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THE EFFECT OF C-3 SPIROCYCLOPROPYL SUBSTITUTION ON SOLVOLYSIS OF EPIMERIC, TERTIARY 2-METHYL-2-BENZONORBORNENYL- AND 2-METHYL-2-NORBORNYL-P-NITROBENZOATES[1].

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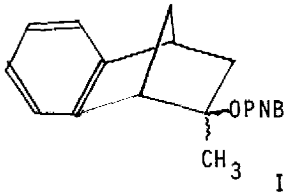
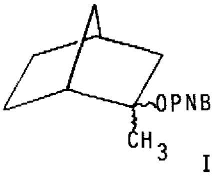
Substituents of increasing eletron demand situated at a carbocation center of systems prone to participation are expected to reduce the solvolysis rate ratio of epimers greatly[3]; such behavior is observed, for example, by alkyl- and aryl groups on the <u>syn</u>/<u>anti</u> ratio of 7-norbornenyl esters[4]. Surprisingly, the large $k_{\underline{exo}}/k_{\underline{endo}}$ values observed in the secondary 2-benzonorbornenyl tosylates[5] (15 000, acetic acid at 25°) and 2-norbornyl tosylates[6] (350, acetic acid at 25°) are not changed substantially in going to the tertiary 2-methyl-compounds: k(I)/k(II) = 6500[5]; k(III)/k(IV) = 895 (60% acetone at 25°)[6].

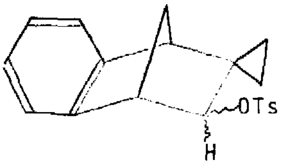


I, CH_3 endo, OPNB exo
II, CH_3 exo, OPNB endo



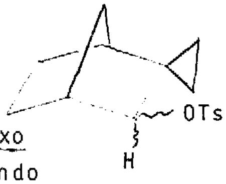
III, CH_3 endo, OPNB exo
IV, CH_3 exo, OPNB endo

In the case of the tertiary esters, where classical or nearly classical behavior is involved[7], steric factors are believed to be responsible for the large exo/endo ratios observed[5,6]. Even though steric effects in tertiary systems are likely to be larger than in secondary, the possibility exists that such factors, rather than participation, may be responsible for the high secondary exo/endo ratios as well[8]. Substituents of increasing electron demand placed at C-3, rather than at the reaction site, preserve the secondary nature of the system but in line with the participation argument, reduce the exo/endo ratios drastically. A spirocyclopropyl group shows this reduction; i.e., to 12 in the 2-benzonorbornenyl[9] and 2.6 in 2-norbornyl system[10]. We have explained this behavior as result of the strong conjugative interaction of the cyclopropyl group which dominates over other neighbouring group effects[5,9]; therefore, the small values can be regarded as due to steric effects in the parent system.



V,H endo,OTs exo

VI,H exo, OTs endo



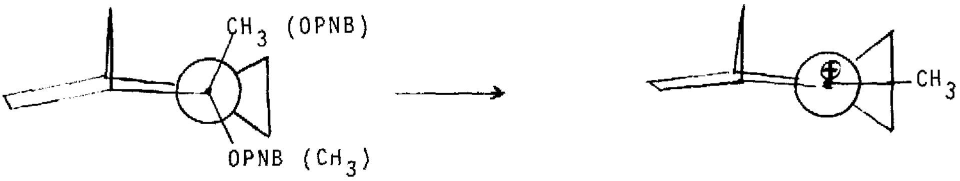
VII,H endo,OTs exo

VIII,H exo,OTs endo

These conclusions have been questioned[11]. More reactive systems, like V and VI, VII and VIII according to Brown should be less selective, and should exhibit lower exo/endo ratios as a consequence[11]. If this were true, and if secondary and tertiary behavior have a common origin, then the tertiary systems related to secondary spirocyclopropyl compounds should also exhibit low exo/endo ratios. We now report results on IX - XII.

