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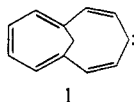
Generation and Properties of 4,9- and 3,8-Methano[11]annulenylenes

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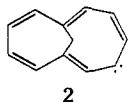
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Abstract: The two carbocyclic aromatic carbenes, 4,9-methano[11]annulenyldiene (**1**) and 3,8-methano[11]annulenyldiene (**2**), have been generated by decomposition of the corresponding ketone tosylhydrazone salts and the sodium salts of the tosylhydrazones of 3- and 2-formyl-1,6-methano[10]annulene (**5** and **14**). The latter reactions are believed to involve carbene-carbene rearrangements which proceed with a high degree of regioselectivity. The facility of rearrangement of these carbenes as compared with other arylcarbenes is discussed. In the absence of substrates 4,9-methano[11]annulenyldiene (**1**) dimerizes to give fulvalene **8**. In the presence of styrenes or dimethyl fumarate it adds to give spirocyclopropane adducts and in the presence of 1,2-cyclononadiene and phenylacetylene it gives 1:1 adducts that are assigned structures that would result from rearrangement of initially formed spirocyclopropane adducts. These properties are all very similar to those of cycloheptatrienyldiene which places **1** in the category of the so-called "nucleophilic" carbenes (a term for which a new definition is suggested). In contrast to **1**, 3,8-methano[11]annulenyldiene (**2**) gives neither a fulvalene in the absence of substrates nor spirocyclopropanes in their presence. Without substrate it gives two isomeric dimethylenecyclobutane products which have structures that can be accounted for by the dimerization of an allene intermediate or initial formation of a fulvalene followed by a 22 π electron electrocyclic ring closure. The stereochemistry of the products is not consistent with a Woodward-Hoffmann controlled ring closure. Generation of **2** in the presence of styrene or dimethyl fumarate gives no isolable adducts. However, in the presence of phenylacetylene, 1,2-cyclononadiene, or 1,1-diphenylethylene, 1:1 adducts are formed. These are assigned structures that could result from either cycloaddition of the substrate and an allene intermediate or rearrangement of an initially formed spirocyclopropane.

As a continuation of our research on carbocyclic aromatic carbenes⁴⁻⁸ and carbene-carbene rearrangements⁹⁻¹² we have now studied some of the chemistry of **1** and **2**,¹³ two of the five



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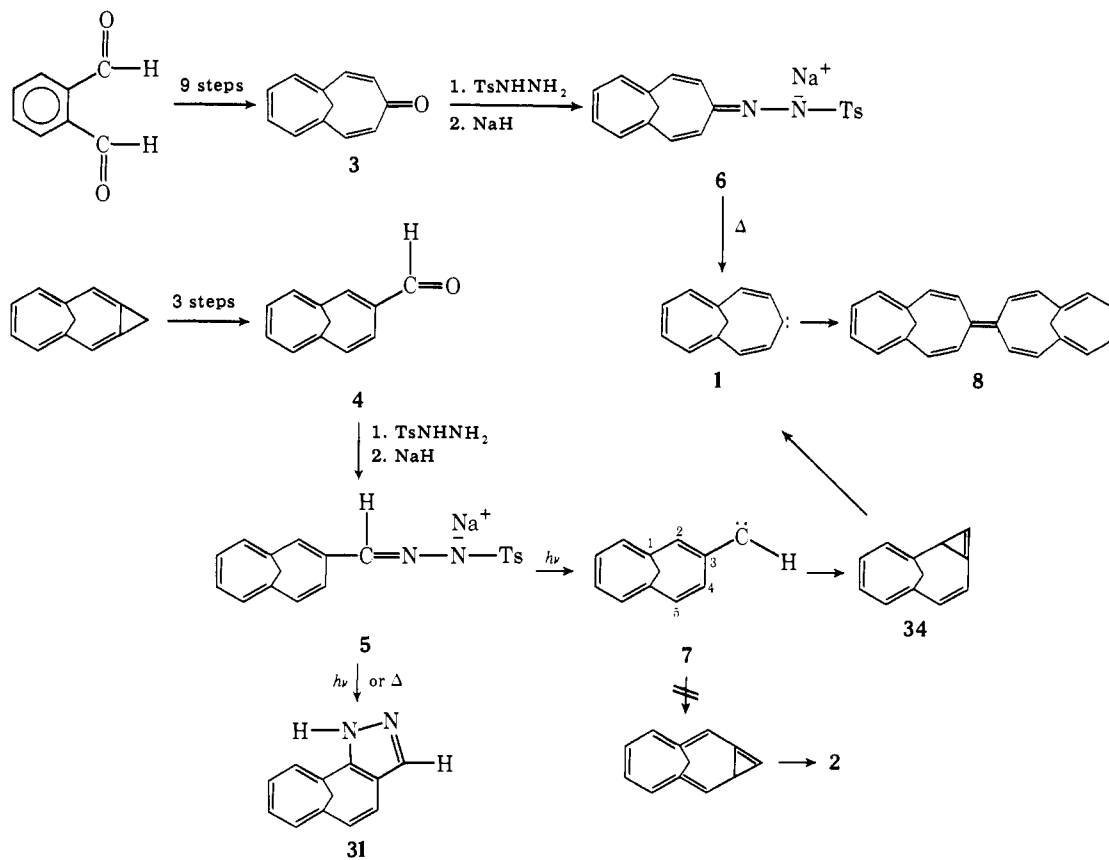
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possible methano[11]annulenylenes. These intermediates have been generated from both the tosylhydrazone salts of the

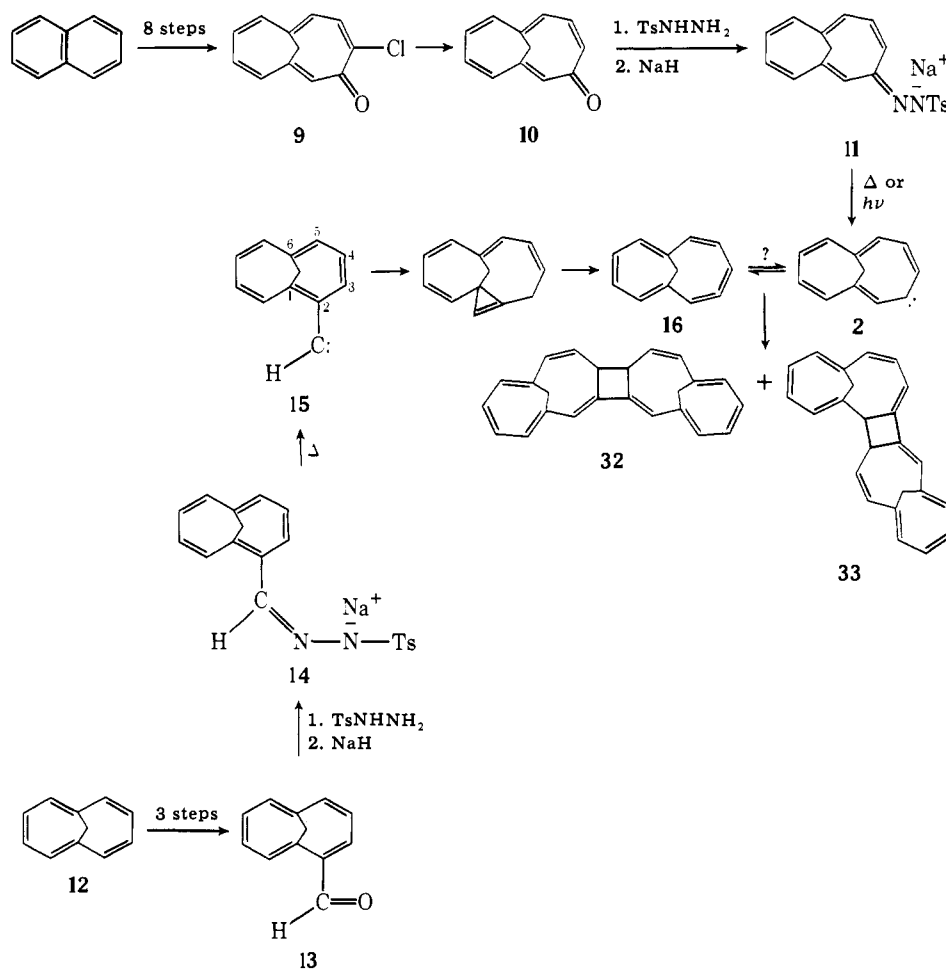
ketones **3**¹⁴ and **10**¹⁵ (Schemes I and II) and carbene-carbene rearrangement of the arylcarbenes **7** and **15**. **1** and **2** constitute the only recorded examples of carbocyclic aromatic carbenes in which the vacant orbital of the singlet state is an integral component of a non-cross-conjugated (such as benzocycloheptatrienyldiene) 10 π electron system.

Generation of the Carbenes. 4,9-Methano[11]annulenyldiene (**1**) was generated by pyrolysis of the tosylhydrazone salts of the ketone **3** and the aldehyde **4**. The ketone was synthesized using a nine-step sequence developed by Vogel.¹⁴ Synthesis of

