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SOLVOLYSES OF EPIMERIC 6,7-BENZOBICYCLO[3.2.2] NONA-2,6,8-TRIEN-4-YL 3,5-DINITROBENZOATES.

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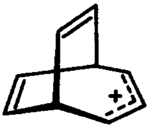
Recent interest[1,2,3] in the possible antibicycloaromatic[4] character of the bicyclo[3.2.2]nonatrienyl cation 1, prompts us to report the results of our studies with the related benzo-fused system 2. The benzo fusion allows the independent study of two epimeric substrates (e.g. 6 and 7), from which, the importance of an anchimerically-assisted route to ionisation in this system might be determined. Direct formation of the barbaryl cation 3, without the intermediacy of 1, seems to predominate in solvolyses of the parent bicyclo [3.2.2]nonatrienyl system.[1,2,3]



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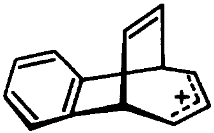

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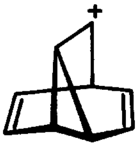

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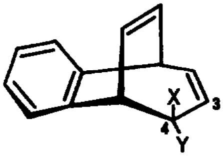
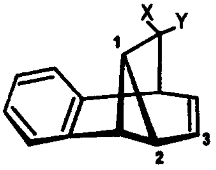
The epimeric 6,7-benzobicyclo[3.2.2]nona-2,6,8-trien-4-ols, 4,[5] m.p. 90-91°(63%) and 5, m.p.107-109°(29%), were obtained by aluminium isopropoxide reduction of 6,7-benzobicyclo[3.2.2]nona-3,6,8-trien-2-one.[6] Conventional esterification afforded the endo and exo 3,5-dinitrobenzoates 6, m.p.192-194° and 7, m.p.184-187° respectively.





4: X = H; Y = OH
5: X = OH; Y = H
6: X = H; Y = ODNB
7: X = ODNB; Y = H

12: X = D; Y = OH
13: X = OH; Y = D
14: X = D; Y = ODNB
15: X = ODNB; Y = D

8: X = H; Y = OH
9: X = OH; Y = H
10: X = H; Y = ODNB
11: X = ODNB; Y = H

ODNB = 3,5-dinitrobenzoate

Preparative solvolyses of 6 and 7 at 120° in 80% aqueous acetone (containing 10% excess lutidine) gave the product mixtures listed in Table 1. Product compositions were very similar in each case, consisting mainly of the epimeric benzobarbarols[7] 8,[8] m.p.106-107° and 9,[8] m.p.120-121°, accompanied by the benzobarbaryl 3,5-dinitrobenzoates 10 and 11, and a smaller amount of the unrearranged endo alcohol 4.

Table 1. Solvolysis data for dinitrobenzoates in 80% aqueous acetone at 120°

	Isolated yields %				
Compound	8	9	10 + 11	4	$k \times 10^5 sec^{-1}$
6 (endo)	37	32	14(1.0:1.6)	10	4.50 ± .04
7 (exo)	39	36	11(4.1:1.0)	4	5.08 ± .04
14 (endo)	30a	31a	15a	10a	

(a) Yields of the corresponding deuteriated products.

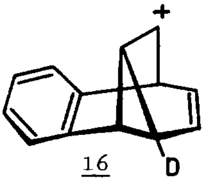
Kinetic solvolyses were performed in 80% aqueous acetone at 120°, and after correction for internal return, the data gave good first order plots. Derived first order rate constants for 6 and 7 are included in Table 1. These may be compared with the value of $9.8 \pm 0.5 \times 10^{-5} sec^{-1}$ obtained[2,3] for the solvolysis of bicyclo[3.2.2]nona-2,6,8-trien-4-yl p-nitrobenzoate in 80% aqueous acetone at 125°. The latter rate is comparable to those of other cyclic allylic p-nitrobenzoates.[2,3]

The strikingly similar solvolysis rates and product compositions for both epimers 6 and 7, and in particular, the consistent[9] observation of *unrearranged* alcohol 4 as a solvolysis product, suggest that there is no unusual instability associated with the benzobicyclo[3.2.2]nonatrienyl cation 2. In keeping with the parent system, however, this cation *is* unstable with respect to rearrangement to the benzobarbaryl system.

