Table I. NMR parameters[7] of $(CH_3)_3CCH_BDCH_AD(X)Zr(Cl)Cp_2$

X	δH_A	δH_B	$\delta (CH_3)_3$	δCp	$J_{H_1H_2}$ (Hz) (erythro)	$J_{H_1H_2}$ (Hz) (threo)
...	*a*	1.38	0.85	5.88	12.9	4.2
CO	2.85	1.66	0.92	5.71	11.7	5.0
SO_2	2.37	1.50	0.74	6.10	12.5	4.8
O	3.90	1.30	0.82	6.01	8.8	6.0

[a] Hidden by $(CH_3)_3$ peak.

Treatment of a benzene solution of **1** with an equivalent amount of Br_2 at 10° yields, after work-up by treatment with aqueous $NaHCO_3$ followed immediately by rapid, reduced pressure distillation at room temperature, the alkyl bromide resulting from *retention* of configuration at carbon. The unavailability, therefore, of an oxidation mechanism changes the stereochemical course of the cleavage reaction from that found with other, oxidizable transition metal complexes. A closed transition state, such as that proposed for halogenation of organomercurials,[9] is a reasonable one to account for retention at carbon. The availability of a vacant, low-lying orbital on Zr in these "16-electron" complexes[10] may facilitate frontside attack[9] on the C–Zr bond. Reaction of **1** with *N*-bromosuccinimide, which also gives good yields of alkyl bromides,[5] and iodination with I_2, both proceed with retention at carbon.

Because halogenation of the C–Zr(IV) bond proved to be mechanistically different from that of other transition metal alkyls, several other cleavage reactions were examined for comparison with results reported for other metal alkyls. Insertion of CO to give the acyl complex[11] proceeds with retention as is the case for all other systems reported.[1] Reaction with SO_2 is complex; $(\eta^5\text{-}C_5H_5)_2Zr(Cl)CH_3$ has been reported to add 2 equiv of SO_2 to give a highly insoluble product formulated as $(C_5H_5)(C_5H_5SO_2)Zr(Cl)(O_2SCH_3)$.[12] We find that addition of less than 1 equiv of SO_2 to a benzene solution of **1** gives rise to a new set of ^1H NMR peaks (Table I) consistent with formulation as an SO_2 insertion product, $(\eta^5\text{-}C_5H_5)_2Zr(Cl)(O_2SCHDCHDC(CH_3)_3)$.[13] The values for $^3J_{HH}$ indicate that SO_2 insertion here proceeds with *retention* at carbon, in contrast to the reaction with $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CHDCHDC(CH_3)_3)$ which goes with >95% *inversion*. These results are in agreement with the mechanistic proposal of Wojcicki[14] that coordinatively saturated complexes react by direct backside attack of SO_2 on the alkyl group followed by rearrangement, resulting in inversion at carbon, while coordinatively unsaturated complexes such as Cp_2MRX (M = Ti, Zr) can coordinate SO_2 to the metal, followed by frontside attack on the alkyl giving retention.

Alkylzirconium complexes $Cp_2Zr(Cl)R$ can be converted to alcohols, ROH, using a variety of reagents,[15] including dry oxygen followed by acid hydrolysis. Such treatment of **1** gives the alcohol $(CH_3)_3CCHDCHDOH$ resulting from approximately one-half racemization and one-half retention of configuration. Loss of stereochemistry does not occur during hydrolytic work-up, since the initial product $Cp_2Zr(Cl)(OCHDCHDC(CH_3)_3)$[16] (Table I) has the same stereochemical composition. Reaction of cobalt alkyls with O_2 to give alkylperoxycobalt complexes proceeds with complete racemization and is thought to involve alkyl radical intermediates;[17] some nonradical pathway must be operating, as well, for zirconium alkyls. For example, the following scheme could account for the observed results.

$$R^*(Zr) + O_2 \longrightarrow R\cdot + \cdot OO(Zr) \longrightarrow ROO(Zr)$$

$$ROO(Zr) + R^*(Zr) \longrightarrow RO(Zr) + R^*O(Zr)$$

R^* = chiral alkyl
R = racemized alkyl
(Zr) = $(\eta^5\text{—}C_5H_5)_2Zr(Cl)$–

The above results clearly demonstrate that d-electron configuration plays a significant role in determining the mechanistic paths followed in reactions of transition metal alkyls. Further work to extend the range of reactions studied and to elucidate details of the mechanisms involved, specifically those for oxygenation, is in progress.

