Table I. Products from Thermolysis and Photolysis of Tetrazene 3

method (conditions)[a]	solvent	% yield[b] 4	5	6	7 + 8
thermolysis[c] (160 °C, 8 h)	THF	36	3	30	9
thermolysis[d] (160 °C, 8 h)	$c\text{-}C_6H_{12}$	33	4	30	9
photolysis[d] (25 °C, 5 h)	THF	15	18	31	14
photolysis[d] (25 °C, 5 h)	ether	10	14	32	18
photolysis[d,e] (25 °C, 5 h)	$c\text{-}C_6H_{12}$	12	16	32	20

[a] Solutions of 3 (0.08 M) were sealed in Pyrex tubes and thermalized or photolyzed with a 450-W high-pressure mercury lamp. [b] Absolute yield determined by GC employing a standard (tetradecane) added after the reaction. [c] Average of five runs. [d] Average of two runs. [e] Similar product ratios were observed at 1-, 2-, and 3-h irradiation.

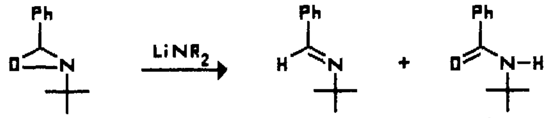
Table II. Products from Reactions of Probe 1 with Oxaziridine 9 in THF at 25 °C[a]

run	[1][b]	[9]/[1][c]	time, h	% yield[d] 4	6	[4]/[10][e]
1	0.10	0	3	<0.1	100	
2	0.10	0.2	3	2.7	93	0.18
3	0.05	0.2	4	2.8	88	0.19
4	0.10	0.4	3	3.8	89	0.13
5	0.05	0.4	4	4.4	80	0.15
6	0.10	0.8	3	5.7	82	0.10
7	0.05	0.8	4	8.8	76	0.14

[a] To a solution of 1 at 25 °C was added the appropriate amount of oxaziridine 9. After 3-4 h at 25 °C, the reaction mixture was quenched, and the products were analyzed by GC. [b] Initial molar concentration of probe 1. [c] Initial ratio of oxaziridine 9 to probe 1. [d] Absolute yield determined by GC employing an internal standard of tetradecane. [e] Ratio of moles of 4 formed to moles of 10 formed.[8]

absolute product yields are given in Table I. These results show that cyclization of aminyl radical **2** occurred as one of the major reaction pathways, that the products were formed to a large degree by disproportionation reactions,[9] and that products **4–8** did not arise by secondary photochemical processes. The details of the reactions of radical **2** are of continuing interest to us, but for this work the important point is that cyclization of **2** occurred in tetrahydrofuran (THF).

We next investigated the potential for applying lithium amide **1** as a mechanistic probe. Lithium amide **1**, prepared by treating the parent amine[8] with n-BuLi in THF at −78 °C, did not rearrange at 25 °C (Table II, run 1). Thus, interfering anionic skeletal rearrangements[7] are not a problem with **1**. Probe **1** was allowed to react with (E)-2-*tert*-butyl-3-phenyloxaziridine (**9**), a substrate that apparently reacts with lithium dialkylamides (eq 3)[2c] and organometallic reagents[10] by electron-transfer processes.



9 10 11 (3)

When oxaziridine **9** was treated with an excess of lithium amide **1**, we observed formation of pyrrolidine **4** (Table II). This implicates aminyl radical **2** as an intermediate in the reaction and strongly suggests that an electron-transfer step occurred. The last column in Table II is the ratio of the moles of pyrrolidine **4** formed in the reactions to the moles of **10** formed.[8] Despite the scatter, the consistency of this ratio leads us to believe that lithium amide probe **1** may provide *quantitative* as well as qualitative evidence of aminyl radical formation, but further studies of the details of these reactions are required before the quantitative utility of probe **1** is known.

