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Acidity Enhancement through Homoconjugation: Selective Introduction of Sodium into Olefinic Positions**

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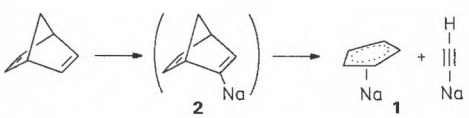
Dedicated to Professor Rolf Huisgen on the occasion of his 65th birthday

Abstract: When treated with butyllithium and sodium *tert*-butoxide, both norbornadiene and norbornene undergo a hydrogen/sodium-exchange at the 2-position. The diene, however, reacts approximately 30 times faster. Bicyclo[3.2.0]hepta-2,6-diene is also more readily metalated than bicyclo[3.2.0]hept-6-ene and its 7-position is preferentially attacked. Finally, cycloheptatriene is smoothly converted into 2-cycloheptatrienylsodium.

Previous attempts to submit norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) to a hydrogen/metal-exchange had failed[1,2]. When treated with a hexane suspension of pentylsodium, the bicyclic substrate decomposed into the fragments sodium cyclopentadienide **1** and sodium acetylide[1].



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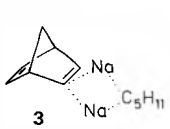
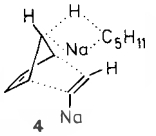
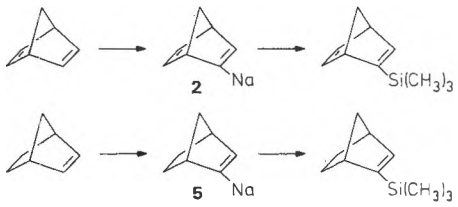
We argued that in the course of this reaction an initial metalation at the exceptionally acidic olefinic position did take place. In the absence of a well complexing solvent, however, the resulting intermediate **2**, can combine with the reagent to form a «mixed aggregate»[3] **3**. The latter should be particularly prone to intramolecular transmetalation and simultaneous[4] fragmentation (transition state **4**).



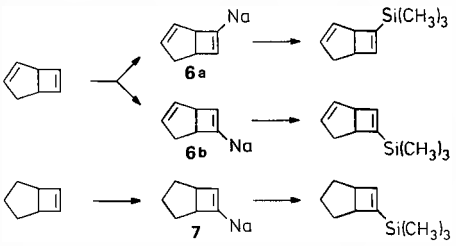


When we repeated the metalation experiment in tetrahydrofuran solution at −50 °C and, after 15 h, trapped the organometallic intermediate **2** with chlorotrimethylsilane, 74% of the corresponding silane was isolated. An excess of the metalating agent (2–4 equiv.) increased the yield to 88% without giving rise to any by-products. The mixture of butyllithium and sodium *tert*-butoxide («LICNAOR»[5]) was found to be just as efficient as pentylsodium itself. Under the same conditions norbornene was converted to the sodium compound **5**, and this, in turn, was silylated in high yield (92%). A competition experiment[6] revealed that norbornene reacts 30 times more slowly than norbornadiene[7].

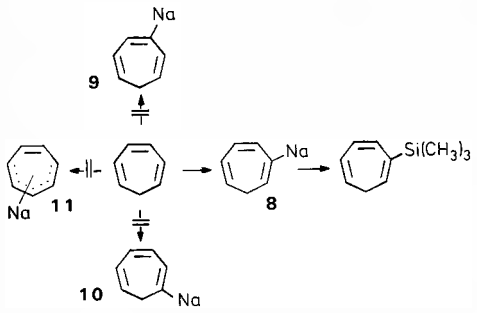


Bicyclo[3.2.0]hepta-2,6-diene and bicyclo[3.2.0]hept-6-ene are isomers of norbornadiene and norbornene, respectively. With butyllithium or pentylsodium in the presence of a potassium *tert*-butoxide suspension in hexane the bicyclic diene shows again an enhanced reactivity, the corresponding monoene being consumed 5 times more slowly in a competition experiment. Due to its higher symmetry, bicyclo[3.2.0]hept-6-ene forms a single organometallic intermediate **7** and also a single silane derivative (66%). In contrast, bicyclo[3.2.0]hepta-2,6-diene is converted into a 4:1 mixture of metalation products **6a** and **6b** as evidenced by the two silanes derived thereof. Unfortunately their combined yield is poor (12%). This may reflect an insufficient stability of intermediates **6a** and **6b** or, more likely, be a consequence of competitive metalation of the precursor

diene at the doubly allylic bridgehead position, thus generating an apparently unstable pentadienylmetal compound.

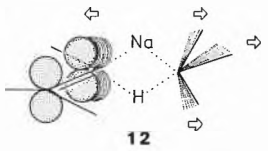


Finally, 1,3,5-cycloheptatriene, a monocyclic isomer of norbornadiene, reacts with amazing selectivity when consecutively treated with the LICNAOR-reagent and chlorotrimethylsilane. A sole product was identified in the reaction mixture, 2-(trimethylsilyl)-1,3,5-cycloheptatriene (isolated in 57% yield), and no derivatives resulting from metalation at the 1-, 3-, or 7-position[8] (intermediates **9**, **10**, and **11**, respectively) were detected.