Acknowledgments. The authors acknowledge generous support for this work provided by the National Science Foundation (GP 43026X) and Mr. D. R. Nordlund for helping us to obtain ^2H decoupled NMR spectra.

References and Notes

(1) P. L. Bock, D. J. Boschetto, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 2814 (1974), and references therein.
(2) F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Am. Chem. Soc.*, **93**, 5283 (1971).
(3) S. M. Anderson, D. H. Ballard, J. Z. Chrastowski, D. Dodd, and M. D. Johnson, *J. Chem. Soc., Chem. Commun.*, 685 (1972).
(4) T. C. Flood and F. J. DiSanti, *J. Chem. Soc., Chem. Commun.*, 18 (1975).
(5) D. W. Hart and J. Schwartz, *J. Am. Chem. Soc.*, **96**, 5115 (1974).
(6) The deuteride was prepared using $LiAlD_4$ as reducing agent.
(7) ^2H Decoupled ^1H NMR spectra were measured at 100 MHz in benzene using an NMR Specialties HD-60 deuterium decoupler.
(8) About 10% of the opposite diastereomer is present in preparations of either *erythro*- or *threo*-**1**; loss of stereochemistry occurs prior to formation of **1** since it is configurationally stable once formed. For all reactions (except O_2) the stereochemical composition of the product is identical with that of the starting alkyl within experimental accuracy (±10%).
(9) F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials", McGraw-Hill, New York, N.Y., 1968.
(10) C. A. Tolman, *Chem. Soc. Rev.*, **1**, 337 (1972).
(11) C. A. Bertelo and J. Schwartz, *J. Am. Chem. Soc.*, **97**, 228 (1975).
(12) P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organomet. Chem.*, **33**, 181 (1971).
(13) Infrared spectral evidence indicates that both the present species and the product reported by Wailes[12] are either *O*- or *O,O'*-sulfinate complexes. The former has a chiral center at sulfur which would cause each doublet due to the methylene protons to split into *two* doublets.[14] The absence of this splitting tends to support the *O,O'*-sulfinate formulation, which would make the sulfinate complex coordinatively saturated.
(14) A. Wojcicki, *Adv. Organomet. Chem.*, **12**, 31 (1974).
(15) T. F. Blackburn, J. A. Labinger, and J. Schwartz, unpublished results.
(16) Characterized by chemical and spectral similarity to known alkoxyzirconium complexes: D. R. Gray and C. H. Brubaker, *Inorg. Chem.*, **10**, 2143 (1971).
(17) F. R. Jensen and R. C. Kiskis, *J. Organomet. Chem.*, **49**, C46 (1973).

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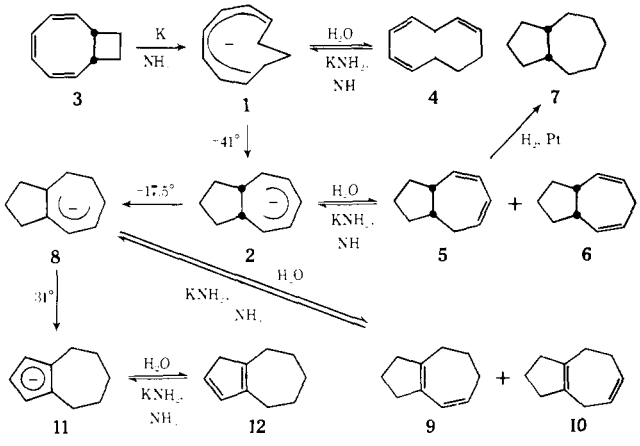
Electrocyclic Reaction of the Cyclodecatrienyl Anion

Sir:

The number of electrocyclic reactions of carbanions which have been reported is limited.[1] In many cases no stereochemical information is available, but most cases in which it is seem to fall within the predictions based on orbital topology. We now report the preparation and direct observation of the cyclodecatrienyl anion (**1**) and its facile electrocyclization to the *cis*-bicyclo[5.3.0]deca-3,5-dien-2-yl anion (**2**),[2] a process not anticipated by orbital topology considerations.

Treatment of *cis*-bicyclo[6.2.0]deca-2,4,6-triene[3] (**3**) with 4 g-atoms of potassium in liquid ammonia cleanly produced the cyclodecatrienyl anion (**1**). The bicyclo[6.2.0]deca-1,3,5,7-tetraene dianion[4] was sometimes pro-

Scheme I



duced as a coproduct, presumably by deprotonation of **3** by the potassium amide produced in the reaction.

