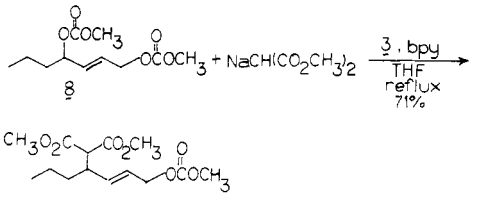
of the carbon bearing the leaving group was sufficiently great to be useful synthetically. Indeed, the dicarbonate **8** permits easy replacement of the secondary carbonate without affecting the primary carbonate for the limited reaction times employed (5 h).



The high regioselectivity of this alkylation presumably reflects the effect of polar substituents to direct the incoming nucleophile to the more distal allyl terminus—an observation we have noted in the other metal-catalyzed reactions.[12,13]

The ability of metals other than palladium, notably less expensive ones, to catalyze allylic displacements offers additional dimensions of selectivity. The tungsten catalyst is less reactive than either the molybdenum[2] or especially the palladium catalysts.[1] However, the electronic and steric demands of this catalyst permit a level of control of regiochemistry not available with the previous metal systems. The timed release of leaving groups as shown in **8** shows how subtle the differences can be and yet be differentiated by this selective template. The use of timed release of leaving groups can be particularly useful in complex synthesis.[13]

Acknowledgment. We thank the National Science Foundation for their generous support of our programs.

Registry No. 1, 62891-99-0; **2**, 18424-76-5; **3**, 16800-47-8; **4**, 87802-71-9; **5**, 87802-72-0; **6**, 87802-73-1; **7**, 87802-74-2; **8**, 87802-75-3; $CH_3OC(O)OCH(Ph)CH{=}CHCH_3$, 87802-76-4; $NaCH_3CE_2$, 62116-54-5; $NaCH(SO_2Ph)E$, 60729-65-9; $NaCH(SO_2Ph)_2$, 34782-39-3; $PhCH(CHE_2)CH{=}CH_2$, 87802-78-6; $PhCH(C(CH_3)E_2)CH{=}CH_2$, 87802-79-7; $PlCH(CH(SO_2Ph)E)CH{=}CH_2$ (isomer 1), 87802-81-1; $PhCH{=}CHCH_2CH(SO_2Ph)E$, 87802-82-2; $PhCH(CH(SO_2Ph)_2)CH{=}CH_2$, 87802-83-3; $PhCH{=}CHCH_2CH(SO_2Ph)E$, 87802-84-4; $PhCH(CHE_2)CH{=}CHCH_3$, 87802-85-5; $PhCH{=}CHCH(CH_3)CHE_2$, 87802-86-6; $CH_2{=}CHCH_2CHE_2$, 40637-56-7; bpy, 366-18-7; *i*-$C_3H_7CH(OC(O)OCH_3)CH{=}CH_2$, 87802-94-6; $CH_3CH{=}CHCH_2O$-$C(O)OCH_3$, 87802-95-7; $CH_3CH(CHE_2)CH{=}CH_2$, 61979-92-8; $CH_3CH{=}CHCH_2CHE_2$, 61979-94-0; *i*-$C_3H_7CH(CHE_2)CH{=}CH_2$, 87802-96-8; *i*-$C_3H_7CH{=}CHCH_2CHE_2$, 87802-97-9; $LiCH(CO_2CH_3)_2$, 74826-01-0; $Br(CH_2)_5CH(CHE_2)CH{=}CH_2$, 87802-99-1; Br-$(CH_2)_5CH{=}CH{-}CH_2CHE_2$, 87803-00-7; $CH_3CH_2CH_2CH(CHE_2)$-$CH{=}CHCH_2OC(O)OCH$, 87803-01-8; $PhCH(CH(SO_2Ph)E)CH{=}CH_2$ (isomer 2), 87803-03-0; 2-(1-((methoxycarbonyl)oxy)-2-propen-1-yl)pyridine, 87802-77-5; methyl 2-hydroxycyclopenten-1-carboxylate sodium salt, 63178-03-0; methyl 1-(1-phenyl-2-propen-1-yl)-2-oxocyclopentan-1-carboxylate (isomer 1), 87802-80-0; dimethyl (3-(2-furyl)-1-buten-4,4-dicarboxylate, 87802-87-7; dimethyl 3-(2-furyl)-1-penten-4,4-dicarboxylate, 87802-88-8; dimethyl 3-(2-thienyl)-1-buten-4,4-dicarboxylate, 87802-89-9; methyl 1-(1-(2-thienyl)-2-propen-1-yl)-2-oxocyclopentan-1-carboxylate (isomer 1), 87802-90-2; methyl 1-(3-(2-thienyl)-2-propen-1-yl)-3-oxocyclopentan-1-carboxylate, 87802-91-3; dimethyl 3-(2-pyridyl)-1-buten-4,4-diocarboxylate, 87802-92-4; dimethyl 1-(2-pyridyl)-1-buten-4,4-dicarboxylate, 87802-93-5; allyl acetate, 591-87-7; methyl *cis*-6-((methoxycarbonyl)oxy)cyclohexen-4-carboxylate, 87802-98-0; 1,10-phenanthralene, 66-71-7; methyl *cis*-6-(bis(methoxycarbonyl)methyl)cyclohexen-4-carboxylate, 64841-68-5; methyl *trans*-6-(bis(methoxycarbonyl)methyl)cyclohexen-4-carboxylate, 74545-66-7; methyl 1-(1-phenyl-2-propen-1-yl)-2-oxocyclopentan-2-carboxylate (isomer 2), 87803-02-9; methyl 1-(1-(2-thienyl)-2-propen-1-yl)-2-oxocyclopentan-1-carboxylate (isomer 2), 87803-04-1.

