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ADDITION OF METHANOL TO endo-TRICYCLO[3.2.1.$0^{2,4}$]OCT-6-ENE: A PROBE OF CYCLOPROPYL CORNER vs EDGE PROTONATION

Merle A. Battiste[a], James M. Coxon[b]*, Alan J. Jones[c], Roy W. King[a], Gregory W. Simpson[b] and Peter J. Steel[b].

(a) Chemistry Department, University of Florida, Gainesville, Florida

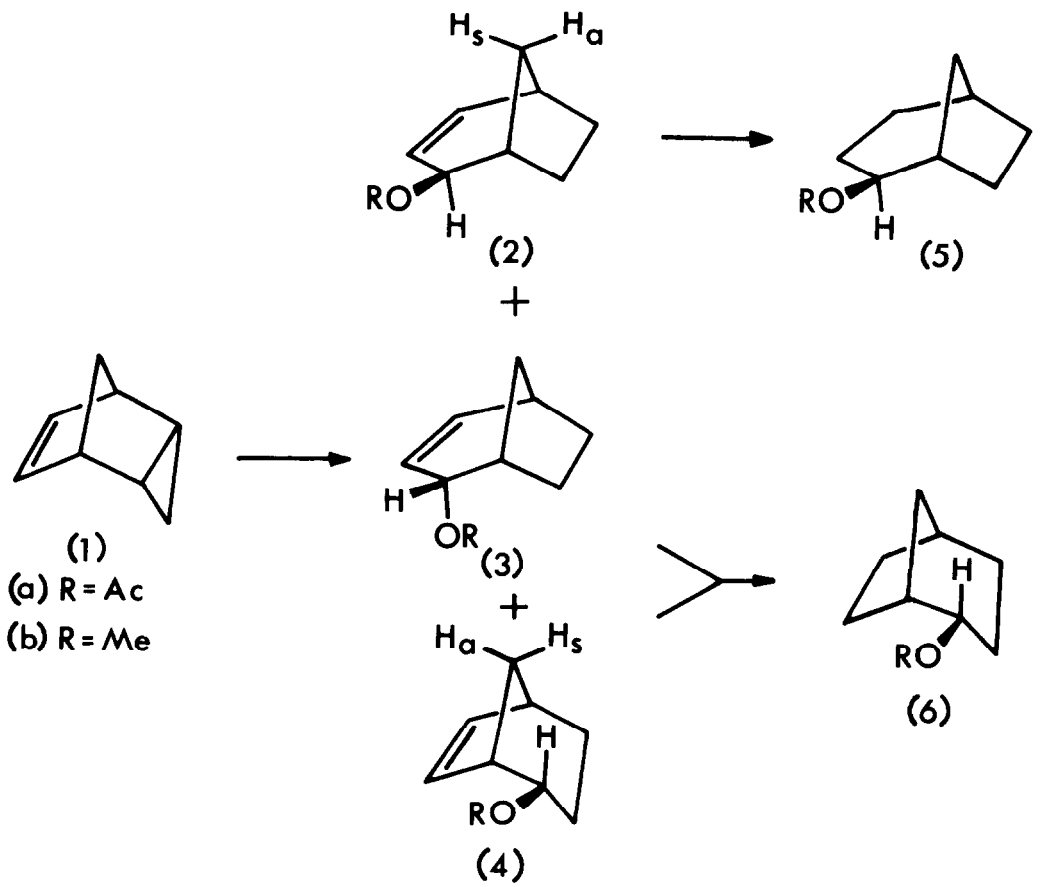
(b) Chemistry Department, University of Canterbury, Christchurch, New Zealand

(c) National N.m.r. Centre, The Australian National University, Canberra, A.C.T., Australia.

