

## A High *exo:endo* Rate Ratio in a Norbornyl Type Ring System due to Factors Other than $\sigma$ -Bond Participation

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Solvolysis of the *p*-nitrobenzoates of the 9-methyltetracyclo[5.2.1.0<sup>2,6</sup>.0<sup>4,8</sup>]decan-9-ols shows an *exo:endo* rate ratio of 2690:1 at 25°. This behaviour is the reverse of that exhibited by the corresponding secondary tosylates.

PREVIOUS work<sup>1</sup> on the tosylates of the tetracyclo[5.2.1.0<sup>2,6</sup>.0<sup>4,8</sup>]decan-9-ol system [(1) and (2)] has shown an extremely unusual *exo:endo* acetolysis rate ratio of 0.33:1. Such a rate ratio (of less than one) appears to be unprecedented in norbornyl-type ring systems where there are no other functional groups. In view of the continuing investigation of the nature of carbonium ions in the norbornyl system<sup>2</sup> it was of interest to see whether tertiary derivatives would show different *exo:endo* rate ratios. If the *exo:endo* rate ratio were to become greater than one this would be the first example of such a reversal of solvolytic behaviour in a norbornyl system and would have to be explained in terms of factors other than  $\sigma$ -bond participation, as will be shown later in this paper.

† Treatment of the olefin (8) with mercury(II) acetate<sup>4</sup> for 3 h yielded only starting material.

<sup>1</sup> I. Rothberg, J. C. King, S. Kirsch, and H. Skidanow, *J. Amer. Chem. Soc.*, 1970, **92**, 2570.

The synthetic procedure involved treatment of the ketone (7) with methylmagnesium iodide to give the carbinol (3), which was converted into the *O-p*-nitrobenzoyl (Pnb) derivative (4). Treatment of the ketone (7) with methylenetriphenylphosphorane<sup>3</sup> gave the olefin (8), epoxidation of which, followed by treatment with lithium aluminum hydride,† gave the carbinol (5). This afforded the *exo-p*-nitrobenzoate (6).

Table 1 shows the solvolysis rates in 60% aqueous acetone and Table 2 the products of solvolysis in 60% aqueous acetone containing a 15% excess of sodium hydrogen carbonate. The *exo:endo* rate ratio is

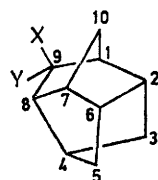
<sup>2</sup> (a) G. D. Sargent in 'Carbonium Ions,' ed. G. Olah and P. von R. Schleyer, Wiley-Interscience, New York, 1972, vol. III; (b) H. C. Brown and K. Takeuchi, *J. Amer. Chem. Soc.*, 1968, **90**, 2693; (c) D. G. Farnum and G. Mehta, *ibid.*, 1969, **91**, 3256; (d) P. von R. Schleyer, *ibid.*, 1967, **89**, 699, 701.

<sup>3</sup> R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, 1963, **28**, 1128.

<sup>4</sup> H. C. Brown and P. Geohegan, *J. Amer. Chem. Soc.*, 1967, **89**, 1522.

2690 : 1 at 25°; this behaviour is completely different from that of the secondary tosylates (1) and (2).

The factors that lead to an *exo* : *endo* rate ratio of less than one for the tosylates (1) and (2) must be one or



	X	Y
(1)	OTs	H
(2)	H	OTs
(3)	Me	OH
(4)	Me	OPnb
(5)	OH	Me
(6)	OPnb	Me
(7)	=O	
(8)	=CH <sub>2</sub>	

more of the following: (a)  $\sigma$ -bond participation in both *exo*- and *endo*-isomers with slightly greater participation in the *endo*-isomer; (b) steric interactions in the ground state of the *endo*-isomer which are relieved in the

TABLE 1

Rates of solvolysis of tertiary *p*-nitrobenzoates in 60% aqueous acetone

Compd.	<i>t</i> /°C	<i>k</i> <sub>1</sub> /s <sup>-1</sup>	$\Delta H^*$ / kJ mol <sup>-1</sup>	$\Delta S^*$ / J mol <sup>-1</sup> K <sup>-1</sup>
(6)	50.0	1.05 ± 0.02 × 10 <sup>-4</sup>	98.0	-18.2
	25.0	4.53 ± 0.14 × 10 <sup>-6</sup>		
(4)	100.0	3.03 ± 0.05 × 10 <sup>-5</sup>	118	-16.0
	75.0	1.85 ± 0.02 × 10 <sup>-6</sup>		
	25.0 <sup>a</sup>	1.68 × 10 <sup>-9</sup>		

<sup>a</sup> Calculated from data obtained at other temperatures.

