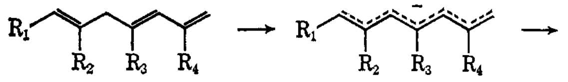
Preparation of Heptatrienyl Anions. The Heptatrienyl–Cycloheptadienyl Anion Rearrangement[1]

Sir:

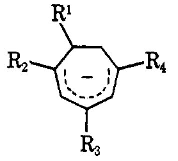
We wish to report the first synthesis of heptatrienyl anions in high concentration and their extremely facile high-yield cyclization to cycloheptadienyl anions.

1,4-Dienes with *n*-butyllithium in THF–hexane give pentadienyl anions, but 1,3-dienes either do not react as rapidly as THF with *n*-butyllithium or undergo addition instead of proton abstraction.[2] In view of the latter, it seemed possible that 1,3,6-trienes would undergo addition, but, in fact, proton abstraction is faster, at least for trienes Ia–d.[3] At $-50°$, Ia and b give excellent yields of heptatrienyl anions IIa,b; the only impurities detected by nmr were the rearrangement products IIIa,b, which form slowly at this temperature. It was necessary to warm Ic to about $-30°$ before it reacted, and nmr showed the resulting solution to contain more IIIc than IIc. Id reacted rapidly only near room temperature, giving an excellent yield of IIId; IId was not observed.



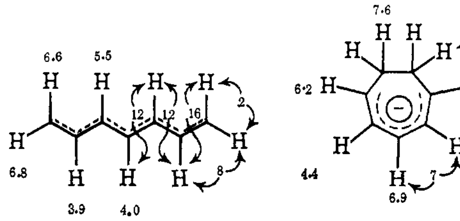
I II

a, $R_1, R_2, R_3, R_4 = H$
b, $R_1 = CH_3$; $R_2, R_3, R_4 = H$
c, $R_1, R_3 = H$; $R_2, R_4 = CH_3$
d, $R_1 = H$; $R_2, R_3, R_4 = CH_3$



III

The nmr parameters for IIa (Figure 1), IIb, and IIc are characteristic of ionic structures, as expected by analogy with pentadienyllithiums[4] and allyllithiums.[5]



IIa ($-50°$) IIIa ($35°$)

Figure 1. Nmr parameters for IIa and IIIa at 100 MHz. Chemical shifts are in τ units and coupling constants in Hz.

The decrease in electron density on the carbon atoms bearing negative charge is reflected in chemical shift decreases in the series allyl (end protons, τ 8.0[5]), pentadienyl (end, τ 7.1; central, τ 5.9[4]), heptatrienyl (end, τ 6.7; internal, τ 5.5). From the relatively large values (12 Hz) observed for the internal vicinal coupling constants in IIa, the extended conformation appears to be favored rather than the "helical all-*cis*" form anticipated by Hoffmann and Olofson;[6] however, the low activation energy for the cyclization described below makes it clear that the helical all-*cis* conformation is also of low energy.

Protonation of a solution of IIa at $-70°$ by ethanol–ether followed by hydrogenation gave a heptane–cycloheptane ratio of 9:1, further indicating the extent of cyclization at this stage and showing the feasibility of carrying out reactions on heptatrienyl anions before they cyclize.

When solutions containing IIa–c were warmed to $-30°$ or above, quantitative first-order cyclization to cycloheptadienyl anions IIIa–c was observed. At $-30°$, $t_{1/2}$ for IIa → IIIa is 13 min; for IIb → IIIb, 300 min; for IIc → IIIc, 200 min. This type of rearrangement, which presumably occurs in a conrotatory manner,[6] has been proposed as the cyclization step in the base-catalyzed conversion of Ib to a mixture of cycloheptadienes.[7] The carbanion equilibrium favors the cyclized forms IIIa–d to the extent that no uncyclized anion IIa–d was detected by nmr, even in the extreme case d, in which a primary, secondary, secondary, primary heptatrienyl anion closes to a tertiary, tertiary, tertiary cycloheptadienyl anion.

The nmr parameters for IIIa are shown in Figure 1. As in cyclooctadienyllithium,[8] the long-range coupling between the protons on the central and terminal carbons of the pentadienyl system is <1, indicating deviation from perfect U shape; models show that in neither cyclooctadienyl nor cycloheptadienyl systems can the p orbitals on the five sp^2-hybridized carbons be coplanar. This carbanion was also generated in quantitative yield by reaction of *n*-butyllithium with 1,4-cycloheptadiene[9] in THF–hexane; on protonation, it gives a 72:28 mixture of 1,3- and 1,4-cycloheptadienes. Unlike cyclooctadienyllithium, which rapidly cyclizes to a bicyclic allyl anion at $35°$,[8] IIIa does not cyclize, even on heating to $100°$.[10] This difference presumably reflects a reversal in the position of equilibrium, a reversal caused by increased strain in the bicyclo[3.2.0] system coupled with especially unfavorable p-orbital overlap in the cyclooctadienyl anion.

Nonatetraenyl anions, which should be similarly formed from 1,3,6,8-tetraenes, are currently under investigation.

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(2) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 199 (1967).

(3) Ia–c were purchased from Chemical Samples Co., and Id from Aldrich Chemical Co.

(4) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 205 (1967).

(5) P. West, J. I. Purmont, and S. V. McKinley, *J. Amer. Chem. Soc.*, **90**, 797 (1968).

(6) R. Hoffmann and R. A. Olofson, *ibid.*, **88**, 943 (1966).

(7) E. A. Zuech, D. L. Crain, and R. F. Kleinschmidt, *J. Org. Chem.*, 33, 771 (1968).

(8) R. B. Bates and D. A. McCombs, *Tetrahedron Lett.*, 977 (1969).

(9) If the reaction mixture from the reduction of cycloheptatriene with sodium in liquid ammonia (A. P. ter Borg and A. F. Bickel, *Rec. Trav. Chim.*, **80**, 1229 (1961)) is added *dropwise to a large excess of ethanol at $-78°$, and extracted with pentane immediately*, instead of obtaining only 1,3-cycloheptadiene, a 3:1 mixture of 1,3- and 1,4-cycloheptadienes is obtained. This mixture was readily separated by preparative glpc on Carbowax 20-M.

(10) It is interesting to note (private communication from S. Winstein) that treatment of 1,4-cycloheptadiene with strong base gives a small amount of bicyclo[3.2.0]hept-2-ene.

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