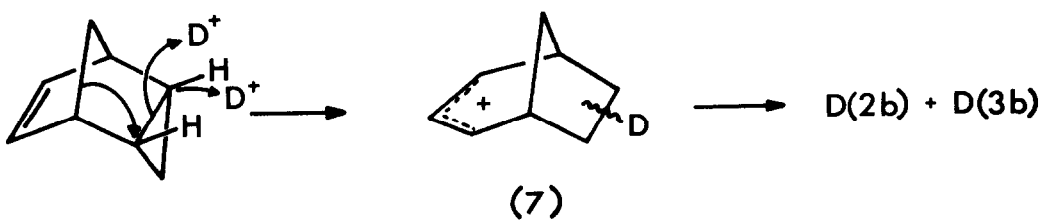
Abstract: Deuterium labelling experiments have shown that acid catalysed reaction of endo-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene with methanol proceeds exclusively by cyclopropyl corner protonation followed by skeletal rearrangement to an allylic ion and formation of 2-exo-methoxybicyclo[3.2.1]oct-3-ene.

endo-Tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (1) on reaction with acetic acid undergoes rupture of the internal cyclopropyl σ-bond to give a (78:22) mixture of exo- and endo-bicyclo[3.2.1]oct-3-en-2-yl acetates[1] (2a) and (3a). We report the reaction of olefin (1) with methanol-(D_1) as a probe of the mechanism of the transformation of the tricyclic to bicyclic skeleton and stereochemistry of electrophilic attack on the cyclopropyl σ-bond.

A 0.136 M solution of olefin (1) in a 0.125 M 4-toluene sulfonic acid-methanol solution at 60° ($k = 4.3(\pm 0.1) \times 10^{-3}$) resulted in the formation of three products (2b), (3b) and (4b) in the ratio 38.6:1.0:5.1 (Scheme 1). The major product (2b), purified by preparative g.l.c. (10% SE30 on Chromosorb W; 16'; 100°), was identified by its spectral properties. [^{1}H n.m.r. ($CDCl_3$) (270 MHz) δ_H 6.10, $J_{H4,H3}$ 9.45, $J_{H4,H5}$ 6.48, $J_{H4,H2}$ 1.08, $J_{H4,H8a}$ 1.08 Hz, H4; 5.51, $J_{H3,H4}$ 9.7, $J_{H3,H2}$ 3.91, $J_{H3,H5}$ 1.75 Hz, H3; 3.38, OMe; 3.26, $J_{H2,H3}$ 3.8, $J_{H2,H1}$ 3.0 Hz, H2; 2.50, Wh/2 20Hz, H1, H5; 1.86, Wh/2 35Hz and 1.60, Wh/2 25Hz, H6exo, H7exo; 1.73, $J_{8s,8a}$ 11.5, ^{4}J 1Hz, H8s; 1.58, Wh/2 25Hz and 1.22 Wh/2 25Hz,



