tions were then examined on tlc in system A. An authentic sample of the DKP -L-Pro-Gly- was used for comparison. Spots were revealed by ninhydrin and with *tert*-butyl hypochlorite, followed by KI-starch.[33] In a solution that was heated for 45 min, no DKP was detected, while in a solution heated for 26 hr more than half of the dipeptide was converted to the DKP.

Acknowledgments. Amphomycin (Ca salt) was obtained as a gift from H. Lundbeck and Co., Copenhagen-Valby, Denmark. The authors express their gratitude to Dr. L. Szabo for the generous samples. Elemental analyses were carried out by Mr. Joseph Alicino of the Squibb Institute for Medical Research, and amino acid analyses by Mrs. Delores J. Gaut. The assistance of Mr. Anthony Severdia in the ir studies is greatly appreciated. The entire study was supported by a grant from the U. S. Public Health Service (NIH AI-07515).

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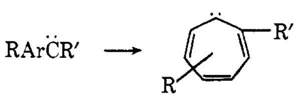
[33] R. H. Mazur, B. W. Ellis, and P. Cammarata, *J. Biol. Chem.*, 237, 1619 (1962).

Communications to the Editor

Generation of a Ten-π-Electron Carbocyclic Aromatic Carbene by a Carbene–Carbene Rearrangement

Sir:

To date, carbene–carbene rearrangements of aryl carbenes to aromatic carbenes have been limited to high temperatures (225–900°), the gas phase, and six-π-electron aromatic carbenes (1).[1] At this time, we



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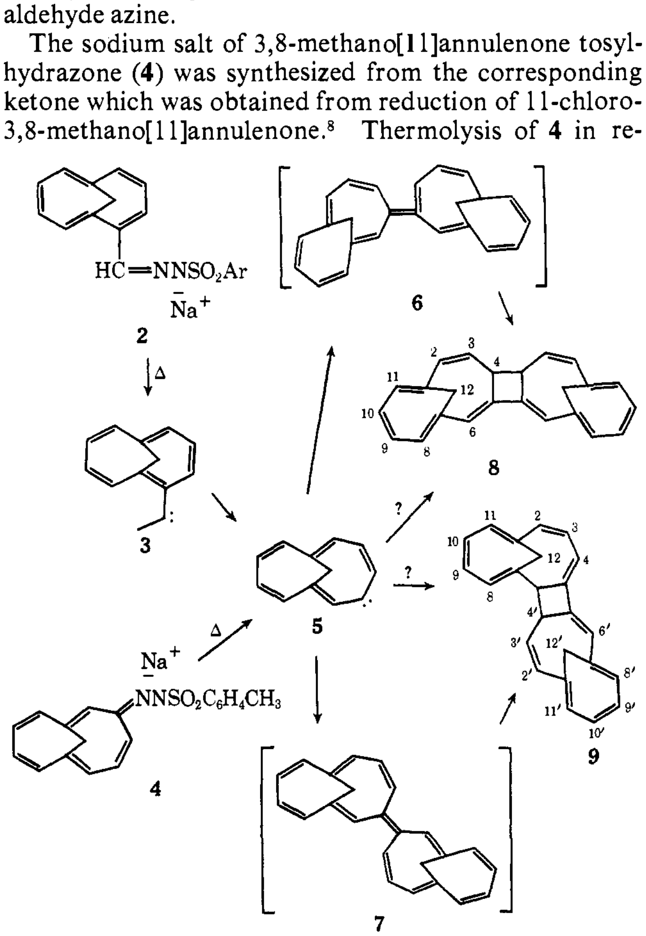
report the isolation and characterization of substantial yields (50–60%) of **8** and **9** from the thermal generation of **3** in diglyme at moderate temperatures (as low as 130°). Taken with the formation of the same products from thermolysis of the sodium salt of the ketone tosylhydrazone **4**, these products constitute strong evidence for the first known rearrangement of an arylcarbene to an aromatic carbene[2] in solution. In addition, the products are also indicative of either an unprecedented 22 π-electron electrocyclic ring closure of the undecafulvalenes **6** and **7** or an atypical aromatic carbene.