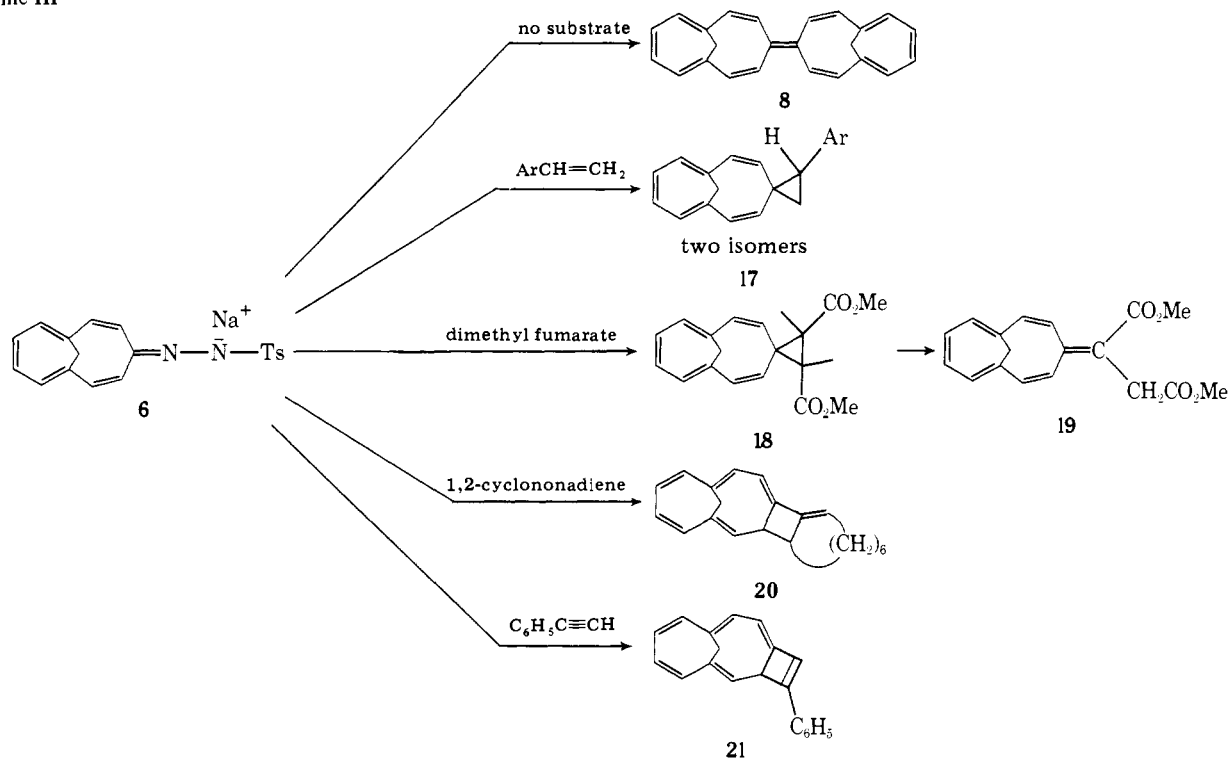
Scheme I



Scheme II

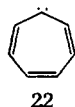


Scheme III

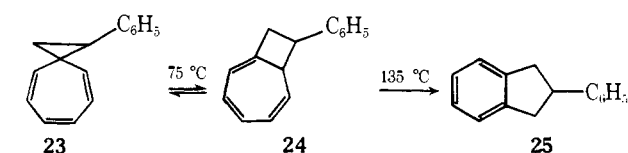


the aldehyde also employed a sequence (nine steps from naphthalene) developed by Vogel.¹⁷ 3,8-Methano[11]annulenylidene (**2**) was generated by both thermolysis (161 °C) and photolysis (−45 °C; low yields) of the tosylhydrazone salt of the ketone **10** which was prepared from naphthalene by a nine-step synthesis developed by Vogel.¹⁵ This same intermediate was also generated by carbene-carbene rearrangement of the arylcarbene **15** which, in turn, was generated by pyrolysis (135 °C, diglyme) of the tosylhydrazone salt of the 1,6-methano[10]annulenylcarboxaldehyde **13**. The aldehyde was prepared from 1,6-methano[10]annulene.¹⁸

Chemistry of 4,9-Methano[11]annulenylidene and Some of Its Products. When generated from **6** the chemical behavior of this intermediate (summarized in Scheme III) is remarkably similar to the 6- π -electron system cycloheptatrienylidene **22**.^{4,19} Thus, in the absence of a reactive substrate it dimerizes

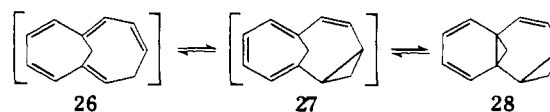


to the fulvalene **8** (stereochemistry unknown). In the presence of an electron-deficient trap such as dimethyl fumarate, it adds to give the spirocyclopropane **18** which, as in the analogous spirononatriene system,¹⁹ isomerizes in the presence of acid to give the corresponding fulvene **19**. The carbene also adds to styrenes to give the spirocyclopropanes **17** (mixtures of stereoisomers). Properties supporting the assigned structures for these compounds are straightforward and are in the Experimental Section and ref 7. The reaction with styrene suggested the possibility of determining a Hammett ρ value for the addition of **1** to substituted styrenes (the ρ value for addition of cycloheptatrienylidene is +1.05)⁵ but attempts to develop a satisfactory method of analysis were futile. The properties of the substituted styrene adducts that were synthesized for this study are included in the Experimental Section. One interesting difference between the spirocyclopropane adducts of cycloheptatrienylidene and 4,9-methano[11]annulenylidene was noted. Thus, whereas spirononatrienes rearrange to bicyclo[5.2.0]nonatrienes²⁰ (e.g., **23** equilibrates with **24** at 75



°C which rearranges to **25** when heated to 135 °C for 60 min) heating **17** at 130 °C for 5 h led to essentially no reaction—only traces of polymer were detected. Thermolysis at 161 °C showed slow disappearance of starting material and formation of a stationary (TLC) product. No trace of any product comparable to the bicyclo[5.2.0]nonatriene or indan was detected.

Adducts (1:1) with both 1,2-cyclononadiene and phenylacetylene were also isolated. However, in these cases, the NMR spectra were not consistent with spirocyclopropane products. In these very complex spectra, the chemical shifts of the high-field bridge hydrogens were particularly informative. In contrast to compounds such as **8**, **17**, and **18** (see Table II) which show methano hydrogen resonances above δ 1.0, the highest field methano hydrogen of both **20** and **21** appears at a much lower field (δ 2.8 and 3.05 for **20** and **21**, respectively). This feature is also found in the ketone **10**¹⁵ (δ 2.07) and the tosylhydrazone **11** (δ 2.7, conjugate acid). The chemical shifts of the lower field methano bridge resonances of **20** and **21** are also reminiscent of **10** and **11** (conjugate acid). These data along with the geminal coupling constants of the bridge hydrogens (excluding cyclopropane structures) and analogy with the cycloheptatrienylidene adducts with these substrates^{20,21} leads us to tentatively assign structures **20** and **21** to the methanoannulenylidene adducts. Perhaps it should be pointed out that if these assigned structures are correct, these molecules must have π systems analogous to the hydrocarbon **26** which

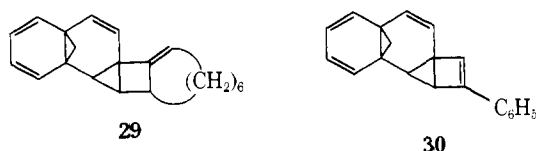


prefers the bicyclopropane form **28**.²² However, it would not be surprising if **20** and **21** preferred the open-ring form since

Table I. Relative Localization Energies

	Point of attack	Electrophilic attack		Nucleophilic attack		Radical attack	
		PPP	SPO	PPP	SPO	PPP	SPO
Benzene ²⁴		0.000	0.000	0.000	0.000	0.000	0.000
Naphthalene ²⁴	C-1	-0.907	-0.905	-0.915	-0.912	-0.424	-0.452
Naphthalene ²⁴	C-2	-0.498	-0.539	-0.500	-0.544	-0.161	-0.248
Phenanthrene ²⁴	C-9	-1.060	-1.066	-1.067	-1.081	-0.460	-0.492
1,6-Methano[10]annulene ²⁵	C-2	-1.361	-1.530	-1.358	-1.525	-0.885	-1.186
1,6-Methano[10]annulene ²⁵	C-3	-1.289	-1.444	-1.289	-1.444	-0.869	-1.166

closure would lead to a methylenebicyclopentane (**29**) and a bicyclopentene (**30**), respectively, structures that would be less



favored than **27** or **28** due to additional strain. Unfortunately, further work could not be done on these systems owing to the difficulty in obtaining the required annulene.

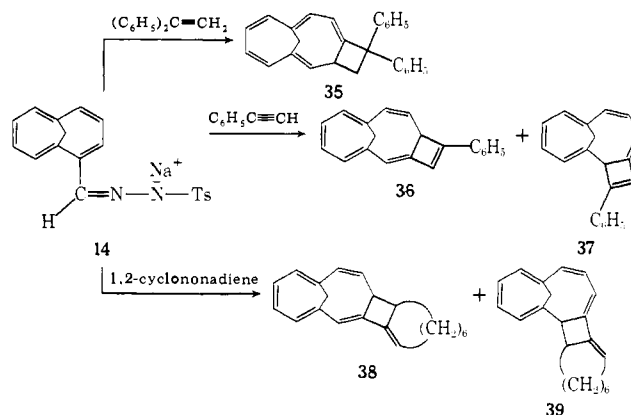
Thermolysis of the tosylhydrazone salt **5** in the absence of substrate gave only the pyrazole **31**. However, photolysis (again in the absence of substrate) gave, in addition to the pyrazole, fulvalene **8**. The yield of this dimer at -45 to -50 °C was 41%. It was also formed at temperatures as low as -70 °C (17% in the presence of furan) indicating a very facile carbene-carbene interconversion. Since the arylcarbene (**7**) could rearrange to give either **1** or **2**, the reaction was carefully examined for the dimers of **2** (**32** and **33**). No trace could be detected. A number of attempts to confirm the presence of both the cyclopropene intermediate **34** and the rearranged carbene **1** were made by carrying out the reaction in the presence of appropriate trapping agents. However, in no case were products other than the pyrazole and fulvalene identified. The results of these experiments are summarized in the Experimental Section.

Chemistry of 3,8-Methano[11]annulenyliene. As in the case of cycloheptatrienyliene and 4,9-methano[11]annulenyliene, generation of 3,8-methano[11]annulenyliene **2** (\rightleftharpoons **16**?) (Scheme II) (from pyrolysis of the tosylhydrazone salt **11**; very low yields were also observed from low-temperature photolysis) in the absence of reactive substrates led to hydrocarbons (in this case, two) which analyzed properly for carbene dimers. However, unlike carbenes **1** and **22** which gave simple fulvalenes, this reaction gave almost exclusively the two hydrocarbons **32** and **33**. Evidence for the assigned structures (including partial proof of stereochemistry) for these two hydrocarbons has been discussed in earlier communications^{6,8} and will not be repeated here. However, detailed experimental information is included in the Experimental Section. The same two dimers were also formed (62%) from pyrolysis of the tosylhydrazone salt **14**.

In contrast to 4,9-methano[11]annulenyliene (**1**), attempts to trap **2** (generated from either **11** or **14**) with either dimethyl fumarate or styrene failed to yield isolable adducts, although quantitative studies with **11** (ca. 5 mg runs monitored by UV) in the presence and absence of substrates showed substantial reduction in **32** and **33** suggesting trapping of either the carbene or a carbene precursor. Difficulty in obtaining quantities of **11** precluded exhaustive preparative studies of these reactions.

On the other hand, 1:1 adducts were isolated when **2** was generated from either **11** or **14** in the presence of 1,2-cyclononadiene (two isomers from **14**; only the major isomer could be detected from a small run with **11**). In addition, adducts believed to have arisen from **2** were obtained when **14** was

Scheme IV



pyrolyzed in the presence of 1,1-diphenylethylene and phenylacetylene (two isomers) (Scheme IV). Comparable attempts to trap the intermediate from **11** with 1,1-diphenylethylene or phenylacetylene were not made owing to a shortage of starting material.

None of the 1:1 adduct structures from **2** can be unambiguously assigned at this time. However, drawing upon analogy to the established structures of the dimers **32** and **33**, the structures suggested in Scheme IV can be assigned with reasonable confidence from the NMR spectra alone (molecular formulas confirmed by mass spectra). In particular, the similarity of the chemical shifts of the methano bridge hydrogens (Table II) and the general vinyl hydrogen patterns (e.g., typical AA'XX' cycloheptatriene patterns for **35**, **36**, and **38**) are striking. Additional support for these fused cyclobutane structures may be found in other isolated facts. For example, formation of a common product from reaction of **14** and **11** with cyclononadiene augers for ring expansion of carbene **15** (the absence of **39** from decomposition of **11** is probably not significant since only 0.16 mg of **38** was formed and **39** was the minor product from **15**). Furthermore, neither of the phenylacetylene adducts showed cyclopropene absorptions in the IR which argues for the cyclobutane structures. Finally, isomer assignments for **36** and **37** as well as **38** and **39** are based on chemical shifts of the methano hydrogens (compared with **32** and **33**) (see Table II) and the positions of the substituents on the cyclobutane rings are based on mechanistic considerations (either a carbene or allene mechanism predicts the same structures). Complete spectral data are included in the Experimental Section.

