priate 1,2-alkyl shift. Withaferin A (V),[8] also obtained from a solanaceae, is perhaps the most closely related substance known.

Nicandrenone (I) has 11 asymmetric centers. It probably possesses the usual plant steroid configurations at C-8, C-9, C-10, and C-20 as shown in Ib; the trans-diaxial relationship of the protons attached to C-8 and C-9 is confirmed by the observed coupling constant between them (11 Hz). The 6–3 ring junctures are presumably cis because of excessive strain if trans. The configuration at C-22 is probably the same as in withaferin A (V) but is not yet known. Our attempts to obtain a crystalline derivative of nicandrenone suitable for X-ray analysis have failed, but we are pursuing this approach in the hope of answering the remaining stereochemical questions.

Acknowledgments. We thank Dr. G. S. Fraenkel for seeds of *Nicandra physalodes*, Dr. D. N. Stephens for isolating the nicandrenone used in this work, the Bruker Company for the cmr spectra, and the Public Health Service (GM-12447 and CA-10944) and Sloan Foundation (Fellowship to R. B. B.) for financial support.

[8] D. Lavie, E. Glotter, and Y. Shvo, *J. Chem. Soc.*, 7517 (1965).

R. B. Bates,* D. J. Eckert
Department of Chemistry, University of Arizona
Tucson, Arizona 85721

Received June 30, 1972

Intramolecular Metal–Double Bond Interaction. III. Intramolecular Cyclization Reactions of Organometallic Compounds

Sir:

Facile cyclization of organometallic compounds by addition across nonconjugated double bonds is presently known only for aluminum derivatives under special conditions,[1,2] and for Grignard reagents.[3,3a] In the former case cyclization takes place on addition of an aluminum hydride to 1,5-hexadiene and in the latter, cyclization or cyclic intermediates have been reported for but-3-enyl, pent-4-enyl, and hex-5-enyl derivatives. No generally successful cyclization process has been outlined, however, for synthetic purposes.

At this time we wish to report that cyclization of hex-5-enyl organometallic compounds is a general reaction and propose that this reaction proceeds through eq 1 and 2 for lithium, magnesium, aluminum, gallium, and indium derivatives. The alkyl group exchange

$$\frac{n}{2}\mathrm{Hg}[(\mathrm{CH_2})_4\mathrm{CH{=}CH_2}]_2 + \mathrm{mM} \longrightarrow \mathrm{mM}[(\mathrm{CH_2})_4\mathrm{CH{=}CH_2}]_n + \frac{n}{2}\mathrm{Hg} \qquad (1)$$

$$\mathrm{M}[(\mathrm{CH_2})_4\mathrm{CH{=}CH_2}]_n \longrightarrow \mathrm{M}(\mathrm{CH_2}(c\text{-}\mathrm{C_5H_9}))_n \qquad (2)$$

indicated in eq 3 also occurs for the Mg and Li systems

$$\mathrm{M}[\mathrm{CH_2}(c\text{-}\mathrm{C_5H_9})]_n + \mathrm{Hg}[(\mathrm{CH_2})_4\mathrm{CH{=}CH_2}]_2 \rightleftharpoons \{\mathrm{M}(\mathrm{CH_2}(c\text{-}\mathrm{C_5H_9}))_{n-1}[(\mathrm{CH_2})_4\mathrm{CH{=}CH_2}] + \mathrm{Hg}(\mathrm{CH_2}(c\text{-}\mathrm{C_5H_9}))[(\mathrm{CH_2})_4\mathrm{CH{=}CH_2}]\} \qquad (3)$$

$$2\mathrm{Hg}(\mathrm{CH_2}(c\text{-}\mathrm{C_5H_9}))(\mathrm{CH_2})_4\mathrm{CH{=}CH_2}) \rightleftharpoons \mathrm{Hg}(\mathrm{CH_2}(c\text{-}\mathrm{C_5H_9}))_2 + \mathrm{Hg}[(\mathrm{CH_2})_4\mathrm{CH{=}CH_2}]_2 \qquad (4)$$

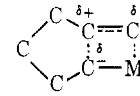
giving rise to formation of the cyclic mercury compound.

The conditions for complete conversion to the methylenecyclopentane derivatives are indicated in Table I.

Table I. Experimental Conditions for Cyclization Reactions of Hex-5-enyl Metal Derivatives

Metal	Time for complete cyclization	Temp, °C	Solvent
Li	8 days	25	C_5H_{10}
Li	96 hr	25	C_6H_6
Li	<1 hr	25	$(C_2H_5)_2O$
Mg	24 hr	110	Neat
Al	48 hr	40	Neat
Al	48 hr	25	C_5H_{10}
Ga	3 weeks	95	Neat
In	3 weeks	110	Neat

The reaction may be depicted as an internal addition across the double bond as indicated in I and appears to proceed more readily for the hex-5-enyl derivatives than for other chain lengths[4] with terminal olefin functionality. It has been demonstrated that the intramolecular cyclization of aluminum derivatives[2] requires a strain-free conformation for facile reaction and it is clear that steric and electronic effects are important. It is also noteworthy that these cyclizations proceed with such facility in contrast to the analogous intermolecular reactions.[5] The cyclization of the lithium derivative has been shown to be solvent dependent; addition of ether results in an increased rate of cyclization. This may be interpreted in terms of stabilization of the polar transition state *via* the solvation of the lithium and from the increased polarity of the lithium–carbon bond also resulting from this solvation.



