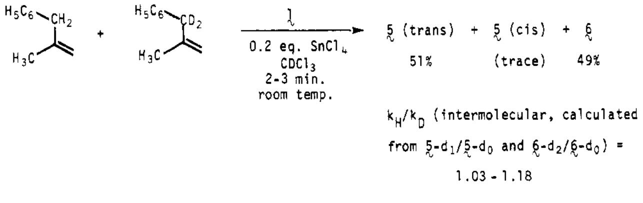
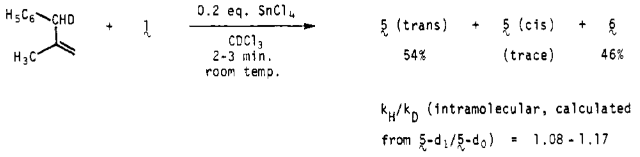
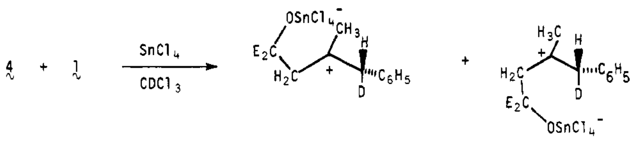
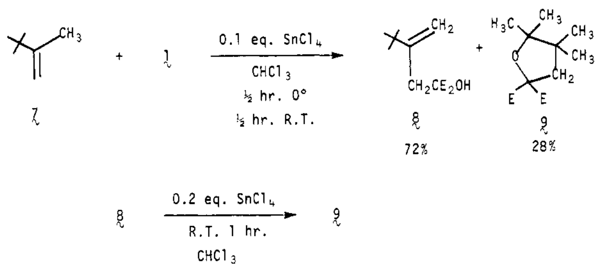


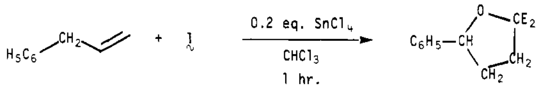




two dipolar species shown below, for example, one would normally expect an isotope fractionation at the CHD grouping since H is competing with methyl CH in the left-hand species, while D is competing with methyl CH in the geometrically equivalent right-hand species. If a fully developed dipolar species is involved in this reaction, the subsequent removal of H or D must proceed essentially without activation energy.[5]

Attempts to measure isotope effects in several other catalyzed reactions have been thwarted by a novel cyclization which may be synthetically useful. In the reaction of **7**, for example, it is obviously possible for $SnCl_4$ to catalyze addition of the OH proton to the olefin in product **8**. In cases where subsequent alkyl (or hydride; see below) shift is favorable, five-membered-ring products, e.g., **9** and **10**, are the only significant species which can be detected by NMR.





10

The previously unrecognized cyclization extends the synthetic usefulness of at least selected reactions in this series and is being actively explored.

Acknowledgment. Professor Harry S. Mosher has provided considerable encouragement to us and financial support for M.O. We also acknowledge support of NSF Grant CHE-80-12233 (to L.M.S.).

Registry No. 1 (E = CO_2Et), 609-09-6; 1 (E = CO_2Me), 3298-40-6; 2, 300-57-2; 2-d_1, 63523-01-3; 3 (E = CO_2Me), 77028-62-7; 3 (E = CO_2Et), 77028-80-9; 3-d_1 (E = CO_2Me), 77028-81-0; 3-d_1 (E = CO_2Et), 77028-82-1; 4, 3290-53-7; 4-d_1, 77028-63-8; 4-d_2, 77028-64-9; *cis*-5 (E = CO_2Me), 77028-65-0; *cis*-5 (E = CO_2Et), 77028-66-1; *cis*-5-d_1 (E = CO_2Et), 77028-83-2; *cis*-5-d_1 (E = CO_2Me), 77028-84-3; *trans*-5 (E = CO_2Me), 77028-67-2; *trans*-5 (E = CO_2Et), 77028-68-3; *trans*-5-d_1 (E = CO_2Me), 77028-85-4; *trans*-5-d_1 (E = CO_2Et), 77028-86-5; 6 (E = CO_2Me), 77028-69-4; 6 (E = CO_2Et), 77028-70-7; 7, 594-56-9; 8 (E = CO_2Me), 77028-71-8; 8 (E = CO_2Et), 77028-72-9; 9 (E = CO_2Me), 77028-73-0; 9 (E = CO_2Et), 77028-74-1; 10 (E = CO_2Me), 77028-75-2; 10 (E = CO_2Et), 77028-76-3; 6-methyl-1,5-heptadiene, 7270-50-0; methyl 2-(carbomethoxy)-3-isopropenyl-2-hydroxy-6-heptenoate, 77028-77-4; ethyl 2-(carboethoxy)-3-isopropenyl-2-hydroxy-6-heptenoate, 73961-90-7; methyl 2-(carbomethoxy)-2-hydroxy-8-methyl-4,7-nonadienoate, 77028-78-5; ethyl 2-(carboethoxy)-2-hydroxy-8-methyl-4,7-nonadienoate, 77028-79-6.

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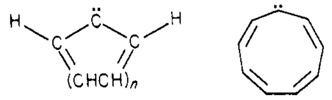
(5) A suitable example for comparison is provided by: Beak, P.; Berger, K. R. *J. Am. Chem. Soc.* **1980**, *102*, 3848. Attack of $(RC{=}O)^+$ on appropriately deuteriated methylenecyclohexane gives ene-like reaction products and shows negligible inter- but high intramolecular isotope effects, 1.0 ± 0.3 and 3.2 ± 0.7, respectively. Here it is clear that an intermediate is produced and that subsequent H(D) removal is an activated process.