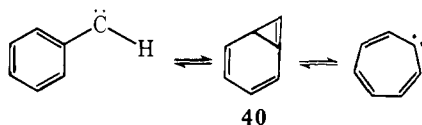
Discussion

Certainly the two most significant results of the studies discussed in the previous sections are (1) the abnormally facile rearrangement of the methanoannulenylicarbenes to their aromatic carbene counterparts as compared with other typical arylcarbenes and (2) the apparent difference in the properties of the two aromatic methanoannulenylicarbenes **1** and **2**.

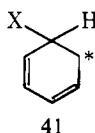
With regard to the former point, it should be noted at the outset that the two methanoannulenylicarbenes **7** and **15** are the only two arylcarbenes to date that have been found to

rearrange to aromatic carbenes in solution. In all other cases, only products of the unrearranged arylcarbene have been detected. Since this is probably due—at least in those cases where the aromatic carbene is the lowest energy isomer—simply to competitive reaction of the unrearranged arylcarbenes with their environment, the unusual behavior of the methanoannulenylicarbenes could be explained by either abnormally slow reaction with environment or abnormally facile rearrangement. There is no obvious reason for the former but the latter is readily rationalized by the following arguments.

All evidence to date points to fused cyclopropenes (e.g., **40**)

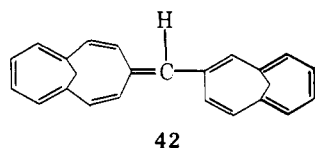


as intermediates in carbene-carbene rearrangements in solution.¹¹ Regardless of the detailed mechanism of the cyclopropene formation,²³ during the ring closure of the arylcarbene aromaticity must be destroyed in much the same way as in electrophilic, nucleophilic, or radical attack on an aromatic ring. The primary difference, of course, is that in the intermediate (**40**) that is analogous to the classical σ complex (**41**),

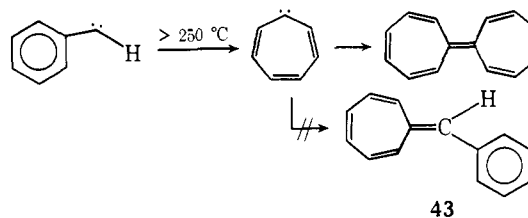


a double bond has replaced the active site. As a result, a comparison of localization energies for substitutions on appropriate aromatic rings could shed light on the relative ease of cyclopropene formation. Fortunately, Dewar and his co-workers^{24,25} have calculated relative localization energies for electrophilic, nucleophilic, and radical substitution on benzene, naphthalene, phenanthrene, and 1,6-methano[10]annulene, four systems in which carbene-carbene rearrangements have been studied. These are summarized in Table I. From these data it is clear that regardless of how the ring closure of the carbene to a cyclopropene is pictured, it should occur more rapidly in the methanoannulene system than any of the other aromatics (including the 9 position of phenanthrene). It is also worth noting that the localization energy for breaking the aromaticity of the methanoannulene ring at C-2 in **7** is more negative (closure more favorable) than at C-3 (which is equivalent to C-4). From this, it is reasonable that carbene **7** should close onto C-2 (which gives the observed carbene products) more rapidly than C-4 which would lead to **2** which should dimerize to **32** and **33**. Neither of these products was observed. One of them (**32**) was tested and found to be stable to the reaction conditions. Unfortunately, the localization energy for breaking the methanoannulene aromaticity at C-1 has not been reported. This would be interesting in light of the apparent tendency of carbene **15** to close at that position. Of course, in this case, closure at C-1 may well also be facilitated by the inductive effect of the methano bridge and, as a result, localization energies would not be as meaningful as in the case of closure of **7**.

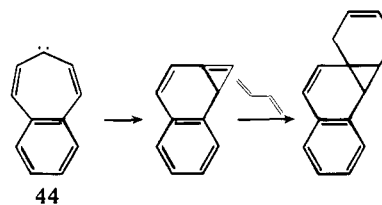
The results of the rearrangement studies suggest one other rather interesting conclusion. If it is assumed that the hydrocarbon **8** is formed from dimerization of the carbene **1** in a process with negligible activation energy, the fact that *mixed dimers* such as **42** were not observed suggests a preferential



accumulation of the aromatic carbene which, in turn, places it at lower energy than its arylcarbene isomer. This is analogous to the phenylcarbene-cycloheptatrienylydene equilibrium in the gas phase^{10,26} where mixed carbene dimers such as **43** are

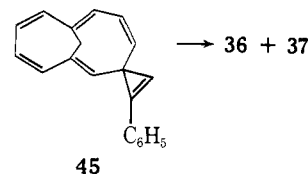


not observed although heptafulvalene is formed in substantial yields. It is also interesting that the cyclopropene **34** could not be trapped with dienes that have been found to be effective for interrupting the rearrangement in benzannelated cycloheptatrienylydenes such as **44**. This may be due to a less favorable



equilibrium between the cyclopropene and the aromatic carbene which, again, suggests a relatively stable aromatic carbene.

With regard to the apparent differences in the properties of the two aromatic carbenes (**1** and **2**) less can be said than would be desirable because many of the results are seriously clouded by rather severe experimental difficulties. However, some generalities do appear to emerge. First, as pointed out above, **1** shows a behavior that is remarkably similar to that of cycloheptatrienylydene in that in the absence of appropriate substrates it dimerizes to a fulvalene and in the presence of electron-deficient olefins, it gives spirocyclopropanes.¹⁹ The latter property would place this carbene in the category of so-called nucleophilic carbenes.^{12,27} In contrast to **1**, the isomeric carbene **2** behaves quite differently from cycloheptatrienylydene. For example, it gives neither fulvalenes in the absence of traps nor spirocyclopropanes in the presence of electron-deficient olefins.³⁰ In fact, all of its products are more in line with what would be expected of an allene such as **16** than with those expected of a carbene. Unfortunately the significance of these differences is uncertain due to a combination of negative results and the possibility of facile rearrangement of initially formed carbene products. For example, products such as **36** and **37** (Scheme IV) could arise from either [2 + 2] cycloaddition of an allene (**16**) and phenylacetylene or carbene addition to give a spirocyclopropene (**45**) followed by



rearrangement. Likewise, in principle the dimethylenecyclobutanes **32** and **33** could arise from either dimerization of the allene **16** or electrocyclic closure of the fulvalenes as illustrated in **46**. At least one strong argument can be made against an

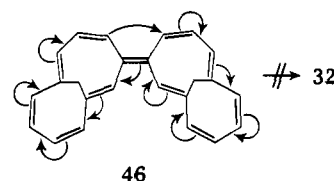


Table II. Chemical Shifts and Coupling Constants of Methano [11]annulenes

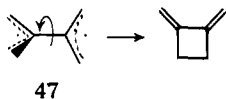
	High-field bridge H, δ	Low-field bridge H, δ	J , Hz	Ref
	0.21	3.72	-11.57	<i>a</i>
	0.7	3.6	-12.0	<i>b</i>
	0.65	3.54	-11.0	<i>b</i>
	1.05	4.27	-12.0	<i>b</i>
	1.1	4.05	-11.5	<i>b</i>
	0.04	1.68	-11.4	<i>c</i>
	0.27	2.72	-11.5	<i>b</i>
	0.69	3.78	-11.0	<i>b</i>
	0.72	3.65	-12.0	<i>b</i>
	-0.1	3.3	-11.5	<i>g</i>
	-0.25	3.25	-11.0	<i>g</i>
	0.63	4.52	-10.4	<i>a</i>
	1.24	6.28	-11.5	<i>a</i>
	>0.92	5.35	-11	<i>b</i>
	1.84	>4.84	-10.5	<i>b</i>
	H _a 1.54 H _b 0.53	H _a 5.01 H _b 3.65	-10.5 -12	<i>b</i>
	-0.02	3.00	-11.0	<i>b</i>
	0.1	2.8	-11.5	<i>d</i>
	0.00	3.12	-11.0	<i>e</i>

Table II. (Continued)

	High-field bridge H, δ	Low-field bridge H, δ	J , Hz	Ref
	0.20	3.53	-11.0	<i>e,f</i>
	-0.2	3.2	-11.5	<i>g</i>
	0.16	2.72	-11.0	<i>b</i>
	2.07	2.52		<i>h</i>
	2.7	3.62	-10.5	<i>b</i>
	2.8	4.75	-11.0	<i>b</i>
	3.0	5.05	-11.0	<i>b</i>

^aE. Vogel, R. Feldmann, and H. Düwel, *Tetrahedron Lett.*, 1941 (1970); E. Vogel, R. Feldmann, H. Düwel, H. D. Cremer, and H. Gunther, *Angew. Chem., Int. Ed. Engl.*, **11**, 217 (1972); *Angew. Chem.*, **84**, 207 (1972). ^bThis work. ^cReference 14. ^dL. Knothe, D. Forster, H. Achenbach, H. Friebolin, and H. Prinzbach, *Tetrahedron Lett.*, 3075 (1970). ^eH. Prinzbach and L. Knothe, *Angew. Chem., Int. Ed. Engl.*, **7**, 729 (1968); *Angew. Chem.*, **80**, 698 (1968). ^fH. Prinzbach and L. Knothe, *Angew. Chem., Int. Ed. Engl.*, **6**, 632 (1967); *Angew. Chem.*, **79**, 620 (1967). ^gH. Prinzbach, L. Knothe, and A. Diffenbacher, *Tetrahedron Lett.*, 2093 (1969) (stereochemistry uncertain). ^hReference 22.

electrocyclic reaction that is controlled by Woodward-Hoffmann rules. Since the allowed mode for this closure is disrotatory, the Woodward-Hoffmann rules predict the cyclobutane hydrogens in **32** and **33** to be *cis*. In fact, using a chirality probe,⁸ the cyclobutane hydrogens in **32** have been unequivocally shown to be *trans*. From this result, it has been further argued that the intermediate from **11** and **15** might, in fact, be best represented by the allene structure **16** since the stereochemistry of the dimerization of allenes to dimethylenecyclobutanes is known to be consistent with that found for **32**. Unfortunately, this conclusion is not valid for the following reason. Recently it has become increasingly clear³¹ that allenes



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dimerize via diradicals such as **47**. Now, if this mechanism is applied to the dimerization of **16**, free rotation of the diradical must lead to fulvalene **46** faster (the planar diradical is simply a resonance form of **46**) than it could close to **32** and **33**. If this is true, then we are forced to conclude that there must be a mechanism for **46** to close with the stereochemistry expected of dimerization of **16**. The obvious answer to this dilemma is facile rotation about the connecting double bond to give the diradical which then closes to give the cyclobutane with *trans* hydrogens. Direct evidence for this will be sought.

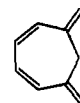
If these arguments are valid, we find ourselves faced with the following important conclusion: the structure of the dimeric products from **11** and **15** can say *nothing* about the structure of the dimerizing monomer. In other words, from the above arguments either the carbene **2** or the allene **16** should give the same product.

Regardless of the point in the dimerization reactions at which the properties of the two intermediates **1** and **2** diverge,

their chemistry shows a property that appears to be rather common among methano[5.4.1]dodecapentaene systems, viz., a tendency to favor structures with the cycloheptatriene moiety **48** and/or avoid structures with the dimethylenecycloheptadiene moiety **49**. This tendency has been noted a number of



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times^{32,33} and has been ascribed to both steric³⁴ and a combination of steric and electronic (homoaromaticity) effects.^{6,33} Whatever the reason(s) for this tendency, it is apparently sufficiently important to change the nature of many of the products from the two isomeric carbenes.³⁵ This is probably also the reason the thermolysis of **17** does not parallel that of the styrene adduct of cycloheptatrienyliene **23** in that the latter equilibrates with the rearranged product **24**²⁰ where thermolysis of **17** gives no sign of rearrangement.

