

## The Reductive Decyclizations of Semibullvalenet

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Reduction of semibullvalene (**5**) with potassium more closely resembles deprotonation of tetrahydropentalenes by n-butyl-lithium-potassium t-pentoxide than it does the reduction of (**5**) with lithium; the former processes both provide the cyclo-octatetraenyl dianion (**4**), plausibly via the intermediate bicyclo[3.3.0]octadienediyl dianion (**3**).

We recently reported that reduction of semibullvalene (**5**) with lithium provides only the 'dilithium semibullvalenides': a mixture of two equilibrating isomeric organolithium clusters, each one possessing (**6**) as a common structural unit<sup>1</sup>. § Indefinitely stable in tetrahydrofuran solution at  $-78^{\circ}\text{C}$ , this mixture generated the cyclo-octatetraenyl dianion (**4**) only slowly at  $0^{\circ}\text{C}$ , albeit exclusively so, and with an apparent first-order rate constant:  $10^5 k = 9.0(1) \text{ s}^{-1}$ . Protonation with methanol at  $-78^{\circ}\text{C}$  provided the expected tetrahydropentalenes (**1**) (39%) and (**2**) (22%) ¶ as the sole isolable products.

We now report the conspicuously different behaviour of (**5**), when it is reduced by a potassium mirror rather than by a lithium wire, also in tetrahydrofuran at  $-78^{\circ}\text{C}$ : (**4**) then appears immediately [ $\delta_{\text{H}}$  (tetrahydrofuran) 5.72, lit.,<sup>3</sup> 5.73]. Under preparatively more amenable conditions [Na-K alloy (1:5), followed by protonation with HCl], only cyclo-octa-1,3,5-triene ¶ (25%) and cyclo-octa-1,3,6-triene ¶ (28%) could be isolated. When excess of lithium bromide was incorporated with the alloy prior to reduction, HCl provided a mixture

containing 18% of (**1**) and (**2**) as well as 18% of cyclo-octa-1,3,5-triene and 14% of cyclo-octa-1,3,6-triene.

We had earlier expected that (**4**) would easily be produced if the transient bicyclo[3.3.0]octadienyl dianion (**3**) could be generated.<sup>1</sup> The intermediacy of (**3**) in the reduction of (**5**) with potassium is consistent with its recently assigned similar role in the deprotonation of isomeric tetrahydropentalenes [(**1**), *inter alia*] by n-butyl-lithium-potassium t-pentoxide (1:1) ( $\text{Bu}^n\text{Li-Pe}^t\text{OK}$ ),<sup>4</sup> presumably a solid dispersion in hexane at elevated temperatures.<sup>5</sup> It is also consistent with the general belief,<sup>6</sup> and occasional demonstration,<sup>7</sup> that deprotonations with such mixed bases initially generate organopotassium compounds.\*\*

The common role of (**3**) in both processes is more a plausible hypothesis than a necessary one. Should it nonetheless be correct, (**3**) cannot then also serve as intermediate in the 12-crown-4 promoted removal of lithium from (**6**).<sup>1</sup> The reactive intermediate in that process deprotonates the ether reagent. This rather different behaviour, the previously reported deuterium incorporation data,<sup>1</sup> and the subsequently reported structural data<sup>2</sup> all implicate instead an incompletely delithiated  $\text{Li}_4(\text{C}_8\text{H}_8)_2$  as reactive intermediate.

In any case, the accumulated results clearly illustrate how the choice of alkali metal can drastically alter the behaviour of organo-alkali metal compounds. They also indicate when such differences are to be expected. The choice of metal is essentially irrelevant if the carbanion is the aromatic (**4**),<sup>3</sup> but crucial if it is the bishomoantiaromatic<sup>8</sup> (**3**). Only lithium permits (**3**) to remain indefinitely stable as its covalent derivative (**6**) at  $-78^{\circ}\text{C}$ . Under identical conditions, the

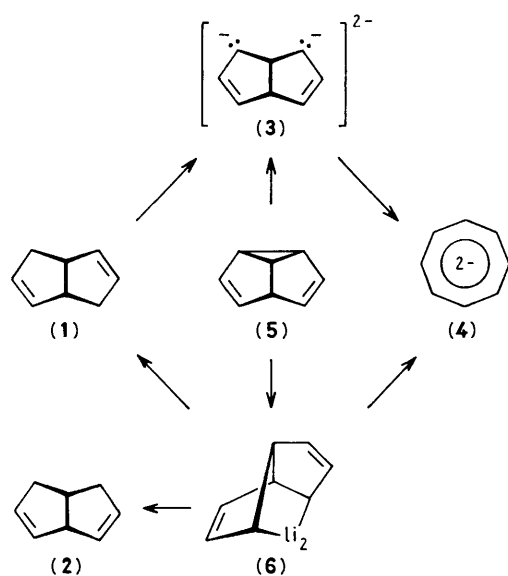
\*\* Wilhelm *et al.*<sup>4</sup> rationalize the facile transformation of (**3**) into (**4**) on grounds that differ from those which we had suggested,<sup>1</sup> but are not inconsistent with them. These same authors unfortunately cite ref. 1 with less than complete accuracy, when they claim that '... (**3**) cannot be an intermediate in the alkali metal-reduction of semibullvalene.' The citation may be accurate only for lithium, the only metal reported in ref. 1.

† Taken in part from the Ph.D. thesis of T. T. W., Cornell University, 1984.

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§ The deliberately ambiguous 'li' serves to indicate carbon-lithium covalency without specifying the full connectivity of the lithium atom or the size of the cluster.<sup>1</sup> A more complete structural characterization is described in the accompanying manuscript.<sup>2</sup>

¶ N.m.r.: (**1**), <sup>13</sup>C,  $\delta$  ( $\text{C}_3\text{D}_6\text{O}$ ) 135.5, 128.3, 48.4, and 38.3. (**2**), <sup>13</sup>C,  $\delta$  ( $\text{C}_3\text{D}_6\text{O}$ ) 132.7, 129.6, 59.3, 41.5, and 39.3; J. K. Whitesell and R. S. Matthews, *J. Org. Chem.*, 1977, **42**, 3878, report  $\delta$  ( $\text{CDCl}_3$ ) 134.2, 129.5, 58.5, 41.2, and 38.7. Cyclo-octa-1,3,5-triene. <sup>1</sup>H,  $\delta$  ( $\text{CDCl}_3$ ) 5.79–5.71 (m, 6.0 H) and 2.42 (m, 4.0 H); M. St. Jacques and R. Prud'homme, *Tetrahedron Lett.*, 1970, 4833, report  $\delta$  ( $\text{CDCl}_3$ ) 5.80–5.71 (m, 6H) and 2.43 (m, 4H). Cyclo-octa-1,3,6-triene, <sup>1</sup>H,  $\delta$  ( $\text{CDCl}_3$ ) 6.21–5.28 (m, 6.2H) and 2.73 (m, 3.8H); irradiation at  $\delta$  2.73 led to 6.13 (dm,  $J$  9.2 Hz), 5.66 (s), and 5.52 (dm,  $J$  9.2 Hz).



presumably ionic dipotassium salt of (3) behaves, at best, like a transient intermediate.<sup>9</sup>

We thank the U.S. National Science Foundation for its support of research and n.m.r. instrumentation.

Received, 14th May 1984; Com. 657

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