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A FACILE ENTRY INTO THE BENZO[7,8] BICYCLO[4.2.1]NONANE SYSTEM

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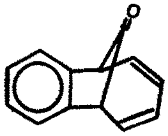
Despite considerable current interest in the bicyclo[4.2.1]nonane ring system[1], only one synthesis of the 7,8-benzo fused skeleton has been reported.[2] The benzobicyclic ketone **1** was produced in low yield from the reaction of benzyne with tropone.[2] A reported[3] synthesis of **2** from reaction of benzyne with cycloheptatriene was shown later to be in error.[4]



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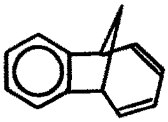


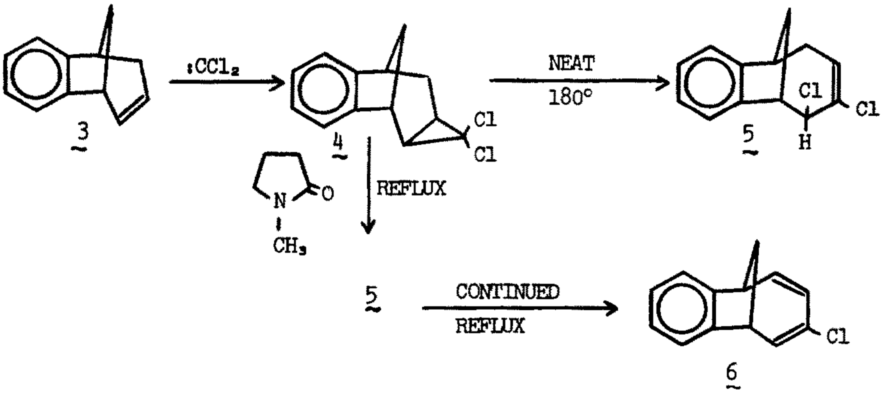
2

We now report a synthesis suitable for large-scale preparation of authentic **2**; the sequence can be diverted conveniently to produce other compounds with the same ring structure.

Addition of dichlorocarbene to benzo[6,7]bicyclo[3.2.1]octa-2,6-diene[5] (**3**) using a phase transfer catalyst[6] gave a 92% yield of **4**: mp 41.6-42.0°, ms m/e 239 ($M^{+\cdot}$), pmr consistent with the proposed structure.

Thermolysis of **4** (neat) for 22 hours at 180° gave *ca*. 40% conversion to dichloroolefin **5**. Similar behavior was reported for the non-benzo analog of **4**.[1b]

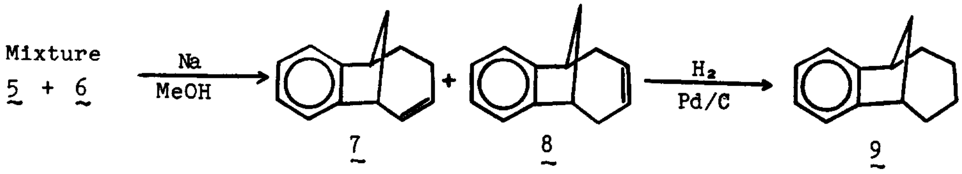
A superior medium for the ring opening of 4 was found to be N-methylpyrrolidone. After 2 hours of refluxing in this solvent (under N_2), a mixture of 5 and the chlorodiene 6 (~ 1:3 Ratio) could be isolated in > 60% yield; no starting material remained. Shorter reflux periods (30 min) gave higher yields (80%) and proportionately more 5 (~ 2:1 Ratio), but some (~ 10%) starting material remained.