Experimental Section

General. Melting points were taken in a Thomas-Hoover Unimelt apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Ga. Accurate mass measurements were performed on an AEI MS 30 with a DS 30 data system. ¹³C NMR were recorded on an XL-100/15 with TTI TT 100 Fourier transform accessory.

Ultraviolet and visible spectra were recorded on a Cary 15 double-beam spectrophotometer using 1-cm silica cells. Infrared spectra were recorded with a Beckman IR-10 spectrophotometer. In all cases where the KBr pellet technique was not used, sodium chloride plates were substituted. Nuclear magnetic resonance spectra were determined on a Varian A-60A high-resolution spectrometer. A Varian XL-100 spectrometer was used for double resonance experiments and for some studies with lanthanide shift reagents. Chemical shifts are

reported in δ values from internal tetramethylsilane standard. Low-resolution mass spectra were determined on a Hitachi Model RMU-6E mass spectrometer.

Analytical thin layer chromatography (TLC) was accomplished on 2 × 8 in. plates coated in these laboratories with 0.25-mm layers of E. Merck HF-254 silica gel; preparative work was conducted on 8 × 8 in. plates coated with 1.0-mm layers of HP-254 silica gel. Components were visualized by their quenching of fluorescence under UV light.

MCB and Baker silica gel (60–200 mesh) or Merck silica gel 60 (particle size 0.063–0.200 mm, 70–230 mesh) were used for column chromatography.

All chemicals were reagent grade used as supplied unless otherwise stated. Dioxane and tetrahydrofuran were dried by distillation from lithium aluminum hydride and passage over activity grade I Woelm basic alumina with subsequent storage over calcium hydride under a nitrogen atmosphere.

Practical grade furan was washed with 5% sodium hydroxide, dried over calcium sulfate, distilled from KOH, passed through basic alumina (Woelm, grade 1), and stored under nitrogen.

4,9-Methano[11]annulenone (3). This ketone was synthesized from phthaldehyde as described in the following sections by a reaction sequence developed by Vogel.^{14,37}

4,5-Benzo-2,7-dicarbethoxycycloheptadienone. The procedure of Tarbell and Wargotz was followed.³⁸ Phthaldehyde (60 g, 0.448 mol), diethyl acetonedicarboxylate (91.2 g, 0.450 mol), dry piperidine (4.0 mL), and glacial acetic acid (16.0 mL) in 400 mL of dry benzene was refluxed until the volume of water in a Dean-Stark trap remained constant (ca. 3–4 h). The benzene solution was concentrated, 50 mL of ethanol added, and after standing for 30 min, the solution was filtered. The resultant solid was washed twice with 20 mL of cold absolute ethanol to give 84.7 g (63%) of 4,5-benzo-2,7-dicarbethoxycycloheptadienone, mp 93–96 °C (lit.³⁹ 96–96.5 °C).

4,5-Benzo-2,7-dicarbethoxycycloheptanone. To 30 g (0.1 mol) of 4,5-benzo-2,7-dicarbethoxycycloheptadienone dissolved in ca. 250 mL of glacial acetic acid was added 1.0 g of 10% Pd/C catalyst. The mixture was hydrogenated by shaking with H₂ at 3 atm of pressure. When the consumption of H₂ ceased, the catalyst was removed by filtration and solvent was removed in vacuo to give 28.9 g (95%) of 4,5-benzo-2,7-dicarbethoxycycloheptanone, mp 98–105 °C (lit.³⁹ 89–101 °C).

4,5-Benzo-5,6,8,9-cycloheptan-7-one. A mixture of 35.8 g (0.118 mol) of 4,5-benzo-2,7-dicarbethoxycycloheptanone, 100 mL of ethanol, and 350 mL of 30% H₂SO₄ was heated at reflux for ca. 30 h at which time no more evolution of CO₂ could be detected. Steam distillation of the product was continued until 3.0 L of distillate had been collected. The distillate was saturated with sodium sulfate and liquid–liquid extracted continuously with ether for 20 h. The ether extract was dried over sodium sulfate and the solvent removed. This gave 11.9 g (63%) of 4,5-benzo-5,6,8,9-cycloheptan-7-one as a colorless oil. No further purification was necessary.

4,5-Benzocycloheptanone Ethylene Ketal. A mixture of 22.9 g (0.144 mol) of 4,5-benzocycloheptanone, 360 mL of ethylene glycol, and 2.4 g of *p*-toluenesulfonic acid monohydrate in 700 mL of toluene was heated at reflux for 20 h and the water was collected in a Dean-Stark trap. The cooled reaction mixture was washed with three portions of saturated NaHCO₃ solution (250 mL each) and the toluene layer was separated. The toluene layer was washed with an additional two 250-mL portions of water. The combined water washings were extracted with two 100-mL portions of benzene. The combined organic layers were dried over sodium sulfate and the solvent was removed at reduced pressure. This gave 25.8 g (87%) of a pale yellow solid, mp 105–108 °C (lit.¹⁴ 110 °C).

Bicyclo[5.4.0]undeca-1,9-dien-4-one Ethylene Ketal. 4,5-Benzocycloheptanone ethylene ketal (34.6 g, 0.169 mol) was dissolved in 250 mL of THF and 150 mL of absolute ethanol. This solution was added to ca. 750 mL of freshly condensed ammonia with rapid stirring. Sodium metal (8.5 g, 0.37 mol) was added at a rate to maintain a gentle reflux until a deep blue persisted for several minutes upon addition of a small piece of sodium. The ammonia was allowed to evaporate and the resultant mixture was poured into 100 mL of water. The aqueous solution was extracted five times with 150-mL portions of ether. The combined ether layers were washed with 200 mL of saturated brine solution and dried (Na₂SO₄) and the ether removed. This gave 29.0 g (83%) of a white solid, mp 65–69 °C (lit.¹⁴ 70 °C).

12,12-Dichlorotricyclo[5.4.1.0.1,7]dodeca-9-en-4-one Ethylene Ketal. To 5.97 g (10% excess) of potassium *tert*-butoxide (Aldrich), 200 mL of dry pentane, and 10.0 g (48.5 mmol) of bicyclo[5.4.0]undeca-1,9-dien-4-one ethylene ketal at 0 °C was added 6.34 g (10% excess) of CHCl₃ over a period of 30 min. The solution was maintained at 0 °C for an additional 2 h and then stirred at room temperature for 4 h. The solution was filtered, the filtration residue washed three times with 100 mL of pentane, and then combined with CH₂Cl₂. Removal of the CH₂Cl₂ gave 5.6 g (78%) of a white solid, mp 49–51.5 °C (lit.¹⁴ 52–53 °C).

4,9-Methano[11]annulenone. Bicyclo[5.4.1]dodeca-7,9,11-trien-4-one (3.0 g, 17 mmol), 12.5 g (55 mmol) of DDQ, and 300 mL of dry benzene were heated with shaking in a stainless steel autoclave at 120–125 °C (external temperature) for 5 h. After cooling, the autoclave was rinsed with acetone and the combined organic layers were concentrated into a red-brown mass under reduced pressure. The red-brown solid was taken up in ether and percolated through a grade III basic alumina column with 50:50 ether–petroleum ether (bp 20–40 °C). The yellow solution was concentrated and the resultant oil was then chromatographed over grade III basic alumina. Elution with 25:75 ether–petroleum ether (bp 20–40 °C) gave two distinct yellow bands.

The first fraction (0.64 g, 22%) gave physical and spectral data consistent with 2,3-dihydro-4,9-methano[11]annulenone.

The second fraction, after removal of solvent and cooling, gave 0.78 g (27%) of 4,9-methano[11]annulenone (3) as a pale yellow solid, mp 72–73 °C (lit.¹⁴ 74 °C) and spectral data consistent with those reported.¹⁴

4,9-Methano[11]annulenone *p*-Toluenesulfonylhydrazone (6). A mixture of 0.600 g (3.53 mmol) of the ketone, 0.707 g (3.80 mmol) of *p*-toluenesulfonylhydrazide, and 4 drops of concentrated HCl in 25 mL of absolute ethanol was heated at reflux for 4 h. The cooled ethanol solution was taken up into 50 mL of methylene chloride and this was washed with two 25-mL portions of saturated NaHCO₃ and finally with 25 mL of H₂O. The methylene chloride was dried (Na₂SO₄), concentrated at reduced pressure, and chromatographed on silica gel. Elution with 25% ether–petroleum ether (bp 20–40 °C) gave 1.077 g (92%) of a bright yellow, amorphous solid, mp 144–145 °C dec. Spectral data: IR (KBr) 3420, 3080, 1590, 1488, 1440, 1400, 1378, 1330, 1180, 1160, 1062, 1030, 920, 850, 808, 790, 740, 660, 573, and 542 cm⁻¹; NMR (CDCl₃) δ 0.28 (d, 1 H), 2.35 (s, 3 H), 2.73 (d, 1 H), 5.51–6.0 (m, 2 H), 6.28–7.0 (m, 6 H), 7.20 (d, 2 H).

Anal. Calcd for C₁₉H₁₈N₂SO₂: C, 67.43; H, 5.36. Found: C, 67.38; H, 5.56.

Sodium Salt of 4,9-Methano[11]annulenone Tosylhydrazone (6). To a solution of 300 mg (0.89 mmol) of 4,9-methano[11]annulenone tosylhydrazone in 20 mL of THF was added 39.0 mg of 57% NaH dispersion. Addition of the NaH resulted in H₂ evolution concomitant with precipitation of an orange solid. After stirring for 1 h, 50 mL of dry pentane was added and the solution was filtered. The separated salt (314 mg, 98%) was dried over CaCl₂ at reduced pressure. The bright yellow solid decomposed at 110 °C with the evolution of gas.

3,8-Methano[11]annulenone (10). This ketone was prepared in a nine-step sequence beginning with naphthalene by a procedure provided by Professor E. Vogel.¹⁵

3,8-Methano[11]annulenone Tosylhydrazone. A solution of 0.25 g (1.5 mmol) of 3,8-methano[11]annulenone, 0.30 g of *p*-toluenesulfonylhydrazide, and 4 drops of concentrated HCl in 10 mL of absolute ethanol was heated at reflux for 30 min. The reaction mixture was poured into 50 mL of saturated NaHCO₃ solution and the mixture was extracted with three 100-mL portions of CH₂Cl₂. The CH₂Cl₂ was dried (Na₂SO₄) and removed at reduced pressure. Chromatography of the blood-red oil on silica gel preparative plates with CH₂Cl₂ as the eluent yielded 0.30 g (60%) of 3,8-methano[11]annulenone tosylhydrazone as an amorphous, golden solid, mp 102–104 °C. Spectral data: IR (neat) 3400, 3010, 3000, 2980, 2964, 1630, 1600, 1500, 1460, 1438, 1390, 1340, 1310, 1298, 1270, 1260, 1230, 1218, 1190, 1170, 1140, 1120, 1060, 1018, 950, 920, 882, 820, 783, 762, 710, 670, and 630 cm⁻¹; UV (ϵ) (ethanol) 293 (3.24 × 10⁴) and 243 nm (3.89 × 10⁴); NMR (CDCl₃) δ 2.40 (s, 3 H), 2.72 (d, 1 H), 3.65 (d, 1 H), 5.7–6.72 (m, 7 H), 7.15–7.99 (m, 6 H).

