the hot mercurial/olefin/benzene solution over 30 min, and the reaction mixture was heated at reflux for an additional 2 hr. At the end of this time tlc showed that none of the starting mercury reagent was present. The cooled reaction mixture (a three-layer system) was trap to trap distilled. Glc analysis of the distillate showed the presence of 7,7-difluoronorcarane in 16% yield.

A similar reaction carried out in benzene at reflux (no DME) for 20 hr gave none of the expected norcarane derivative.

The reaction of 10 mmol of $CF_3HgO_2CCF_3$ and 40 mmol of NaI in the presence of 30 ml of allyltrimethylsilane in 20 ml of benzene and 20 ml of DME, carried out using the procedure described above, gave 1,1-difluoro-2-(trimethylsilylmethyl)cyclopropane in 24% yield.

C. **Trifluoromethylmercuric Chloride.**—A solution of 30 mmol of NaI in 20 ml of dry DME was added over a 30-min period to a stirred and heated solution of 5 mmol of CF_3HgCl[18] and 30 mmol of cyclohexene in 10 ml of benzene. A white solid deposited as the NaI was added. This became gradually green and oily as the addition progressed and finally went into solution. The reaction was heated at reflux for 1 hr and then was cooled to room temperature. A two-layer system resulted. The upper light yellow layer contained no 7,7-difluoronorcarane (by glc). Trap-to-trap distillation at 0.05 mm gave a water-white distillate which was shown by glc to contain only trace amounts of 7,7-difluoronorcarane. None of this product was present in a similar reaction mixture in which the solvent contained no DME.

Very similar behavior was observed with trifluoromethylmercuric bromide.[18]

Registry No.—Phenyl(trifluoromethyl)mercury, 24925-18-6; sodium iodide, 7681-82-5; trifluoromethylmercuric iodide, 421-11-4; trifluoromethylmercuric trifluoroacetate, 675-25-2; trifluoromethylmercuric chloride, 421-10-3; phenylmercuric iodide, 823-04-1.

Acknowledgments.—The authors are grateful to the U. S. Air Force Office of Scientific Research (NC)-OAR for generous support of this work (Grant AF-AFOSR-72-2204) and to M & T Chemicals, Inc., for gifts of chemicals.

Synthesis of (Fluoren-9-ylidene)(dibenzo[*a,d*]cyclohepten-5-ylidene)methane. Allenes as Ground-State Carbenes. I[1]

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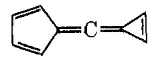
The first representative of a novel class of allenes (**3**) was synthesized by dehydrogenation of the dihydro precursor **9**, the latter compound being formed by the reaction of the phosphonium ylide **8** with the aldehyde **7**. Interest in the allene was based on the possibility that polarization of the cumulene linkage, resulting from the special properties of the end groups, would impart divalent character to the central carbon. Spectroscopic data on the allene indicated that this expectation was only minimally realized in this tetraannelated representative.

Hine[2] has suggested that a stable carbene might be formed if the electron-deficient carbon is attached to an electron donor and an electron acceptor.

$$\ddot{X}-\ddot{C}-Y \longleftrightarrow \overset{+}{X}=C=\overset{-}{Y}$$

Using what might be considered an inversion of this concept, it occurred to us that allenes, appropriately substituted, might exhibit divalent character in the ground state. Two prototypical allenes (**1** and **2**) exemplify this concept.



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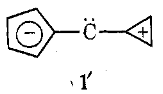
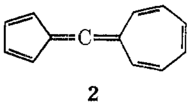


1′



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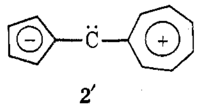
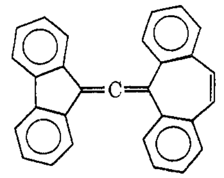


2′

Neither **1** nor **2**, which are obviously closely related to the calicenes,[3] nor any of their derivatives are known compounds. In order, then, to examine the feasibility of this concept, the synthesis of the tetraannelated derivative, (fluoren-9-ylidene)(dibenzo[*a,d*]cyclohepten-5-ylidene)methane (**3**), was undertaken. The representative **3** of this novel class of allenes was chosen as the initial goal because of the added stability that annelation should impart to such a system and because of the commercial availability of certain suitable starting materials.