We are continuing studies with probe **1** and are attempting to find aminyl radicals that rearrange more efficiently than **2**. However, the results presented herein demonstrate the utility of our approach for implicating aminyl radical formation and, by inference, electron-transfer processes in reactions of hindered lithium dialkylamides.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Robert A. Welch Foundation for support of this research. We thank Professors M. A. Fox and N. A. Kornblum for discussions that led to the inception of this work.

Registry No. 1, 88015-36-5; **2**, 88015-37-6; **3**, 88015-30-9; **4**, 88015-31-0; **5**, 88015-32-1; **6**, 88015-33-2; **7**, 88015-34-3; **8**, 88015-35-4; **9**, 7731-34-2; **10**, 6852-58-0; **11**, 5894-65-5; 5-methyl-4-hexen-1-ol tosylate, 61755-53-1; 1-butanamine, 109-73-9; pyrrolemagnesium bromide, 6123-07-5; 2-bromopropane, 75-26-3.

Supplementary Material Available: Brief description of the syntheses of **6**, **3**, and **4**, references for the syntheses, and methods used to identify products in eq 2 and to determine the yield of **10** from reaction of **1** with **9** (1 page). Ordering information is given on any current masthead page.

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[9] Aminyl radicals are feeble hydrogen atom abstractors: Michejda, C. J.; Hoss, W. P. *J. Am. Chem. Soc.* **1970**, *92*, 6298–6301.

[10] Davis, F. A.; Mancinelli, P. A.; Balasubramanian, K.; Nadir, U. K. *J. Am. Chem. Soc.* **1979**, *101*, 1044–1045.

Decamethyl[5]pericyclyne. A Novel Homoconjugated Cyclic Polyacetylene[1]

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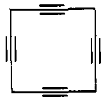
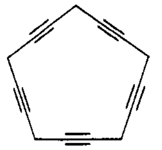
Received September 19, 1983

Cyclic hydrocarbons composed of N acetylenic units and N CH_2 groups alternating around the ring, e.g., **1**, **2**, and **3**, constitute


1


2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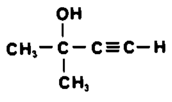
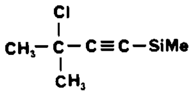
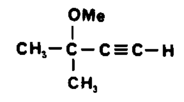
an intriguing family of compounds, which we refer to as the [N]pericyclynes. Such molecules, especially the smaller ones, should offer an excellent opportunity to assess the importance of "homoconjugation" in neutral systems.[2] We report here a synthesis of decamethyl[5]pericyclyne,[3] the first member of this family to be prepared, and present evidence for a strong electronic interaction among the five acetylenic units therein.

All 25 carbon atoms of the title compound have been assembled from a common five-carbon unit: the readily available 2-methyl-3-butyn-2-ol (**4**). By literature methods, two basic building


$$\mathrm{CH_3{-}\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}{-}C{\equiv}C{-}H}$$
4


$$\mathrm{CH_3{-}\overset{\displaystyle Cl}{\underset{\displaystyle CH_3}{C}}{-}C{\equiv}C{-}SiMe_3}$$
5


$$\mathrm{CH_3{-}\overset{\displaystyle OMe}{\underset{\displaystyle CH_3}{C}}{-}C{\equiv}C{-}H}$$
6

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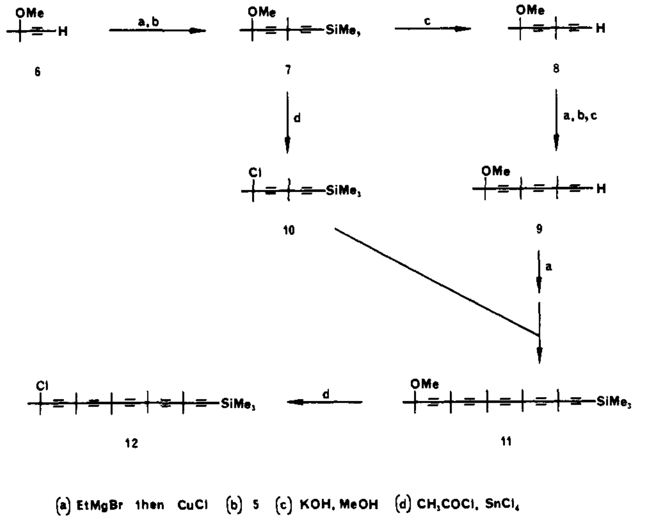
[1] Part 3 in the series on "Cyclynes". For preceding papers in this series, see: Santiago, C.; Houk, K. N.; DeCicco, G. J.; Scott, L. T. *J. Am. Chem. Soc.* **1978**, *100*, 692–696 and references cited therein.