(12) Cf.: Trost, B. M.; Klun, T. P. *J. Am. Chem. Soc.* **1979**, *101*, 6756. Trost, B. M.; Schmuff, N.; Miller, M. *Ibid.* **1980**, *102*, 5979. Trost, B. M.; Molander, G. A. *Ibid.* **1981**, *103*, 5969. Also see: Tsuji, J.; Kataoka, H.; Kobayashi, Y. *Tetrahedron Lett.* **1981**, *22*, 2575. Valpey, R. S.; Miller, D. J.; Ester, J. M.; Godleski, S. A. *J. Org. Chem.* **1982**, *47*, 4717.

(13) Genet, J. P.; Balabane, M.; Backvall, J. E.; Nystrom, J. E. *Tetrahedron Lett.* **1983**, *24*, 2745. Genet, J. P.; Balabane, M.; Charbonnier, F. *Ibid.* **1982**, *23*, 5027. Tanigawa, Y.; Nishimura, K.; Kawasaki, A.; Murahashi, S. I. *Ibid.* **1982**, *23*, 5549. Backvall, J. E.; Nordberg, R. E.; Nystrom, J. E. *Ibid.* **1982**, *23*, 1617. Genet, J. P.; Balabane, M.; Legras, Y. *Ibid.* **1981**, *23*, 331. Backvall, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 4959. Genet, J. P.; Piau, F. *J. Org. Chem.* **1981**, *46*, 2414. Genet, J. P.; Piau, F.; Ficini, J. *Tetrahedron Lett.* **1980**, *21*, 3183.

Cyclization of the *N*-Butyl-5-methyl-1-hex-4-enaminyl Radical and the Use of *N*-Lithio-*N*-butyl-5-methyl-1-hex-4-enamine as a Mechanistic Probe for Electron-Transfer Processes

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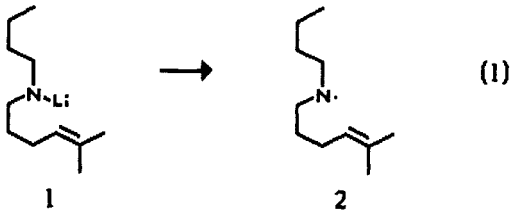
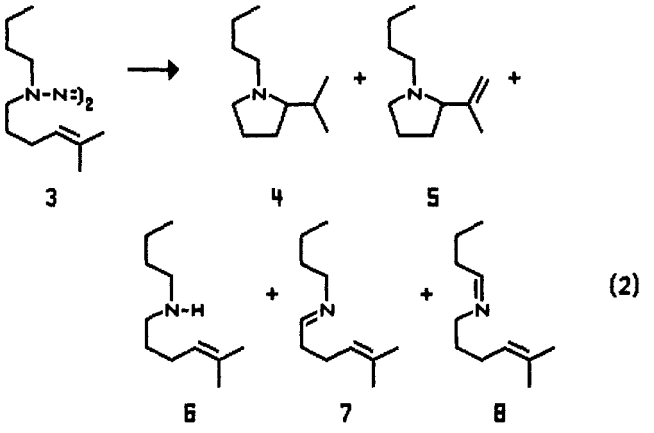
Evidence has been presented that lithium dialkylamides can react with selected substrates by an electron-transfer process rather than a conventional two-electron process.[2] Generally mechanistic conclusions have been reached by studying the reduced substrates of these reactions. An alternative approach would be to study the oxidized product, an aminyl radical, which was designed to undergo a characteristic skeletal rearrangement.[3,4] In this communication we report that *N*-lithio-*N*-butyl-5-methyl-1-hex-4-enamine (**1**) can be used as a mechanistic probe.[5] Oxidation of **1** gives radical **2** (eq 1) which has been found to cyclize.