The NMR spectrum of **1** (δ 5.72 (d of d, H_2, H_6, $J_{12} = J_{67} = 11.7$, $J_{23} = J_{56} = 9.9$ Hz), 5.57 (t, H_4, $J_{34} = J_{45} = 12.8$ Hz), 4.7 (m, H_1, H_7), 3.82 (d of d, H_3, H_5) 1.1–1.7 (m, H_8–H_{10})) indicates a symmetrical species on the NMR time scale at −65°. The vicinal coupling constants are all significantly larger than the corresponding values in the cyclononatrienyl anion.[5] This may be rationalized on the basis of a C_2 (spiral) conformation[6] for **1** (Scheme I) in which there is a minimum of twist between adjacent carbon atoms in the π system.

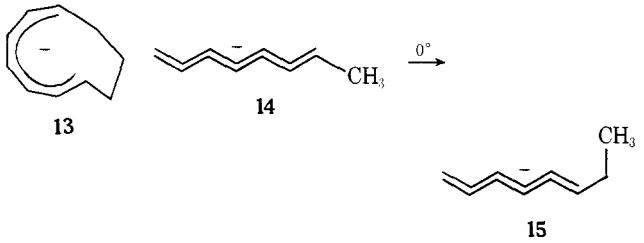
The all-cis conformation of **1** is consistent with the observation that a single product, identified as **4**,[7,8] is obtained on quenching **1** (after 1 min at −33°) with water. The all-cis conformation of **4** is supported by (a) the absence of a strong infrared band at ca. 965 cm^{-1} (out-of-plane HC=CH bending in trans double bonds), (b) the absence of a λ_{max} above 220 nm,[9] and (c) the fact that all of the *HC=CH* coupling constants ≤11 Hz.[10] The latter information was obtained from a 220-MHz NMR spectrum[11] of a mixture of the *8,8,9,9-d_4* and *9,9,10,10-d_4* derivatives of **4** and from a 300-MHz NMR spectrum of **4.** It should be noted, however, that we cannot exclude the possibility that anion **1** is actually a rapidly (on the NMR time scale) interconverting mixture of various conformations which possess one or more trans π bonds and which give a symmetrical time-averaged NMR spectrum at −65°.

Anion **1** (prepared from **4**) is converted essentially completely ($t_{1/2} \approx 23$ min) to anion **2** on raising the temperature to −41°. The structure of **2** is based on its NMR spectrum (δ 5.72 (d of d, H_3, H_5, $J_{34} = J_{45} = 8.2$, $J_{23} = J_{56} = 10.0$ Hz), 3.53 (d of d, H_2, H_6, $J_{12} = J_{67} = 4.2$ Hz), 3.21 (t, H_4), 2.4–2.8 (m, H_1, H_7), 1.2–1.6 (m, H_8–H_{10})), its quenching with water to produce a 5:1 mixture of **5** and **6**,[12] and on the catalytic hydrogenation of **5** to afford **7**, which has an infrared spectrum identical with that of an authentic sample.[13,14]

The NMR spectrum of **2** is completely replaced by that of **8** (δ 5.79 (d of d, H_3, $J_{23} = 7.8$, $J_{34} = 9.2$ Hz), 3.33–3.70 (m, H_4), 3.20 (d of d, H_2, $J_{24} = 1.4$ Hz), 2.01–2.59 (m with four major lines, H_5, H_6, H_8, H_{10}), 1.47—1.85 (m, H_9)) on raising the temperature to −17.5° ($t_{1/2} \approx 47$ min). Quenching of **8** with water afforded a 2:1 mixture of **9** and **10.** Finally, **8** is cleanly converted to **11** (AB_2 multiplet at 5.30 (H_9) and 5.18 (H_8, H_{10}, $J_{89} = J_{9,10} = 3.0$ Hz), 2.45–2.70 (m, H_2, H_6), 1.4–1.7 (m, H_3–H_5)) on warming to 31° ($t_{1/2} \approx 19$ min), and diene **12**[15] is produced on quenching the latter anion with water. The isomerization of **2** to **11** via **8** presumably occurs by a protonation-deprotonation mechanism since **11** showed extensive deuterium uptake at C_2–C_6 when the reaction was performed in ammonia-d_3.

The key observation is, of course, the closure of **1** to **2.** The latter unequivocally possesses cis stereochemistry at the ring fusion so that if **2** has an all-cis conformation then the closure follows an apparent "nonallowed" course.