Cyclononatetraenylidene

Summary: Cyclononatetraenylidene has been generated and is found to give a dimeric product via its triplet state.

Sir: The interest in cyclic, completely conjugated carbenes has been evident.[1] The potential for alternating properties (e.g., the electronic nature of the ground state, the electrophilicity or nucleophilicity of the singlet state) adds theoretical importance to the **1**–**3** series of carbenes. To date, the largest monocyclic conjugated carbene which has been approached is cycloheptatrienylidene, **3**.[2] The generation of the C_9 carbene, cyclononatetraenylidene (**4**), is now reported.[3]



1, $n = 0$
2, $n = 1$
3, $n = 2$

4

The logical precurser of **4**, diazocyclononatetraene (**5**), had been reportedly isolated from the reaction of lithium cyclononatetraenide (**6**) with *p*-toluenesulfonyl azide.[4] Actually, the isolated product of this reaction was 9-azidobicyclo[4.3.0]nonatriene (**7**).[5] It is now found that the use of 4-nitrobenzenesulfonyl azide with **6** all but eliminates the formation of **7** and a $C_{18}H_{18}$ hydrocarbon (**8**) is isolated in 33% yield. The proton and carbon NMR spectra and the UV spectrum are identical with the spectra

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(1) Dürr, H. *Top. Cur. Chem.* **1973**, *40*, 103–142.

(2) (a) Jones, W. M.; Ennis, C. L. *J. Am. Chem. Soc.* **1969**, *91*, 6391–6397. (b) It is quite possible that the chemistry of **3** is better ascribed to 1,2,4,6-cycloheptatetraene instead.

(3) The classical approach to 1,2,4,6,8-cyclononapentaene, which produces indene, has been reported. Waali, E. E.; Allison, N. T. *J. Org. Chem.* **1979**, *44*, 3266–3268.

(4) Lloyd, D.; Preston, N. W. *Chem. Ind.* (*London*) **1966**, 1039.

(5) Waali, E. E.; Taylor, J. L.; Allison, N. T. *Tetrahedron Lett.* **1977**, 3873–3874.

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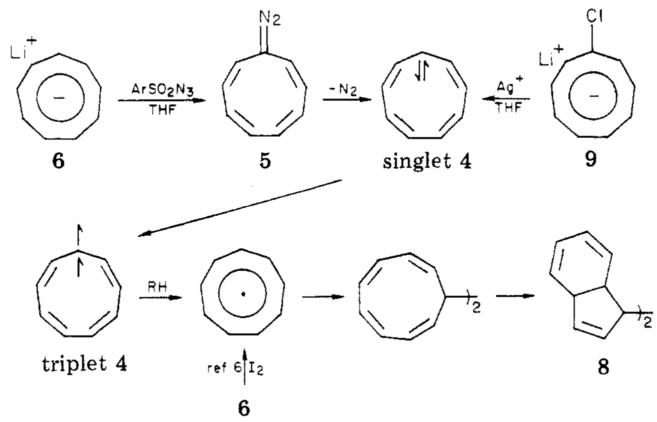
Scheme I



of the 9,9′-bibicyclo[4.3.0]nona-2,4,7-triene prepared by Hafner and co-workers from the dimerization of the cyclononatetraenyl radical.[6,7] A reaction scheme can be written as shown in Scheme I.

One could argue that the formation of **8** in the present work merely involves the oxidation of **6** by some unspecified oxidizing agent. The following speaks against this.[8] If lithium chlorocyclononatetraenide (**9**)[9] is treated with silver nitrate,[10] **8** is isolated (19%). In this case the possible direct oxidation of **6** is eliminated. The facile removal of chloride ion from **9** by silver ion is an indication that the carbenic electrons in singlet **4** are in the π system.[11] Intersystem crossing to a more stable triplet state[11] and hydrogen abstraction would give the cyclononatetraenyl radical. Dimerization of the radical followed by electrocyclic ring closures would give **8**. Indene, an important product of other C_9H_8 intermediates,[3,13] is not observed in the present work.

Further work on the interception of the various intermediates in Scheme I and the reaction of silver ion with other stable chloro anions is planned.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. **4**, 76947-27-8; **8**, 2177-49-3; **9**, 76947-28-9.

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(6) Hafner, K.; Braun, S.; Nakazawa, T.; Tappe, H. *Tetrahedron Lett.* **1975**, 3507–3510.

(7) If a tetrahydrofuran (THF) solution of 4-nitrobenzenesulfonyl azide is rapidly injected into a THF solution of **6**, a transient red color appears at the tip of the syringe needle. The red color has a half-life of about 0.4 s at 22 °C as measured at 520 nm by using a stopped-flow kinetic apparatus. Since nitrogen evolution occurs over a much longer period of time it is unlikely that the red color is due to the diazo compound **5**.

(8) An infrared spectrum of the reaction solution shows a band at 2060 cm^{-1} (which is quite possibly due to **5**) in addition to bands at 2130 (4-nitrobenzenesulfonyl azide) and 2090 cm^{-1} (weak, **7**).[5] The 2060-cm^{-1} material was not stable to workup.

(9) LaLancette, E. A.; Benson, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 1941–1946.

(10) Two equivalents of silver nitrate is used since there is 1 equiv of lithium chloride produced from the preparation of **9**.

(11) MNDO[12] calculations, to be published elsewhere, indicate that **4** is a π carbene in its singlet state but is a ground-state triplet.

(12) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4907.

(13) Rajan Babu, T. V.; Shechter, H. *J. Am. Chem. Soc.* **1976**, *98*, 8261–8262. Freeman, P. K.; Swenson, K. E. Northwest Regional American Chemical Society Meeting, Seattle, WA, June 1978.