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SYM-BENZVALENO-BENZO-BENZVALENE, A DOUBLE VALENCE ISOMER OF ANTHRACENE

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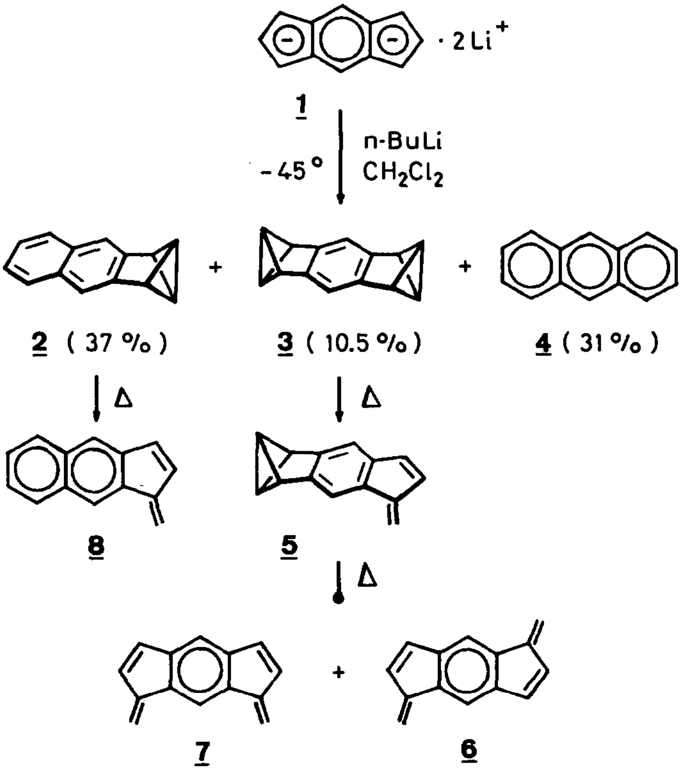
Abstract. Dilithio-s-indacene (1) on reaction with excess chlorocarbene produces s-benzvaleno-benzo-benzvalene (3). Unlike benzvalene, it does not aromatize on heating but decomposes stepwise to 1,5- and 1,7-bis-methylene-dihydro-indacene (6 and 7).

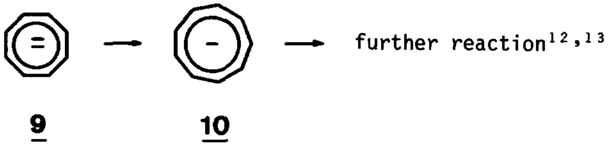
Lithium salts of several carbo and heteroaromatic anions have been successfully converted into benzvalene type compounds by reaction with chlorocarbene generated from methylene chloride and alkyl lithium.[1,2] Equal attention has been devoted to both the mechanistic and preparative aspects of this reaction.[3] So far, no answer has been provided to the question of how aromatic di-anions behave under corresponding conditions. We now wish to report that multiple bicyclobutane formation can be achieved by reacting suitable di-anions with excess chlorocarbene.

When dilithio-s-indacene (1)[4] is treated with a fourfold excess each of n-butyl lithium and dichloromethane in dimethylether at -45°C, three isomeric $C_{14}H_{10}$-hydrocarbons are formed which are in order of decreasing yield: naphtho[2,3]benzvalene (2) (37%), anthracene (4) (31%) and the title compound, s-benzvaleno-benzo-benzvalene (3) (10.5%). All products have been isolated by filtration of the crude reaction mixture over celite, followed by column chromatography on magnesia/celite (2:1) (n-pentane, 0°C). The structures of the valence isomers 2 and 3 have been established unambiguously from their spectra and by their $AgClO_4$ catalyzed interconversion to anthracene.[5] The ^{1}H-NMR spectrum of compound 2 (benzene-d_6, 100 MHz) shows an $[A_2B_2]$spin system for the bicyclobutane moiety at δ (ppm) 2.44 and 3.55 with the characteristic coupling $^3J_{AB}$ = 1.66 Hz. In addition to the aromatic [AA'BB'] system at δ (ppm) 7.28-7.74, a singlet (2H) is found at δ (ppm) 7.41. Compound 3 (benzene-d_6, 100 MHz) is characterized by an $[A_2B_2]$system of double intensity at δ (ppm) 2.29 and 3.74 ($^3J_{AB}$ = 1.62 Hz), and a single aromatic line (2H) at δ (ppm) 7.06.