Anal. Calcd for C₁₉H₁₈N₂SO₂: C, 67.43; H, 5.36. Found: C, 67.36; H, 5.51.

Sodium Salt of 3,8-Methano[11]annulenone Tosylhydrazone (11). The same procedure for the preparation of the sodium salt of 4,9-

methano[11]annulene tosylhydrazone was used except that the addition of 100 mL of pentane was required after completion of the reaction to cause precipitation of the salt. The sodium salt was filtered, washed with pentane, and dried over CaCl_2 at reduced pressure.

3-Formyl-1,6-methano[10]annulene Tosylhydrazone. To a solution of 850 mg (5 mmol) of 3-formyl-1,6-methano[10]annulene (**4**)¹⁷ and 1.02 g (5.5 mmol) of *p*-toluenesulfonylhydrazide in 30 mL of absolute ethanol at room temperature was added 3 drops of concentrated HCl. The mixture was stirred for 3 h at room temperature and allowed to stand at 0 °C overnight. The resulting precipitate was collected and washed three times with 15 mL of cold ethanol. After drying under vacuum 1.59 g (94%) of 3-formyl-1,6-methano[10]annulene tosylhydrazone was obtained (mp 163–164 °C). Recrystallization of 100 mg from 3 mL of methanol gave a sample with the same melting point. Spectral data: IR (KBr) 3400, 3140, 2900, 2930, 1590, 1435, 1355, 1305, 1155, 1080, 1035, 925, 890, 800, 760, 650, 565, 550 cm^{-1} ; ¹H NMR (CDCl_3) δ 8.09–6.98 (m, 12 H), 2.37 (s, 3 H), 0.28 ($\frac{1}{2}(\delta_A + \delta_B)$) (AB system, 2 H, AB \approx 9 Hz) N–H (s) varies; exact mass 338.1088 (calcd for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$, 338.1088).

Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$: C, 67.43; H, 5.36; N, 8.28; S, 9.48. Found: C, 67.47; H, 5.36; N, 8.27; S, 9.40.

3-Formyl-1,6-methano[10]annulene Tosylhydrazone Sodium Salt (5). To a solution of 1.487 g (4.4 mmol) of 3-formyl-1,6-methano[10]annulene tosylhydrazone in 50 mL of dry THF was added over a period of ca. 15 min 212 mg of NaH (50% in mineral oil). The salt immediately began to precipitate. The reaction was allowed to stir for an additional 1 h after which 100 mL of pentane was added. The salt was filtered, washed with 50 mL of pentane, and dried under vacuum to give 1.481 g (93%) of **5**.

2-Bromo-1,6-methano[10]annulene. 1,6-Methano[10]annulene¹⁸ (15 g, 0.10 mol) was dissolved in 500 mL of methylene chloride along with *N*-bromosuccinimide (19 g, 0.10 mol). The mixture was then refluxed for 3 h. The reaction mixture was cooled to room temperature, poured into 500 mL of pentane, and filtered. The filtrate was reduced by rotary evaporator and the residue chromatographed on silica gel eluting with pentane yielding 20 g (86%) of 2-bromo-1,6-methano[10]annulene, bp 87–88 °C (0.05 mm). All physical properties are in accord with those reported.¹⁸ NMR (CDCl_3) δ 7.9–6.8 (m, 7 H), –0.48 (pair of doublets, 2 H).

1,6-Methano[10]annulene-2-carboxylic Acid. 2-Bromo-1,6-methano[10]annulene (17.9 g, 0.081 mol) in 50 mL of dry ether was slowly added to 2.0 g (0.082 mol) of magnesium metal with rapid stirring. After the initial reaction had subsided 400 mL of dry ether was added to the reaction mixture. This mixture was then cooled to –10 °C and dry carbon dioxide was passed into the flask above the surface of the liquid until no more reaction was apparent (about 15 min). To this was then added about 100 mL of 6% hydrochloric acid and stirring continued for 1 h. The ether was separated and the aqueous portion extracted thoroughly with ether. The combined ether extracts were washed with water, 10% sodium bicarbonate, then water, and dried on anhydrous magnesium sulfate. Removal of the ether by rotary evaporator yielded 9.5 g (63%) of the desired acid. All physical properties agree with those reported.^{18a} NMR (CDCl_3) δ 10.6 (s, 1 H), 8.5–7.0 (complex multiplet, 7 H), –0.4 (s, 2 H).

1,6-Methano[10]annulene-2-carbinol. 1,6-Methano[10]annulene-2-carboxylic acid (5 g, 25.9 mmol) was slowly added as a solid to a solution of 1 g (26.3 mmol) of lithium aluminum hydride in dry ether at reflux. The mixture was refluxed for 3 h, then cooled and the excess hydride destroyed with ethyl acetate. The ethereal solution was washed with three 100-mL portions of water and then dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporator and the residue chromatographed on silica gel with ether–pentane (1:1) to yield 4.55 g (95%) of the desired alcohol: IR (neat) 3300, 2900, 1440, 1245, 990 cm^{-1} ; NMR (CDCl_3) δ –0.55 (m, 2 H), 4.68 (s, 2 H), 6.9–7.9 (m, 7 H).

Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{O}$: C, 83.69; H, 7.02. Found: C, 83.51; H, 7.09.

2-Formyl-1,6-methano[10]annulene (13). 1,6-Methano[10]annulene-2-carbinol (7 g, 40.6 mmol), 75 g of freshly prepared manganese dioxide, and 400 mL of acetonitrile were stirred at room temperature for 9 h. The reaction mixture was poured into water and extracted with ether, and the combined ether extracts were washed with water and then dried over anhydrous magnesium sulfate. Removal of the solvent and chromatography of the residue on silica gel with ether–pentane (1:2) yielded 5.26 g (30.9 mmol) of the pure aldehyde (76%): IR (neat) 2960, 2730, 1680, 1490, 1165, 810, 775 cm^{-1} ; NMR (CDCl_3) δ –0.3

(s, 2 H), 6.93–7.85 (m, 6 H), 8.17 (d, 1 H), 10.08 (s, 1 H).

Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{O}$: C, 84.68; H, 5.92. Found: C, 84.51; H, 5.86.

2-Formyl-1,6-methano[10]annulene Tosylhydrazone. 2-Formyl-1,6-methano[10]annulene (5.26 g, 30.9 mmol) was dissolved in 100 mL of absolute alcohol containing 5.75 g (30.9 mmol) of *p*-toluenesulfonylhydrazide. One drop of concentrated sulfuric acid was added and the mixture stirred at room temperature for several hours. The crystals were filtered and dried in vacuo to give 7.6 g (70%). Recrystallization from hot chloroform gave an analytical sample: mp 171–173 °C dec; IR (KBr) 3175, 2940, 1599, 1325, 1160, 1020, 945, 909, 762, 670, 550 cm^{-1} ; NMR (CDCl_3) δ –0.48 (m, 2 H), 2.39 (s, 3 H), 7.0–8.2 (m, 12 H); mass spectrum M^+ at *m/e* 338.

Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$: C, 67.43; H, 5.36; N, 8.28; S, 9.46. Found: C, 67.44; H, 5.37; N, 8.25; S, 9.37.

2-Formyl-1,6-methano[10]annulene Tosylhydrazone Sodium Salt (14). To 2.0 g (5.91 mmol) of the tosylhydrazone dissolved in 30 mL of dry THF (distilled from LiAlH_4 and stored over CaH_2) 1 equiv of sodium hydride (mineral oil dispersion) was slowly added with stirring. After the hydride was all added stirring was continued for 15 min. Reagent grade pentane was added (200 mL) to precipitate the salt which was then filtered and dried in vacuo.

Bicyclo[5.4.1]dodeca-2,5,7,9,11-pentaene (8). Dry diglyme (50 mL) was saturated with N_2 and then heated to 130 °C under a N_2 atmosphere. A suspension of 0.180 g of the sodium salt of 4,9-methano[11]annulene tosylhydrazone (**6**) in 10 mL of dry diglyme was added over a 5-min period, and after complete addition the reaction was maintained at 130 °C for an additional 3 min. The solution was immediately quenched in an ice bath and 500 mL of H_2O was added to the reaction mixture. The H_2O solution was extracted with four 50-mL portions of pentane and finally with two 100-mL portions of H_2O , dried over Na_2SO_4 , concentrated at reduced pressure, and chromatographed over 50 g of silica gel. Elution with pentane followed by removal of the solvent gave 51.6 mg (67%) of a red-brown solid: mp 254–256 °C dec; IR (KBr) 3010, 3000, 2992, 1600, 1550, 1451, 1444, 1260, 1238, 1082, 1011, 968, 959, 900, 855, 848, 785, 746, 719, 682, 611, 590, 560, and 510 cm^{-1} ; UV and visible (ϵ) (*n*-hexane) 413 (17 600), 320 (41 200), and 222 nm (26 700); NMR (CDCl_3) δ 6.5–6.9 (m, 8 H), 6.5 (d, 4 H), 5.63 (d, 4 H), 3.75 (d, 2 H), and 0.69 (d, 2 H); mass spectrum found, $P = 308.1563$ (calcd for $\text{C}_{24}\text{H}_{20}$, $P = 308.1564$).

1-Phenyl-(6,11-methano)spiro[2.10]tetradeca-4,6,8,10,12-pentaene (17). To a solution of 0.520 g (5 mmol) of styrene in 50 mL of dry, N_2 -saturated diglyme maintained at 125 °C was added over a 5-min period 0.180 g (0.5 mmol) of the sodium salt of 4,9-methano[11]annulene tosylhydrazone **6** as a suspension in 5 mL of diglyme. After complete addition, the solution was maintained at 125 °C for an additional 2 min and then cooled in an ice bath. The reaction mixture was flooded with 500 mL of water and extracted with three portions (100 mL) of pentane and two portions (50 mL each) of ether. The combined organic phase was washed with water, dried over Na_2SO_4 , and concentrated under reduced pressure. The excess styrene was removed by vacuum distillation. The pot residue was eluted through an activity III neutral alumina column with 10% ether–pentane to remove traces of polystyrene. After removal of the solvent, the red-brown residue was triturated with 50 mL of pentane, heated to reflux, and then cooled in an ice bath. Filtration of the red-brown precipitate gave 15.3 mg (19.8% yield) of **8** and a yellow filtrate. The concentrated filtrate was chromatographed over activity III neutral alumina with 10% ether–petroleum ether. This gave 40.3 mg (31.2%) of a pale yellow oil which proved to be a mixture of geometrical isomers which could not be separated by normal chromatographic techniques. The spectral data for the mixture: IR (KBr) 2999, 2960, 2920, 1600, 1490, 1450, 1268, 1090, 955 cm^{-1} ; UV (ϵ) (*n*-hexane) 318 (4500) and 262 nm (29 800); NMR (CCl_4) δ 7.20 (m, 5 H), 6.84 (m, 2 H), 6.38 (m, 4 H), 5.10–3.78 (m, 3 H), 2.70–2.24 (m, 1 H), 1.79–1.18 (m, 2 H), and 0.10 (superimposable d, 1 H); mass spectrum *m/e* 258 (parent and base peak).

Anal. Calcd for $\text{C}_{20}\text{H}_{18}$: C, 92.98; H, 7.02. Found: C, 92.72; H, 7.01.