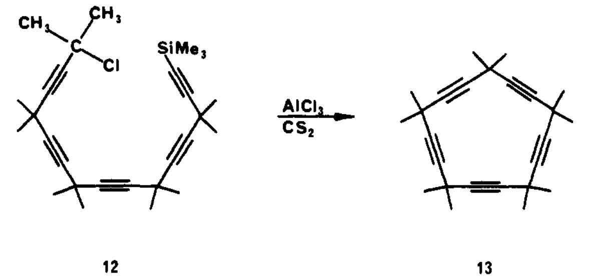
[2] For one recent theoretical treatment, see: Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797–6802. See also: Klingensmith, K. A.; Püttmann, W.; Vogel, E.; Michl, J. *Ibid.* **1983**, 3375–3380. Paquette, L. A.; Snow, R. A.; Muthard, J. L.; Cynkowski, T. *Ibid.* **1979**, *101*, 6991–6996.

[3] IUPAC name: 3,3,6,6,9,9,12,12,15,15-decamethylcyclopentadeca-1,4,7,10,13-pentayne.

Scheme I



Scheme II



blocks, **5** and **6**, can be easily prepared from **4** on a large scale.[4] Deprotonation of **6** with EtMgBr followed by CuCl-catalyzed coupling[5] with **5** gives the diacetylene **7**. Desilylation of **7** with KOH/MeOH then yields **8**, a simple homologue of **6**. Now **8** can likewise be deprotonated and coupled with **5** to give, after desilylation, the triacetylene **9**. Repetition of this homologation sequence through two more cycles builds up compounds containing all five acetylenic units. Alternatively, the convergent synthesis depicted in Scheme I represents a more efficient route. Thus, the last two acetylenic units can be attached to **9** in a single reaction by coupling with **10**, a homologue of **5**.

Preparation of **10** was conveniently accomplished by treatment of **7** with acetyl chloride at room temperature. This reaction presumably entails acylation of the ether oxygen followed by an S$_N$1 reaction; Lewis acids have an accelerating effect but are not essential. The same procedure converts the pentaacetylene ether **11** to the corresponding chloride **12**. Since the reactions in Scheme I all proceed in reasonable yield (couplings 65–70%, chlorinations 75–85%, desilylations >90%), pentaacetylene **12** can be easily prepared in multigram quantities.

Cyclization of **12** to the title compound (**13**) was achieved in 35% yield by the slow addition of **12** to AlCl$_3$ in refluxing carbon disulfide (Scheme II). This reaction undoubtedly involves electrophilic attack on the alkynyl silane by a tertiary propargylic cation to form the last C–C bond.[6] Decamethyl[5]pericyclyne[3] is a colorless, air-stable compound: mp 201–202 °C. Anal. C, H. Mass spectrum M$^+$ calcd for C$_{25}$H$_{30}$ 330.2348, found 330.2346, *m/z* (rel intensity) 330 (24), 315 (100), 300 (7), 285 (30), 270 (12), 257 (17), 255 (11); ^{1}H NMR (CDCl$_3$) δ 1.42; ^{13}C NMR (CDCl$_3$) δ 82.2, 31.1, 25.6; IR (KBr) no C≡C str; Raman (crystal) 2276 (s), 2256 (w), 2244 (m), 2230 (s) cm^{-1}; UV (pentane) end absorption, no max >200 nm, 230 sh (ε 30).