TABLE 2

Product studies of solvolysis in 60% aqueous acetone

	Product <sup>a</sup> (%)		
	Olefin (8)	(5)	(3)
(6)	94.6	3.5	< 0.3
(4)	94.3	5.0	0.40

<sup>a</sup> Absolute yields.

transition state and  $\sigma$ -bond participation in the *exo*-isomer; and (c) a lack of  $\sigma$ -bond participation in the *exo*-isomer and slight relief of steric strain in the *endo*-isomer.

If there is  $\sigma$ -bond participation in the solvolysis of both (1) and (2) there is no reason why the ratio of participation should be drastically changed in the tertiary derivatives to lead to a high *exo* : *endo* rate ratio. A decrease in participation in the case of (4) and no decrease in participation in that of (6) would be unreasonable.

If there is participation of the single bond in the case of the *exo*-isomer (1) and steric acceleration in that of the *endo*-isomer (2), the high tertiary *exo* : *endo* ratio cannot

be due to an increase in participation in the case of the *exo*-isomer. All previous work has suggested that the extent of  $\sigma$ -bond participation in tertiary ions is small.<sup>2</sup> It would be unreasonable to believe that  $\sigma$ -bond participation should be markedly increased in the case of the tertiary derivative.

The change to a high *exo* : *endo* rate ratio can most reasonably be explained in terms of steric hindrance to ionization<sup>5</sup> in the *endo*-isomer (4) and steric acceleration of ionization in the *exo*-isomer (6), as the methyl group moves upward to become coplanar during the solvolysis. Possibly the larger bulk of the methyl group in (4) as compared to hydrogen in (2) leads to an increase in steric hindrance to ionization in the former. This work supports the theory that high *exo* : *endo* rate ratios in tertiary norbornyl systems are not caused by  $\sigma$ -bond participation.<sup>2</sup>

## EXPERIMENTAL

M.p.s were determined with a Thomas-Hoover apparatus. I.r. spectra were recorded on a Beckman IR-10 instrument. N.m.r. spectra were taken on a Varian A-60 instrument with tetramethylsilane as internal standard. For g.l.c. a Hewlett-Packard 5750 instrument was used, with flame ionization detectors and columns (10 ft × 0.25 in o.d.) packed with 10% of either UCW-98 or FFAP on Chromosorb W. Standard kinetic techniques were used, which involved immersion of ampoules in a constant temperature bath, removal of the ampoules, and titration of *p*-nitrobenzoic acid with standardized aqueous 0.02M-sodium hydroxide. Products were identified by g.l.c. retention time and peak enhancement and by comparison of material isolated by preparative g.l.c. with authentic materials. The product studies were carried out with use of a 15% excess of sodium hydrogen carbonate to neutralize the liberated *p*-nitrobenzoic acid.

9-Methyltetracyclo[5.2.1.0<sup>2,6</sup>.0<sup>4,8</sup>]decan-endo-9-ol (3).—The ketone (7)<sup>1</sup> was treated with methylmagnesium iodide in tetrahydrofuran at reflux temperature for 18 h and the product was worked up with ammonium chloride in the usual way. Gradient elution chromatography (hexane-ether) on alumina and sublimation (at 0.1 mmHg) gave the carbinol (3) (50%), m.p. 75–76°,  $\nu_{\max}$  (CCl<sub>4</sub>) 3620 cm<sup>-1</sup>,  $\delta$  2.90 (1H, d, *J* 12 Hz, *endo* H-3) and 1.20 (3H, s, tert. Me) (Found: C, 80.35; H, 9.65. C<sub>11</sub>H<sub>16</sub>O requires C, 80.45; H, 9.8%).