3

Results and Discussion

The synthesis of **3** was accomplished using the reaction sequence shown in Scheme I.

Synthesis of **9** was straightforward and proceeded in good yield. Reaction of **9** with DDQ in benzene provided a soluble fraction consisting of the allene and unreacted **9** and an insoluble fraction consisting of the hydroquinone and the tropylium salt **13**. Based on the analogy of the reaction of tropylidene itself with DDQ,[4] it was initially assumed that the structure of the salt was **11**. However, treatment of the salt with a variety of bases failed to convert it to the allene. Furthermore, the elemental analysis correlates substantially better with structure **13** than with **11**.

The allene is a colorless solid, mp 242°, and its structure was established by several lines of evidence. Thus, the elemental analysis, molecular weight deter-

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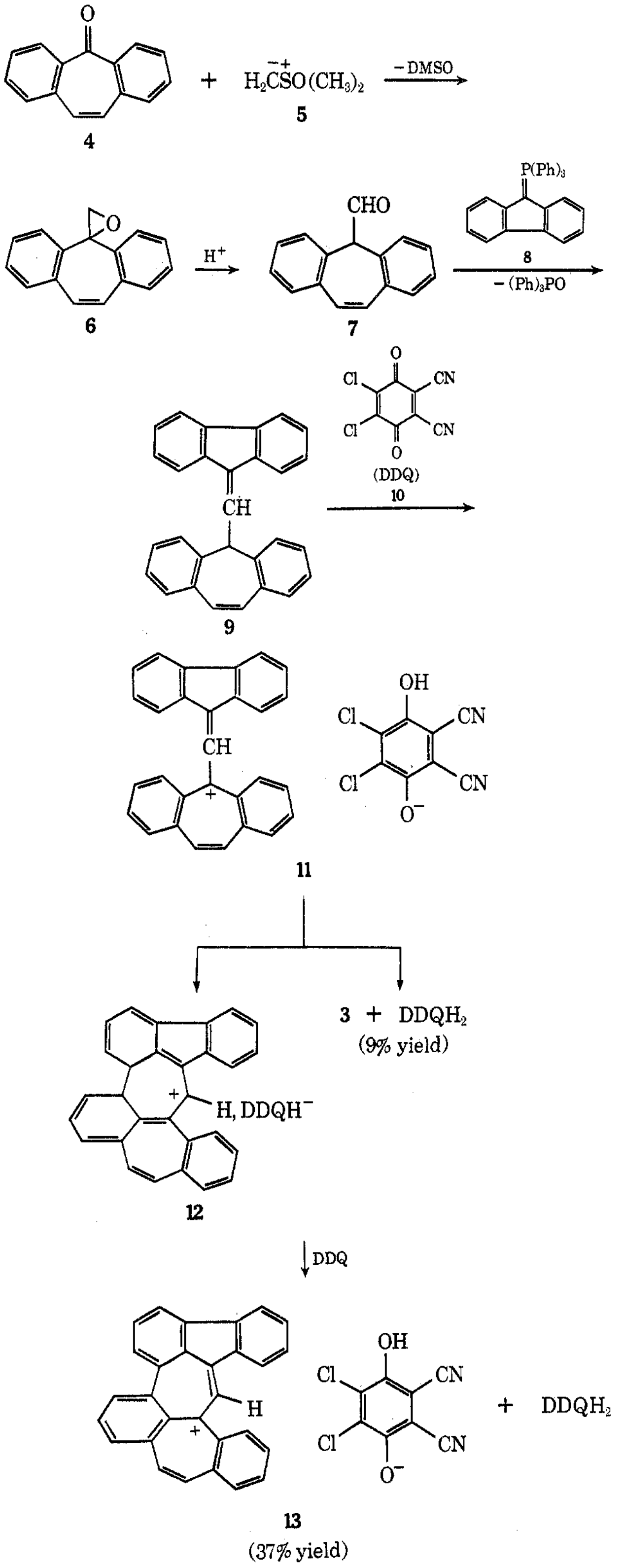
[1] This work was supported by The Petroleum Research Fund, administered by The American Chemical Society, Grant 1339-G1.