The parent methanoannulene was synthesized according to the method of Vogel[3] as modified by Untch.[4] The hydrocarbon was converted to the carboxylic acid[3] and the acid converted to the aldehyde by initial quantitative reduction (lithium aluminum hydride), followed by oxidation (76% yield) of the primary alcohol with freshly prepared MnO_2[5] in acetonitrile. The tosylhydrazone[6] and its sodium salt (**2**) were prepared in the conventional way.

In a typical reaction, the carbene was generated by addition over a 10-min period of 0.5 g of **2** in 15 ml of dry diglyme to 50 ml of rapidly stirred dry diglyme (dry nitrogen swept) maintained at about 135° (minimum of 130°). The reaction mixture was then rapidly cooled to room temperature (to minimize product polymerization), poured into water, and extracted with pentane. Careful column chromatography on silica gel eluting with pentane typically resulted in isolation of two major hydrocarbon products,[7] **8** and **9**, in 50–60% total yield along with a modest amount of annulenyl aldehyde azine.

The sodium salt of 3,8-methano[11]annulenone tosylhydrazone (**4**) was synthesized from the corresponding ketone which was obtained from reduction of 11-chloro-3,8-methano[11]annulenone.[8] Thermolysis of **4** in re-



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[1] R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, 91, 7754 (1969); J. A. Myers, R. C. Joines, and W. M. Jones, *ibid.*, 92, 4740 (1970); T. Mitsuhashi and W. M. Jones, *ibid.*, 94, 677 (1972); E. Hedaya and M. E. Kent, *ibid.*, 93, 3283 (1971); P. Schissel, M. E. Kent, D. J. McAdoo, and E. Hedaya, *ibid.*, 92, 2147 (1970); G. G. Vander Stouw, A. R. Kraska, and H. Shechter, *ibid.*, 94, 1655 (1972), and references cited therein; W. J. Baron, M. Jones, Jr., and P. P. Gaspar, *ibid.*, 92, 4379 (1970).

[2] For a report on the properties of an isomeric ten-π-electron carbocyclic aromatic carbene, see R. A. LaBar and W. M. Jones, *ibid.*, 95, 2359 (1973).

[3] E. Vogel, *Chem. Soc., Spec. Publ.*, No. 21, 113 (1967).

[4] P. H. Nelson and K. G. Untch, *Tetrahedron Lett.*, 4475 (1969).

[5] J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

[6] Except where noted, all new compounds gave satisfactory elemental analyses.

[7] Subjection of **8** and **9** to the original reaction conditions resulted in no detectable interconversion but only polymerization to colorless solids.

[8] We thank Professor E. Vogel for generously providing a sample of the chloroannulenone.

