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Solvolysis of *p*-2-Norbornyl-*tert*-cumyl Chlorides. σ^+ Constants for *p*-*exo*- and -*endo*-Norbornyl and the Question of an Unusual Polarizability of the σ -Bonds in the 2-Norbornyl Group¹

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Abstract: *p*-*exo*-Norbornyl- and *p*-*endo*-norbornyl-*tert*-cumyl chlorides were synthesized and their rates of solvolysis in 90% aqueous acetone determined in order to establish whether there is in this system a significant difference in the ability of the 2-norbornyl group to stabilize an electron deficiency from the *exo* and *endo* directions. The relative rates and σ^+ constants are as follows: *p*-hydrogen, 1.00, 0.00; *p*-isopropyl, 18.8, -0.280; *p*-*exo*-norbornyl, 25.2, -0.309; *p*-*endo*-norbornyl, 21.8, -0.295; *p*-cyclopentyl, 23.7, -0.302; *p*-cyclohexyl, 19.6, -0.285; *p*-cyclopropyl, 125, -0.462. It is concluded that this probe, although capable of revealing the modest hyperconjugative contributions of a *p*-methyl substituent and the much larger contributions of a *p*-cyclopropyl substituent in stabilizing an electron deficiency, fails to reveal an appreciable difference in the relative abilities of *p*-*exo*-norbornyl and *p*-*endo*-norbornyl to achieve such stabilization. It is pointed out that the 2-aryl-2-norbornyl system provides far greater electron demand. Yet even this probe fails to reveal a directed electron supply in the *exo* position varying with electron demand.

The physical basis for the high *exo*:*endo* rate ratio in the solvolysis of 2-norbornyl derivatives³ has fascinated chemists for nearly a quarter of a century. The effect was originally attributed to σ -participation in the transition state for the *exo* isomer.³

It was then discovered that equally high *exo*:*endo* rate ratios can be observed in tertiary 2-norbornyl derivatives where such σ -participation cannot be a factor.⁴ It was proposed that steric hindrance to ionization⁵ must be responsible for the high *exo*:*endo* rate ratios observed in such stabilized tertiary derivatives.

The problem remaining is that of extrapolating the results realized in the tertiary 2-norbornyl derivatives back to

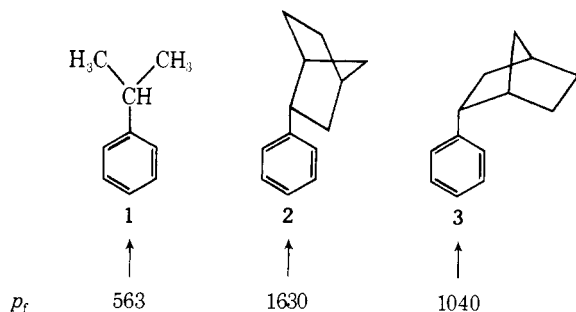
the secondary parent derivatives. Is the large *exo*:*endo* rate ratio in 2-norbornyl the result of comparable steric forces, or is there a large electronic component not present in the stabilized tertiary derivatives?

It has been suggested that the *exo*:*endo* rate ratios in 2-norbornyl may be the result neither of σ -participation³ nor of steric effects,⁴ but of a hyperconjugative contribution by the strained σ -bonds of the norbornyl structure.⁶⁻⁸

Traylor and his coworkers have pointed out that strained or polarized σ -bonds can afford large stabilization of neighboring cations.^{11,12} They have suggested that such stabilization takes place through a vertical electronic effect involving σ - π conjugation, with such conjugation not requiring

any changes of the carbon-carbon bond length or any movement of the stabilizing group toward the cationic center.⁷ This provides an interesting new approach to account for the unique characteristics of the norbornyl system in solvolytic processes.

An attempt was made to probe for such electronic contributions from the norbornyl group by determining the partial rate factors at 25° for the reaction of benzoyl chloride-aluminum chloride in ethylene dichloride solution with the 1- and 2-phenylnorbornanes.⁶ The results reveal a consistent increase in rate over isopropylbenzene, consistent with a larger hyperconjugative contribution from the strained carbon-carbon bonds. The data also reveal a small, but possibly significant greater reactivity for the *exo* isomer (**2**), as compared with isopropylbenzene (**1**) or the *endo* isomer (**3**).



