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SOLVOLYSIS OF 2-ARYL-*EXO*-5,6-TRIMETHYLENE-2-NORBORNYL *p*-NITROBENZOATES AS A REFERENCE OF 2-ARYL-2-NORBORNYL *p*-NITROBENZOATES SOLVOLYSIS

FURTHER EVIDENCE FOR THE UNIMPORTANCE OF σ-PARTICIPATION IN THE SOLVOLYSIS OF 2-ARYL-2-NORBORNYL DERIVATIVES

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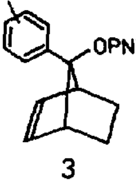
Abstract—The rates of solvolysis of 2 - aryl - *exo* - 5,6 - trimethylene - *exo* - and *endo* - 2 - norbornyl *p*-nitrobenzoates (**7** and **8**, respectively) with representative substituents [*p*-CH$_3$O, *p*-CH$_3$, H, *m*-CF$_3$, *p*-CF$_3$, and 3,5-(CF$_3$)$_2$] were determined in 80% aqueous acetone and compared with those of the parent 2-aryl-*exo*- and *endo*-2-norbornyl *p*-nitrobenzoates (**5** and **6**, respectively). The rate ratios for the *endo*-*p*-nitrobenzoates (**6**/**8**) are essentially constant and close to unity for these substituents, indicating that the perturbation of the trimethylene bridge toward the C$_2$-position is virtually negligilbe. The rate ratios for the *exo*-*p*-nitrobenzoates (**5**/**7**) can also be regarded as invariant over the reactivity range studied. The *exo*/*endo* rate ratios (**7**/**8**) are 246 (*p*-CH$_3$O), 196 (*p*-CH$_3$), 129 (H), 80 (*m*-CF$_3$), 90 (*p*-CF$_3$), and 89 [3,5-(CF$_3$)$_2$], being similar to the corresponding **5**/**6** rate ratios. The solvolyses of these *p*-nitrobenzoates (**7** and **8**) afford predominantly (>97%) *exo*-alcohols. Since the secondary *exo*-5,6-trimethylene-2-norbornyl system, with its low *exo*/*endo* rate ratio, 11.2, is known to solvolyse without significant σ-participation, the tertiary derivatives should also undergo solvolysis without σ-participation. Consequently, the similarities in the solvolytic behaviors between the two systems (**5** vs **7**; **6** vs **8**) strongly support the previous conclusion that σ-participation is unimportant in the solvolysis of **5**.

In spite of tremendous efforts devoted by many physical organic chemists, the problem of the significance of σ-participation in the solvolysis of *exo*-2-norbornyl derivatives has not been settled.[1,2] As important criteria supporting σ-participation and the formation of a symmetrical σ-bridged norbornyl cation in the solvolysis of *exo*-2-norbornyl derivatives, the high *exo*/*endo* rate ratio, high predominance of *exo* substitution, and the formation of the racemised substitution product from optically active *exo*-2-norbornyl brosylate, have long been employed.[1,3] However, there has been accumulated evidence that such phenomena may also be interpreted in terms of steric origin.[2] In addition, the recent work from our laboratories on the solvolysis of *exo* - 2 - norbornyl - *exo* - 3 - *d* tosylate in carboxamide solvents provided evidence for the existence of an unsymmetrical 2-norbornyl cation in such solvolytic solvents.[4] More recently, Grob *et al.* pointed out the importance of C$_1$–C$_6$ hyperconjugation,† not σ-participation, in the ionisation of *exo*-2-norbornyl tosylate, from extensive studies of the rates and products of solvolysis of 2-norbornyl tosylates containing varying substituents at the *exo*-6-position.[5,6]

A beautiful tool for detecting participation phenomena was developed by Gassman and Fentiman, who showed that the rate enhancement of 10^{11} observed in the solvolysis of *anti*-7-norbornenyl brosylate (**1**) as compared with the saturated homologue (**2**) decreases with the introduction of electron-donating groups at the 7-position and it effectively vanishes with the *p*-anisyl group in the solvolysis of the *p*-nitrobenzoates, **3** and **4**.[9]



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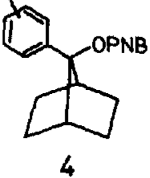

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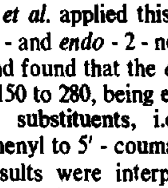

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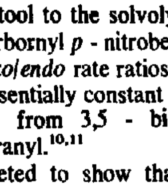