Photoelectron spectroscopy (PES) provides the most compelling evidence for cyclic homoconjugation in **13**: the spectrum[7] shows one sharp π ionization potential (π-IP) at 9.07 eV, three additional (incompletely resolved) strong π-IPs at 9.31, 9.64, and 9.90 eV, and a final sharp π-IP at 10.20 eV. In the absence of any electronic interaction among the acetylenic units, the molecule would have five degenerate in-plane π bonds and five degenerate out-of-plane π bonds.[8] Such an arrangement would give rise to just one π-IP for the in-plane π electrons and to one π-IP for the out-of-plane electrons, i.e., to only two π-IPs, which might or might not be distinguishable by PES. Any cyclic homoconjugative interaction among the 10 p orbitals within each set, on the other hand, would split the bonding orbitals into an extensive array of delocalized molecular orbitals (LCAO-MOs) spanning a range of energies. Clearly, the PES of **13** cannot be accommodated by the "localized orbital" picture. The large number of π-IPs observed is difficult to explain without invoking cyclic homoconjugation, and the range of π-IPs (1.13 eV) indicates that the orbital interactions in **13** must be quite substantial. A more detailed analysis of the PES of **13**, aided by theoretical calculations, has been initiated.

We are currently preparing other members of this family and exploring the potentially novel chemistry of pericyclynes, e.g., transition-metal complexation.

Acknowledgment. We are indebted to Prof. K. N. Houk for the first PES of the title compound. Financial support from the National Science Foundation and the National Institutes of Health is gratefully acknowledged.

Registry No. **5**, 18387-63-8; **6**, 13994-57-5; **7**, 88057-35-6; **8**, 88057-36-7; **9**, 88057-37-8; **10**, 18306-51-9; **11**, 88057-38-9; **12**, 88057-39-0; **13**, 88057-40-3.

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(4) Shostakovskii, M. F.; Shikhiev, I. A.; Komarov, N. V. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1956**, 1271; *Chem. Abstr.* **1957**, *51*, 5690*a*. Hennion, G. F.; Sheehan, J. J.; Maloney, D. E. *J. Am. Chem. Soc.* **1950**, *72*, 3542–3545. Corey, E. J.; Floyd, D.; Lipshutz, B. H. *J. Org. Chem.* **1978**, 3418–3420.

(5) Zimmerman, H.; Pincock, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 3246–3250.

(6) Cf. the intramolecular *acylations* of alkynyl silanes that give macrocyclic ketones: Utimoto, K.; Tanaka, M.; Kitai, M.; Nozaki, H. *Tetrahedron Lett.* **1978**, 2301–2304.

(7) The PES of **13** was recorded at LSU in collaboration with K. N. Houk. The numbers reported here were obtained from six independent spectra and are all ±0.08 eV or better.

(8) Assuming D_{5h} symmetry in the gas phase. A planar ring with perfectly linear acetylenes would have internal angles at the vertices of 108°.

Confirmation of the Mayo Mechanism for the Initiation of the Thermal Polymerization of Styrene

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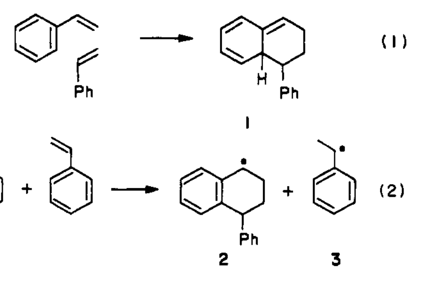
Received August 22, 1983
Revised Manuscript Received October 28, 1983

The mechanism of initiation in the thermal polymerization of styrene has challenged chemists for many years. The most widely accepted pathway for the spontaneous generation of radicals was proposed by Mayo in 1961 and is outlined in eq 1 and 2.[1] In



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(1) Mayo, F. R. *Polym Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1961**, *2*, 55; *J. Am. Chem. Soc.* **1968**, *90*, 1289.