On the other hand, if anion **2** is formed by an "allowed" closure, then anion **13** is expected to be its immediate precursor. The half-life for the isomerization of **14** to **15** (potassium counterion) in liquid ammonia is ca. 4 hr at 0°.[2c] It is therefore conceivable that conversion of **1** (which is undoubtedly more strained than **14**) to **2** occurs via an initial slow isomerization to **13** followed by a rapid ring closure.



In our view, the mechanism of the electrocyclization of **1** is probably closely linked with the currently unsolved problem of the mechanism of rotation around π bonds in carbanions.[1,16] While we cannot definitely specify a pathway for conversion of **1** to **13,** we can rule out the possibility of protonation of **1** at C_1 followed by rotation around the resulting C_1–C_2 σ bond and deprotonation at C_1, due to the fact that there is no deuterium incorporation at C_1 in **2** when **1** is isomerized to **2** in ammonia-d_3. Further investigation of the mechanism of this unusual cyclization is planned.

Acknowledgment. We thank the National Science Foundation for support of this work.

References and Notes

(1) Review: D. H. Hunter in "Isotopes in Organic Chemistry", Vol. 1, E. Buncel and C. C. Lee, Ed., Elsevier, Amsterdam, 1975.

(2) Although electrocyclic reactions of heptatrienyl anions are known, no stereochemical aspects of this reaction have been reported: (a) D. L. Crain, R. F. Kleinschmidt, and H. A. Hartzfeld, *Abstracts*, 148th National Meeting of the American Chemical Society, Chicago, Ill., p 86S, 1964; (b) E. A. Zeuch, D. L. Crain, and R. F. Kleinschmidt, *J. Org. Chem.*, **33**, 771 (1968); (c) H. Kloosterziel and J. A. A. van Drunen, *Recl. Trav. Chim. Pays-Bas*, **88**, 1084, 1471 (1969); (d) R. B. Bates, W. H. Dienes, D. A. McCombs, and D. E. Potter, *J. Am. Chem. Soc.*, **91**, 4608 (1969); (e) R. B. Bates, S. Brenner, W. H. Dienes, D. A. McCombs, and D. E. Potter, *ibid.*, **92**, 6345 (1970); (f) G. Dauphin, L. David. A. Kergomard, and H. Veschambre, *Bull. Soc. Chim. Fr.*, 3162 (1970); (g) L. David and A. Kergomard, *Tetrahedron*, **26**, 5045 (1970); **27**, 653 (1971); (h) R. B. Bates, S. Brenner, and C. M. Cole, *J. Am. Chem. Soc.*, **94**, 2130 (1972).

(3) S. W. Staley and T. J. Henry, *J. Am. Chem. Soc.*, **92**, 7612 (1970).

(4) S. W. Staley, G. M. Cramer, and A. W. Orvedal, *J. Am. Chem. Soc.*, **96**, 7433 (1974).

(5) S. W. Staley and N. J. Pearl, *J. Am. Chem. Soc.*, **95**, 3437 (1973).

(6) We refer to all *Z,E* isomers as *conformational* isomers. See H.-O. Kalinowski and H. Kessler, *Top Stereochem.*, **7**, 295 (1973).

(7) This compound was previously assigned the cis,trans,cis conformation; H. V. Cortez, Ph.D. Thesis, The University of Texas at Austin, 1964.

(8) NMR (60 MHz, CCl_4, 34°), δ 4.96–5.92 (m, 6 H, olefinic), 2.56–3.12 (m, H_5), 1.83–2.43 (m, H_8, H_{10}), 1.18–1.68 (m, H_9); uv (hexane) end absorption (shoulder at 220 nm (ϵ 320)). This overall reaction is analogous to the reductive cleavage of *cis*-bicyclo[6.1.0]nona-2,4,6-triene with alkali metals in liquid ammonia to afford *cis,cis,cis*-1,3,6-cyclononatriene; W. H. Okamura, T. I. Ito, and P. M. Kellett, *Chem. Commun.*, 1317 (1971).

(9) The cis,trans isomer of 1,3-cyclodecadiene has a strong ir band at 976 cm^{-1} and λ_{max} (solvent unspecified) 222 nm (ϵ 9350) whereas the cis,cis isomer showed no absorption at 970–980 cm^{-1} and only end absorption in the region 215–230 nm; A. T. Blomquist and A. Goldstein, *J. Am. Chem. Soc.*, **77**, 998 (1955).