An unexpected feature of these results is the observation that the data give σ^+ values for both *p-exo*-norbornyl (-0.357) and *p-endo*-norbornyl (-0.336) that are considerably more negative than the values for *p-isopropyl* (-0.280) or even *p-methyl* (-0.311). This is a highly important result. As far as the present authors are aware, this is the first experimental result in a 2-norbornyl derivative revealing a differential electronic effect which is larger from the *exo* direction than from the *endo* direction.

The benzoylation reaction possesses both favorable and unfavorable characteristics for such a study of electronic contributions.¹³ On the favorable side is the high electron demand, with $\rho = ca. -9.0$, and predominant substitution ($\sim 95\%$) in the position para to an alkyl substituent, presumably resulting from a large steric factor for the reagent. On the negative side, there is the possibility that the large steric requirements could influence in a modest way the rates of substitution of the *exo*- and *endo*-phenyl groups.

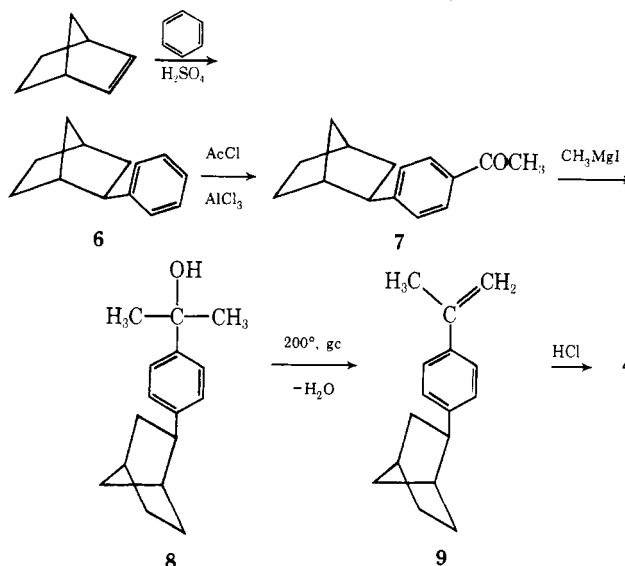
The solvolysis of *tert*-cumyl chlorides appears to be remarkably free of complications and it has been applied as a probe to a large number of systems without the appearance of any significant complications.¹⁴ It appeared desirable therefore to apply this probe to explore the relative ability of *exo*-norbornyl and *endo*-norbornyl groups in the para position to stabilize the electron deficiency in the developing cation. Accordingly, we undertook to synthesize *p-exo*-nor-

bornyl-*tert*-cumyl chloride (**4**) and *p-endo*-norbornyl-*tert*-cumyl chloride (**5**) and to determine their rates of solvolysis in 90% aqueous acetone.^{15,16}

Results and Discussion

The desired derivative (**4** and **5**) were synthesized by the synthetic routes outlined in Schemes I and II.

Scheme I. Synthesis of *p-exo*-Norbornyl-*tert*-cumyl Chloride (**4**)



Scheme II. Synthesis of *p-endo*-Norbornyl-*tert*-cumyl Chloride (**5**)

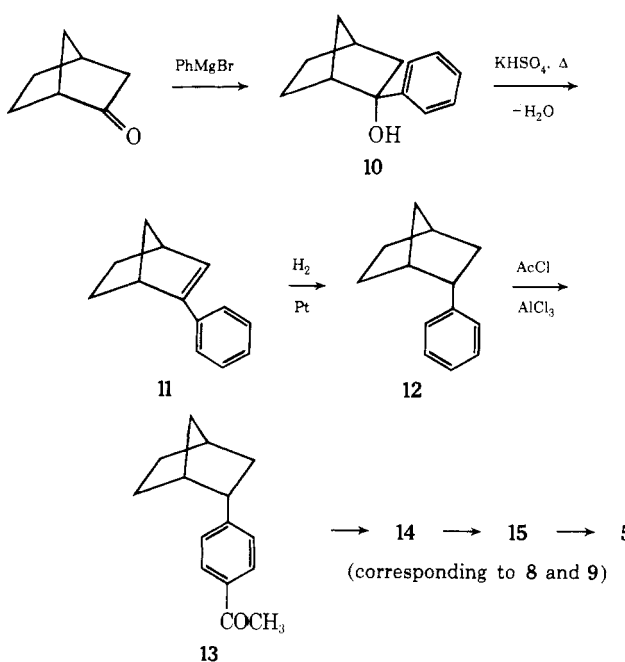


Table I. Rates of Solvolysis of *p*-Alkyl-*tert*-cumyl Chlorides in 90% Aqueous Acetone at 25.0°