[2] J. S. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964, p 170.

[3] G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, Cambridge, England, 1969, p 76.

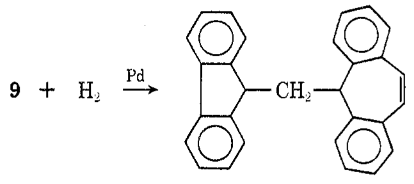
[4] D. H. Reid, M. Frazer, B. B. Molloy, H. A. S. Payne, and R. G. Sutherland, *Tetrahedron Lett.*, 530 (1961).

SCHEME I



mination, and mass spectrum were all consistent with the molecular formula $C_{29}H_{18}$. The infrared spectrum, in addition to bands characteristic of ortho-disubstituted benzene, exhibited a band of medium intensity at 1933 cm^{-1}, consistent with the presence of an allene group. The nmr spectrum showed the correct proton ratio and the ultraviolet spectrum was similar to that of a model allene, 2-(fluoren-9-ylidene)-1,1-diphenylethene.[5]

The allene appears to be indefinitely stable in the solid state, although solutions of **3** yellow on standing, presumably to give oxidation products. Attempts to reduce the allene by catalytic hydrogenation failed. The precursor **9** readily absorbs 1 equiv of hydrogen to give (fluoren-9-yl)(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)methane (**14**). Hydrogenation of **3** to **14** would have



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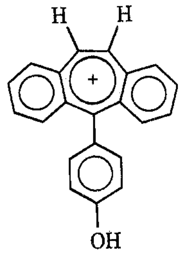
provided a rigorous proof of structure. Chemical reduction of **3** using $NaBH_4$, $LiAlH_4$, or Na/EtOH occurs rapidly but gives a variety of products, none of which is either **9** or **14**.

Having secured the allene **3**, it was of considerable interest to determine the electron distribution in its ground state, *i.e.*, to determine to what extent, if any, the dipolar carbene form contributes to the ground state of **3**. The simplest probe for this purpose appears to be the chemical shift of the protons of the seven-membered ring. Any development of positive charge in this ring should cause the protons in question to be deshielded compared to those in uncharged systems. Thus, in the charged model compound **15** the



15

chemical shift of the protons on the seven-membered ring is reported to be 535 Hz.[6] In the uncharged model compound, 5-methylene-5*H*-dibenzo[*a*,*d*]cycloheptene, the chemical shift of these protons is 403 Hz. In the allene **3** the chemical shift is observed at 408 Hz. It would appear then that, based on the nmr analysis, the carbene resonance form makes at best a meager contribution to the ground state of **3**. Further support for this conclusion is found in the fact that the ultraviolet spectrum of **3** is insensitive to solvent polarity, methanol and cyclohexane solutions of **3** having identical spectra.

The absence of significant carbene character in **3**, while disappointing, was not altogether unexpected, for, although the annelation of the central rings by four benzene rings can be expected to stabilize the system, a counter effect, the tendency to suppress the development of aromatic character in the central rings through bond localization, will reduce the contribution from the polar carbene form.[7] With this in mind the nonannelated representatives **1** and **2** remain attractive candidates for synthesis.

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[5] H. Fischer and H. Fischer, *Chem. Ber.*, **97**, 2978 (1964).

[6] B. Foehlisch, *Justus Liebigs Ann. Chem.*, **721**, 52 (1969).

[7] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 109.

Experimental Section

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Ir spectra were recorded on a Perkin-Elmer Infracord, Model 137; uv spectra on a Cary 14 spectrophotometer; and nmr spectra on a Varian Associates A-60 instrument, chemical shifts relative to tetramethylsilane.