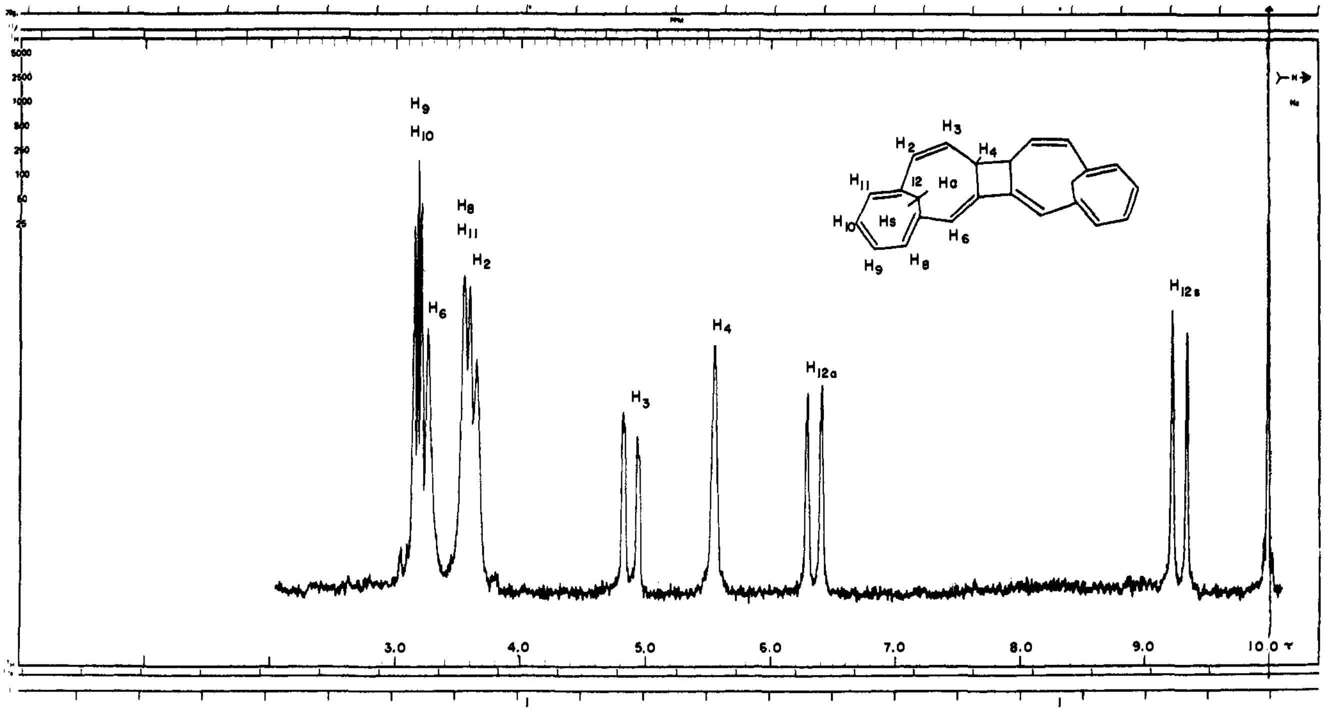

Figure 1. The 100-MHz proton magnetic resonance spectrum of **8**.

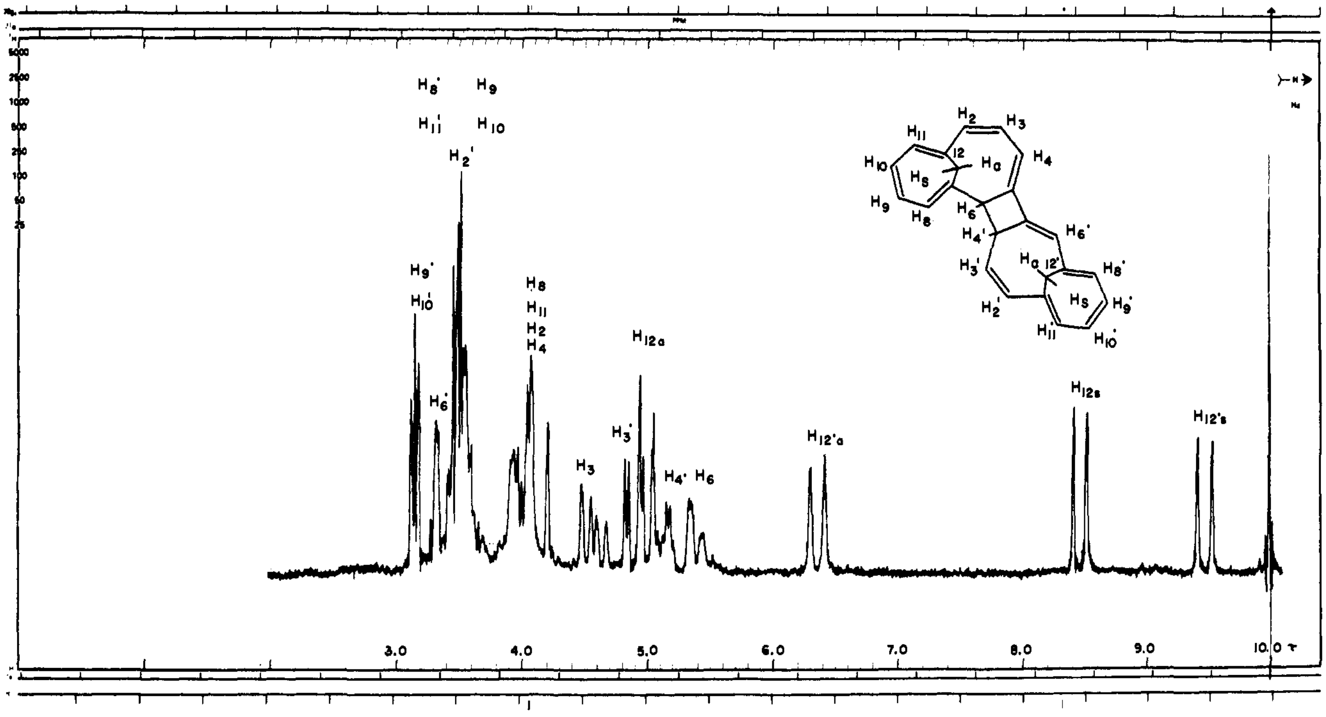

Figure 2. The 100-MHz proton magnetic resonance spectrum of **9**.

