high concentration of the trapping agent without using high pressure equipment, if sulfur dioxide is the trapping agent. Furthermore, the sulfones that are formed are not particularly sensitive to ultraviolet radiation as are the peroxides formed in oxygen trapping experiments. Therefore, while an argon laser source with an output of about 2 W accelerates the rate of formation of the sulfones by a factor of about 70 over a conventional ultraviolet light source, the sulfones can easily be isolated from uncomplicated reaction mixtures using a conventional 3600 Å light source.

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(9) All attempts to resolve this mixture by silica gel chromatography led to the complete and selective destruction of a very unstable trioxane isomer; whereupon, it becomes possible to isolate the stable isomer 1c in pure form by trap-to-trap distillation at 10^{-6}.mm.
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Solvolysis of the 2-Aryl-5-methyl-2-norbornenyl *p*-Nitrobenzoates. Evidence for π Participation as a Factor in the Variation of the Rates and Products with Increasing Electron Demand at the Cationic Center

Sir:

The exo:endo rate ratio in the solvolysis of the 2-aryl-5-methyl-2-norbornenyl *p*-nitrobenzoates (**1** and **2**) increases

1

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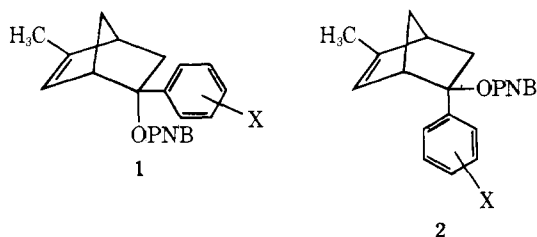
as the electron demand of the 2-aryl substituent is increased. Moreover, the reaction products reveal increasing involvement of the double bond. These results indicate that the double bond activated by the 5-methyl substituent is strongly involved in the solvolysis, in contrast to the behavior of the parent 2-aryl-2-norbornenyl derivative[1] (**3** and **4**).

3

4
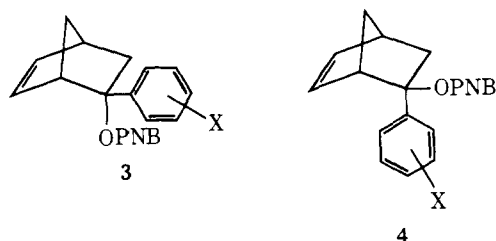
The tool of increasing electron demand has been applied as a test for π and σ participation in a number of systems. The results confirm the presence of such participation in 7-aryl-*anti*-norbornenyl,[2] arylcyclopropylmethylcarbinyl,[3] and 3-aryl-3-nortricyclyl.[4] However, the data indicate the absence of such participation in the solvolysis of 2-aryl-2-norbornenyl[1] (**3** and **4**) and 2-aryl-2-norbornyl[5] (**5** and **6**) derivatives.

5

6
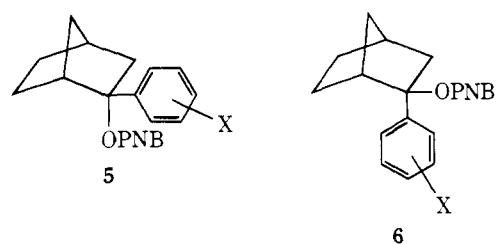
It has been suggested that tertiary benzylic cations are so stable that participation could be detected only in systems where such participation is of very large magnitude,[6] such as the *anti*-norbornenyl[2] and the cyclopropylcarbinyl systems.[3,4] Accordingly, we undertook to activate the double bond of **3** and **4** moderately in order to test whether with such activation the tool of increasing electron demand could detect moderate participation. (We are also seeking to increase the electron demand at the cationic center of **3** and **4** in the hope of establishing the incursion of π participation by such means.)

