Stereospecific Quenching of the Bicyclo[5.4.1]dodecapentaenyl Cation. Evidence of Orbital Symmetry Control

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Summary. Quenching of the title cation (**3**) with lithium methoxid results in stereo- and regio-specific incorporation of the methoxy group to give (**4**); the high specificity of the quench reaction is controlled by orbital symmetry.

IT has recently[1] been demonstrated that, in contrast with earlier reports, the stereospecific incorporation of electrophiles in the bicyclo[4.3.1]decatetraenyl anion takes place from the *exo*-face. We report here the highly stereospecific *exo*†-quenching of the iso-electronic bicyclo[5.4.1]dodeca-

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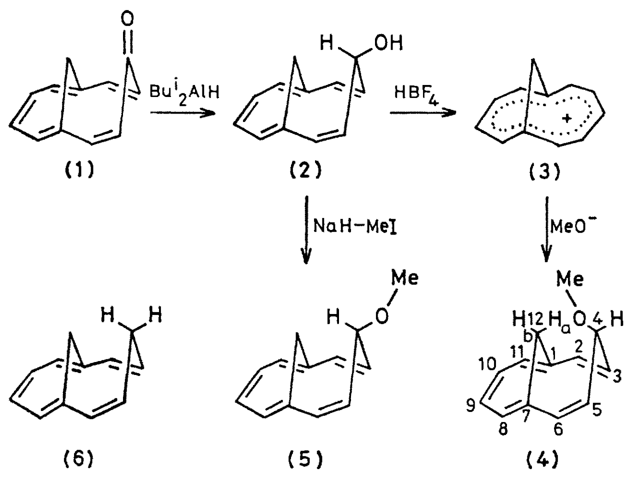
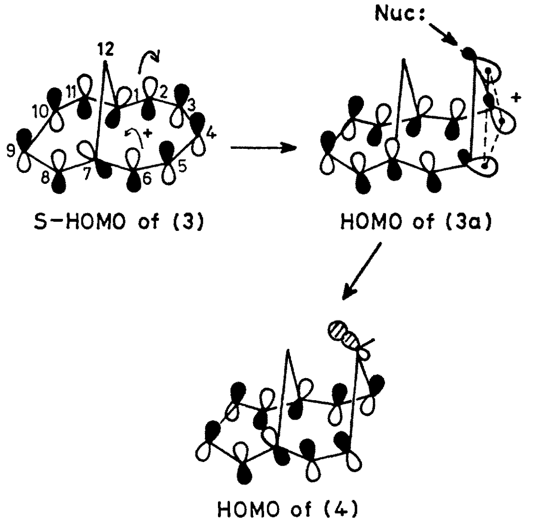
† In this communication the designation *exo*/*endo* for ring positions in the bicyclo[5.4.1]system is analogous to that in the bicyclo-[4.3.1] system, which is according to the rules for bicyclo[*X*.*Y*.*Z*.]anes in which the positions on the same side as the *Z*-bridge are designated *exo*, 'Selection of Index Names for Chemical Substances,' *Chem. Abstr.*, 1972, **76**, Index Guide.

pentaenyl cation (**3**), a methano-bridged 10π-electron aromatic cation.

The cation (**3**) was prepared by reducing the ketone (**1**)[2] with di-isobutylaluminium hydride to give the *endo*-alcohol (**2**) exclusively, which upon treatment with HBF_4 yielded the cation (**3**). When (**3**) was quenched with LiOMe–MeOH, only the methoxy derivative (**4**) could be isolated. Its epimer (**5**) was obtained by treatment of the alcohol (**2**) with NaH–MeI (Scheme).