Under similar conditions 1,3-cycloheptadiene and cycloheptene undergo smooth metalation at an allylic rather than olefinic position. At first sight the different chemical behavior of 1,3,5-cycloheptatriene appears only to manifest its reluctance to generate an «antiaromatic»[9] entity by deprotonation at the 7-position. Actually the acidity of cycloheptatriene (proton loss to afford a delocalized 8π-anion: $pK \approx 36$[10]) is hardly higher, presumably even a bit lower than that of cycloheptadiene. On the other hand, however, the ease with which metalation occurs at the 2-position of cycloheptatriene also suggests that the extra double-bond across the ring («extra» with respect to 1,3-cycloheptadiene as a reference) exerts a distinct activating effect. A similar role must be attributed to the extra double-bond in norbornadiene (when compared to norbornene) and the double-bond in the five-membered ring of bicyclo[3.2.0]hepta-2,6-diene depending on its proximity to the site of metalation.

With respect to the reaction center, all these activating extra double-bonds occupy a homoallylic or even more distant position. A pictorial explanation of this rate enhancing effect can be based on the presumed four-center transition state **12**[3]



of the hydrogen/metal-exchange process. When a monomeric butylsodium molecule enters into an encounter complex such as **12**, electron-deficient bonds are established between a metal, a hydrogen, and the carbon atom. The change from tetra- to pentavalency around the pivotal carbon atom obliges the three remaining «ordinary» σ-bonds to draw back by compressing their bond angles. The p-electrons of the olefinic substrate do basically the same by drifting away from the four-center core of transition state **12**. This motion appears to be facilitated by other double-bonds being located in the direction of this p-electron flow.

Typical working procedure: A solution of 30 mmol butyllithium in petroleum ether was evaporated under reduced pressure and the residue dissolved at −90 °C in precooled tetrahydrofuran. After addition of sublimed sodium *tert*-butoxide and cycloheptatriene (30 mmol each), the mixture was kept at −50 °C for 15 h before it was treated with chlorotrimethylsilane (32 mmol) and allowed to reach 25 °C. The solvent was carefully removed by distillation through a Widmer column (30 cm length), and the 2-trimethylsilyl-1,3,5-cycloheptatriene[11,12] distilled under reduced pressure; *b.p.* 99–102 °C/10 mmHg; 2.8 g (57%).

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[1] R.A. Finnegan, R.S. McNees, *Tetrahedron Lett.* (1962) 755.
[2] See also: G. Wittig, J. Otten, *Tetrahedron Lett.* (1963) 601; G. Wittig, G. Klumpp, *ibid.* (1963) 607.
[3] M. Schlosser: *Struktur und Reaktivität polarer Organometalle*, Springer-Verlag, Berlin 1973, p. 11, 136–138.
[4] Since the reaction proceeds spontaneously at ordinary temperature, it requires only a small activation energy and hence it should be an exothermal process. As simple thermochemical comparisons show, only such fragmentations satisfy the exothermicity condition which produce immediately cyclopentadienide (rather than cyclopentadiene), i.e., which are accompanied by concerted deprotonation at the 7-position.
[5] M. Schlosser, *Proc. Jpn. Chem. Soc. Annu. Meet. Tokyo 1984, 3* (1984) 1820.
[6] R. Huisgen, in *Houben-Weyl: Methoden der organischen Chemie*, Vol. *3/1*, p. 101, 143, Thieme Verlag, Stuttgart 1955.
[7] The higher kinetic acidity of norbornadiene with respect to norbornene had already been noted by other authors although in a merely qualitative fashion [A. Streitwieser, R.A. Caldwell, *J. Org. Chem. 27* (1962) 3360; G. Schröder, *Chem. Ber. 96* (1963) 3178].
[8] It has been claimed, that 7-cycloheptatrienylpotassium can be obtained by metalation of cycloheptatriene with benzylpotassium and by cleavage of 7-methoxy-cycloheptatriene or 7-triphenylmethyl-cycloheptatriene with potassium/sodium-alloy [H.J. Dauben, M.R. Rifi, *J. Am. Chem. Soc. 85* (1963) 3041; for details see: M.R. Rifi, Ph. D. thesis, University of Washington 1964 (microfilm service order nr. 64–8782)]. Although four coworkers tried hard to repeat this work, each of them carrying out at least half a dozen of individual reactions and using powerful analytical methods (including, e.g., ^{13}C-DEPT-NMR spectroscopy), all of them failed to find a trace of the alleged quenching product 2,4,6-cycloheptatriene-1-carboxylic acid.
[9] See also: M. Schlosser, P. Schneider, *Angew. Chem. 91* (1971) 515; *Angew. Chem. Int. Ed. Engl. 18* (1979) 489.
[10] R. Breslow, W. Chu, *J. Am. Chem. Soc. 95* (1973) 411; see also C.A. Wight, J.L. Beauchamp, *ibid. 103* (1981) 6499.
[11] ^{1}H-NMR (360 MHz): δ = 6.77 (d, J = 10.7 Hz, 1 H); 6.58 (dd, J = 10.6, 5.3, 1 H); 6.19 (dd, J = 9.0, 5.3, 1 H); 5.52 (t, J = 6.6, 1 H); 5.38 (dt, J = 9.0, 6.7, 1 H); 2.33 (t, J = 6.7, 2 H); 0.12 (s, 9 H). – ^{13}C-NMR (90.6 MHz): 138.3 (s); 134.3 (d, J = 155.3 Hz); 129.3 (d, J = 156.3); 126 (2C, beide d; J = 155); 120.4 (d, J = 159.3); 30.3 (t, J = 131.6); −1.27 (3C, q, J = 118.9).
[12] All new compounds gave correct elemental analyses.