The most remarkable finding of our experiment is that the heptacyclic bis-valene 3 is a stable compound at all. Its heat of formation (ΔH_f) is computed by the MINDO/3 method[6] to be 200.8 kcal/mole. Although this certainly overestimates the real energy content, it is obvious that 3 is protected against aromatization by high kinetic barriers. In fact, the bis-valene 3 when warmed in benzene does not give anthracene, but rearranges ($t_{1/2}$(70°C) 15 min.) to the 1,5- and 1,7-bis-methylene-dihydro-s-indacenes 6 and 7 in a 1:1 ratio.[7] Monitoring the thermolysis in the NMR spectrometer at 70°C readily reveals the intermediacy of benzvaleno-benzo-fulvene (5). This structure was deduced from the simultaneous and transient appearance of a new bicyclobutane resonance pattern (apparent $[A_2B_2]$ system at δ (ppm) 2.34 and 3.81 with $^3J_{AB}$ = 1.63 Hz) and the characteristic exo-methylene signals at δ (ppm) 5.48 and 5.88.[8] Thus the two bicyclobutane units of 3 undergo stepwise and independent breakdown like benzo-benzvalene.[1a] This is also observed for the simple valence isomer 2 which rearranges into fulveno[b]napthalene (8) ($t_{1/2}$ at 160°C in benzene, ca. 15 min).[9]

So far, 1 is the only salt of an aromatic dianion known that undergoes double bicyclobutane formation with chlorocarbene. We have also tested the lithium salt of cyclooctatetraene dianion (9).[10] However, the number of compounds obtained from reaction of 9 with methylene chloride/n-butyl lithium in dimethyl ether or THF was discouraging (at least 14). The major products (>95% of total material isolated) turned out to result from either direct reaction of 9 with methylene chloride[11] or were identical with the products obtained by Katz[12] and Masamune[13] from the reaction of cyclononatetraenide (10) with chlorocarbene. Clearly, initial ring enlargement (9 → 10) is the dominant reaction and bicyclobutane formation occurs at best in trace amounts.



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4) (a) The dilithium salt of s-indacene (1) was obtained by reacting a mixture of 1,5- and 1,7-dihydro-s-indacene[4b] with 2.1 equiv. of methyl lithium in dimethyl ether at -45°C. ^{1}H-NMR of 1 in THF-d_8 (100 MHz): [A_2B] spin system of double intensity at δ (ppm) 5.68 (A) and 6.60 (B) with $^3J_{AB}$ = 3.6 Hz, and a singlet at δ (ppm) 7.48 for the equivalent protons of the central ring. For chemical shifts cf. ref. 4c. (b) L. Trogen & U. Edlun, Acta Chem. Scand. B33, 109 (1979); (c) K. Hafner, private communication cited by B.M. Trost & P.L. Kinson, J. Am. Chem. Soc. 97, 2438 (1975).

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7) The ^{1}H-NMR spectrum of (6 + 7) shows two strongly overlapping four spin patterns in the olefinic region strongly reminiscent of the non-aromatic part of benzo-fulvene.[8] Fast polymerization prohibited the isolation.

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9) The ^{1}H-NMR spectrum of 8 (benzene-d_6, 100 MHz) shows four non-aromatic protons at δ (ppm) 5.44 (narrow m), 5.89 (narrow m) and [AB] type at 6.53 and 6.83 ($^3J_{AB}$ = 5.6 Hz) with further fine structure. The complex aromatic [ABCD] system at δ (ppm) 7.2-7.8 overlaps with two aromatic singlets at δ (ppm) 7.48 and 7.90.

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