fluxing diglyme (5 min) gave 40% of a mixture of **8** and **9**.[9]

The two hydrocarbons exhibited similar spectral properties: uv (λ_{max} in pentane) 293 nm (ϵ 40,600), 425 (15,100) for **8** and 289 (23,000), 440 (8730) for **9**; high-resolution mass spectra for both, 308.1563 (calcd for $C_{24}H_{20}$, 308.1564); ir 3000, 1450, 1265, 1070, 880, 790 cm^{-1} for **8** and 3000, 1445, 1360, 1265, 880, 750 for **9**.

Detailed structural assignments of **8** and **9** rest primarily on their pmr spectra (Figures 1 and 2) including spin decoupling data.[10]

Spin decoupling has unequivocally established the following relationships in **8** (see spectrum): H_{12a}–H_{12s} (6.35 and 9.28 τ), a two-hydrogen AB system of 12.0 Hz coupling (eliminating a norcaradiene structure); H_2–H_3 (3.6 and 4.88 τ), a two-hydrogen AB system of 12.0 Hz coupling; H_6–H_{12s} (3.26 and 9.28 τ), long-

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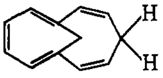
(9) A more complete account of the chemical properties of **5** generated from both precursors will be reported in a later publication.

(10) Complete detailed decoupling data will be presented in the full paper.

range coupling of 0.5 Hz; H_2–H_{12s} (3.26 and 9.28 τ), long-range coupling of 0.5 Hz; $H_8{}'H_{11}$–H_{12a} (3.6 and 6.35 τ), long-range coupling of 0.5 Hz; H_3–H_4 (4.88 and 5.54 τ) with 1-Hz coupling; H_2–H_4 (3.6 and 5.54 τ), long-range coupling <0.5 Hz.

Although more complex, the nmr spectrum of **9** also yielded to extensive decoupling[10] as follows: two sets of two-hydrogen AB resonances, H_{12a}–H_{12s} (4.99 and 8.46 τ) of 10.5-Hz coupling and $H_{12'a}$–$H_{12's}$ (6.35 and 9.47 τ) of 12-Hz coupling; a complex ABMX system, $H_{2'}$–$H_{3'}$–$H_{4'}$–H_6 (3.5, 4.89, 5.10, and 5.39 τ), with 11.5-, 3.0-, and 9.5-Hz coupling, respectively; an AMX system, H_2–H_3–H_4 (4.14, 4.57, and 4.01 τ) with 12.5- and 7.5-Hz coupling. Long-range coupling (0.5–1 Hz) was found for H_2–H_{12s} (4.14 and 8.46 τ) and also $H_{6'}$–$H_{12's}$ (3.32 and 9.47 τ). Taken with the similarity of the nmr spectra with closely related compounds[2,11] (such as **8** compared with **10** and **11** or **9** compared with **10** or **11** superimposed on **12**), there is no question of the gross structures of **8** and **9**, although their stereochemistry remains an open question.



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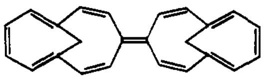

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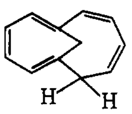

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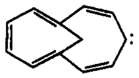
Formation of **8** and **9** from **4** as well as **2** leaves little question but that the arylcarbene **3** undergoes carbene–carbene rearrangement to **5**. Furthermore, the known propensity of both cycloheptatrienylidene[12] and 4,9-methano[11]annulenylidene[2] (**13**) to dimerize is certainly sound precedent for the formation of **6** and **7**[13] which could then undergo electrocyclic ring closures[13,15] to give **8** and **9**. On the other hand, unless **6** and **7** can actually be detected and shown to undergo the necessary ring closures under the reaction conditions, we do not feel that the possibility of a direct dimerization of **5** to give the final products can be excluded.



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Finally, it is worth noting that, if **8** and **9** are formed *via* **6** and **7**, a gain in homoaromaticity is an attractive rationale for this unique tendency to undergo ring closure (especially when compared with other fulvalenes such as heptafulvalene and the undecafulvalene **11**).

