued for another 0.5 h. Volatiles (mainly peroxytrifluoroacetic acid and trifluoroacetic acid, ∼90 mL) were vacuum transferred into a liquid nitrogen-cooled trap. In another 500 mL round-bottom flask, tetrachlorothiophene (13 g, 60 mmol) was dissolved in 80 mL of methylene chloride. The peroxytrifluoroacetic acid solution was added dropwise over 1 h at room temperature, and the mixture was stirred overnight. Volatiles were removed using an aspirator, and the residue was dried further on the vacuum line to obtain 14.5 g of **7** as a white solid: mp 88−90 °C (lit.[6] 90−91 °C). Yield: 97%.

6-Dimethylaminofulvene (8). To a 250 mL round-bottom flask containing dimethylformamide dimethylacetal (30 g, 250 mmol) was attached a reflux condenser fitted with N_2 inlet. Freshly cracked cyclopentadiene (20 g, 300 mmol) was added. The mixture was refluxed under N_2 on the steam bath for 2 h. Then another portion of cyclopentadiene (20 g, 300 mmol) was added and refluxing was continued for 3 h. Volatiles were removed on a rotary evaporator. The fulvene was recrystallized from hexane to afford 24 g of yellow crystals: mp 67 °C (lit.[7] 67 °C). Yield: 77%.

4,5,6,7-Tetrachloroazulene (5). To a 250 mL round-bottom flask containing a solution of tetrachlorothiophene dioxide (12.7 g, 50 mmol) in methylene chloride (40 mL) was added a solution of 6-dimethylaminofulvene (5.5 g, 50 mmol) in methylene chloride (20 mL) over 5 min at 0 °C. The mixture was allowed to warm to room temperature and stirring was continued for an additional 2 h. After volatiles were removed by rotary evaporation, the residue was triturated with 10 mL hexane. The resulting mixture was chromatographed on two successive columns of silica gel (50 g, Acros, 0.035−0.07 mm), with hexane as eluent. After concentration of the blue eluate, the residue was further purified by sublimation at 70 °C/30 mTorr to afford 1.3 g of **5** as blue solid: mp 137−139 °C (lit. 137−139 °C;[12] 147−149 °C[8]). Yield: 10%. A reaction run as above but with 2 g of the thiophene dioxide was worked up after only 0.5 h at room temperature, and the azulene yield was 16%.

1,3,4,5,6,7-Hexachloroazulene (10). 4,5,6,7-Tetrachloroazulene (0.20 g, 0.75 mmol) and anhydrous cupric chloride (0.6 g, 4.5 mmol) were placed in a 50 mL round-bottom flask. Dry acetonitrile (15 mL) was added, and the mixture was refluxed overnight. After concentration of the reaction mixture, the residue was extracted with methylene chloride (60 mL). The mixture was filtered, and the solution was washed with hot water (50 mL), then dried over anhydrous $MgSO_4$. After concentration of the blue solution, the residue was further purified by sublimation at 70 °C/30 mTorr to afford 0.20 g of **10** as a blue solid: mp 138−139 °C (lit.[12] 138−139 °C). Yield: 80%. IR (KBr, cm^{-1}): 1588, 1493, 1412, 1306, 1227, 1125, 1096, 1017, 912, 855, 821, and 696. UV−vis (cyclohexane, nm): λ_{max} 272 (27 000), 309 (40 900), 381 (5540), 399 (4530), and 678 (471).

