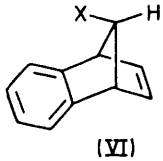
Pronounced Solvolytic Reactivity of *endo*-Tetracyclo[5,4,0,$0^{2,4}$,$0^{3,6}$]undeca-1(7),8,-10-trien-5-yl *p*-Nitrobenzoate compared with the *exo*-Epimer

By JOSEPH J. TUFARIELLO* and DONALD W. ROWE

(*Department of Chemistry, State University of New York at Buffalo, Buffalo, New York* 14214)

Summary The solvolytic reactivities of the title compounds have been investigated; the *endo*-epimer is more than 10^5 as reactive as its *exo*-counterpart.

WE have recently described[1] the synthesis of the highly reactive *exo*- and *endo*-undecatrienyl *p*-nitrobenzoates (I) and (II), respectively. The results of our investigation of the solvolytic reactivity of these *exo*- and *endo*-benzotricyclic derivatives are summarized in the Table. These data afford an *endo*/*exo* rate ratio of *ca.* 4×10^5, indicative of an important stereochemical requirement for participation in this system.



(VI)

a; X = OH
b; X = OPNB
c; X = Cl
d; X = O_2CMe

Hydrolysis of both epimers under the conditions of the kinetic runs affords *syn*-alcohol (VIa) and *syn*-*p*-nitrobenzoate (VIb). That the product composition from

		syn-alcohol(VIa)	+ *syn*-OPNB (VIb)
exo-OPNB (I)	→	82%	18%
endo-OPNB (II)	→	85%	15%

either epimer is nearly identical suggests that the products are largely, if not entirely, derived from the same cationic intermediate; presumably, the same cation is derived from the *syn*-benzotricyclic system since it has been shown[2] that acetolysis of *syn*-7-chlorobenzonorbornadiene (VIc) gives the acetate with retained configuration (*i.e.* VId) exclusively.

The Scheme shows that the *endo*-benzotricyclic *p*-nitrobenzoate (II) possesses a reactivity nearly as great as that of the *endo*-tricyclic *p*-nitrobenzoate (III),[4a] and exceeds the reactivity of the *p*-nitrobenzoate (V) by a factor of 10^{21}. The small diminution in rate of the benzo-analogue when compared with (III) may be ascribed largely to the inductive effect of the benzene ring.[3] The enhanced rate of (II) relative to its bicyclic isomer (VIb) ($k_{rel} = 5{\cdot}5 \times 10^8$; *cf.*, Table) is apparently due to the substantial ground-state strain of (II) and to the release of some of this strain in the solvolytic transition state.[4]

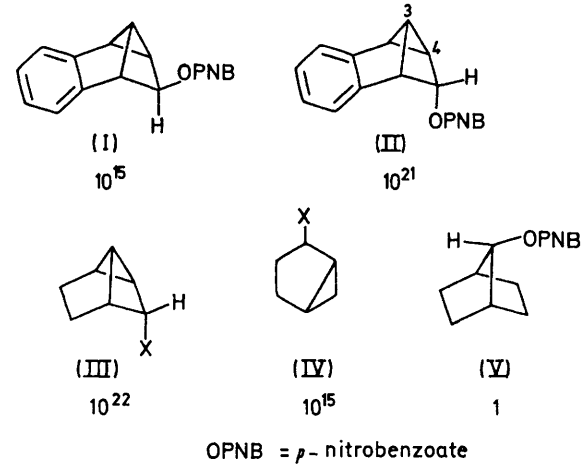
Comparison of either benzotricyclic epimer with a typical secondary cyclopropyl carbinyl system[5,6] [*e.g.* (IV); Scheme] reveals that the *exo*-epimer (I) hydrolyses normally; however, the *endo*-epimer is about 10^6 more reactive. The recently reported[7] solvolysis data for the epimeric 2-substituted bicyclo[2,1,0]pentanes reveal a similar order-

TABLE

Solvolysis data in 80% *aqueous acetone*

Temp./°C	k_{obs}/s^{-1}	k_{rel} at 25°
exo-Benzotricyclic OPNB (I)		
120·5	$(2{\cdot}81 \pm 0{\cdot}15) \times 10^{-4}$	
100·1[a]	$(5{\cdot}67 \pm 0{\cdot}26) \times 10^{-5}$	
25·0[b]	$2{\cdot}3 \times 10^{-8}$	2×10^4
endo-Benzotricyclic OPNB (II)		
25·0	$(9{\cdot}38 \pm 0{\cdot}16) \times 10^{-3}$	7×10^9
syn-Benzonorbornadien-7-yl OPNB (VIb)		
160·5	$(5{\cdot}34 \pm 0{\cdot}08) \times 10^{-5}$	
140·4[c]	$(1{\cdot}02 \pm 0{\cdot}05) \times 10^{-5}$	
25·0[b]	$1{\cdot}7 \times 10^{-11}$	14
anti-Norbornen-7-yl OPNB		
25·0[d]	$1{\cdot}2 \times 10^{-12}$	1

[a] $\Delta H^{\ddagger} = 22{\cdot}4$ kcal/mol; $\Delta S^{\ddagger} = -10{\cdot}1$ cal K^{-1} mol^{-1}. [b] Extrapolated from data at higher temperatures. [c] $\Delta H^{\ddagger} = 27{\cdot}3$ K cal/mol; $\Delta S^{\ddagger} = -7{\cdot}22$ cal K^{-1} mol^{-1}. [d] From data in ref. 4b, extrapolated to 25° and 80% aqueous acetone using the Arrhenius equation and the mY relationship, with Y values of 1·398, 0·130, and −0·693 for 50, 70, and 80% aqueous acetone, respectively; A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2770.



SCHEME. *Relative solvolytic reactivities are given below each compound.*

ing, with the *endo*-epimer [*i.e.* corresponding to (II)] being 10^7 more reactive than its *exo*-counterpart.[7] The reactivity ratio of (II) compared to (I) appears to be due to the favourable geometry for participation of the central bond[6] [*i.e.* C(3)–C(4) in (II)].

We thank the donors of the Petroleum Research Fund for partial support.

(*Received, 14th July* 1972; *Com.* 1227.)

[1] J. J. Tufariello and D. W. Rowe, *J. Org. Chem.*, 1971, **36**, 2057.
[2] S. W. Cristol and G. W. Nachtigall, *J. Amer. Chem. Soc.*, 1968, **90**, 7132, 7133.
[3] (a) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, 1952, **74**, 1117; (b) W. Pritzkow and K. H. Schloppler, *Chem. Ber.*, 1962, **95**, 834.
[4] (a) J. J. Tufariello and R. J. Lorence, *J. Amer. Chem. Soc.*, 1969, **91**, 1546; (b) J. Lhomme, A. Diaz, and S. Winstein, *ibid.*, p. 1548.
[5] L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *J. Amer. Chem. Soc.*, 1966, **88**, 2316.
[6] K. B. Wiberg, V. Z. Williams, jun., and L. Friedrich, *J. Amer. Chem. Soc.*, 1970, **92**, 564.
[7] J. J. Tufariello, T. F. Mich, and R. J. Lorence, *Chem. Comm.*, 1967, 1202.