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Received September 12, 1972

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(11) For **10** and **12**, see E. Vogel, F. Feldmann, and H. Duwell, *Tetrahedron Lett.*, 1941 (1970); for other closely related compounds, see H. Prinzbach, *Pure Appl. Chem.*, **28**, 281 (1971).

(12) W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, **91**, 6391 (1969).

(13) On the basis of steric considerations alone, formation of a predominance of two of the four possible dimers of **5** would be expected if aromatic carbenes dimerize by the same mechanism as has been proposed for the dimerization of methylene.[14] Furthermore, on these same grounds it would be predicted that **6** and **7** would be the syn isomers. Finally, the thermally allowed electrocyclic ring closure of the two syn isomers would lead to structures with the symmetry required by the nmr spectra of **8** and **9**.

(14) R. Hoffmann, R. Gleiter, and F. B. Mallory, *J. Amer. Chem. Soc.*, **92**, 1460 (1970); H. Kellmar, *Tetrahedron Lett.*, 3337 (1970).

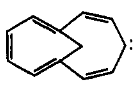
(15) For an example of ring closure of a vinylfulvalene, see H. Sauter and H. Prinzbach, *Angew. Chem., Int. Ed. Engl.*, **11**, 296 (1972).

4,9-Methano[11]annulenylidene. An Example of a Ten-π-Electron Carbocyclic Aromatic Carbene

Sir:

The chemistry of singlet carbenes in which the vacant orbital is integrated into a conjugated carbocyclic ring system with two or six π electrons has been found to be significantly different from that of their less highly perturbed relatives.[1,2] For example, neither diphenylcyclopropenylidene nor cycloheptatrienylidene shows any tendency to insert into single bonds or add to electron-rich double bonds.[3] On the other hand, both intermediates add readily to electron-deficient double bonds and, in addition to a strong tendency to dimerize, cycloheptatrienylidene has recently been found to add to substituted styrenes as a nucleophilic species[4] ($\rho = +1.0$; $\rho_{CCl_2} = -0.619$ at 80°,[5] -0.378 at 0° [6]).

At this time we present a preliminary report of the apparently successful generation of 4,9-methano[11]annulenylidene, an example of a ten-π-electron carbocyclic aromatic carbene.[7]



The ten-π-electron carbene was generated by the Bamford–Stevens[8] reaction. The requisite 4,9-methano[11]annulenone[9] (**1**) was synthesized by the method developed by Vogel.[10] The ketone was converted to its tosylhydrazone[11] **2** by refluxing with *p*-toluenesulfonhydrazide for 3 hr in acidic absolute ethanol.

The sodium salt was generated by treating a solution of **2** in dry THF with 10% excess sodium hydride (dry-

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(1) For a theoretical treatment, see R. Gleiter and R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 5457 (1968).

(2) (a) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1971, Chapter 8; (b) J. Hine, "Divalent Carbon," Roland Press, New York, N. Y., 1964, p 43.

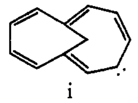
(3) W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, **91**, 6391 (1969), and references cited therein.

(4) L. W. Christensen, E. E. Waali, and W. M. Jones, *ibid.*, **94**, 2118 (1972).

(5) D. Seyferth, J. Y.-P. Mui, and R. Damrauer, *ibid.*, **90**, 6182 (1968).

(6) J. H. Sadler, *J. Chem. Soc. B*, 1024 (1969).

(7) For a report of the generation of 3,8-methano[11]annulenylidene (i), see P. H. Gebert, R. W. King, R. A. LaBar, and W. M. Jones, *J. Amer. Chem. Soc.*, **95**, 9357 (1973).



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(8) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952); W. Kirmse, B. G. von Bulow, and H. Schepp, *Justus Liebigs Ann. Chem.*, **691**, 41 (1966).

(9) W. Grimme, J. Reisdorff, W. Junemann, and E. Vogel, *J. Amer. Chem. Soc.*, **92**, 6335 (1970).

(10) We are indebted to Professor Vogel for his encouragement and helpful suggestions in all of our work on the methanoannulenylidenes.

(11) Except where noted, all new compounds gave satisfactory elemental analyses and spectra consistent with the assigned structures.