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Brown *et al.* applied this tool to the solvolysis of 2 - aryl - *exo* - and *endo* - 2 - norbornyl *p* - nitrobenzoates (**5** and **6**), and found that the *exo*/*endo* rate ratios are in the range of 150 to 280, being essentially constant for a wide range of substituents, i.e. from 3,5 - bis(trifluoromethyl)phenyl to 5′ - coumaranyl.[10,11]

The results were interpreted to show that σ-participation is not important in stabilising the incipient carbonium ions from these tertiary *exo* - *p* - nitrobenzoates. Steric hindrance to ionisation in *endo* - *p* - nitrobenzoates (**6**) was considered to be principally responsible for the high *exo*/*endo* rate ratios.

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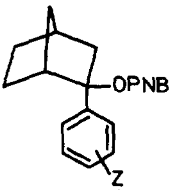
†The hyperconjugative model had been proposed by Jensen[7] and Traylor.[8]



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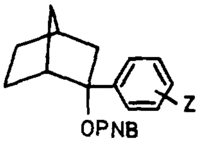

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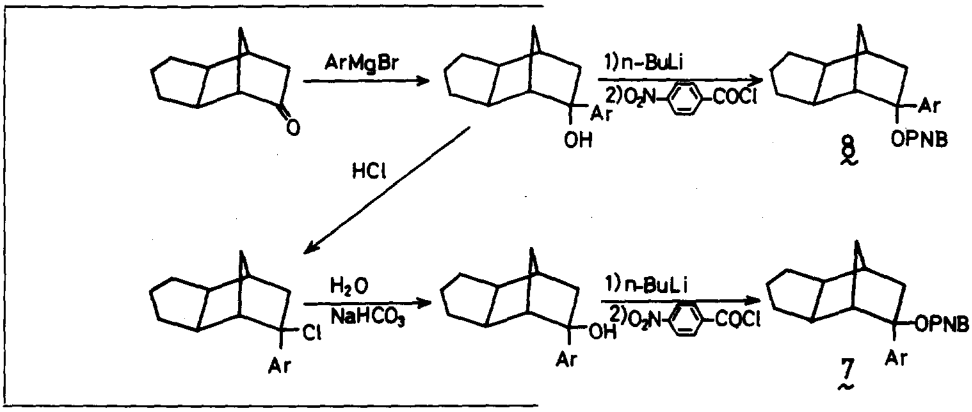
The test of the significance of σ-participation based on the *exo*/*endo* rate ratios for **5** and **6**, however, appeared to the present authors to have a drawback since the rates of the *exo*- are compared over a wide reactivity range with those of the *endo*-*p*-nitrobenzoates which have considerably different steric circumstances, such as steric hindrance to ionisation[2] and torsional strain.[12] Thus, it appeared more advisable to compare the rates of **5** with those of a reference system which is structurally similar to **5** but is believed to solvolyse without participation. As such a reference system 2 - aryl - *exo* - 5,6 - trimethylene - *exo* - 2 - norbornyl system (**7**) was employed. In order to establish validity for the choice of **7** as the reference system, the rates of **8** were also compared with those of **6**.

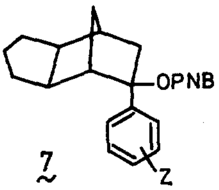
The rates of solvolyses of 2-methyl-, 2-phenyl-, and 2 - (5' - coumaranyl) - *exo* - 5,6 - trimethylene - 2 - norbornyl *p*-nitrobenzoates were previously studied by Brown *et al.* and it was shown that these tertiary derivatives exhibit the rates and the *exo*/*endo* rate ratios which are similar to those for the corresponding parent norbornyl compounds, **5** and **6**.[14]

In the present work, the rates of a series of **7** and **8** containing the substituents, *p*-CH_3O, *p*-CH_3, *m*-CF_3, *p*-CF_3, and 3,5-$(CF_3)_2$, have been determined in 80% aqueous acetone and the previous rate data for **5** and **6** were reassessed in the light of the rates of **7** and **8**.

RESULTS

Syntheses. Appropriate Grignard reagents were added to *exo* - 5,6 - trimethylene - 2 - norbornanone. The tertiary *endo*-alcohols were converted into *endo* - *p* - nitrobenzoates by treating their lithium salts with *p*-nitrobenzoyl chloride in THF. The *endo*-alcohols were converted into tertiary *exo*-chlorides with dry hydrogen chloride in methylene chloride and the chlorides hydrolysed in 60% aqueous acetone in the presence of excess sodium bicarbonate or silver nitrate. The resulting tertiary *exo*-alcohols were then converted into *p*-nitrobenzoates. The properties of the alcohols and the *p*-nitrobenzoates are listed in Tables 4 and 5, respectively.