Table I. Rates of Solvolysis of 5-Methyl-2-aryl-2-norbornenyl *p*-Nitrobenzoates in 80% Acetone at 25.0°

Substituent in 2-aryl[a]	Isomer	Rate constant $10^6 k_1$, sec^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, eu	$k_1{}^{5-Me}/k_1{}^{5-H}$[b]	Exo:endo rate ratio
p-CH₃O	2[c]	3000[d]			1.19	354
	1[e]	8.48			1.05	
p-H	2[f]	9.18			7.4	1260
	1[g]	7.28×10^{-3}[h]	26.4	−7.2	1.21	
p-CF₃	2[i]	0.0794[i]			26	6700
	1[j]	1.19×10^{-5}[h]	30.4	−6.4	0.93	

[a] All new compounds gave spectral and microanalytical data consistent with the proposed structure. [b] Values of $k_1{}^{5-H}$ (**3** and **4**) from ref 1. [c] Benzoate. ROBz, liquid; $k_1{}^{25°} = 1.44 \times 10^{-4}$ sec^{-1}; ROH mp 68–69°. [d] Rate constant for *p*-nitrobenzoate estimated by multiplying the rate constant for the benzoate by the factor 20.8[5]. [e] ROPNB mp 112–113° dec; ROH bp 108–110° (0.02 mm). [f] ROPNB mp 116–118°; ROH bp 90° (0.03 mm). [g] ROPNB mp 109–110°; $k_1{}^{100°} = 69.3 \times 10^{-6}$ sec^{-1}, $k_1{}^{75°}$ 5.07 $\times 10^{-6}$ sec^{-1}; ROH bp 82° (0.12 mm). [h] Value calculated from data at other temperatures. [i] Value calculated from values for *p*-H and *p*-MeO using the equation log $(k/k_H) = \rho\sigma^+$ (ref 9). [j] ROPNB mp 155°; $k^{150°} = 62.5 \times 10^{-6}$ sec^{-1}, $k_1{}^{125°} = 6.16 \times 10^{-6}$ sec^{-1}; ROH bp 103° (0.15 mm).

Table II. Exo:Endo Rate Ratios as a Function of Increasing Electron Demand

	Exo/Endo Rate Ratio		
	$k_1{}^6/k_1{}^5$	$k_1{}^4/k_1{}^3$	$k_1{}^2/k_1{}^1$
p-CH$_3$O	284	312	354
p-H	127	202	1260
p-CF$_3$	187	283	6700

Table III. Products of the Solvolysis of the 2-Aryl-5-methyl-2-norbornenyl p-Nitrobenzoates

| Compound solvolyzed (1, 2)	Products, %	
	7	8
p-CH$_3$O (exo or endo)	75 ± 3	25 ± 3
p-H (exo or endo)	18 ± 3	82 ± 3
p-CF$_3$ (endo)	<2	>98

The introduction of a methyl group on a double bond greatly increases its ability to participate by relatively small factors.[7] Accordingly, we undertook to synthesize 1 by the addition of the appropriate Grignard to 5-methyl-2-norbornenone[8] and 2 from the hydrolysis products of an appropriate derivative of 1. Unfortunately, as described later, the alcohol corresponding to 2-p-CF$_3$ could not be obtained by this procedure. However, all of these derivatives follow the log $(k/k_H) = \rho\sigma^+$ relationship[9] closely. Consequently, this relationship was utilized to calculate the rate for 2-p-CF$_3$. The rate data are summarized in Table I.

The 5-CH$_3$ substituent has practically no effect upon the rates of the endo isomers. Thus $k_1{}^3/k_1{}^1$ is 1.05 for p-CH$_3$O, 1.21 for p-H, and 0.93 for p-CF$_3$. On the other hand, the 5-CH$_3$ substituent enhances the rates of the exo isomer, with the enhancement increasing with increasing electron demand: $k_1{}^4/k_1{}^2 = 1.19$ for p-CH$_3$O, 7.4 for p-H, and 26 for p-CF$_3$.

The effect of the 5-CH$_3$ is also indicated by the ρ values: 3, -4.17; 1, -4.19; 4, -4.21; 2, -3.28.