SCHEME



S–HOMO of (3) HOMO of (3a)

HOMO of (4)

FIGURE

The structural assignment of (**4**) and (**5**) [implying that of (**2**)] is evident from a comparison of their ^{1}H n.m.r. spectra with that of the protic analogue[3] (**6**) and by application of the lanthanide shift reagent $Pr(fod)_3$. The coupling constants $J_{3,4} = J_{4,5}$ in (**4**) and (**5**) (8·5 and 4·5 Hz, respectively) do not vary significantly from comparable couplings in (**6**) and indicate that the methoxy group in (**4**) must occupy a pseudo-axial position, whereas the methoxy group in (**5**) must occupy a pseudo-equatorial position. Since the positions at C(4) in (**2**), (**4**), (**5**), and (**6**) can be distinguished by means of their different coupling constants, $J_{3,4a}$ and $J_{3,4e}$, the C(2)–C(6) fragment must be non-planar, leaving two possible orientations for the C(3)–C(5) unit; either *syn* or *anti* with respect to the C(1)–C(7) methylene bridge. On account of the large upfield shift of H(12a) in (**4**) [even larger than the shift for H(3,5)] when $Pr(fod)_3$ is used as the lanthanide shift reagent, the *anti*-conformation can be excluded. For (**5**) also a *syn*-structure can be assigned on the basis of the larger upfield shift of H(12a) with respect to that of H(2,6).

The formation of the thermodynamically unfavourable structure (**4**), in which the methoxy-group occupies a highly crowded *exo*-position in the *syn*-conformer, points to prevailing electronic factors and can most adequately be explained on the basis of MO symmetry arguments. Quenching of ion (**3**), which contains a nearly planar peripheral 11-membered ring,[4] generates the *syn*-conformer (**4**) suggesting a non-planar *syn*-transition state. The preferential formation of this transition state (**3a**) is interrelated with the *S*-symmetry‡ of the degenerate highest-occupied molecular orbital (HOMO) of the 10π-electron system in cation (**3**) (see Figure). The presence of the methylene bridge causes the p_π-orbitals at C(1,7) (bridgehead orbitals) to be distorted with respect to the other p_π-orbitals in the 11-membered ring. In order to gain a maximum overlap with the inward-twisted bridgehead orbitals, the p_π-orbitals at C(2) and C(6) will tend to make a disrotatory motion as illustrated in the Figure, resulting in a parallel orientation of the atomic orbitals at C(1,2) and C(6,7), respectively. This mode of motion gives rise to the orientation of the C(3)–C(5) unit *syn* with respect to the C(1)–C(7) methylene bridge. The alternative motion, *i.e.* disrotation of the atomic orbitals at C(2) and C(6) in the opposite direction, leading to an *anti*-transition state, is highly unfavourable since, in this case, the bridgehead orbitals and the p_π-orbitals at C(2) and C(6) are orthogonal, as can be derived from model studies. In (**3**) and (**3a**), the p_π-orbitals of the C(3)–C(5) unit have analogous symmetry in the HOMO of the 10π-electron system. Furthermore, in (**3a**) these orbitals have sp_3 character due to *endo*-twisting, which results in an enhanced orbital overlap of C(3) and C(5) with C(4) to form a homocyclopropenyl-type cation at the *endo*-face of the carbon skeleton.§ The intermediacy of the homocyclopropenyl-type cation (**3a**) results in reactions in which the nucleophile is captured *anti* with respect to the interacting side, in this case the *exo*-side of the ion, to give (**4**). The conversion of the HOMO of (**3a**) into that of (**4**) is 'allowed,' since they are interrelated by the same plane of

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‡ The HOMO is twofold degenerate. The A-MO has a nodal plane [*i.e.* the plane through C(12) bisecting the bridgehead–bridgehead axis] and is therefore unable to participate in the described process.

§ In spite of the non-coplanarity of the pπ-orbitals at C(2) and C(3) [respectively C(5) and C(6)], some conjugation of the homocyclopropenyl-type cation with the rest of the π-electron system may be present.

symmetry, which is the plane through C(12) bisecting the bridgehead–bridgehead axis

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