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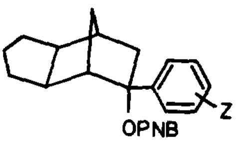

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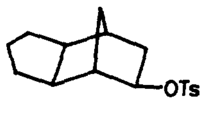
Secondary *exo* - 5,6 - trimethylene - 2 - norbornyl tosylates (**9** and **10**) exhibit a small *exo*/*endo* rate ratio (11.2) in acetolysis and solvolyse without appreciable Wagner–Meerwein rearrangement.[13] Such solvolytic behaviour has been ascribed to unimportance of σ-participation in **9**.[1] It is claimed that the trimethylene bridge prohibits the incipient carbonium ion to assume a non-classical structure because of the steric difficulties in achieving σ-bridging.[1]



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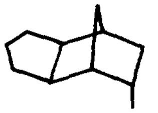

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Rate studies. The rates of solvolysis of the *p*-nitrobenzoates were determined in 80% aqueous acetone. Since *p*-anisyl-**7** was too unstable to be isolated, the rate was calculated from that of the benzoate utilising the conversion factor 20.8 observed for the relative rates at 25.0° of 2 - phenyl - *exo* - 2 - norbornyl *p* - nitrobenzoate and benzoate.[15] The rate data are summarized in Table 1. The present work required precise comparison of the rates among **5**, **6**, **7**, and **8**. Therefore, some of the previously published rates for **5** and **6** were subjected to reinvestigation and the data given in Table 2. In addition, the rates of **5**, **6**, **7**, and **8** with the substituent 3,4-$(CF_3)_2$ were also checked in Professor Brown's laboratory, and it was revealed that the results of the reexamination did not alter the conclusion of this paper.

Product studies. The products of solvolysis of **7** and **8** in 80% aqueous acetone were determined at different temperatures for the substituents *p*-CH_3, H, and 3,5-$(CF_3)_2$. The products, alcohol and olefin, were separated by means of elution chromatography and identified by means of ^1H NMR. The results are summarised in Table 3.

Table 1. Rates of solvolysis of 2 - aryl - *exo* - 5,6 - trimethylene - 2 - norbornyl *p*-nitrobenzoates (**7** and **8**) in 80% aqueous acetone

Substituent	Temp.	—— k_1 x 10^6, sec^{-1} ——		$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
Z	°C	7	8	kcal/mol	eu
p-CH_3O	0	10.3[a]		7 22.3[a]	+0.6[a]
	25	356[a]		8 22.4	-4.1
	25	7400[b]	30.1		
	50		607		
p-CH_3	0	1.98		7 23.2	+0.4
	25	78.0	0.398[d]	8 25.6	-1.8
	50		12.2		
	75		229		
H	25	4.22(4.24)[c]	0.0327[d](0.036)[c]	7 24.2[c]	-1.8[c]
	50	(109)[c]	1.13	8 26.6	-3.7
	75		23.5(24.6)[c]		
	100		(337)[c]		
m-CF_3	25	0.0270[d,e]	3.37x10^{-4}[d,g]	7 27.5	-0.9
	50	1.05±0.00[f]		8 29.2	-4.0
	75	25.05±0.05[f]			
	100	369	8.27±0.08[f]		
	125		103±1[f]		
p-CF_3	25	0.0128[d]	1.43x10^{-4}[d]	7 27.5	-2.3
	50	0.504		8 29.4	-4.9
	75	11.7			
	100		3.81		
	125		48.4		
3,5-$(CF_3)_2$	25	5.98x10^{-4}[d,h]	6.72x10^{-6}[d,i]	7 28.9	-4.0
	75	0.756±0.002[f]		8 30.5	-7.5
	100	13.1 ±0.1[f]	0.253±0.004[f]		
	125		3.51 ±0.06[f]		

[a] For benzoate. [b] $k_1^{25°}$(benzoate) x 20.8; see Ref. 15. [c] Ref. 14. [d] Extrapolated from data at other temperatures. [e] Accurate to ±9%. [f] Average of two data. [g] Accurate to ±9%. [h] Accurate to ±3%. [i] Accurate to ±16%.