5-Methylene-5*H*-dibenzo[*a*,*d*]cyclohepten-5,12-oxide (6).—The epoxide **6** was prepared by a modification of the Corey-Chaykovsky reaction.[8] A stirred solution of trimethyloxosulfonium iodide (1.76 g, 8 mmol) in 10 ml of dry dimethyl sulfoxide (DMSO) at 10° under nitrogen was treated with 5 ml of 1.6 *M* *n*-butyllithium in hexane (Foote Mineral Co.). After 10 min, 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (1.03 g, 5 mmol, Aldrich Chemical Co.) in 10 ml of dry DMSO was added in one portion. The mixture was warmed to 50–55° and stirred for 3 hr, then cooled and diluted with water (50 ml) and 1:1 benzene–hexane (50 ml). The organic layer was separated, washed five times with water, dried ($MgSO_4$), and filtered. Evaporation of the filtrate gave the crude epoxide **6** as a pale yellow oil (1.01 g) which crystallized on cooling. Recrystallization from benzene–hexane gave the pure epoxide (0.88 g, 86%) as colorless prisms: mp 92–93°; uv (EtOH) 221 nm (ϵ 25,000) and 228 (14,000); ir (KBr) 6.75, 7.64, 9.85, 10.81, 11.21, 11.65, 12.43, 12.70, 13.02, 13.15, 13.40, and 13.92 μ; nmr ($CDCl_3$) 7.2–7.8 (m, 8, aromatic), 7.0 (s, 2, seven-membered ring), and 2.67 ppm (s, 2, CH_2).

Anal. Calcd for $C_{16}H_{12}O$: C, 87.24; H, 5.49. Found: C, 86.97; H, 5.46.

The epoxide decomposes at room temperature but is stable at freezer temperature. The crude epoxide was found to be suitable for conversion to the aldehyde **7**.

5*H*-Dibenzo[*a*,*d*]cyclohepten-5-carboxaldehyde (7).—A solution of crude **6** (2.0 g) and *p*-toluenesulfonic acid (150 mg) in dry benzene (100 ml) was refluxed for 5 hr under nitrogen. The cooled solution was washed successively with bicarbonate and water, dried ($MgSO_4$), and filtered. Evaporation of the filtrate provided a yellow solid which was recrystallized from benzene–hexane to give the aldehyde **7** as colorless needles (1.0 g), mp 109–111° (lit.[9] mp 112–114°).

(Fluoren-9-ylidene)(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)methane (9).—Fluoren-9-ylidene triphenylphosphorane (**8**) (9.0 g), prepared by the method of Pinck and Hilbert,[10] was combined with the aldehyde **7** (4.66 g) in benzene (40 ml) in a sealed tube and heated at 100° for 20 hr. The tube was cooled and opened, and the benzene was evaporated. The yellow, oily residue was chromatographed on a 5 × 100 cm column of silica gel using benzene (4 l.) as the eluent. Evaporation of the eluent provided a yellow solid (6.56 g), uniform by tlc, which was recrystallized from benzene–hexane to give **9** as very pale yellow prisms (5.11 g, 66%): mp 157–159°; uv (EtOH) 220 nm (ϵ 59,000), 245 (37,300), 255 (52,400), 280 (31,100), 298 (25,900), and 313 (21,900); ir (KBr) 6.77, 6.95, 12.60, 12.82, 12.99, 13.10, 13.49, 13.55, and 13.85 μ; nmr ($CDCl_3$) 7.1–8.2 (m, 19) and 5.67 ppm (d, J = 10.5 Hz, 1, methine H of the seven-membered ring).

Anal. Calcd for $C_{29}H_{20}$: C, 94.54; H, 5.46. Found: C, 94.29; H, 5.54.