(10) NMR (CCl_4): δ 5.70 (H_2, d, $J_{12} = 11$ Hz), 5.64 (H_3, d, $J_{34} = 10$–11 Hz), 5.51 (H_6, m), 5.49 (H_4, m), 5.31 (H_1, apparent q), 5.18 (H_7, apparent q, $J_{67} = 10$ Hz); at 220 MHz and 21° the upfield region showed three multiplets at δ 2.9–3.7 (1 H, H_5), 1.7–2.8 (5 H, H_{10}, H_6, and the other H_5), and 1.3–1.6 (broadened s, H_9). This is different from the 60-MHz data in ref 7 because the averaging due to ring reversal in **4** has been largely eliminated in the high field spectrum.

(11) We are most grateful to Drs. E. D. Becker and H. Ziffer of the National Institutes of Health for assistance in obtaining the 220-MHz spectra and to Professor W. H. Okamura of the University of California, Riverside, for obtaining the 300-MHz spectra.

(12) Diene **5**: NMR (220 MHz, CCl_4) δ 5.55–5.95 (m, H_2–H_5), 2.18–2.78 (major peaks at 2.27 and 2.53, H_1, H_6), 1.0–2.1 (major peaks at 2.0 and 1.4, H_7–H_{10}); uv (hexane) λ_{max} 240 nm (ϵ 6940). Diene **6**: NMR (220 MHz, CCl_4) δ 5.58 (5 line m, H_3, H_5), 5.40 (d, H_2, H_6, $J_{23} = J_{56} = 11$ Hz), 2.93 (H_{4a}, m of at least 14 lines consistent with a d ($J_{4a,4b} = 19$ Hz) of t (4 Hz) of t (2 Hz)), 2.69 (broadened s, H_1, H_7), 2.49 (d of t, H_{4b}, $J_{3,4b} = J_{4b,5} = 6.5$ Hz), 1.48–1.82 (m, major peaks at 1.6 and 1.7, H_8–H_{10}); uv (hexane) end absorption ($\epsilon_{220\ nm}$ 120).
(13) N. L. Allinger and V. B. Zalkow, *J. Am. Chem. Soc.*, **83**, 1144 (1961). We thank Professor Allinger for sending us copies of the ir spectra of 7 and its trans isomer.
(14) We thank Professor R. B. Bates for providing us with a sample of the reaction mixture from the catalytic hydrogenation of azulene, which turned out to be >90% **7**.
(15) NMR and uv data were essentially identical with data reported by L. M. Dané, J. W. de Haan, and H. Kloosterziel, *Tetrahedron Lett.*, 2755 (1970).
(16) (a) F. J. Kronzer and V. R. Sandel, *J. Am. Chem. Soc.*, **94**, 5750 (1972). (b) Further discussion will be found in a forthcoming review: S. W. Staley in "Pericyclic Reactions", A. P. Marchand and R. P. Lehr, Ed., Academic Press, New York, N.Y., 1976.

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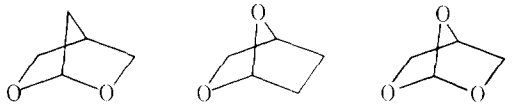
2,6,7-Trioxabicyclo[2.2.1]heptane

Sir:

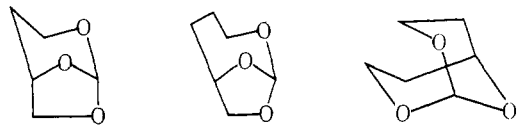
We recently reported the synthesis of bicyclic acetals **1** and **2,** and noted that their rates of dichloracetic acid catalyzed hydrolysis exceeded those of an acyclic reference compound by factors of 10^6 and 10^5, respectively.[1]



1 2 3

We now report the synthesis of 2,6,7-trioxabicyclo-[2.2.1]heptane[2] and note that, despite expected high ring strain, it undergoes acetic acid catalyzed hydrolysis at a rate slightly *less* than those of acyclic model compounds.

Compound **3** was prepared in 73% yield by the interchange reaction of glycerol with ethyl orthoformate in dilute dioctyl phthalate solution at 110–140° with a trace of anhydrous *p*-toluenesulfonic acid as catalyst with vigorous stirring at 0.1 mm. The bicyclic compound distilled out as formed and was condensed in a liquid nitrogen-chilled receiver. Alternatively the first two molecules of ethanol could be removed without catalyst or dilution as described by Crank and Eastwood[3] and the final molecule of ethanol removed as above using dibutyl phthalate. This technique avoids oligomerization of very acid-sensitive compounds such as **3,** which may account for its absence from the chemical literature to the present time. The hydrolysis rate constant for **3,** given in Table I, is smaller than those for trimethyl and triethyl orthoformates by factors of 2 and 1.5, respectively.