DISCUSSION

Comparison of the rates of endo - p - *nitrobenzoates*, **6** *and* **8**. In order that **7** and **8** can be the good reference systems of **5** and **6**, it is essential that the attachment of the trimethylene bridge does not affect much the reactivities inherent to **5** and **6**, except that only σ-participation, if present, is eliminated. This can best be tested by comparing the rates of **8** with those of **6** and by examining if both systems react with similar rates. As summarised in Table 2 the **6**/**8** rate ratios are close to unity and essentially constant over a wide reactivity range studied, showing that the perturbation of the trimethylene bridge toward the C_2-position is virtually negligible.† Reflecting the above results, the ρ^+ values obtained in the $\rho^+\sigma^+$ relations‡ (Fig. 1) for **6** and **8** are

Table 2. Rates of solvolysis of 2 - aryl - 2 - norbornyl *p*-nitrobenzoates (**5** and **6**) in 80% aqueous acetone at 25° and various rate ratios[a]

Substituent	—— k_1x10^6, sec^{-1} at 25°——		—— Rate ratios at 25°——			
Z	5	6	5/6	7/8	5/7	6/8
p-OCH_2CH_2-m[b]	6.66x10^{4}[c]	278[c]	240	286	1.26	1.50
p-CH_3O	1.14x10^{4}[d]	40.2[d]	284	246	1.54	1.34
p-CH_3	131[d]	0.564[d]	232	196	1.68	1.42
H	7.56[d]	0.0594[d]	127	129	1.79(1.52)[m]	1.82
m-CF_3	0.0713[e,f]	4.72x10^{-4}[e,g]	151	80±7	2.64(1.89)[m]	1.40
p-CF_3	0.0275[h,i]	1.83x10^{-4}[h,j]	150	90	2.15(2.25)[m]	1.28
3,5-$(CF_3)_2$	1.31x10^{-3}[h,k]	9.27x10^{-6}[h,l]	141	89±14	2.16(2.07)[m]	1.38

[a] For the rate constants of 7 and 8, see Table 1 and Ref. 14. [b] 5-Coumaranyl. [c] Ref. 11. [d] Ref. 10. [e] This work. [f] k_1x10^6 sec^{-1}: 47.4 (75.3°), 2.32 (50°). [g] k_1x10^6 sec^{-1}: 10.8 (100°), 0.615 (75°). [h] Redetermined in this work; see Ref. 10 for previous values. [i] k_1x10^6 sec^{-1}: 26.3 (75°), 1.11 (50°). [j] k_1x10^6 sec^{-1}: 5.22 (100°), 0.279 (75°). [k] k_1x10^6 sec^{-1}: 26.9 (100°), 1.58 (75°). [l] k_1x10^6 sec^{-1}: 5.12 (125°), 0.365 (100°). [m] At 75°.

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†*endo*-2-Norbornyl tosylate reacts faster than **10** in *methanolysis at* 25° *by a factor of* 1.84,[13,16] *which is close to the present rate ratios.*

‡The σ^+ constant (0.946) for 3,5-bis(trifluoromethyl), which was newly determined in this work, was used instead of 2× $\sigma^+_{m\text{-}CF_3}$ (=1.040);[17] see Experimental.

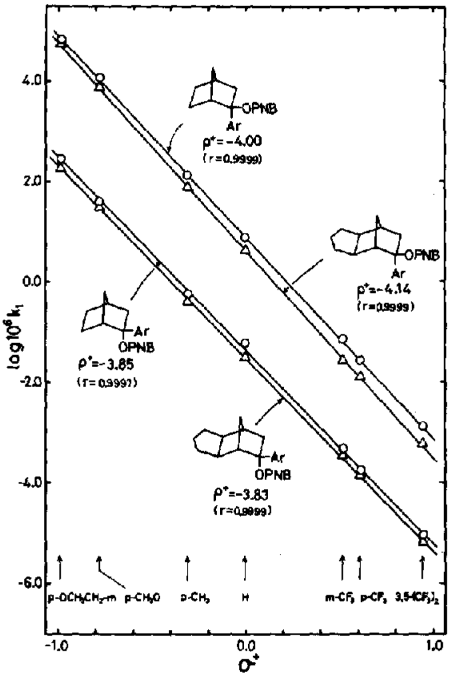


Fig. 1. Log $k_1 - \sigma^+$ plot for the 2 - aryl - 2 - norbornyl and 2 - aryl - *exo* - 5,6 - trimethylene - 2 - norbornyl *p* - nitrobenzoates in 80% aqueous acetone at 25°.