(1)

1 **2**

To study the cyclization reaction, we generated radical **2** by photolysis or thermolysis of tetrazene **3**.[8] In reactions in various solvents both cyclic and acyclic products were obtained[8] (eq 2);



(2)

3 **4** **5** **6** **7** **8**

(1) Camille and Henry Dreyfus Teacher-Scholar, 1980–1985.

(2) (a) Scott, L. T.; Carlin, K. J.; Schultz, T. H. *Tetrahedron Lett.* **1978**, 4637–4638. (b) Creary, X. *J. Org. Chem.* **1980**, *45*, 2419–2425. (c) Newcomb, M.; Reeder, R. A. *Ibid.* **1980**, *45*, 1489–1493. (d) Ashby, E. C.; Goel, A. B.; DePriest, R. N. *Ibid.* **1981**, *46*, 2429–2431. Ashby, E. C.; Goel, A. B.; DePriest, R. N. *Tetrahedron Lett.* **1981**, *22*, 4355–4358. (e) Balogh, D. W.; Paquette, L. A.; Engel, P.; Blount, J. F. *J. Am. Soc.* **1981**, *103*, 226–228. Paquette, L. A.; Balogh, D. W. *Ibid.* **1982**, *104*, 774–783. (f) Newkome, G. R., Hager, D. C. *J. Org. Chem.* **1982**, *47*, 599–601.

(3) For example, see: Ashby, E. C.; Bowers, J. S., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 8504–8505.

(4) Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; deMayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 4. Surzer, J. M. *React. Intermed.* **1982**, *2*, 121–295.

(5) Ring openings of cyclopropyl- and cyclobutylaminyl radicals have been reported[6a] as has the cyclization of a pentenylaminyl radical.[6b] However, the corresponding lithium amide derivatives undergo complicating *anionic* rearrangements.[7]

(6) (a) Maeda, Y.; Ingold, K. U. *J. Am. Chem. Soc.* **1980**, *102*, 328–331. (b) Michejda, C. J.; Campbell, D. H. Sieh, D. H.; Koepke, S. R. In "Organic Free Radicals"; Pryor, W. A., Ed.; American Chemical Society: Washington, D.C., 1978; Chapter 18.

(7) Newcomb, M.; Williams, W. G.; Reeder, R. A. *Tetrahedron Lett.* **1982**, *23*, 4863–4866. Newcomb, M.; Burchill, M. T. *Ibid.* **1982**, *23*, 4867–4870.

(8) The supplementary material contains a brief description of the syntheses of **6**, **3**, and **4**, references for the syntheses, the method used to identify the products in eq 2, and the method used to determine the yield of **10** from the reactions of **1** with **9**.

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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-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-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.

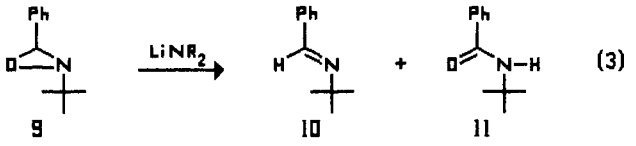
Table II. Products from Reactions of Probe 1 with Oxaziridine 9 in THF at 25 °C[a]

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.

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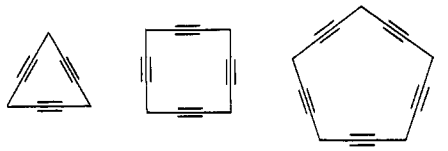
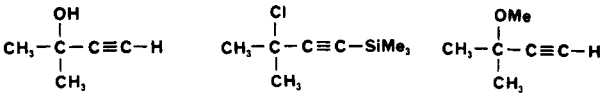
Cyclic hydrocarbons composed of N acetylenic units and N CH_2 groups alternating around the ring, e.g., **1**, **2**, and **3**, constitute



1 2 3

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



4 5 6

(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.

0002-7863/83/1505-7760$01.50/0