I

This reaction appears to provide an interesting and readily available procedure for formation of five-membered ring systems which is potentially significant for synthetic purposes. It also provides a convenient system for the examination of the initial stages of addition to π systems. These features are now under further investigation.

---

[1] C. Zweifel, G. M. Clark, and R. Lynd, *Chem. Commun.*, 1593 (1971).

[2] G. Hata and A. Miyaki, *J. Org. Chem.*, **28**, 3237 (1963).

[3] H. G. Richey, Jr., and W. C. Kossa, Jr., *Tetrahedron Lett.*, 2313 (1969); H. G. Richey, Jr., and T. C. Rees, *ibid.*, 4297 (1966); H. G. Richey, Jr., and A. M. Rothman, *ibid.*, 1457 (1968); M. S. Silver, P. R. Shafer, J. E. Norlander, C. Ruchart, and J. D. Roberts, *J. Amer. Chem. Soc.*, **82**, 2646 (1960).

[3a] NOTE ADDED IN PROOF. V. N. Drozd, Yu. A. Ustynyuk, M. A. Tsel'eva, and L. B. Dimitriev, *Zh. Obshch. Khim.*, **38**, 2114 (1968), have reported the cyclization of hex-4-enyllithium species to yield methylcyclopentane derivatives similar to those reported in this work.

[4] We have prepared a series of but-3-enyl and pent-4-enyl metal derivatives and have found no cyclization reactions. However, for the pent-4-enyl derivatives we have established the presence of an intramolecular metal–olefin association which we believe to be intimately related to the cyclization processes observed for the hex-5-enyl derivative. A preliminary report has been submitted with respect to the pent-5-enyl derivatives: J. Smart, J. St. Denis, and J. P. Oliver, *J. Organometal. Chem.*, in press.

[5] K. Ziegler in "Organometallic Chemistry," H. H. Zeiss, Ed., Reinhold, New York, N. Y., 1960, pp 220–231.

Di(hex-5-enyl)mercury was prepared from the corresponding Grignard reagent and $HgCl_2$. The remaining hexenyl metal derivatives were then all prepared by the reaction of $Hg[(CH_2)_4CH{=}CH_2]_2$ with the respective metal in a sealed tube under the conditions indicated in Table I. The independent existence of the hexenyl metal derivative was not established in all cases, and, in fact, attempts to prepare tri(hex-5-enyl)aluminum indicated that only the cyclic product was detectable after exchange of aluminum for mercury.

All compounds were characterized by hydrolysis with 10% HCl-H_2O, which gave methylcyclopentane, and by their nmr spectra. In addition the Al and Li derivatives yielded $H_2C{=}(c\text{-}C_5H_8)$ on pyrolysis. These products were characterized by their nmr spectra. The formation of the cyclic mercury compound indicated in eq 4 was shown both by its nmr spectrum and by its mass spectrum.

Acknowledgment. This work was supported by National Science Foundation grants GP-8323 and 19299.

J. St. Denis, T. Dolzine, J. P. Oliver*
Wayne State University
Detroit, Michigan 48202
Received August 12, 1972

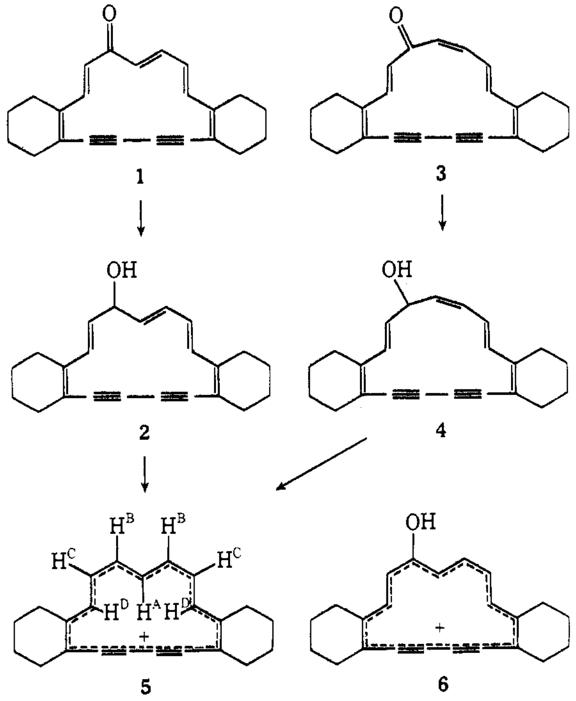
Synthesis of the 5,6:14,15-Bis(tetramethylene)-1,3-bisdehydro[15]annulenium Cation, an Aromatic 15-Membered Carbocyclic System[1]

Sir:

$(4n + 3)$-Membered conjugated carbocyclic cations contain $(4n + 2)$ π electrons and are therefore expected to be aromatic (diatropic),[2] provided they are reasonably coplanar. Well-known examples are the aromatic cyclopropenium ($n = 0$) and tropylium ($n = 1$) cations,[3] and recently some bridged derivatives of higher members ($n = 2, 3$) have been synthesized.[4] However, it has previously not been possible to prepare an unbridged macrocyclic annulenium cation. We now report the synthesis of the bisdehydro[15]annulenium cation **5** ($n = 3$) which, as expected, proved to be strongly diatropic.

