Ring Opening of a Bicyclo[3.3.0]octadienediyl Dianion

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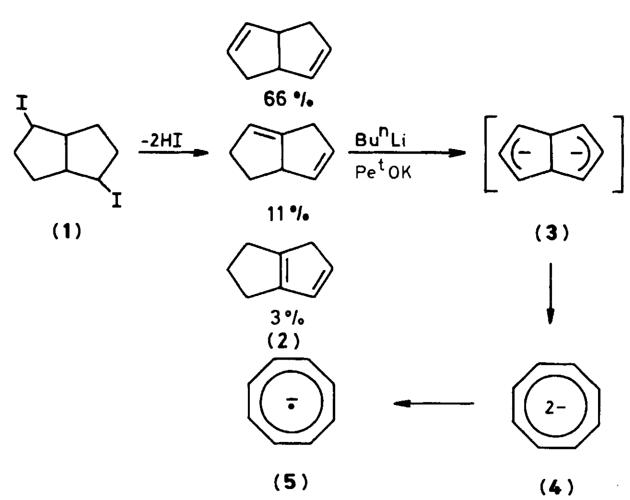
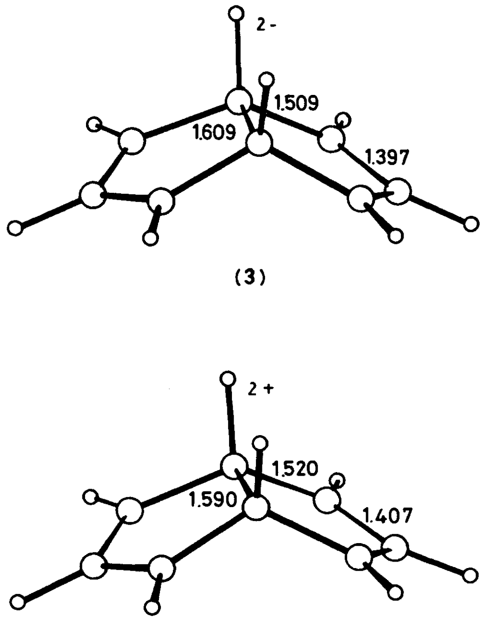
The bicyclo[3.3.0]octadienediyl dianion (**3**) ring opens to give the cyclo-octatetraene dianion (**4**), the reverse of the behaviour shown by the corresponding dication.

Transannular ring closure to give bicyclo[3.3.0]octane systems is a common feature of eight-membered ring chemistry. Pyrolysis of cyclo-octatetraene,[1] treatment of cyclo-octadienes with bases,[2,3] or iodine,[4] thermolysis or chlorination of octachlorocyclo-octatetraene,[5] and rearrangements of homotropylium cations[6] and of cyclo-octatetraene dication derivatives[7] all lead to the bicyclo[3.3.0]octane skeleton. As part of our investigations of the metallation–elimination reaction sequence,[3,8] we were interested in generating the pentalene dianion[9] by a simple elimination route. The results, however, reveal a new aspect of dianionic eight-membered ring chemistry and open a new route to the cyclo-octatetraene dianion.

When the mixture of tetrahydropentalenes[10] (**2**) obtained by elimination from the readily available di-iodide (**1**)[4] with potassium t-pentoxide is allowed to react under standard conditions[3] with a fourfold excess of a 1:1 n-butyllithium:potassium t-pentoxide (Bu^{n}Li–Pe^{t}OK) mixture and the resulting precipitate filtered off and dissolved in ($^2H_8$) tetrahydrofuran (THF), a clean proton n.m.r. spectrum consisting of a single line at δ 5.7 relative to Me_4Si is obtained. A solution in dry THF gives a nine line e.s.r. spectrum with a coupling constant of 3.20 G[†] and with ^{13}C satellites showing a coupling constant of 1.35 G when treated with dry oxygen. These data are characteristic of the cyclo-octatetraene dianion[11] (**4**) and radical anion[12] (**5**) produced by oxidation with O_2.



Treatment of the dienes (**2**) with less than one equivalent of Bu^{n}Li–Pe^{t}OK to favour monoanion formation gave no cyclo-octatriene products on quenching with D_2O. We therefore



(3)

(6)

Figure 1. MNDO Structures of (**3**) and (**6**).

[†] 10^4 G = 1 T.

Table 1. MNDO Heats of formation of C_8H_8 systems in kcal mol^{-1}.‡

Species	Bicyclo[3.3.0]octadienediyl	Cyclo-octatetraene
Dication,$^{2+}$	537.6 (**6**)	537.7 (**7**)
Neutral	148.7 (Diradical)	55.5 (D_{2d})
Dianion,$^{2-}$	148.8 (**3**)	121.1 (**4**)

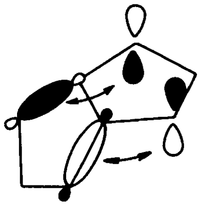


Figure 2

conclude that the dianion (**3**) ring opens to give the cyclo-octatetraene dianion COT^{2-} (**4**).

The disrotatory ring opening of (**3**) to give (**4**) is thermally allowed, in contrast to the equivalent reaction in the dication case,[7] but the direction of the reaction is reversed, in comparison to most of the known chemistry of such systems.[1–7] MNDO Semi-empirical molecular orbital theory[13] also indicates a change in behaviour between the dication and dianion. MNDO Structures for (**3**) and the corresponding dication (**6**) are shown in Figure 1. The calculated heats of formation (Table 1) indicate that the ring closure of the cyclo-octatetraene dication to give (**6**) is thermoneutral, whereas experimentally only (**6**) is observed as the reaction products of methylated systems.[7] In the dianion case, however, the aromatic dianion (**4**) is calculated to be 27.7 kcal mol^{-1}‡ more stable than the bicyclic isomer (**3**) in accord with our experimental results.

The shift in the relative stabilities is due to two factors: the widened CCC bond angle (*ca.* 130°) preferred by allyl anions,[14] which leads to extra strain in (**3**), and strong hyperconjugative stabilisation of the bicyclic dication (**6**). This strong interaction between the allyl system and the carbon–carbon sigma framework is stabilising for the dication (**6**) but destabilising for the dianionic counterpart (**3**) (Figure 2).

The behaviour of the diradical corresponding to (**3**) and (**6**) appears to be intermediate between the dication and the dianion. Bicyclo[3.3.0]octadienediyl diradicals have been suggested as intermediates in the ring closure of cyclo-octatetraene to give dihydropentalene and the ring opening of substituted semibullvalenes to give cyclo-octatetraenes.[15] Finally, we note that (**3**) cannot be an intermediate in the alkali metal reduction of semibullvalene.[16]

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‡ 1 kcal = 4.18 kJ.