The *endo*-*p*-Nitrobenzoate (4).—The alcohol (3) (3.4 g 20 mmol) in tetrahydrofuran (20 ml) was treated with 1.68M-methyl-lithium in ether (12.0 ml) for 1 h at room temperature. This mixture was cooled to -60° and *p*-nitrobenzoyl chloride (1 mol. equiv.) in tetrahydrofuran (20 ml) was added. The mixture was then allowed to warm to room temperature, set aside for 4 h, and then heated at reflux for 1 h. After cooling, the mixture was added to saturated aqueous sodium carbonate (100 ml) and the product extracted into ether. The extract was washed with saturated aqueous sodium carbonate and water, dried (MgSO<sub>4</sub>), and evaporated to give the ester (4) (45%), m.p. 119–120° (from ether-pentane),  $\nu_{\max}$  (CCl<sub>4</sub>) 1720, 1550,

<sup>5</sup> H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Nat. Acad. Sci. U.S.A.*, 1966, **56**, 1653; H. C. Brown, I. Rothberg, and D. L. Vander Jagt, *J. Amer. Chem. Soc.*, 1967, **89**, 6380.

and  $1340\text{ cm}^{-1}$  (Found: C, 69.05; H, 6.15; N, 4.45.  $\text{C}_{18}\text{H}_{16}\text{NO}_4$  requires C, 69.0; H, 6.1; N, 4.45%).

9-Methylenetetrahydro[5.2.1.0<sup>2,6</sup>.0<sup>4,8</sup>]decane (8).—The ketone (7) (4.0 g, 27.0 mmol) was treated with methylene-triphenylphosphorane essentially according to the Corey procedure<sup>3</sup> and the product was distilled (b.p. 91–92° at 35 mmHg) to give the olefin (8) (2.4 g, 61%),  $n_D^{20}$  1.5207;  $\nu_{\text{max}}$  (neat) 3080, 1680, and 870  $\text{cm}^{-1}$ ;  $\delta$  4.60 (1H, d,  $J$  1.5 Hz, =CH), 4.40 (1H, d,  $J$  1.5 Hz, =CH), 2.60br (1H, m, H-1?), 2.25 and 2.0 (5H, complex broad m, tertiary H), and 1.7–0.8 (6H, complex m,  $\text{CH}_2$ ) (Found: C, 90.3; H, 9.8.  $\text{C}_{11}\text{H}_{14}$  requires C, 90.35; H, 9.65%).

The Epoxide derived from the Olefin (8).—The olefin (8) (2.0 g, 13.7 mmol) in chloroform was treated with 40% peracetic acid buffered with sodium acetate essentially according to the procedure of Walborsky and Loncrini<sup>6</sup> to give, after sublimation at 1 mmHg, the epoxide (72%), m.p. 92–93°;  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 3050, 950, and 930  $\text{cm}^{-1}$ ;  $\delta$  2.75 (2H, s, O- $\text{CH}_2$ ), 2.4–1.8 (6H, complex m, tertiary H), and 1.8–0.8 (6H, complex m,  $\text{CH}_2$ ) (Found: C, 81.45; H, 8.75.  $\text{C}_{11}\text{H}_{14}\text{O}$  requires C, 81.45; H, 8.7%).

9-Methyltetrahydro[5.2.1.0<sup>2,6</sup>.0<sup>4,8</sup>]decan-exo-9-ol (5).—The foregoing epoxide was treated with an excess of lithium

aluminium hydride in ether at room temperature for 24 h. Addition of a solution of sodium potassium tartrate (30%), extraction into ether, and evaporation of the extract (dried with  $\text{MgSO}_4$ ) gave the crude alcohol (5) (98%). Sublimation (at 1 mmHg) and recrystallization (ether–pentane) gave a sample of m.p. 122–124°,  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 3640  $\text{cm}^{-1}$ ,  $\delta$  1.52 (3H, s, tert. Me) (Found: C, 80.05; H, 9.7%).

The exo-p-Nitrobenzoate (6).—The p-nitrobenzoate (6) was prepared as described for compound (4) and recrystallized from ether–pentane (35% yield), double m.p. 110–112° and 233–234°,  $\nu_{\text{max}}$  ( $\text{CHCl}_3$ ) 1710  $\text{cm}^{-1}$  (Found: C, 69.3; H, 6.0; N, 4.65%).

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<sup>6</sup> H. M. Walborsky and D. F. Loncrini, *J. Amer. Chem. Soc.* 1954, **76**, 5396.