The exo:endo rate ratio has long been the standard criterion to estimate participation. The summary of the data in Table II clearly reveals in the present system an increase in the exo:endo rate ratio with increasing electron demand by the 2-aryl substituent and the absence of the effect in the 2-aryl-2-norbornenyl[1] and 2-aryl-2-norbornyl systems.[5]

The products produced in the solvolysis of the 1 and 2 derivatives in aqueous acetone containing 10 mol % excess sodium acetate were determined by nmr examination (eq 1).

(1)
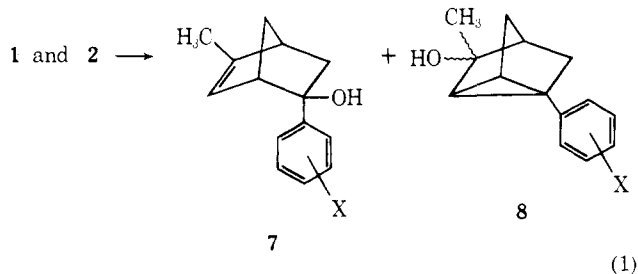
The results (Table III) clearly correspond to the effect anticipated for increasing participation of the double bond with increasing electron demand of the 2-aryl group.

In the case of the 2-aryl-2-norbornenyl p-nitrobenzoates[1] (3, 4), not only does the exo:endo rate ratio fail to reflect any influence of increasing electron demand (Table II) but the predominant solvolysis product, in all three cases, is the corresponding 2-aryl-exo-norbornenol.[1] This contrasts with the behavior of the 5-CH$_3$ derivatives. Here, only the p-CH$_3$O derivative yields the exo alcohol as the major product. The other derivatives, involving greater electron de-

mand, yield chiefly the rearranged product, 1-aryl-3-methyl-3-nortricyclanol, resulting from a homoallylic rearrangement.

In conclusion, the present study reveals that the tool of increasing electron demand is capable of responding to and detecting relatively small participations. The failure of this tool to detect any measurable electronic contributions in the 2-aryl-2-norbornyl (5 and 6) and the 2-aryl-2-norbornenyl (3 and 4) systems supports the conclusion that the high exo: endo rate ratios observed in these systems must be the result of other than electronic factors, presumably steric.[10] On this basis, the exo:endo rate ratio of 6700 observed for 2-p-CF$_3$/1-p-CF$_3$ would be made up of a factor of approximately 25 representing π participation and one of approximately 270 representing the steric factor.

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Long Range Effect in the Exciton Chirality Method

Sir:

The method for determining the absolute configuration of organic compounds from coupled Cotton effects, e.g., exciton chirality method,[1,2] is theoretically well grounded and nonempirical.[1,3] From a practical viewpoint it is important to clarify the relation between the observed $\Delta\epsilon$ of split Cotton effects and the geometrical factors which affect these values, especially the distance dependency.[4,5]

The following data for a series of steroidal glycol dibenzoates show excellent agreement between experimental and theoretical values. In particular the strong interaction still operating between the 3β- and 15β-benzoate functions in the D-homo-steroidal 1,8-glycol[6] 10 (Table I), which was prepared in order to avoid complications arising from a flexible five-membered D-ring, is noteworthy as it shows that the exciton chirality method can be applied to configurational studies of molecules containing quite remote groups. In 10 the distance is ca. 12.8 Å but the $\Delta\epsilon$ is still more than ten times stronger than ordinary carbonyl n,π^* Cotton effects. Although the present communication is for dibenzoate systems,[7] the same treatment should hold for interactions between other chromophores, e.g., enone–benzoate,[2,8] and others.[1]

The p-dimethylaminobenzoyloxy group was chosen as the chromophore since: (i) the strong uv intensity of its 309-nm intramolecular charge transfer band leads to large amplitudes of the coupled Cotton effects;[9] (ii) the 309-nm band is well separated from the shorter wavelength band and thus facilitates theoretical treatments.

CD curves were calculated on the basis of the point-di-