Attempted Thermal Rearrangement of 1-Phenyl-(6,11-methano)spiro[2.10]tetradeca-4,6,8,10,12-pentaene (17). A solution of 64.0 mg (0.24 mmol) of the spirotetradecapentaene **17** in 5 mL of diglyme was heated at reflux under an inert atmosphere. The reaction was followed on silica gel TLC plates using pentane as the solvent. After 6 h the TLC showed no more starting material present. The reaction mixture

was poured into 100 mL of H₂O and extracted three times with 50 mL of ether. The ether solution was dried and the solvent was removed at reduced pressure. NMR of the crude product gave a complex pattern from δ 0.5 to 7.5 indicating a polymeric material. Attempts to elute monomeric products from the crude reaction product by chromatography over a short silica gel column were unsuccessful. When an identical reaction was carried out at 130 °C, the crude reaction mixture contained mostly unreacted starting material plus some polymeric product.

1-(4-Bromophenyl)-(6,11-methano)spiro[2.10]tetradeca-4,6,8,10,12-pentaene. To a stirred solution of 1.50 g of *p*-bromostyrene in 30 mL of dry diglyme maintained at 100 °C was added 0.150 g (0.5 mmol) of the sodium salt of 4,9-methano[11]annulene tosylhydrazone in 15 mL of diglyme over a period of 8 min. The mixture was then heated for an additional 7 min. The cooled solution was poured into 300 mL of H₂O and extracted four times with 50-mL portions of pentane. The pentane solution was washed with H₂O, dried over Na₂SO₄, and concentrated on a rotary evaporator and finally excess *p*-bromostyrene was removed by distillation at reduced pressure. Elution of the crude product over an activity III neutral alumina column afforded 74 mg (52.8%) of a white solid, mp 92–97 °C. Spectral data indicate the solid to be a mixture of geometrical isomers. Spectral data: IR (melt) 3000, 2980, 2940, 1590, 1550, 1488, 1450, 1400, 1378, 1260, 1234, 1190, 1110, 1072, 1010, 960, 910, 850, 840, 790, 770, 730, and 640 cm⁻¹; UV (ϵ) (*n*-hexane) 323 (2800) and 260 nm (38 200); NMR (CCl₄) δ 7.54–6.71 (m, 6 H), 6.51–6.24 (m, 4 H), 5.04–3.62 (m, 3 H), 2.76–1.27 (m, 3 H), and 0.32 to –0.21 (m, 1 H).

Anal. Calcd for C₂₀H₁₇Br: C, 71.22; H, 5.04. Found: C, 70.97; H, 5.18.

1-(4-Chlorophenyl)-(6,11-methano)spiro[2.10]tetradeca-4,6,8,10,12-pentaene. The same procedure and workup used for the preparation of 1-(4-bromophenyl)-(6,11-methano)spiro[2.10]tetradeca-4,6,8,10,12-pentaene was used. In addition to 14 mg (21.9%) of **8**, 67.1 mg (55.1%) of a mixture of two isomers of the title compound was isolated as an oil. Spectra data: IR (melt) 3000, 2970, 2930, 1600, 1552, 1494, 1450, 1408, 1370, 1260, 1240, 1190, 1112, 1098, 1017, 960, 915, 850, 837, 780, 740, 687, 647, 610, and 590 cm⁻¹; UV (ϵ) (*n*-hexane) 320 (3900) and 263 nm (30 500); NMR (CCl₄) δ 7.40–6.68 (m, 6 H), 6.51–6.22 (m, 4 H), 5.04–3.58 (m, 3 H), 2.74–1.17 (m, 3 H), and 0.30 to –0.23 (m, 7 H); mass spectrum found, P = 294.0991 and 292.1018 (calcd for C₂₀H₁₇Cl, P = 294.0989 and 292.1018).

1-(3-Bromophenyl)-(6,11-methano)spiro[2.10]tetradeca-4,6,8,10,12-pentaene. The same procedure and workup used for the preparation of 1-(4-bromophenyl)-(6,11-methano)spiro[2.10]tetradeca-4,6,8,10,12-pentaene was used. This yielded, in addition to dimer **8**, 84.0 mg (74.7%) of a pale yellow solid, mp 45–50 °C. Again spectral data indicates a mixture of isomers for the product. Spectral data: IR (melt) 3000, 2980, 1600, 1640, 1460, 1450, 1420, 1360, 1270, 1240, 1190, 1175, 1130, 1070, 1020, 960, 918, 910, 882, 858, 850, 785, 745, 718, 700, and 685 cm⁻¹; UV (ϵ) (*n*-hexane) 321 (1800) and 263 nm (15 300); NMR (CCl₄) ϵ 7.51–6.25 (m), 3.55 (d), 4.94–4.60 (m), 3.72 (d), 2.33–1.04 (m), 0.63 (d), and 0.02 (d); mass spectrum found, P = 338.0508 and 336.0513 (calcd for C₂₀H₁₇Br, P = 338.0506 and 336.0526).

Attempted Formation of 1-(4-Methoxyphenyl)-(6,11-methano)spiro[2.10]tetradeca-4,6,8,10,12-pentaene. The same procedure and workup for the preparation of 1-(4-bromophenyl)-(6,11-methano)spiro[2.10]tetradeca-4,6,8,10,12-pentaene was used except that a 50-fold excess of *p*-methoxystyrene was used as the trap. This afforded mostly dimer **8** and ca. 2 mg of an uncharacterized material which appeared to be an adduct.

1,2-Dimethyl (6,11-Methano)spiro[2.10]-tetradeca-4,6,8,10,12-pentaenedicarboxylate (18). The same procedure for the preparation of **17** was used except that 0.720 g (50 mmol) of dimethyl fumarate was used as the trap instead of styrene. After completion of the reaction, the mixture was flooded with 500 mL of H₂O and extracted with four portions of pentane (100 mL each) and twice with 100-mL portions of ether. The combined organic layers were washed twice with 125 mL of H₂O, dried over Na₂SO₄, and concentrated at reduced pressure. Elution of crude product over an activity III neutral alumina column with 10% ether–pentane gave a fast-moving yellow band which upon removal of solvent gave 1.3 mg (1.7%) of the dimer **8**. Continued elution gave a second fraction which proved to be unreacted dimethyl fumarate. This was followed by a third very pale yellow band which

upon removal of solvent yielded 78.2 mg (52.5%) of **18** as a white, crystalline solid, mp (recrystallized from pentane) 100–101 °C. Spectral data: IR (KBr) 3010, 3000, 2942, 1720, 1630, 1600, 1438, 1405, 1382, 1350, 1280, 1258, 1198, 1180, 1020, 1010, 910, 880, 770, 620, 582, and 555 cm⁻¹; UV (ϵ) (*n*-hexane) 317 (2700), 258 (25 100), and 240 nm (21 900); NMR (CDCl₃) δ 7.04–6.60 (m, 6 H), 4.98 (d, 1 H), 4.81 (d, 1 H), 3.88 (s, 3 H), 3.72 (m, 4 H), 3.02 (d, 1 H), 2.72 (d, 1 H), and 0.16 (d, 1 H); mass spectrum *m/e* P = 298, base peak 180.

Anal. Calcd for C₁₈H₁₈O₄: C, 72.50; H, 6.04. Found: C, 72.69; H, 6.08.

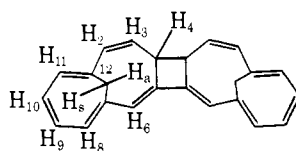
Dimethyl Bicyclo[5.4.1]dodeca-2,5,7,9,11-pentaene- $\Delta^{4,a}$ -succinate (19). A solution of 15.0 mg of 1,2-dimethyl (6,11-methano)spiro[2.10]tetradeca-4,6,8,10,12-pentaenedicarboxylate (**18**) 25 mL of methanol, and 6 drops of concentrated HCl was heated at reflux. The formation of the fulvene product was followed by TLC and complete reaction was observed in 3 h. The solution was neutralized with 100 mL of saturated aqueous NaHCO₃ solution. Extraction with pentane and removal of solvent followed by preparative plate chromatography on silica gel with 10% ether–pentane afforded a fast-moving, intense yellow band which upon isolation gave 10.5 mg (70%) of dimethyl bicyclo[5.4.1]dodeca-2,5,7,9,11-pentaene- $\Delta^{4,a}$ -succinate (**19**) as a bright yellow oil. Spectral data: IR (melt) 2996, 2970, 1733, 1702, 1600, 1430, 1330, 1290, 1255, 1180, 1118, 1082, 840, 780, 732, and 620 cm⁻¹; UV (ϵ) (EtOH) 370 (4200), 305 (19 100), and 237 nm (23 100); NMR (CCl₄) δ 7.13–6.97 (m, 2 H), 6.79–6.38 (m, 5 H), 5.56 (d, 1 H), 3.79 (s, 3 H), 3.70 (s, 3 H), 3.48 (s, 2 H), 3.00 (d, 1 H), and –0.06 (d, 1 H).

Anal. Calcd for C₁₈H₁₈O₄: C, 72.50; H, 6.04. Found: C, 72.79; H, 6.25.

Tetracyclo[14.4.1.0^{3,13}.0^{4,12}]heneicosa-1,11,13,15,17,19-hexaene (20). The same procedure for the preparation of 1-phenyl-(6,11-methano)spiro[2.10]tetradeca-4,6,8,10,12-pentaene (**17**) was used except that 0.610 g of cyclononadiene was used as the trap instead of styrene. The reaction mixture was rapidly cooled, flooded with water, and extracted with portions of pentane and finally with ether. The combined organic layer was washed with water, dried (Na₂SO₄), and concentrated at reduced pressure. The residue was triturated with pentane, heated to reflux, cooled in an ice bath, and filtered to remove the dimeric product (17.7 mg, 22.2%). The filtrate was concentrated and chromatographed over an activity III neutral alumina column. Elution with 10% ether–pentane afforded 38.2 mg (27.6%) of the desired product as a yellow oil. Spectral data: IR (melt) 3000, 2950, 2920, 1630, 1562, 1440, 1350, 1270, 1018, 910, 840, and 808 cm⁻¹; UV and visible (ϵ) (*n*-hexane) 405 (3100), 292 (21 600), 284 (20 600), and 246 nm (14 200); NMR (CDCl₃) δ 6.50–5.38 (m, 8 H), 4.69 (d, 1 H), and 3.44–0.87 (m, 16 H); mass spectrum found, P = 276.1875 (calcd for C₂₁H₂₄, P = 276.1877).

4-Phenyltricyclo[7.4.1.0^{3,6}]tetradeca-1,4,6,8,10,12-hexaene (21). To a solution of 2 mL of phenylacetylene in 10 mL of dry, N₂-saturated diglyme maintained at 100 °C was added 0.120 g of the sodium salt of 4,9-methano[11]annulene tosylhydrazone as a suspension in 10 mL of dry diglyme. The total time of addition of the salt was 5 min, after which the solution was heated for an additional 5 min. The cooled solution was flooded with 300 mL of saturated NaCl solution and then extracted three times with 100-mL portions of ether. The ether solution was washed with H₂O and dried over Na₂SO₄ and the ether was removed at reduced pressure. The crude product was chromatographed over activity III neutral alumina with 10% ether–petroleum ether (bp 20–40 °C). This yielded a bright red solution which upon removal of the solvent gave 47.0 mg (55.1%) of a deep red oil which was unstable in air. Spectral data: NMR (CDCl₃) δ 7.48–7.14 (m, 5 H), 6.96–5.35 (m, 8 H), 5.28–4.78 (m, 2 H), and 3.00 (d, 1 H); mass spectrum found, P = 256.1247 (calcd for C₂₀H₁₆, P = 256.1251).