4 5 6

To extend this finding, orthoesters **4–6** were prepared in yields of 70–73%, as described for **3.**[4] Their hydrolysis rate constants (Table I) are even slower than those of **3.**

These results may be attributable to a very early transition state, with very little C–O bond breaking and consequently very little strain release. Work is underway, particularly to determine whether the hydrolysis is specific or general-acid catalyzed, to explore the problem further.

Table I. Rates of Hydrolysis of Bicyclic Orthoesters[a]

Compound	$10^4 k_1$, sec^{-1}	Compound	$10^4 k_1$, sec^{-1}
$(CH_3O)_3CH$	19	6	4.3
$(C_2H_5O)_3CH$	15	4	4.1
3	10	5	3.2

[a] Conditions: temperature 35°; 0.084 *M* acetic acid catalyst; solutions are initially 1.4 *M* in orthoester in solvent 0.6 ml of acetone-d_6 and 0.2 ml of D_2O; rates were followed by monitoring O_3CH NMR absorption intensity as a function of time. Good pseudo-first-order plots were obtained.

Recent studies of orthoester hydrolysis[5–7] as models for the behavior of the tetrahedral intermediates in enzyme-catalyzed hydrolysis, and studies of the stereoelectronic preferences in these intermediates,[8–10] have focused attention on the need for models with rigidly defined geometry. Crank and Eastwood[3] had earlier suggested that experimental information could be provided by the synthesis and determination of the properties of rigid bicyclic orthoesters. The ready availability of bicyclic orthoesters means that the suggestion of Crank and Eastwood can now be pursued. Moreover, these compounds will be useful new monomers for studies of ring-opening polymerization to polysaccharide analogs.[11,12]

Acknowledgment. We are deeply indebted to the National Institutes of Health Grant GM 18595 for support of this work and to a referee for helpful comments.

References and Notes

(1) H. K. Hall, Jr., and Fr. DeBlauwe, *J. Am. Chem. Soc.*, **97**, 655 (1975).
(2) F. Pauer, *Monatsh. Chem.*, **58**, 1 (1931), had reported compound **1** as displaying bp 126° (12 mm). However, R. H. de Wolfe, "Carboxylic Ortho Acid Derivatives", Academic Press, New York, N.Y., 1974, p 8, noted that this is much higher than expected and is probably that of a dimer. Our authentic compound **1** boils at 80° (37 mm).
(3) G. Crank and F. W. Eastwood, *Aust. J. Chem.*, **17**, 1385 (1964).
(4) Compounds **4–6** had previously been reported by Crank and Eastwood (ref 3), although in low yields (2, 3, and 39%, respectively). Our NMR spectra agreed with their reported values.
(5) T. H. Fife, *Acc. Chem. Res.*, **5**, 264 (1972).
(6) J. Hine and A. W. Klueppal, *J. Am. Chem. Soc.*, **96**, 2924 (1974).
(7) Y. Chiang, A. J. Kresge, P. Salomaa, and C. I. Young, *J. Am. Chem. Soc.*, **96**, 4494 (1974).
(8) J. P. Guthrie, *J. Am. Chem. Soc.*, **95**, 6999 (1973).
(9) J. M. Lehn and G. Wipff, *J. Am. Chem. Soc.*, **96**, 4048 (1974).
(10) (a) P. Deslongchamps, C. Moreau, D. Fréhel, and P. Atlani, *Can. J. Chem.*, **50**, 3402 (1972); (b) P. Deslongchamps, P. Atlani, D. Fréhel, and A. Malaval, *ibid.*, **50**, 3405 (1972); (c) P. Deslongchamps, C. Lebreux, and R. Taillefer, *ibid.*, **51**, 1665 (1973).
(11) Review: C. Schuerch, *Acc. Chem. Res.*, **6**, 184 (1973).
(12) N. K. Kochetkov and A. F. Bochkov, *Carbohydr. Res.*, **9**, 61 (1969).

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Simple Alkyl Methylenecyclopropenes via Addition of Unsaturated Carbenes to Alkynes[1]

Sir:

Strained small ring systems have long fascinated chemists, and the methylenecyclopropene system, **1,** in particular has been of special interest to theoreticians[2] as well as being a synthetic challenge.[3] The first successful synthesis of a methylenecyclopropene was a diphenylquinocyclopropene reported by Kende[4] in 1963, and, although numerous other stable methylenecyclopropenes have been prepared since, they all have strongly electron stabilizing substituents, such