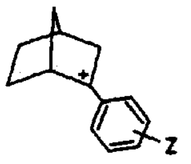
almost identical, being −3.85† (r: 0.9997) and −3.83 (r: 0.9999), respectively.

Comparison of the rates of exo-p-*nitrobenzoates,* **5** and **7**. Since it has been demonstrated that the attachment of the trimethylene bridge to 2 - aryl - *endo* - 2 - norbornyl *p*-nitrobenzoates **6** does not affect much their solvolytic behaviour, we are in a position to utilise 2 - aryl - *exo* - 5,6 - trimethylene - *exo* - 2 - norbornyl *p*-nitrobenzoates **7** as the reference of the parent 2 - aryl - *exo* - 2 - norbornyl *p*-nitrobenzoates **5**. If the **5**/**7** rate ratios exhibit either gradual or sudden increase with the increase of the electron-withdrawing ability of the substituent Z, we are able to conclude that the σ-participation is operative in the solvolysis of **5**.[2] The **5**/**7** rate ratios are given in Table 2. The interpretation of the results is subtle. The ratios appear to show a slightly increasing trend as the substituent Z is made more and more electron-withdrawing. As an immediate consequence of the trend, the ρ^+ value (−4.00)‡ for **5** is slightly less negative than that (−4.14) for **7** (Fig. 1). It is tempting to explain the results in terms of the onset of σ-participation in **5** with the substituents more electron-withdrawing than H. However, we prefer to interpret the results in the manner that the trend is too subtle to be ascribed to the onset of σ-participation. In order to avoid the error inevitable in calculating the rate constants at 25° by the long extrapolation from data at higher temperatures, the **5**/**7** rate ratios at 75° were also calculated and listed in parentheses in Table 2. However, these results cannot change the above interpretation. In addition, the correlation coefficient (0.9999) of the $\rho^+\sigma^+$ relation for **5** is excellent, excluding any possibility of curvature. Thus, the previous conclusion that σ-participation is not important in the solvolysis of **5** even with the substituent $3,5\text{-}(CF_3)_2$[10] has been again confirmed by the use of the reference system **7**.

Exo/Endo *rate ratios.* The **7**/**8** (*exo*/*endo*) rate ratios vary from 1×10^2 to 3×10^2, being comparable with the **5**/**6** ratios (Table 2). Since the system **7** is known to solvolyse without participation, the similarity of the *exo*/*endo* rate ratios (**5**/**6** vs **7**/**8**) ascertains the conclusion that the σ-participation is not important in the solvolysis of **5**. Steric hindrance to ionisation and the torsional effect in *endo*-*p*-nitrobenzoates must be responsible for the high *exo*/*endo* rate ratios.

Products of solvolysis. The formation of the *exo*-alcohol as the major substitution product (>97%) in the solvolysis of **7** and **8** [Z = *p*-CH_3, H, and $3,5\text{-}(CF_3)_2$] (Table 3) is in accord with what has been realised in the solvolysis of **5** and **6**. It is to be noted that the amount of the elimination product from **7** is generally greater than that from **8**, although precise comparison is not permitted because of the differences in the temperature of solvolysis. Presumably, because the *exo* direction is less congested than the *endo* direction, the *p*-nitrobenzoate anion in the ion-pair formed from **7** is more favorably situated as a deprotonating agent than the case of **8**.

Relation with the ^{13}*C NMR results under stable ion conditions.* Olah[18] and Farnum[19] independently carried out the ^{13}C NMR studies of 2 - aryl - 2 - norbornyl cations (**11**) with varying substituents under stable ion conditions and concluded that they observed the onset of σ-bridging with the cation containing *p*-CF_3 group. Farnum further mentioned, based on the analysis of the substituent effects on the rates of solvolysis of 2 - aryl - 2 - norbornenyl *p*-nitrobenzoates and on the ^{13}C NMR chemical shift values of the corresponding cations, that more powerfully electron-withdrawing aryl groups than 3,5-bis(trifluoromethyl)phenyl would be required in order that σ-bridging becomes manifest in the solvolysis of **5**. Unfortunately, we are not in a position at present to examine his estimate.