Thermolysis of 3-Formyl-1,6-methano[10]annulene Tosylhydrazone Sodium Salt (5). In a 25-mL Morton flask, equipped with a high-speed stirrer, 10 mL of dry diglyme was heated to 150 °C and swept with argon for 30 min. A slurry of 180 mg (0.5 mmol) of the salt **5** in 5 mL of diglyme was added during 5 min. The reaction mixture was poured into 100 mL of ice water and extracted five times with 50 mL of pentane. The combined pentane phases were washed five times with water and dried over MgSO₄. Evaporation of the solvent and drying via a high-vacuum pump (overnight) gave a semicrystalline residue which was chromatographed (quartz column *l* = 45 cm, *d* = 8 mm) on silica gel with ether–pentane (1:1) to give 75.6 mg (83%) of pyra-

Table III. NMR Data for 32⁴⁰

32

Proton	Chemical shifts, δ	Coupling constant, Hz	Pattern	Irradiation position, δ	Results
H ₂	6.4 doublet	$J_{2,3}$ 12.0	AB	0.72 H _{1,2S}	3.65 doublet to singlet
H ₃	5.12 doublet	$J_{3,2}$ 12.0	AB	3.65 H _{1,2a}	0.72 doublet to singlet
H ₄	4.46 broad singlet			5.12 H ₃	6.4 singlet arises from complex multiplet
H ₆	6.74 broad singlet			6.74 H ₆	0.72 doublet sharpens
H ₈			AA'BB'	6.4 H _{2,8,11}	5.12 doublet partially collapses to singlet
H _{1,1}	6.4 multiplet			(low power)	
H ₉	6.82 multiplet		AA'BB'		4.46 broad singlet sharpens
H ₁₀					3.65 doublet sharpens
H _{1,2a}	3.65 doublet	$J_{1,2a,1,2S}$ 12.0	AB	(high power)	0.72 doublet sharpens
H _{1,2S}	0.72 doublet	$J_{1,2S,1,2a}$ 12.0	AB	4.46 H ₄	5.12 doublet sharpens

zole **31** with the following properties: mp 122.5–124.5 °C (from ether–pentane, 1:1); UV λ (ϵ) (cyclohexane) 262 nm (26 200), 302 (4700); IR (KBr) 3200–2820, 1500, 1440, 1355, 1250, 1085, 960, 935, 915, 860, 845, 800, 750, 710, 700, 630, 580, 535, 465 cm⁻¹; ¹H NMR (CCl₄) δ 7.89 (s, 1 H), 7.29–6.65 (m, 6 H), 1.5 and –0.08 (2 H, AB system, J = 9.8 Hz), N–H varies; ¹³C NMR [decoupled spectrum (CDCl₃), from Me₄Si] 34.7, 104.8, 117.4, 119.0, 119.6, 122.8, 123.4, 125.4, 127.9, 128.1, 135.6, and 143.8 ppm; exact mass 182.0839 (calcd for C₁₂H₁₀N₂, 182.0843).

Anal. Calcd for C₁₂H₁₀N₂: C, 79.09; H, 5.53; N, 15.37. Found: C, 78.84; H, 5.60; N, 15.48.

Photolysis of the Sodium Salt of 3-Formyl-1,6-methano[10]annulene Tosylhydrazone (5). A solution of 180 mg (5 mmol) of the sodium salt in 100 mL of dry diglyme was photolyzed in a Pyrex vessel under a nitrogen atmosphere at –45 to –50 °C for 4.5 h with a 550-W Hanovia “high pressure quartz mercury vapor lamp”. The reaction mixture was poured into 300 mL of water and extracted three times with 100 mL of pentane and then twice with 100 mL of ether. The combined organic layers were washed five times with 100 mL of water and dried over MgSO₄. Evaporation of the solvent followed by high vacuum drying gave a dark brown solid. Chromatography with pentane on silica gel (column, l = 45 cm, d = 8 mm) gave 31.4 mg (41%) of fulvalene **8** and 30.2 mg (33%) of pyrazole **31**.

Photolysis of the Sodium Salt of 3-Formyl-1,6-methano[10]annulene Tosylhydrazone (5) in the Presence of Trapping Agents. The sodium salt was dissolved in diglyme and photolyzed under the conditions described above at temperatures ranging from –45 to –74 °C in the presence of different trapping agents (1,3-butadiene, furan, dimethyl fumarate, and styrene). In no case were products other than fulvalene **8**, pyrazole **31**, or 3-formyl-1,6-methano[10]annulene tosylhydrazone isolated.

Thermolysis of the Sodium Salt of 3,8-Methano[11]annulene Tosylhydrazone (11). To 50 mL of diglyme at reflux (161 °C) under a N₂ atmosphere was added all at once 141 mg (0.39 mmol) of the sodium salt of 3,8-methano[11]annulene tosylhydrazone (**11**) as a solid. The solution was maintained at reflux for an additional 5 min. The reaction mixture was quenched in an ice bath, flooded with 300 mL of saturated NaCl solution, and extracted four times with 100-mL portions of pentane. The pentane solution was dried over Na₂SO₄ and the solvent removed on a rotary evaporator. The crude product was chromatographed on preparative silica gel plates with pentane as the eluent. This afforded two major products which proved to be *anti*-pentacyclo[16.4.1.1.6¹¹.0^{2,14}.0^{3,13}]tetracos-4,6,8,10,12,14,16,18,20,22-decaene (**33**, 17.6 mg, 29.4%) and *anti-trans*-pentacyclo[16.4.1.1.6¹¹.0^{3,15}.0^{4,14}]tetracos-2,4,6,8,10,12,16,18,20,22-decaene (**32**, 6.7 mg, 11.2%).

Spectral data for **32**: IR (film) 3000, 1445, 1360, 1265, 880, 850, 750 cm⁻¹; UV (pentane) (ϵ) 289 (23 000), 440 nm (8730); NMR (see Table III). Spectral data for **33**: IR (KBr) 3000, 1450, 1265, 1070, 880, 790, 740 cm⁻¹; UV (pentane) (ϵ) 293 (40 600), 425 (15 100); NMR (see Table IV).

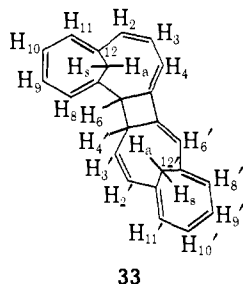
Mass spectrum for **32**, found, P = 308.1563 (calcd for C₂₄H₂₀, P = 308.1564).

Mass spectrum for **33**, found, P = 308.1563 (calcd for C₂₄H₂₀, P = 308.1564).

Photolysis of the Sodium Salt of 3,8-Methano[11]annulene Tosylhydrazone (11). A vigorously stirred solution of 20 mg (0.055 mmol) of the sodium salt of 3,8-methano[11]annulene tosylhydrazone in dry THF maintained at –45 °C was photolyzed by a 550-W Hanovia high-pressure mercury lamp (quartz filter) for 4 h. The reaction mixture was poured into 100 mL of saturated NaCl solution and the aqueous phase was extracted with three 50-mL portions of ether. The ether was dried (Na₂SO₄) and removed on a rotary evaporator. The crude product was chromatographed on a preparative silica gel plate with pentane as the eluent. Product analysis by UV–visible spectrum gave **33** in less than 1% yield and **32** in 2.5% yield as the only isolable products. A considerable amount of polymeric residue remained on the preparative plate.

Pyrolysis of the Sodium Salt of 2-Formyl-1,6-methano[10]annulene (14) Tosylhydrazone in Diglyme. One gram (2.77 mmol) of the sodium salt was dissolved in 10 mL of dry diglyme that had been swept for 10 min with a nitrogen stream. This solution was added dropwise over a 30-min period to 50 mL of dry diglyme that had also been previously swept with a dry nitrogen stream. The diglyme was maintained at approximately 160 °C and agitated by a high-speed stirrer. Air was excluded by means of a very slow nitrogen sweep. After addition was complete the deep red solution was cooled to room temperature and poured into 300 mL of water. The aqueous solution was then extracted several times with pentane. The combined pentane extracts were washed with water and dried over anhydrous magnesium sulfate. The pentane was removed by rotary evaporator and the residue submitted to column chromatography on silica gel, eluting first with pentane and then increasing the polarity of the eluent by increasing the percentage of added ether. Typically 50 fractions (20 mL) were taken. These fractions were monitored by TLC and then combined according to content. This procedure usually resulted in eight fractions each of which was submitted to preparative TLC (silica, pentane) utilizing the multiple pass development method. This gave 0.085 g of **32** and 0.120 g of **33** (total yield 48%). All properties of these materials were identical with those described above.

Thermolysis of 2-Formyl-1,6-methano[10]annulene Tosylhydrazone Sodium Salt (14) in the Presence of 1,1-Diphenylethylene. To a solution of 50 mL of dry diglyme and 2 mL of 1,1-diphenylethylene at reflux under a N₂ atmosphere was added 0.361 g (1.0 mmol) of 2-formyl-1,6-methano[10]annulene tosylhydrazone sodium salt (**14**) as a suspension in 20 mL of diglyme. The salt was added over a 7-min period. The reaction mixture was cooled, poured into 500 mL of saturated NaCl solution, and extracted with four 100-mL portions of pentane. The combined pentane layers were washed with water and dried over Na₂SO₄, and the volatile materials were removed at reduced pressure. Chromatography on silica gel with pentane afforded 91.4 mg (27.4%) of 5,5-diphenyltricyclo[7.4.1.0^{3,6}]tetradeca-2,7,9,11,13-pentaene (**35**)

Table IV. NMR Data for 33⁴⁰

Proton	Chemical shift, δ	Coupling constant, Hz	Pattern	
H ₂	5.86	doublet	$J_{2,3}$ 12.5	AMX
H ₃	5.43	doub of doub	$J_{3,2}$ 12.5 $J_{3,4}$ 7.5	AMX
H ₄	5.99	doublet	$J_{4,3}$ 7.5	AMX
H ₆	4.61	doublet	$J_{6,4}$ 9.5	ABMX
H ₁₁	6.06	multiplet		AA'BB'
H ₉				
H ₁₀	6.5	multiplet		AA'BB'
H _{12a}	5.01	doublet	$J_{12a,12s}$ 10.5	AB
H _{12s}	1.54	doublet	$J_{12s,12a}$ 10.5	AB
H _{2'}	6.5	doublet	$J_{2',3'}$ 11.5	ABMX
H _{3'}	5.11	doub of doub	$J_{3',2'}$ 11.5 $J_{3',4'}$ 3.0	ABMX
H _{4'}	4.90	doub of doub	$J_{4',3'}$ 3.0 $J_{4',6}$ 9.5	ABMX
H _{6'}	6.68	br singlet		
H ₈	6.55	multiplet		AA'BB'
H ₁₁				
H ₉	6.87	multiplet		AA'BB'
H ₁₀				
H _{12'a}	3.65	doublet	$J_{12'a,12's}$ 12.0	AB
H _{12's}	0.53	doublet	$J_{12's,12'a}$ 12.0	AB

Irradiation position, δ	Results
6.68 H _{6'}	4.90 doub of doub to trip 0.53 doub sharpens
6.5 H _{2'}	5.11 11 Hz doub of 3 Hz to 3 Hz doub
5.86 H ₂	5.43 12.5 Hz doub of 7.5 Hz doub to 12.5 Hz doub 1.54 doub sharp.
5.43 H ₃	5.86 mult changes
5.11 H _{3'}	6.5 sing. arises from mult
4.90 H _{4'}	5.11 11.5 Hz doub of 3 Hz to 11.5 Hz doub
4.61 H ₆	5.99 mult changes
5.99 H ₄	4.61 br doub sharp
3.65 H _{12'a}	0.53 doub to sing.
1.54 H _{12s}	5.01 doub to sing.

as a bright orange solid, mp 140–141 °C. spectral data: IR (KBr) 3000, 2990, 2978, 2950, 2910, 1590, 1482, 1440, 1350, 1320, 1250, 1200, 1170, 1070, 1050, 890, 860, 850, 838, 800, 770, 740, 690, 620, 600, and 588 cm⁻¹; UV and visible (ϵ) (*n*-hexane) 415 (1200), 338 (3400), and 254 nm (32 600); NMR (CDCl₃) δ 7.59–6.80 (m, 10 H), 6.75–5.60 (m, 7 H), 4.42–3.81 (m, 2 H), 3.56–3.32 (m, 2 H), and 1.10 (d, 1 H); mass spectrum found, P = 334.1723 (calcd for C₂₆H₂₂, P = 334.1721).