Products 5 and 6 were separated by silica gel chromatography[8] and characterized spectroscopically. Data for 5 include: ir 1638 cm^{-1}, pmr($CDCl_3$) τ 2.80(s, 4H, arom.), 4.41(quart., 1H, vinyl), 5.23(d, 1H, H_2), 6.22-6.78 (m, 2H, H_1, H_6), and 7.10-8.00(m, 4H, $2H_5$, $2H_9$). Data for 6 include: ir 1620 cm^{-1} (strong); λ_{max}^{EtOH} mμ (log ε) 213(3.92), 256.5(sh, 3.49), 267(3.59), 276 (3.57), 2.89(3.34); pmr($CDCl_3$) τ 2.83(s, 4H, arom.), 3.50-4.50(m, 2H, H_2, H_5), 4.12-4.18(dd, J=12, 2Hz, 1H, H_4), 6.18-6.55(m, 2H, H_1, H_6), 7.30-7.82(quintet further split, 1H, H_9 syn) and 8.00-8.28(d, J=11.5Hz, 1H, H_9 anti). The vinylic region of 6 is closely comparable with that of the non-benzo analog.[7,1c] Solutions of 6 gradually form hexane-insoluble material on standing.

Reduction of the 1:3 mixture of 5 and 6, from thermolysis, with sodium in methanol gave a mixture of 7 and 8 (~ 1:1 Ratio) in 55% overall yield (based on 4). These were separated easily by column chromatography on silica gel or by preparative high pressure liquid chromatography, and characterized spectroscopically.

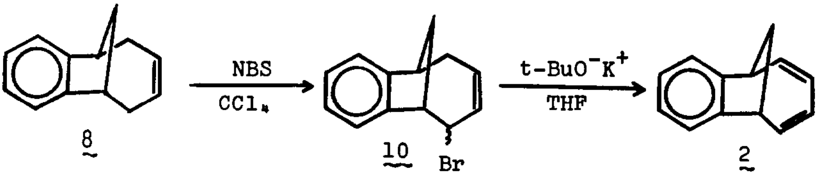
Data for 7 include: ir 1640 cm^{-1} (weak); pmr($CDCl_3$) τ 2.85(s, 4H, arom.), 3.62-4.08(dtd, 1H, H_2), 4.23-4.78(dtd, 1H, H_3), 6.28-6.78(m, 2H, H_1, H_6), and



7.42-8.40(m, 6H). For compound 8: ir 1650 cm^{-1} (weak); pmr($CDCl_3$), τ2.85(s, 4H, arom.), 4.73(narrow m, 2H, H_3, H_4), 6.64(quint., 2H, H_1, H_6), 7.20-7.90(m, 5H, $2H_2$, $2H_4$, H_9 syn), and 8.12-8.40(d, J=11.3Hz, 1H, H_9 anti).

Both 7 and 8 were catalytically reduced to give benzo[7,8]bicyclo[4.2.1]non-7-ene (9): pmr($CDCl_3$) τ2.83(s, 4H, arom.), 6.66(symmetrical m, 2H, H_1, H_6), and 7.52-8.90(m, 10H).

Allylic bromination of 8 with N-bromosuccinimide gave a mixture of monobromides. Without further purification, this was treated with potassium-t-butoxide in THF to give benzo[7,8]bicyclo[4.2.1]nona-2,4,7-triene (2) in 60% yield. Recrystallization under N_2 (pentane) gave colorless crystals of 2, mp 79-80.5°. Solutions of 2 also form hexane-insoluble material on standing.



Data for 2 include: ms m/e 168 ($M^{+\cdot}$ and base peak); λ_{max}^{EtOH} mμ (log ε) 208 (4.20), 281.9(3.51), 270.4(3.70), 261.0(3.65), 252.7(3.50); pmr($CDCl_3$) τ 2.81 (s, 4H, arom.), 3.53-4.00(m, 2H, H_2, H_5), 4.10-4.48(5-line pattern, 2H, H_3, H_4), 6.25(t, J=7Hz, 2H, H_1, H_6), 7.24-7.77(quintet further split, 1H, H_9 syn), 7.99-8.26(d, J=11.5Hz, 1H, H_9 anti). The aliphatic region of 2 shows an AA'BB'XX'YY' pattern, characteristic of symmetrical bicyclic dienes. A close comparison was found with vinyl patterns for bicyclo[4.2.1]nona-2,4-diene[7,1c], ketone 1, and several other published spectra.[1]

Further chemistry of 2, 5, 6, 7 and 8 is under investigation.

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(7) We wish to thank Professor C.W. Jefford and F. Delay for spectra of several bicyclo[4.2.1]nonane compounds.

(8) Very active silica gel isomerizes **5** to a compound believed to be a benzobicyclo[3.2.2] derivative.