Hydrogenation of 9 to (Fluoren-9-yl)(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)methane (14).—A mixture of **9** (189 mg, 0.5 mmol), absolute EtOH (35 ml), and 10% Pd/C (23 mg) was treated with hydrogen at atmospheric pressure and room temperature. Hydrogen uptake (0.5 mmol) was complete after 90 min. The catalyst was filtered (Celite) and evaporation of the filtrate gave a white, crystalline solid which was recrystallized from EtOH (30 ml) to give **14** (80 mg, 42%) as colorless needles: mp 147–150°; uv (EtOH) 266 nm (ϵ 22,300), 290 (16,400), and 300 (16,900); ir (KBr) 6.73, 6.93, 10.66, 12.50, 13.09, 13.50, 13.70, and 13.81 μ; nmr ($CDCl_3$) 6.75–7.85 (m, 18), 3.98 (t, J = 7.5 Hz, 1, methine H of the fluorenyl group), 3.66 (t, J = 5.0 Hz, 1, methine H of the seven-membered ring), and 2.59–2.41 ppm (doublet of doublets, J = 5.0 Hz, 2, CH_2). The hydrogenation equivalent and nmr spectrum indicate that the endocyclic double bond of the seven-membered ring was not reduced.

Anal. Calcd for $C_{29}H_{22}$: C, 94.01; H, 5.99. Found: C, 94.06; H, 5.94.

Reaction of 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) with 9. Formation of the Allene 3 and the Tropylium Quinolate Salt 13.—To a refluxing solution of **9** (368 mg, 1 mmol) in benzene (10 ml) was added a solution of DDQ (Aldrich Chemical Co., 250 mg, 1.1 mmol) in benzene (10 ml) over a 2-min period. A copious precipitate formed during the addition and after an additional 5 min the mixture was cooled and the precipitate was filtered. The precipitate was labeled fraction A and the filtrate fraction B.

Fraction A. Isolation of the Salt 13.—This fraction consisted of a mixture of the hydroquinone (146 mg) and the salt **13** (162 mg). Washing the precipitate with MeOH (20 ml) selectively dissolved the hydroquinone and left the insoluble salt **13** as glistening gold platelets: mp 280° dec (blackens without melting on continued heating); ir (KBr) 3.00 (-OH), 4.49 (-CN), 7.00, 7.12, 7.54, 7.72, 7.91, 8.27, 8.49, 10.02, 10.74, 12.27, and 13.32 μ; uv (dioxane) 225 nm (ϵ 75,900), 268 sh (41,700), 314 (15,800), 327 (17,000), 342 (12,600), and 360 (9330).

Anal. Calcd for $C_{37}H_{18}Cl_2N_2O_2$: C, 74.87; H, 3.06; Cl, 11.95; N, 4.72. Found: C, 74.84; H, 3.08; Cl, 12.44; N, 5.07.

Fraction B. Isolation of the Allene 3.—The filtrate was evaporated to dryness and the residue was chromatographed on a thick layer of silica gel G using 50% benzene in hexane as the eluent. The uppermost band was eluted and recrystallized from benzene–hexane to give the allene **3** as colorless needles (32 mg, 9%): mp 242–245° dec; ir (KBr) 5.17 (C=C=C), 6.67, 6.85, 12.28, 12.69, 12.91, and 13.37 μ; uv (cyclohexane) 227 nm (ϵ 83,200), 246 (57,500), 255 (64,600), 279 sh (39,800), 287 (45,700), 302 (41,700), 315 (43,700); the uv spectrum is identical in MeOH; nmr ($CDCl_3$) 7.00–8.17 (m, 16, aromatic), 6.82 ppm (s, 2, seven-membered ring H); mass spectrum molecular ion m/e 366 (base peak; calcd for $C_{29}H_{18}$, 366); mol wt (osmometric in benzene), found 351.

Anal. Calcd for $C_{29}H_{18}$: C, 95.05; H, 4.95. Found: C, 94.74; H, 4.68.

Registry No.—**3**, 36146-49-3; **6**, 16036-73-0; **9**, 36146-51-7; **13**, 36079-64-8; **14**, 36079-65-9.

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[8] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1358 (1965).

[9] S. J. Cristol and L. K. Bly, *ibid.*, **82**, 6155 (1960).

[10] L. A. Pinck and G. A. Hilbert, *ibid.*, **69**, 723 (1947).