Thermolysis of 2-Formyl-1,6-methano[10]annulene Tosylhydrazone Sodium Salt (14) in the Presence of Phenylacetylene. The same procedure and workup given above was used except that 2 mL of phenylacetylene rather than 1,1-diphenylethylene was used as the trapping agent. Repeated passes with pentane on a silica gel preparative plate separated the crude reaction mixture into five products. Isolation of a bright orange band afforded 21.4 mg (17.5%) of an adduct believed to be 5-phenyltricyclo[7.4.1.0^{3,6}]tetradeca-2,4,7,9,11,13-hexaene (36) as a red-orange solid, mp 141–143 °C. Spectral data: IR (CCl₄) 3000, 2960, 2940, 1635, 1590, 1480, 1450, 1440, 1428, 1356, 1260, 1020, 952, 910, 875, 710, 682, and 610 cm⁻¹; UV (ϵ) (*n*-hexane) 393 (8600), 303 (32 900), 292 (34 200), and 241 nm (2600); NMR (CDCl₃) δ 7.68–7.19 (m, 5 H), 6.88–5.48 (m, 9 H), 4.17 (d, 1 H), and 1.05 (d,

1 H); mass spectrum found, P = 256.1240 (calcd for C₂₀H₁₆, P = 256.1251).

Isolation of a fast-moving yellow band gave 13 mg (10.6%) of an adduct believed to be 3-phenyltricyclo[7.4.1.0^{2,5}]tetradeca-1,3,6,8,10,12-hexaene (37) as an orange oil. Spectral data: IR (CCl₄) 3000, 2985, 2960, 1642, 1592, 1480, 1440, 1350, 1256, 1110, 960, 900, 872, 860, 840, 720, 685, and 640 cm⁻¹; UV (ϵ) (*n*-hexane) 395 (5300), 296 (33 900), and 248 nm (19 300); NMR (CDCl₃) δ 7.64–7.10 (m, 5 H), 6.65–6.18 (m, 2 H), 6.00–4.84 (m, 8 H), and 1.80 (d, 1 H); mass spectrum found, P = 256.1233 (calcd for C₂₀H₁₆, P = 256.1251).

Two other unidentified products totaling 13.2 mg were isolated in addition to the above products.

Thermolysis of the Sodium Salt of 2-Formyl-1,6-methano[10]annulene Tosylhydrazone (14) in the Presence of 1,2-Cyclonadiene. To a solution of 50 mL of dry, N₂-saturated diglyme and 1 mL of 1,2-cyclonadiene maintained at reflux was added 0.180 g (0.5 mmol) of 1,6-methano[10]annulene-2-carboxaldehyde tosylhydrazone sodium salt over a 5-min period as a suspension in 5 mL of diglyme. The reaction mixture was cooled, poured into 500 mL of saturated NaCl solution, and extracted with four 100-mL portions of pentane. The combined pentane layers were washed with water and dried over NaSO₄, and the volatile substances were removed at reduced pressure. Chromatography over a silica gel column with pentane as the eluent afforded a fast-moving bright yellow band. Chromatography of this material on a preparative silica gel plate with pentane as the eluent gave two distinct yellow compounds. The first band yielded an adduct assigned structure tetracyclo[14.4.1.0^{2,12}.0^{3,11}]heneicoso-10,12,14,16,18,20-hexaene (39) in 27.6% yield (38.2 mg) as a bright yellow oil. Spectral data: IR (neat) 3000, 2955, 2920, 1600, 1440, 1410, 1350, 1252, 1148, 1082, 1060, 1030, 952, 900, 850, 800, 750, and 730 cm⁻¹; UV and visible (ϵ) (*n*-hexane) 405 (3100), 292 (21 600), 284 (20 600), and 246 nm (14 200); NMR (CCl₄) δ 6.45–6.22 (m, 2 H), 5.90–5.05 (m, 7 H), 3.70–2.89 (m, 2 H), and 2.47–0.92 (m, 13 H); mass spectrum found, P = 276.1875 (calcd for C₂₁H₂₄, P = 276.1877).

The second band afforded a pale yellow oil (11.5 mg, 8.3%) which appears from its spectral properties to be tetracyclo[14.4.1.0^{3,13}.0^{4,12}]heneicoso-2,4,14,16,18,20-hexaene (38). Spectral data: UV (ϵ) (*n*-hexane) 382 (4200) and 263 nm (15 100); NMR (CCl₄) δ 6.74–6.02 (m), 5.52–4.62 (m), 3.54 (d), 3.37–1.02 (m), and 0.65 (d); mass spectrum found, P = 276.1875 (calcd for C₂₁H₂₄, P = 276.1877).

Further elution of the silica gel column with pentane yielded 17.1 mg (22.2%) of dimers 32 and 33.

Thermolysis of the Sodium Salt of 3,8-Methano[11]annulene Tosylhydrazone (11) in the Presence of 1,2-Cyclonadiene. To a solution of 15 μ L of 1,2-cyclonadiene in 2.5 mL of dry diglyme maintained at 160 °C was added 7.71 mg of the sodium salt of 3,8-methano[11]annulene tosylhydrazone (11) in 1 mL of diglyme. After ca. 1 min the solution was quenched and the reaction mixture was poured into 50 mL of saturated NaCl solution and extracted with three 25-mL portions of ether. The ether layer was concentrated and then chromatographed on silica gel with pentane as the eluent. This afforded a total of 1.19 mg (35.9%) of dimeric products 32 and 33 and 0.16 mg (3.2%) of an adduct which was identified as 39 by quantitative UV analysis. None of the isomeric adduct was detected.

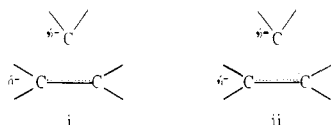
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References and Notes

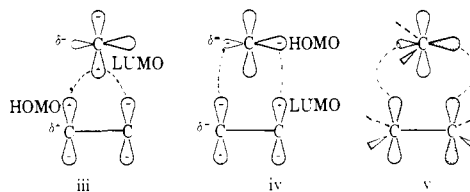
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- (2) University of Florida Postdoctoral Fellow.
- (3) Fulbright-Hays Fellow.
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 (15) Our first batch of this ketone was prepared by reduction of a sample of 11-chloro-3,8-methano[11]annulene¹⁶ which was generously furnished to us by Professor Vogel. Later batches were synthesized by the method developed and furnished to us by Professor Vogel. The authors are deeply grateful for both assistance and encouragement of Professor Vogel during the course of this work.
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 (27) Although articulated in a number of ways,²⁸ carbenes have generally been defined as electrophilic or nucleophilic when they lead to transition states with charge distributions as pictured in i and ii, respectively. As an elaboration of this definition, we would like to suggest that the concept of electrophilicity and nucleophilicity can also be viewed in terms of the contributions of HOMO and LUMO orbitals,¹² an approach which has some very real advantages over the simple charge distribution picture. Recognizing that iii and iv are equivalent to v (the more traditional representation of the only symmetry-allowed mechanism, for concerted cycloaddition of a carbene to a multiple bond), it is apparent that if, in the transition state, the contribution of iii outweighs that of iv, the charge distribution in i obtains and the carbene could be called "electrophilic". On the other hand, if the contribution of iv outweighs iii, the charge distribution of ii obtains and the carbene could then be said to be "nucleophilic". Among the advantages this definition or picture has over the simpler charge distribution definition: (1) It emphasizes the importance of the substrate in dictating the so-called



ration of this definition, we would like to suggest that the concept of electrophilicity and nucleophilicity can also be viewed in terms of the contributions of HOMO and LUMO orbitals,¹² an approach which has some very real advantages over the simple charge distribution picture. Recognizing that iii and iv are equivalent to v (the more traditional representation of the only symmetry-allowed mechanism, for concerted cycloaddition of a carbene to a multiple bond), it is apparent that if, in the transition state, the contribution of iii outweighs that of iv, the charge distribution in i obtains and the carbene could be called "electrophilic". On the other hand, if the contribution of iv outweighs iii, the charge distribution of ii obtains and the carbene could then be said to be "nucleophilic". Among the advantages this definition or picture has over the simpler charge distribution definition: (1) It emphasizes the importance of the substrate in dictating the so-called



- electrophilicity or nucleophilicity of the carbene. (2) It accommodates the influence of uncharged multiple bonds such as vinyl and phenyl (on the substrate) on the reactivity of both "electrophilic" and "nucleophilic" carbenes since the HOMO is raised (increasing the contribution of iii) and the LUMO is lowered (increasing the contribution of iv). (3) It emphasizes the " π " approach (v) for both types of carbenes; this is consistent with both the stereospecificity of addition of cycloheptatrienyliene to electron-deficient double bonds and its reluctance to undergo 1,4-additions, a reaction that would be allowed by a " σ " approach. (4) It suggests a number of interesting experiments to probe the effects of substituent groups in both carbenes and substrates.²⁸ This approach does not more satisfactorily accommodate the apparent anomalies that arise from so-called carbene selectivity or, more precisely, the position of the transition state on the reaction coordinate.
- (28) Cf. R. A. Moss in "Carbenes", Vol. 1, M. Jones, Jr., and R. A. Moss, Ed., Wiley, New York, N.Y., 1973.
 (29) For a recent use of the HOMO-LUMO approach to explain substituent group effects on intramolecular reactions of vinyl carbenes, see C. Mayor and C. Wentrup, *J. Am. Chem. Soc.*, **97**, 7467 (1975).
 (30) For example, both cycloheptatrienyliene and the methanoannulenyliene 1 efficiently add to electron-deficient olefins such as dimethyl fumarate to give spirocyclopropanes. In contrast, thermal decomposition of the tosylhydrazone salt 11 in the presence of dimethyl fumarate gave no isolable adduct. Interestingly, quantitative studies (monitored by UV) of the influence of potential substrates on the formation of the dimeric hydrocarbons **32** and **33** showed a significant diminution by dimethyl fumarate. At this time it is not known at what point in the reaction sequence the fumarate interrupts dimer formation.
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 (40) NMR data were obtained and interpreted by R. W. King, to whom the authors are grateful.