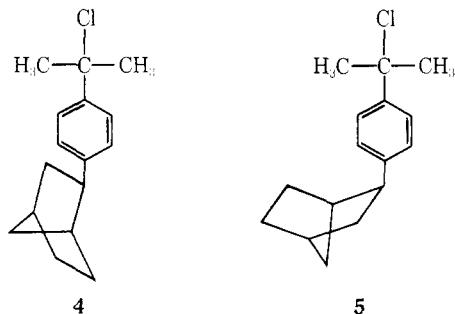
Alkyl group	$10^6 \times k_1^{25^\circ}$, sec ⁻¹	Relative rate	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , eu	σ^+
Hydrogen ^a	1.24	1.00	18.8	-12.4	(0.00)
Isopropyl ^a	23.3	18.8	17.4	-12.2	-0.280
2- <i>exo</i> -Norbornyl ^b	31.2	25.2	17.3	-11.8	-0.309
2- <i>endo</i> -Norbornyl ^c	27.0	21.8	17.9	-10.3	-0.295
Cyclopentyl ^d	29.4	23.7	17.4	-11.6	-0.302
Cyclohexyl ^d	24.3	19.6	17.6	-11.6	-0.285
Cyclopropyl ^d	155	125	16.7	-10.6	-0.462

^a Data for this compound taken from ref 15. ^b $k_1^{15^\circ} = 11.4 \times 10^{-6}$ sec⁻¹, $k_1^{25^\circ} = 2.05 \times 10^{-6}$ sec⁻¹. ^c $k_1^{15^\circ} = 9.53 \times 10^{-6}$ sec⁻¹, $k_1^{25^\circ} = 1.63 \times 10^{-6}$ sec⁻¹. ^d Data for this compound taken from ref 16.

The rate constants, kinetic parameters, and σ^+ constants for these and related compounds are summarized in Table I.

The results reveal that the effect of the *p-exo*-norbornyl (**4**) is slightly greater than the effect of the *p-endo*-norbornyl (**5**).

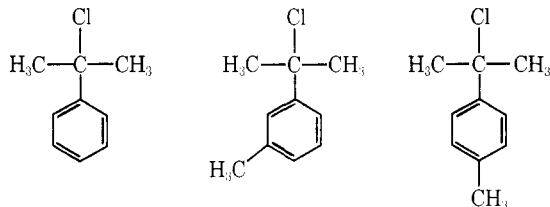
The difference in rates is smaller than that observed in the benzoylation reaction, even smaller than that anticipated from the difference in the ρ values (benzoylation, $\rho \approx -9$;¹³ solvolysis of *tert*-cumyl chlorides, $\rho = -4.54$ ¹⁷). In view of the small difference realized, it appears desirable to consider the magnitude of other structural effects in the *tert*-cumyl system in order to provide a scale for compari-



rel rate 25.2 21.8

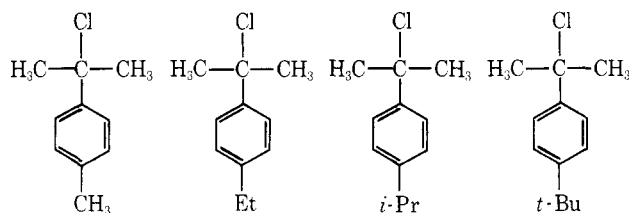
son and a basis for a decision as to the significance of the results for the proposed directed electronic effect.

The hyperconjugative effect of a *p*-methyl substituent (18) leads to a rate enhancement by a factor of 26.¹⁵



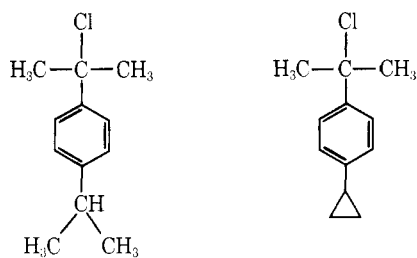
rel rate 1.00 2.00 26.0

The small Baker-Nathan effects of branching in the alkyl group (18–21) are revealed.^{15,18}