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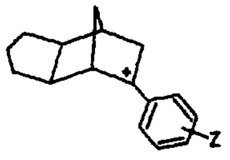
In his same article Farnum reported that σ-bridging occurs also in the 2 - aryl - *exo* - 5,6 - trimethylene - 2 - norbornyl cations (**12**), and that it becomes observable with the *p*-CF_3 substituent, which is the substituent that makes σ-bridging in **11** observable. This is a puzzling situation since more electron-withdrawing substituent will be required in **12** than in **11** in order that the stabilisation gained by σ-bridging can compensate for the increased strain between the trimethylene bridge and the



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†The previous ρ^+ value was −3.76.[11]
‡The previous ρ^+ value was −3.85.[11]

Table 3. Product distributions in the solvolysis of 2 - aryl - *exo* - 5,6 - trimethylene - 2 - norbornyl *p* - nitrobenzoates (7 and 8) in 80% aqueous acetone[a]

Substrate		Temp.	Product yield,[b] %		
Substituent	7 or 8	°C	Alcohol[c]		Elimination
p-CH_3	7	25	53 (54	 :	45 46)[e]
	8	75	76 (84	 :	14 16)[e]
H	7	25	75 (77	 :	22 23)[e]
	8	75	96 (96	 :	4 4)[e]
3,5-$(CF_3)_2$	7	100	27 (31	 :	61 69)[e]
	8	125	55 (69	 :	24 31)[e]

[a]The reaction was conducted for more than ten half-lives. [b]Isolated yields. [c]^{1}H NMR showed that the exo-alcohol was formed predominantly (>97%). [d]A mixture of an olefin and a small amount of unidentified product, possibly nortricyclene derivative. [e]Ratio of the alcohol to the elimination product.

7-methylene bridge due to σ-bridging. It appears that the ^{13}C chemical shifts correlation should be handled cautiously.

EXPERIMENTAL

M.ps and b.ps are uncorrected. Elemental analyses were performed by the Microanalytical Center, Kyoto University, Kyoto, Japan. ^{1}H NMR spectra were taken on a Hitachi R-24 (60 MHz) spectrometer.

exo-5,6-*Trimethylene-2-norbornanone*. This compound was prepared by the chromic acid oxidation of *exo* - 5,6 - trimethylene - *exo* - 2 - norbornanol[13] following the procedure of Brown,[20] b.p. 103°/14 mmHg – 109°/15 mmHg (lit.[21] 130–132°/29 mmHg).

2 - *Aryl* - exo - 5,6 - *trimethylene* - endo - 2 - *norbornanols*. These alcohols were prepared by treating *exo* - 5,6 - trimethylene - 2 - norbornanone with the appropriate Grignard reagents in ether. The tertiary alcohols were purified by recrystallisation from hexane. The properties of the alcohols are listed in Table 4.

2 - *Aryl* - exo - 5,6 - *trimethylene* - exo - 2 - *norbornanols* (*p*-CH_3O, *p*-CH_3, H, *m*-CF_3, *p*-CF_3). These alcohols were prepared by the hydrolysis of the corresponding *exo*-2-chlorides. The *endo*-alcohols were hydrochlorinated with dry HCl in CH_2Cl_2 at 0°. Evaporation of the CH_2Cl_2 after drying over $CaCl_2$ afforded the corresponding *exo*-chlorides. The crude chlorides were hydrolysed in 60% aqueous acetone in the presence of 50% molar excess of $NaHCO_3$ to yield the *exo*-alcohols. These were recrystallised from hexane. The properties are listed in Table 4.

2 - [3,5 - *Bis(trifluoromethyl)phenyl*] - exo - 5,6 - *trimethylene* - exo - 2 - *norbornanol*. The hydrochlorination of the tertiary *endo*-alcohol was too slow for preparative purposes. Consequently, 2 - [3,5 - bis(trifluoromethyl)phenyl] - *exo* - 5,6 - trimethylene - 2 - norbornene was prepared and hydrochlorinated. A mixture of 2 - [3,5 - bis(trifluoromethyl)phenyl] - *exo* - 5,6 - trimethylene - *endo* - 2 - norbornanol (11.25 g, 30.9 mmol) and $KHSO_4$ (6.56 g, 48.1 mmol) was subjected to distillation *in vacuo*, giving 10.24 g of colorless liquid, b.p. 111–142°/4.5 mmHg; NMR (CCl_4) δ 0.65–2.9 (m, 12H), 6.50 (d, 1H, $J = 4$ Hz), 7.65 (s, 3H). The olefin (6.79 g, 19.6 mmol) was treated with dry HCl in CH_2Cl_2 in the presence of 350 mg of $FeCl_3$ for 40 min at 0°. The reaction mixture was washed with chilled water