1,1,2,3,3,4,5,6,7,8-Decachloro-1,2,3,4-tetrahydroazulene (11). In a 50 mL round-bottom flask, **5** (0.70 g, 2.6 mmol) was dissolved with freshly distilled sulfuryl chloride (25 mL). The blue color of the solution quickly turned to yellow. The solution was irradiated with a tungsten lamp (150 W) overnight. Volatiles were removed by a rotary evaporator, and the resulting pale yellow, viscous liquid was chromatographed on a column of silica gel (50 g, Acros, 0.035−0.07 mm) with hexane as eluent. Removal of the solvent left a colorless liquid which was crystallized from hexane to give 0.88 g of **11** as colorless solid: mp 109−111 °C Yield: 70%. ^1H NMR ($CDCl_3$): δ 5.08 (s, 1H), 5.74 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 52.1, 79.0, 85.6, 85.8, 129.5, 131.3, 131.9, 136.9, 138.1, 139.1. UV (cyclohexane, nm): λ_{max} 227 (12 800), 251 (15 400), 259 (15 100), 283 (9140). IR (KBr, cm^{-1}): 2960, 1563, 1511, 1294, 1264, 1240, 1166, 1051, 877, 829, 696, 629 and 538. Anal. Calcd for $C_{10}H_2Cl_{10}$: C, 25.20; H, 0.42; Cl, 74.38. Found: C, 25.27; H, 0.46; Cl, 74.55.

X-ray Crystal Structure of 11.[20] A colorless, block crystal (triclinic, approximate dimensions 0.32 × 0.30 × 0.26 mm) of **11** ($C_{10}H_2Cl_{10}$, M.W. 476.62) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a CCD area detector diffractometer for a data collection at 173(2) K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrixes determined from 97 reflections. The data collection was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 10 s and a detector distance of 4.9 cm. A randomly oriented region of reciprocal space was surveyed to the extent of a full sphere and to a resolution of 0.84 Å. Three major sections of frames were collected with 0.20° steps in ω at 3 different ϕ settings and a detector position of −28° in 2θ. The intensity data were corrected for absorption and decay (SADABS).[21] Final cell constants were calculated from the xyz centroids of 3008 strong reflections from the actual data collection after integration (SAINT 6.01, 1999).[22] Unit cell dimensions were as follows: $a = 5.8505(5)$ Å, $b = 8.3803(7)$ Å, $c = 17.609(2)$ Å; $\alpha = 82.391(2)°$, $\beta = 80.494(2)°$, $\gamma = 72.591(2)°$, $Z = 2$.

The structure was solved using SIR92[23] and refined using SHELXL-97.[24] The space group P-1 was determined based on intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0370$ and $wR2 = 0.0930$ (F^2, all data). Goodness-of-fit on $F^2 = 1.108$. The program PLATON[25] was used in checking for errors.

Octachloroazulene (3). Triene **11** (0.4480 g, 0.9392 mmol) was dissolved with anhydrous THF (5 mL) in a 25 mL three-necked flask fitted with a dropping funnel. When the system had been flushed with argon, Schwesinger base **12** (285 μL, 0.923 mmol) and 3 mL anhydrous THF were placed in the funnel. The mixture was cooled to −40 °C with dry ice/acetonitrile slush. The base solution was then slowly added during 0.5 h, and the mixture was kept at −40 °C with stirring for another 0.5 h. After addition of anhydrous $CaCO_3$ (3.6 g, 36 mmol), the reaction mixture was warmed to room temperature and stirring was continued overnight. Solvent was removed and the resulting dark green residue was chromatographed on a column of silica gel (50 g, Acros, 0.035−0.07 mm), with hexane as eluent. After rotary evaporation a green solid was obtained. HPLC showed the purity of the octachloroazulene to be 95%. The material was further purified to 98% by recrystallization from hexane and acetone. Mp: 131−133 °C. Yield: 0.16 g, 42%. ^{13}C NMR ($CDCl_3$): δ 124.0, 129.1, 131.0, 137.4, 138.5, and 140.1. IR (cm^{-1}): 1636, 1487, 1383, 1278, 1230, and 1145. MS (m/e): 400 (M^+), 330 ($C_{10}Cl_6^+$), 260 ($C_{10}Cl_4^+$), 225 ($C_{10}Cl_3^+$), 190 ($C_{10}Cl_2^+$), 120 (C_{10}^+), 108 (C_9^+), and 84 (C_7^+). HRMS (m/e): 399.750 599 (found), 399.750 822 (theor.). UV−vis (cyclohexane, nm): λ_{max} 244 (13 900), 301 (20 300), 330 (25 200), 360 (sh, 10 400), 586 (br, 594). Anal. Calcd for $C_{10}Cl_8$: C, 29.75; H, 0.0; Cl, 70.25. Found: C, 30.25; H, 0.0; Cl, 69.85.