The tertiary spiro compounds IX - XII (see Table) have been prepared by procedures[12] analogous to the parent compounds I - IV[5b,6b]. Starting from the corresponding ketones, spiro [5.6-benzonorbornen-3.1'-cyclopropan] -2-one[13]and spiro [norbornan -3.1-cyclopropan] -2-one[9] either 2-exo-methyl-2-endo-alcohol were obtained by reaction with CH$_3$MgI. Wittig reaction of either ketone yielded the 2-methylene compound, which was converted into the 2-endo-methyl-2-exo alcohol by oxymercuration-demercuration. The tertiary alcohols were obtained stereochemically pure and converted into their p-nitrobenzoates IX - XII by the n-butyl-Li/p-benzoyl chloride method. IX - XII were solvolysed in 60% aque. acetone; the kinetic results are summarized in the Table.

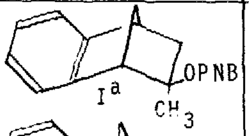
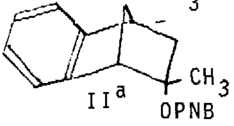
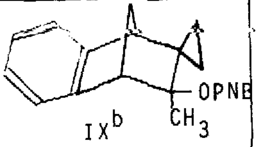
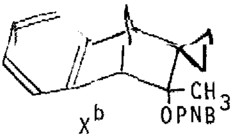
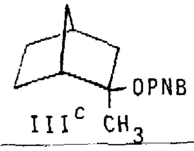
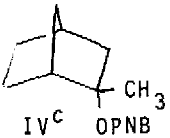
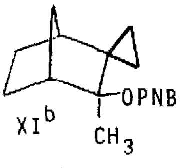
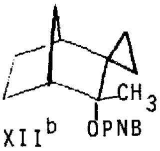
In sharp contrast to the secondary behavior, the tertiary exo/endo ratios are virtually unaffected by C-3 spirocyclopropane substitution. This occurs despite the ca. 10^4 acceleration in all instances by cyclopropylcarbinyl resonance[13]. There is no evidence for the operation of a selectivity effect in these systems. The cyclopropyl group at C-3 bisects the reaction site and should not affect the steric environment of exo or endo ground and transition states differentially[15,16].



Our work shows that high exo/endo ratios in related secondary and tertiary benzonorbornenyl and norbornyl systems do not have a common origin. Steric effects[15] are largely responsible for the high ratios exhibited by tertiary derivatives, but electronic effects (i.e.,participation) dominate the behavior of the unstabilized secondary cases. Only a small steric factor, ca. 2-10, can contribute to these secondary exo/endo ratios.

That sigma-aryl systems can participate is no longer disputed[5a];the benzonorbornenyl system can thus be taken as a model for a participating norbornyl system, and the identical pattern of behavior observed in either series strongly supports our interpretation.

Table. Summary of Solvolysis Rates of p-Nitrobenzoates IX-XII in aque.Acetone

Compound	Temp. [°C]	k [sec^{-1}]	ΔH‡[kcal/mole]	ΔS‡[e.u.]	k_{exo}/k_{endo}
 I[a]	100.0 [d] 25.0 [d]	7.48×10^{-7} 3.6×10^{-10}			1133 6545
 II[a]	100.0 [d] 25.0 [d]	6.6×10^{-10} 5.5×10^{-15}			
 IX[b]	100.0 [d] 75.6 52.2 25.0	1.61×10^{-2} 1.70×10^{-3} 1.44×10^{-4} 5.06×10^{-6}	23.1	-5.2	1192 5200
 X[b]	124.7 100.0 [d] 98.5 25.0 [d]	1.50×10^{-4} 1.35×10^{-5} 1.20×10^{-5} 9.73×10^{-10}	27.5	-7.3	
 III[c]	100.0 25.0 [d]	9.46×10^{-5} 1.02×10^{-8}			240 895
 IV[c]	100.0 25.0 [d]	3.95×10^{-7} 1.14×10^{-11}			
 XI[b]	100.0 [d] 0.1 25.0	1.99×10^{0} 1.38×10^{-4} 2.71×10^{-3}	18.8	-7.3	172 831
 XII[b]	100.0 [d] 66.7 50.3 89.8 25.0 [d]	1.16×10^{-2} 5.10×10^{-4} 7.50×10^{-5} 4.50×10^{-3} 3.26×10^{-6}	23.4	-5.0	

[a] In 80% acetone, ref. 5b [b] In 60% acetone, determined conductometrically; average of two runs; deviations not more than ±3% [c] In 80% acetone, ref. 6b [d] Calculated from rates at other temperatures.

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