In order to gain insight into the detailed mechanism of this solvolytic rearrangement, the preparative solvolysis was repeated using the deuteriated 3,5-dinitrobenzoate 14.[10] The extent of deuterium scrambling was determined by repeated integration of the nmr spectra of the isolated solvolysis products (Table 1). Within experimental error (± 5%), the epimeric benzobarbarols 8 and 9 had identical scrambling patterns; 45% of the deuterium appeared at C-2 while

55% was scrambled almost statistically amongst the remaining non-benzo positions. A similar analysis of the mixture of dinitrobenzoates 10 and 11 indicated corresponding figures of 54 and 46%. Unfortunately, the relatively small amount of unrearranged alcohol 4 obtained in this experiment prevented measurement of the extent of deuterium scrambling with the same accuracy. Despite this, it was evident that significant scrambling of the label had occurred.[11]

Perhaps the most economical explanation of the present results, is that solvolysis of the endo ester 14 proceeds by two pathways; one involving direct formation of an unscrambled benzobarbaryl cation or ion pair 16, and the other, leading by way of the benzobicyclo[3.2.2]nonatrienyl cation 2, to a scrambled benzobarbaryl cation 17. Whether these two routes are truly independent, cannot be judged from the present work.



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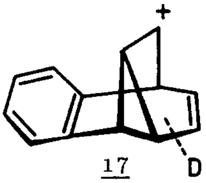

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Implication of the unrearranged cation 2 in the solvolysis of 6, is in direct contrast to the situation observed with the parent system.[1,2,3] This difference may be due in part, to the reluctance of the benzo π electrons to participate as part of an antibicycloaromatic system.[12]

Direct, anchimerically-assisted formation of the benzobarbaryl cation from the exo ester 7 is precluded on geometrical grounds. By implication, a different mechanism must be operative in its solvolysis, yet the solvolysis rate and products are virtually identical with those of 6. Worthwhile speculation on this point must await a practical synthesis of the deuteriated exo 3,5-dinitrobenzoate 15, and measurement of the scrambling accompanying its solvolysis. Such a study is in progress,[10] along with related investigations of partially reduced, and organometallic derivatives of 4 and 5.

Acknowledgement

One of us (J.S.B.) thanks the S.R.C. for the award of a research studentship.

References and Footnotes

1. J. C. Barborak and P.v.R. Schleyer, *J.Amer.Chem.Soc.*, **92**, 3184 (1970).
2. J. B. Grutzner and S. Winstein, *ibid.*, **92**, 3186 (1970).
3. Idem., *ibid.*, **94**, 2200 (1972).
4. (a) M. J. Goldstein, *ibid.*, **89**, 6357 (1967);
   (b) M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971).
5. All new compounds gave satisfactory analyses and high resolution mass spectra. Structural assignments were made on the basis of 100 MHz nmr spectra in conjunction with spin-decoupling and paramagnetic shift reagent [Eu(fod)$_3$] studies. The details of these spectra will be supplied on request.
6. J. Ciabattoni, J. E. Crowley, and A. S. Kende, *J.Amer.Chem.Soc.*, **89**, 2778 (1967).
7. The trivial name is used to conserve space; correctly named, these compounds would be 6,7-benzotricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-yl derivatives.
8. Benzobarbarols **8** and **9** have been reported recently but without experimental details; Z. Goldschmidt and A. S. Kende, *Tetrahedron Letters*, 4625 (1971), footnote 12.
9. The small and irreproducible yield of unrearranged alcohol originally observed[2] in the solvolysis of the parent system, has now been shown[3] to be an experimental artefact.
10. Obtained by esterification of endo alcohol **12**, the major product from the sodium borodeuteride reduction of 6,7-benzobicyclo[3.2.2]nona-3,6,8-trien-2-one. The exo alcohol **13** is also formed in this reduction, but has resisted chromatographic purification. Alternative routes to **13** are currently under investigation.
11. For example, the absorption (broad singlet at 4.15 δ) for H-4 was now *ca.* 80% of the intensity of the H-3 absorption. The former absorption was completely absent from the spectrum of starting alcohol **12**.
12. 6,7-Benzobicyclo[3.2.1]octadiene undergoes exchange eight times slower than bicyclo[3.2.1]octadiene in KOBu^t/DMSO-d_6 at 45°.[13] This has been interpreted as providing evidence for a smaller degree of participation by the arene, even when forming part of a bishomoconjugatively *stabilised* system.
13. J. M. Brown, E. N. Cain, and M. C. McIvor, *J. Chem. Soc.*, (B), 730 (1971).