1,2,3,4,5,6,7-Heptachloroazulene (13). Triene **11** (0.1356 g, 0.2842 mmol) was treated with the base **12** (90 μL, 0.290 mmol) in the same manner as described above. After the reaction mixture was warmed to about 0 °C, mercury (0.1 mL, 6.8 mmol) was added. The mixture was stirred at room-temperature overnight. The deep blue solution was isolated from the unreacted mercury by a pipet. After the solvent had been removed by rotary evaporation, the residue was chromatographed on a column of silica gel (50 g, Acros, 0.035−0.07 mm) with hexane as eluent to give 0.05 g of **13** as a green solid: mp 148−150 °C. Yield: 48%. ^1H NMR ($CDCl_3$): δ 8.42 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 116.9, 119.3, 123.7, 129.7, 129.9, 132.6, 140.4, 141.1, and 142.7. MS m/e: 366 (M^+), 296 ($C_{10}HCl_5^+$), 226 ($C_{10}HCl_3^+$), 156 ($C_{10}HCl^+$), 120 (C_{10}^+). UV/Vis (cyclohexane, nm): λ_{max} 247 (13 000), 277 (24 500), 322 (44 200), 368 (4750), 386 (6050), 654 (366), and 704 (336). IR (KBr, cm^{-1}): 1583, 1484, 1474, 1380, 1304, 1224, 1106, 910, 840, and 716. Anal. Calcd for $C_{10}HCl_7$: C, 32.50; H, 0.27; Cl, 67.22. Found: C, 32.62; H, 0.25; Cl, 67.47.

Pyrolysis of Triene 11. The triene (32 mg, 0.07 mmol) was placed in an ampule which was evacuated and sealed under vacuum. It was then heated at 250 °C for 1 h. The resulting pale yellow crystals were washed with acetone until colorless. Recrystallization from hexane afforded 10 mg of 1*H*-heptachloronaphthalene as white crystals (40% yield). Mp 180−182 °C. (lit.[26] 183.5−184.5 °C; cf. mp of 2*H*-heptachloronaphthalene, 110.0−110.5 °C). ^1H NMR ($CDCl_3$): δ 8.45 (s, 1H); lit.[26] ($CDCl_3$) δ 8.73; cf δ for 2*H*-heptachloronaphthalene, 7.78). ^{13}C NMR ($CDCl_3$): δ 135.8, 135.1, 134.3, 132.6, 131.3, 130.3, 129.8, 129.3, 127.3, and 125.4. GC/MS (m/e): 366 (M^+), 331 ($C_{10}HCl_6^+$), 296 ($C_{10}HCl_5^+$), 261 ($C_{10}HCl_4^+$), 226 ($C_{10}HCl_3^+$). Octachloronaphthalene[27] was identified in the pyrolysis product by GC/MS, m/e: 400 (M^+), 330 ($C_{10}Cl_6^+$), 260 ($C_{10}Cl_4^+$), 190 ($C_{10}Cl_2^+$), 120 (C_{10}^+).

Acknowledgment. The authors are grateful to the National Science Foundation for support of this work. We also thank Neil R. Brooks, Victor G. Young, Jr., and the X-ray Crystallographic Laboratory in the Department of Chemistry, University of Minnesota for the X-ray crystal structure.

Supporting Information Available: Tables of X-ray crystallographic data for **11**; X-ray crystallographic data (CIF). A table of decachlorotetrahydroazulene energies (AM1) is also included. This material is available free of charge via the Internet at http://pubs.acs.org.

JA012051H

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