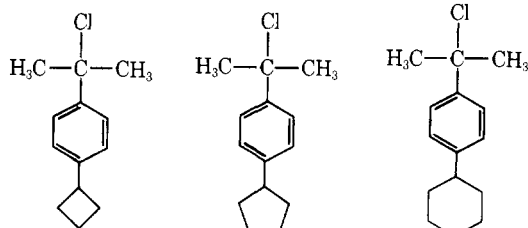
rel
rate 26.0 22.0 18.8 14.4

The enhanced ability of a *p*-cyclopropyl ring (22) to supply electrons to an electron deficient center is unambiguously indicated.¹⁶



rel rate 18.8 125

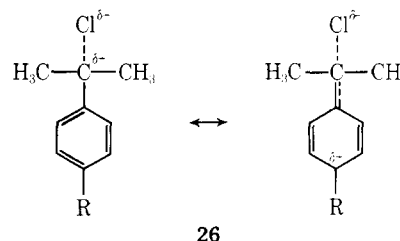
On the other hand, a *p*-cyclobutyl group (23) does not cause any unusual rate acceleration¹⁹ compared to *p*-isopropyl (20), *p*-cyclopentyl (24), or *p*-cyclohexyl (25).¹⁶



rel rate 20.7 23.7 19.6

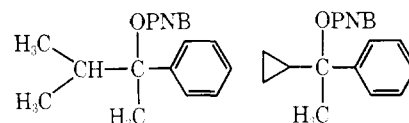
It should be noted that the differences observed for *p*-*exo*- (4) and *p*-*endo*-norbornyl (5) are comparable to those observed for 23–25.

It can be argued that the partial electron deficiency delocalized to the para position of the *tert*-cumyl system in the transition state (26) makes too small an electron demand on



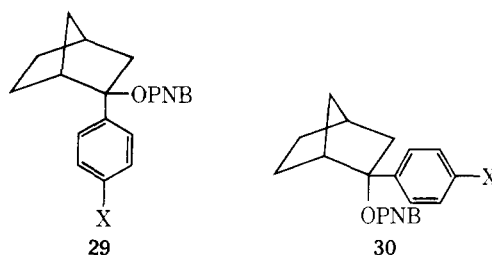
the norbornyl system to reflect any significant differences in the directed electron supply from the *exo* and *endo* positions. However, the demand is clearly able to reveal the other electronic effects tested, as discussed earlier.

In the 2-aryl-2-norbornyl derivatives⁴ the positive charge is developed to a considerable extent directly in the 2-position. This approach should provide a far more powerful electron demand. That this is indeed the case is clearly revealed by comparing the relative effects of cyclopropyl and isopropyl in 20–22 with that in 27–28.²⁰



rel rate 1.00 6.6 1.00 25,300

Yet the *exo:endo* rate ratio of 29 and 30 is essentially constant, revealing no detectable increase with increasing electron demand over a wide range ($X = p\text{-OCH}_3, p\text{-H}, p\text{-CF}_3$).²¹



It is clear that this far more powerful probe fails to reveal any increases in electron supply to the *exo* position of the norbornyl system with increasing electron demand at the 2-position. This makes it hazardous to accept as significant the small differences in reactivity indicated by 4 and 5 and 2 and 3. Clearly we require a probe utilizing electron demand much more powerful than that provided by 29 and 30 to test the proposal that vertical stabilization⁷ or carbon-carbon hyperconjugation⁶ in the norbornyl system accounts for a significant part of the *exo:endo* rate ratio in the parent system.²² Clearly, if there is such a hunger for a directed electronic contribution in the *exo*-norbornyl system,^{3,6–8} one can only hope that someone will devise the experiment to provide the data that will demonstrate unambiguously the existence of such a directed electronic effect.

Experimental Section

exo-2-Phenylnorbornane (6) was prepared by the alkylation of benzene with norbornene.²³

A solution of 100 g (1.06 mol) of norbornene in 340 g (4.3 mol) of benzene was added with stirring to a mixture of 300 g of concentrated sulfuric acid and 220 g (2.9 mol) of benzene at 5°. After

stirring at $0 \pm 1^\circ$ for 4 hr, the solution was poured into ice water and the organic layer was washed several times with water prior to drying over magnesium sulfate. Vacuum distillation gave 116 g (63.5%) of product: bp 76° (0.8 mm), n_D^{20} 1.5452.

exo-2-(p-Acetylphenyl)norbornane (7) was prepared by acetylation of **exo-2-phenylnorbornane (6)** in accordance with the procedure described for *p-tert*-butylacetophenone.¹⁵ An 82% yield of material was obtained: bp 164° (1.5 mm), n_D^{20} 1.5625.