Reduction of *all-trans*-4,5:10,11-bis(tetramethylene)-6,8-bisdehydro[15]annulenone (**1**)[5] in ether with ethanolic $NaBH_4$ for 2 hr at room temperature led to the orange-yellow alcohol **2**: λ_{max} (ether) 260 (ϵ 26,600), 269 (27,700), 285 sh (17,500), 354 (11,000), 375 sh (8300), 404 sh nm (2600).[6] Similar reduction of the mono-*cis*-bisdehydro[15]annulenone **3**[5] gave the lemon yellow alcohol **4**: λ_{max} (ether) 272 (ϵ 25,300), 283 sh (23,400), 312 sh (13,900), 340 sh nm (8600).[6] Both **2** and **4** were unstable substances which readily decomposed in the neat state at room temperature or on attempted chromatography on SiO_2 or Al_2O_3. Their structures were confirmed by the ir spectra (presence of OH bands, absence of C=O bands) and by oxidation in ether with MnO_2 to **1** and **3**, respectively, in high yield.

Several methods for converting **2** and **4** to the cation **5** were investigated. The best results were obtained by treatment of either **2** or **4** in the neat state with CF_3COOH or CF_3COOD at $\sim -78°$, followed by gradual warming to room temperature. Removal of the black insoluble polymer resulted in a deep violet solution of the trifluoroacetate of **5**: λ_{max} (CF_3COOH) 324 (ϵ 14,800), 387 (54,200), 550 sh (8400), 582 nm (22,200),[7] with absorption >700 nm. The structure of **5**, obtained from either **2** or **4**, follows unequivocally from the rather simple nmr spectrum (CF_3COOD, 100 MHz, $-7°$[8]), which consisted of a 2 H double doublet at τ -0.31 (H^B; $J_{B,A} = 14$, $J_{B,C} = 7.5$ Hz), a 2 H double doublet at τ 0.13 (H^C; $J_{C,D} = 15$, $J_{C,B} = 7.5$ Hz), an 8 H multiplet at τ 5.65–6.05 (allylic CH_2), an 8 H multiplet at τ 7.3–7.7 (nonallylic CH_2), a 1 H triplet at τ 13.13 (H^A; $J_{A,B} = 14$ Hz), and a 2 H doublet at τ 13.91 (H^D; $J_{D,C} = 15$ Hz). Although the trifluoroacetate of **5** was relatively stable in CF_3COOH solution, it could not be isolated since decomposition occurred on removal of the solvent or on addition of water.



The nmr spectrum of **5** trifluoroacetate clearly shows the substance to be strongly diatropic, since the inner olefinic protons resonate at very high field and the outer olefinic, allylic, and nonallylic protons at low field (the downfield shift is much greater than could be explained by the positive charge). The diamagnetic ring current in the cation **5** is considerably greater than in **6** (obtained by protonation of **1** or **3** with CF_3COOH),[5] in which the inner olefinic protons resonate at τ 9.61–9.88, the outer olefinic protons at τ 0.37–1.49, the allylic protons at τ 6.2–6.8, and the nonallylic protons at τ

---

(1) Unsaturated Macrocyclic Compounds. XCVII. For part XCVI, see E. LeGoff and F. Sondheimer, *Angew. Chem.*, in press.

(2) See F. Sondheimer, *Accounts Chem. Res.*, 5, 81 (1972).

(3) See P. J. Garratt, "Aromaticity," McGraw-Hill, Maidenhead, Berkshire, England, 1971, Chapter 4.

(4) See E. Vogel, *Int. Congr. Pure Appl. Chem., 23rd, Suppl.*, 1, 275 (1971); H. Ogawa, M. Kubo, and H. Saikachi, *Tetrahedron Lett.*, 4859 (1971).

(5) P. D. Howes, E. LeGoff, and F. Sondheimer, *ibid.*, 3695 (1972).

(6) The ϵ values represent minimum ones due to the instability of the substance.

(7) Complete conversion of **2** and **4** to **5** has been assumed in calculating the ϵ values which represent minimum ones. The electronic spectrum of **5** derived from **2** was essentially identical with that derived from **4**, although some variations in ϵ values were naturally observed.

(8) The nmr spectrum at room temperature was essentially identical, but the lowest field band was obscured by the solvent peak.