Table 4. Melting points and elemental analyses of 2 - aryl - *exo* - 5,6 - trimethylene - 2 - norbornanols

Substituent	Isomer	M.p.[a]	Carbon, %		Hydrogen, %	
Z		°C	Calcd	Found	Calcd	Found
p-CH_3O	exo-OH	84.0-84.8	79.03	78.76	8.58	8.79
	endo-OH	56.0-56.5	79.03	79.12	8.58	8.65
p-CH_3	exo-OH	96.4-97.3	84.24	84.21	9.15	9.45
	endo-OH	88.3-88.8	84.24	84.28	9.15	9.42
m-CF_3	exo-OH	79.5-82.0	68.90	68.89	6.46	6.64
	endo-OH	75.8-76.4	68.90	68.89	6.46	6.34
p-CF_3	exo-OH	101.7-102.7	68.90	69.19	6.46	6.57
	endo-OH	75.2-76.2	68.90	69.20	6.46	6.63
3,5-$(CF_3)_2$	exo-OH	73.5-74.5	59.34	59.60	4.98	4.79
	endo-OH	118.2-119.2	59.34	59.45	4.98	4.79

[a]Uncorrected.

and dried over $CaCl_2$. The CH_2Cl_2 was evaporated and the residue hydrolysed in 60% aqueous acetone in the presence of 20% molar excess of $AgNO_3$ at room temp. for 20 hr to give the *exo*-alcohol. This was recrystallised from hexane, and the properties shown in Table 4.

Preparation of p*-nitrobenzoates.* The *p*-nitrobenzoates were prepared by treating the Li salts of the alcohols with *p*-nitrobenzoyl chloride[22] and purified by recrystallisation from hexane. The m.ps and analytical data are summarised in Table 5.

2 - (m - *Trifluoromethyl)phenyl* - exo - *and* endo - 2 - *norbornyl* p - *nitrobenzoates.* The corresponding alcohols were prepared in the manner similar to that described in the lit.:[10] *exo*-OH, m.p. 105.7–106.6° (Found: C, 65.48; H, 6.06. $C_{14}H_{15}F_3O$ requires: C, 65.61; H, 5.90%). *endo*-OH, m.p. 46.9–47.8° (Found: C, 65.32; H, 6.17. $C_{14}H_{15}F_3O$ requires: C, 65.61; H, 5.90%). The *p*-nitrobenzoates were prepared in the manner described above: **5**, m.p. 79.9–81.5° (Found: C, 62.33; H, 4.35; N, 3.65. $C_{21}H_{18}F_3NO_4$ requires: C, 62.22; H, 4.47; N, 3.46%): **6**, m.p. 95.7–97.1° (Found: C, 61.78; H, 4.63; N, 3.74. $C_{21}H_{18}F_3NO_4$ requires: C, 62.22; H, 4.47; N, 3.46%).

2 - p - *Anisyl* - exo - 5,6 - *trimethylene* - exo - 2 - *norbornyl benzoate.* This was prepared by treating the Li salt of the corresponding tertiary alcohol with benzoyl chloride in the manner described in the lit.[22] Even the benzoate was unstable at room temp. and slowly decomposed to give an olefin and benzoic acid; the olefin exhibited an olefinic proton at δ 6.1 ppm on NMR analysis. This benzoate could not be crystallised; therefore, the crude product was used for kinetic runs without purification. Infinity titers exhibited the purity of 45 wt%.

3,5-*Bis(trifluoromethyl)cumyl chloride.* The reaction of acetone (2.60 g, 45 mmol) with 3,5-bis(trifluoromethyl)-phenylmagnesium iodide prepared from Mg turnings (1.09 g, 45 mmol) and 3,5-bis(trifluoromethyl)phenyl iodide (10.2 g, 30 mmol) in ether afforded 3,5-bis(trifluoromethyl)cumyl alcohol. After one recrystallisation from hexane the alcohol was obtained in 75% yield; m.p. 60.5–61.5°; NMR (CCl_4) δ 1.60 (s, 6H), 2.2 (s, 1H), 7.75 (s, 1H), 7.92 (s, 2H). The alcohol, when heated with equal weight of $KHSO_4$ at 140° and 100 mmHg afforded 3,5 - bis(trifluoromethyl) - α - methylstyrene in 79% yield as a distillate; b.p. 100–110°/100 mmHg; NMR (CCl_4) δ 2.21 (s, 3H), 5,26 (br. s, 1H), 5.47 (s, 1H), 7.7–8.0 (br. s, 3H). The olefin (2.2 g, 8.7 mmol) was treated with dry HCl in CH_2Cl_2 (5 ml) in the presence of $FeCl_3$ (250 mg) for 70 min at 0°. To the mixture was added water (10 ml) and pentane (15 ml), and the organic layer washed with water and then dried over $CaCl_2$. Distillation afforded the chloride in 28% yield; b.p. 74–75°/8 mmHg; NMR (CCl_4) δ 2.00 (s, 6H), 7.80 (s, 1H), 8.00 (s, 2H). The infinity titer exhibited the purity of 99.2%.