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.20; H, 8.56.

p-(exo-2-Norbornyl)phenyldimethylcarbinol (8) was prepared by reaction of **7** with the methyl Grignard reagent in a yield of 60%: mp $67-71^\circ$ (from pentane cooled in Dry Ice).

exo-2-(p-Isopropenylphenyl)norbornane (9) was obtained by the thermal dehydration of **8** in an attempt to isolate pure **8** by preparative gc. The tertiary alcohol is rather unstable and injected samples completely dehydrated on the 10% SE-30 column at 200° , giving the olefin **9**. A 70% yield of **9** was obtained.

The product was established to be homogeneous by gas chromatographic examination, using a 150-ft Apiezon L capillary column at 170° . The nmr and ir spectra of the material are in agreement with the structure of **exo-2-(p-isopropenylphenyl)norbornane**, n_D^{20} 1.5640.

Anal. Calcd for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: C, 90.80; H, 9.33.

p-(exo-2-Norbornyl)-tert-cumyl chloride (4) was prepared by hydrochlorination of **9** with automatic generation of hydrogen chloride.²⁴ Methylene chloride was employed as solvent and the reaction was carried out at 0° . The nmr spectra of the chloride obtained shows the presence of one proton at the endo position of the norbornyl (triplet centered at 2.65 ppm). The chloride was neutral and was used for rate measurements without any further purification.¹⁵

2-Phenyl-endo-norborneol (10) was prepared by the addition of phenyl Grignard to norcamphor:²¹ mp $42.5-45^\circ$.

2-Phenylnorbornene (11) was the product of dehydration of 2-phenyl-2-endo-norborneol (**10**) with potassium bisulfate. Into a distilling flask 81 g (0.43 mol) of **13** and 42.6 g (0.31 mol) of potassium bisulfate crystals were placed. The mixture was heated and all material distilling at 6 mm was removed. A total of 65.1 g (89%) of a material distilling at $110-117^\circ$ was obtained (bp $124-128^\circ$ at 17 mm),²¹ n_D^{20} 1.5812 (n_D^{20} 1.5810).²²

The 1-phenylnortricyclene reported to be present in 6% in the olefin²² was not separated and the material was utilized directly for hydrogenation.

endo-2-Phenylnorbornane (12) was prepared by the hydrogenation of **11**: bp 71° (0.6 mm), n_D^{20} 1.5481.

endo-2-(p-Acetylphenyl)norbornane (13) was prepared, following the procedure described for **7**: bp $144-145^\circ$ (0.9 mm), n_D^{20} 1.5476.

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.40; H, 8.31.

p-(endo-2-Norbornyl)phenyldimethylcarbinol (14) was prepared by the procedure described for **8**: mp $27-30^\circ$.

2-endo-(p-Isopropenylphenyl)norbornane (15) was the product of thermal dehydration of **14** under the conditions utilized for **8**: n_D^{20} 1.5665.

Anal. Calcd for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: C, 89.10; H, 9.43.

p-(endo-2-Norbornyl)-tert-cumyl chloride (5) was prepared in accordance with the procedure described for **4**. The nmr spectrum of the chloride shows the presence of one proton at exo position of norbornyl group (broad multiplet centered at 3.15 ppm). This material was utilized for rate measurements without additional purification.¹⁵

Kinetic measurements were similar to those previously de-

scribed.¹⁵ A possibility of isomerization of endo compound in the process of solvolysis of the chloride was also checked. In an erlenmeyer flask were placed 50 ml of 90% acetone and 1.1 g of **5**. The reaction mixture was permitted to stand overnight and then was poured into water. The alcohol was extracted with ether. The ether solution, after drying over sodium sulfate, was concentrated and utilized for preparation of olefin, as described previously. The nmr spectrum of the olefin obtained is consistent with the structure of **2-endo-(p-isopropenylphenyl)norbornene (15)**. Thus, no isomerization occurs in the course of the solvolysis of *p*-(endo-2-norbornyl)-tert-cumyl chloride, at least within the limits of precision of the nmr analysis.

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