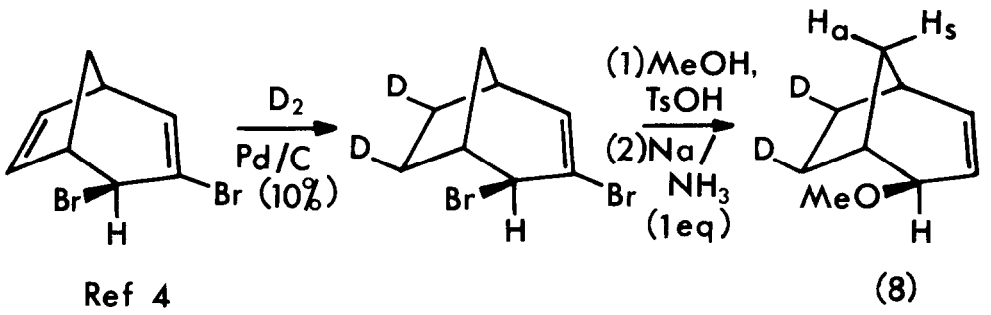
Scheme 1



Scheme 2

H6endo,H7endo; 1.22, $J_{8a,8s}$ 11.5Hz, H8a. ^{13}C n.m.r. ($CDCl_3$) δ_C 138.5, C4; 123.1, C3; 81.3, C2; 56.3, OMe; 36.2, 35.8, C1, C5; 31.4, C8; 31.3, 24.9, C6, C7] and by hydrogenation (5% Pd/C) to methyl ether (5b) identical with an authentic sample[2]. Methoxy-olefin (4b) was isolated by preparative g.l.c. and identified by its spectral properties [^1H n.m.r. ($CDCl_3$)(100 MHz) δ_H 5.92, Wh/2 4Hz, H6, H7; 3.34, OMe; 3.26, $J_{H2,H1}$ 3, $J_{H2,H3exo}$ 4, $J_{H2,H3endo}$ 8Hz, H2; 2.84, $J_{H1,H8a}$ 6Hz, H1; 2.53, $J_{H5,H8a}$ 5, $J_{H5,H4exo} = J_{H5,H4endo}$ 3Hz, H5; 2.05, $J_{H8a,H8s}$ 10, $J_{H8a,H4endo}$ 1.0 Hz, H8a; 1.95-1.4, $H_2$3, $H_2$4; 1.31, $J_{H8s,H8a}$ 10Hz, H8s] which showed CHOMe coupled to H1 which is deshielded by the olefin group. Hydrogenation (5% Pd/C) gave methyl ether (6b) identical to an authentic sample[2]. The minor reaction product (3b) was isolated free of (4b) but not free of (2b) by preparative g.l.c. Capillary column g.l.c. analysis showed the product had the same retention as an authentic sample[2] of (3b) and hydrogenation of this mixture free of (4b) gave a reaction product enriched in methoxy-ether (6b).

Reaction of olefin (1) with methanol-D_1 should allow edge vs corner attack[3] at the cyclopropyl carbon to be differentiated (Scheme 2). For edge attack the configuration of deuterium in (2b) would be exo and for corner attack would be endo. The mass spectrum of (2b) prepared from reaction with methanol-D_1 showed incorporation of one deuterium and the ^2H n.m.r. spectrum showed two signals at 1.54 and 1.14 p.p.m. The predominance of exo-methoxy olefin vs endo-methoxy olefin (3b) and the presence of two distinct sets of carbon signals for C6 and C7 in the spectrum of deutero- (2b) supports the intermediacy of the allylic cation (7). Thus the signals at 31.3 and 24.9 p.p.m. (C6 and C7) were reduced in intensity and triplets centred at 31.2 and 24.6 p.p.m. were apparent. To confirm the assignament of C6 and C7 protons of methoxy olefin (2b) an authentic sample of C6,C7-exo-dideuteromethoxy olefin (8) was prepared (Scheme 3) [^2H n.m.r. δ_D 1.80 and 1.55. ^1H n.m.r. ($CDCl_3$) δ_H 1.86 absent; 1.6 reduced in intensity by one-half; 1.73, J_{8s8a} 11.5, ^4J 1Hz, H8s; 1.55, $J_{H6endo,H7endo}$ 8.98, J 1.29, (C6)- or (C7)-endo-H; 1.22, Wh/2 20Hz, (C6) or (C7)-endo-H, H8a]. From the ^2H n.m.r. spectrum of methoxy olefin (8) the C6-exo and C7-exo protons of the undeuterated olefin (2b) were assigned. The chemical shifts of the C6-exo and C7-exo deuteriums in the ^2H n.m.r. spectrum of the methoxy olefin (8) facilitated assignment of the C6 and C7 protons in the ^1H n.m.r. spectrum of olefin (2b). The ^1H n.m.r. spectrum of olefin (2b)



Ref 4 (8)

Scheme 3

shows H8b coupled to H8a, the signal due to H8a being readily discernable in the simplified spectrum of (8). The remaining proton signals at 1.6 and 1.2 p.p.m. are therefore due to the C6-endo and C7-endo protons. The reduction of these two signals for the methoxy olefin (2b) formed by reaction with methanol-D_1 confirms corner protonation of the cyclopropyl σ-bond.

The olefin (1) has been shown previously to exhibit high stereoselectivity and regiospecificity in its reaction with tetracyanoethene[5]; the above results demonstrate protonation occurs in the same sense - by corner attack of the cyclopropyl σ-bond.

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