

Stereospecific *exo*-Incorporation of Deuterium into the Bicyclo[4.3.1]-decatetraenyl Anion

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Summary The title annulenyl anion (**4**) shows an overwhelming tendency for *exo*-face (*cis* to the methylene bridge) deuterium incorporation to give (**5**), contrary to a previous report describing the *endo*-deuteriation of (**4**).

WE have recently¹ demonstrated that the methoxycarbonyl bicyclo[4.3.1]decatetraenyl anion (**1**) shows a high *exo*-(*cis* to the methylene bridge)-stereoselectivity in its reaction with electrophiles giving the *exo*-incorporation products (**2**) (R=H, Me, and CH₂Ph). This selectivity of the anion (**1**) is the opposite to that obtained by Radlick and Rosen² for D₂O quenching of the anion (**4**) in Me₂SO. They indicated

that incorporation of deuterium into (**4**) occurred from the *endo* face because the ¹H n.m.r. signal at δ 2.71 of (**3**) disappeared in the deuteriated tricyclo[4.3.1.0]decatiene (**5**). It is, however, unlikely that the stereospecificity of the reaction with electrophiles is reversed according to whether an ester group is present or absent. Although Radlick and Rosen assigned the signals at δ 2.71 and 2.47† to H-9-*endo* and H-9-*exo*, respectively, in bicyclo[4.3.1.0]decatiene (**3**), this assignment is rather ambiguous, since an anisotropic effect of the olefinic units is also conceivable in addition to the effect of the cyclopropane ring. For example, both the C-4 methylene protons of bicyclo[3.1.0]hex-2-ene have nearly identical chemical shifts.

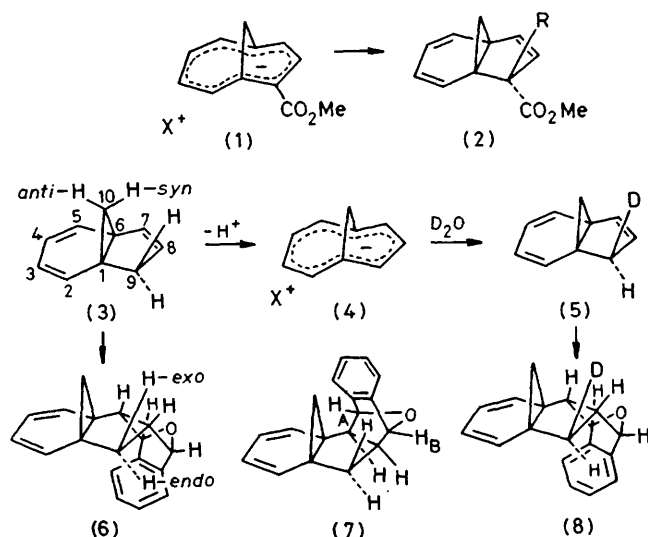
† The chemical shifts, δ 2.65 and 2.35, of the C-9 methylene protons reported in ref. 2 should be corrected as given here.

TABLE. ^1H N.m.r. data for (6) at 100 MHz, in CDCl_3

Assignment	$\delta/\text{p.p.m.}$	Multiplicity	J/Hz
H-7	3.40	dd	$J_{7,A}$ 5.0, $J_{7,B}$ 9.0
H-8	2.81	dddd	$J_{8,B}$ 6.0
H-9-endo	1.05	ddd	$J_{10,9\text{-endo}}$ 2.0; $J_{8,9\text{-endo}}$ 4.8
H-9-exo	2.01	dd	$J_{8,9\text{-exo}}$ 9.0, $J_{9\text{-exo},9\text{-endo}}$ 13.0
H-10-syn	1.20	d	$J_{10\text{-syn},10\text{-anti}}$ 3.5

To substantiate further the assignment of the ^1H n.m.r. spectra of the tricyclic triene (3) and to determine the mode of the deuteration of (4), the triene (3) was allowed to react with isobenzofuran to afford a single adduct (6) [m.p. 73–75 °C; m/e 248 (3.7%), 130 (100), and 118 (75)]. Proof of the structure of (6) was based on its ^1H n.m.r. data, which are summarized in the Table. The values of $J_{7,A}$ and $J_{8,B}$ indicated a *cis*-arrangement of these pairs of protons, eliminating the two isomeric structures having a *trans*-arrangement of the corresponding protons. Of the two remaining structures, (6) was preferred to (7) on the basis of the following. (a) The chemical shift of H-10-*syn* in the adduct was comparable with shifts of the corresponding protons which are not shielded by the aromatic ring in tricyclo[4.3.1.0]deca-2,4-diene³ and its 8-*endo*-chloro⁴ derivative. (b) W coupling was observed between H-10-*anti* and the C-9 proton at δ 1.05 (J 2.0 Hz), but not H-7. (c) Of the two C-9 methylene protons, the resonance of that coupled with H-10-*anti* was *ca.* 1.0 p.p.m. to higher field than the non-coupled proton. This can be reasonably explained only by the structure (6) where H-9-*endo* is located in the shielding region of the aromatic ring.

Reaction of the monodeuteriated triene (5), obtained from the anion (4) by D_2O quenching,[‡] with isobenzofuran gave the deuteriated adduct (8) [m.p. 75–76 °C; m/e 249 (1.9%), 131 (100), and 118 (52)]. The signal at δ 2.01 for (6) was absent from the spectrum of (8) and the signals at δ 1.05 (H-9-*endo*) and 2.81 for (6) collapsed to a lower multiplicity for (8), indicating unequivocally that (8) contains the deuterium in the C-9-*exo* position. In the two



double triplets centred at δ 2.71 and 2.47 for the C-9 methylene protons of (3), the former disappeared in the spectrum of deuteriated (5) and therefore should be assigned to H-9-*exo* in accordance with stereospecific *exo*-face incorporation of deuterium into the 1,5-methano[9]-annulenylium anion (4).

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[‡] Quenching with D_2O , AcOD, or MeOD of solutions of the lithium salt of the anion (4) in tetrahydrofuran, the sodium salt in dimethyl sulphoxide, and the potassium salt in 1,2-dimethoxyethane led to the same compound (5) in each case.

¹ K. Takahashi, T. Kagawa, and K. Takase, *Chem. Letters*, 1979, 701.

² P. Radlick and W. Rosen, *J. Amer. Chem. Soc.*, 1967, **89**, 5308.

³ H. Günther and T. Keller, *Chem. Ber.*, 1970, **103**, 3231.

⁴ P. Radlick and W. Rosen, *J. Amer. Chem. Soc.*, 1966, **88**, 3461.