Determination of σ^+ constant for 3,5-*bis(trifluoromethyl).* The rates of solvolysis of 3,5 - bis(trifluoromethyl) - t - cumyl chloride were determined in 90% aqueous acetone which had been adjusted to afford the first-order rate constant of $12.4 \times 10^{-5}\ \text{sec}^{-1}$ for t-cumyl chloride,[17] giving k_1 (75°) 0.181×10^{-5}, k_1 (100°) 1.74×10^{-5}, and k_1 (25°) $6.27 \times 10^{-9}\ \text{sec}^{-1}$ (extrapolated); $\Delta H^{\ddagger}$ 22.8 kcal/mol, $\Delta S^{\ddagger}$ −19.7 e.u. The σ^+ constant for 3,5-bis(trifluoromethyl) was calculated from the equation; $\sigma^+ = [\log 6.27 \times 10^{-9}/12.4 \times 10^{-5})]/(-4.54)$.[17]

Products of solvolysis of **7** and **8**. To the *p*-nitrobenzoate (0.32 mmol) in an ampoule was added purified acetone (32.00 ml) and 0.042 M aqueous NaOAc (8.00 ml) at 25°. The ampoule was sealed under N_2 and immersed in a constant temp. bath controlled at an appropriate temp. After more than ten half-lives most of the acetone was evaporated and the residue extracted with ether. The ethereal soln was worked up in a usual manner. The product mixture was chromatographed on a Florisil (100–200 mesh) column. The elimination product and the alcohol were eluted with hexane and hexane–ether (1:1), respectively. The separated products were identified with NMR.

Kinetic procedure. Most of the *p*-nitrobenzoates were sparingly soluble in 80% aqueous acetone. Therefore, following method was adopted. The *p*-nitrobenzoate (0.6–0.8 mmol) was dissolved in 100 ml of purified acetone and equilibrated to 25°. Aliquots (4.000 ml each) of the acetone soln were taken into ampoules under N_2, and to these were added 1.000 ml aliquots of distilled water and the ampoules cooled in an ice bath. At this stage somewhat amounts of the *p*-nitrobenzoate precipitated. The ampoules were sealed, immersed in a constant temp. bath and shaken for 5 min until the crystals dissolved. The reaction was followed by titrating the produced *p*-nitrobenzoic acid with 0.02 N NaOH in acetone under N_2 using Bromthymol blue as indicator. For the reaction at 25 and 0° the usual pipetting out method was used.

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Table 5. Melting points and elemental analyses of 2 - aryl - *exo* - 5,6 - trimethylene - 2 - norbornyl *p* - nitrobenzoates (**7** and **8**)

Substituent Z	**7** or **8**	M.p.[a] °C	— Carbon, %— Calcd	Found	—Hydrogen, %— Calcd	Found	—Nitrogen, %— Calcd	Found
p-CH_3O[b]	**8**	178.0(d)	70.74	71.02	6.18	6.30	3.44	3.25
p-CH_3	**7**	99.4(d)	73.63	73.54	6.44	6.21	3.58	3.68
	8	149.0(d)	73.63	73.49	6.44	6.62	3.58	3.73
m-CF_3	**7**	132.0(d)	64.71	64.96	4.98	5.21	3.14	3.27
	8	149.8-150.6	64.71	64.75	4.98	5.23	3.14	3.19
p-CF_3	**7**	136.0(d)	64.71	64.72	4.98	5.16	3.14	3.34
	8	133.6-134.5	64.71	64.72	4.98	5.12	3.14	3.26
3,5-$(CF_3)_2$	**7**	139.6-139.9	58.45	58.72	4.12	4.24	2.73	2.92
	8	123.8-124.8	58.45	58.51	4.12	4.03	2.73	2.83

[a] Uncorrected. [b] The exo-p-nitrobenzoate was too unstable to be isolated in pure state.

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