Structural Effects in Solvolytic Reactions. XIII. Effect of Increasing Electron Demand on the Rates of Solvolysis of 1-Arylcyclopent-3-en-1-yl and 1-Arylcyclopentyl *p*-Nitrobenzoates. Evidence for the Absence of π-Participation

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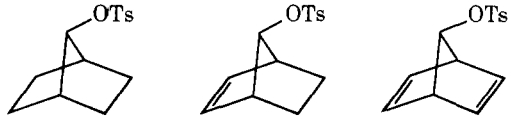
Abstract: The rates of solvolysis of 1-arylcyclopent-3-en-1-yl *p*-nitrobenzoates were measured in 80% aqueous acetone and compared with the corresponding saturated derivatives in order to establish whether there is in this system increasing π-participation with increasing electron demand. The rates of solvolysis of cyclopentenyl derivatives compared with their saturated analogs are 1/2.24 for *p*-OCH_3, 1/3.26 for *p*-H, 1/4.0 for *p*-CF_3, and 1/3.24 for 3,5-$(CF_3)_2$. The 1-arylcyclopent-3-en-1-yl system yields a ρ^+ value of -3.92 as compared with -3.82 for cyclopentyl derivatives. It is concluded that the tool of increasing electron demand reveals no significant 1,3-interaction between the π electrons and the cationic center.

The introduction of one or two double bonds in 7-norbornyl tosylate (**1**) greatly increases the rate of solvolysis. Thus the rate of *anti*-7-norbornenyl (**2**) is increased by a factor of 10^{11} [2] and that of 7-norbornadienyl (**3**) by a factor of 10^{14}.[3] These major increases in rate are attributed to π-participation by the double bond.



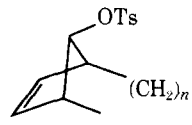
	1	2	3
rel rate:	1.0	10^{11}	10^{14}

Bartlett and Rice have examined the solvolysis of 4-bromocyclopentene (**5**).[4] They noted that the system reacted slower than cyclopentyl bromide (**4**). Thus the amount of

	4	5
rel rate:	1.0	1/4.7

orbital overlap between C_1 and C_4 must be negligible, and the molecule of the unsaturated bromide is not bent sufficiently toward the form of 7-norbornenyl to produce any significant overlap. Calculation showed that the strain energy involved in reaching a suitable conformation is greater than the stabilization afforded by the orbital overlap.[4] These results are in line with the conclusion that the degree of puckering in the cyclopentene ring and hence the distance between the π-electron cloud of the double bond and the developing cationic center must be crucial in determining the overall effect of anchimeric assistance.[5]

The importance of this steric requirement can be seen by comparing the homologous series of bicyclo[2.1.*n*] compounds (**6**) where n = 1-3 (n = 0 for cyclopentene). Thus



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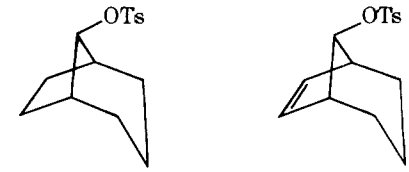
in 1969 Masamune and co-workers[6] reported that the acetolysis of *exo*-6-bicyclo[2.1.1]hex-2-en-6-yl tosylate (**8**) is 5 $\times$ 10^{16} times faster than that of *exo*-bicyclo[2.1.1]hex-6-yl tosylate (**7**).[7]

	7	8
rel rate:	1.0	5×10^{16}

In 1955, Winstein et al. noted that *anti*-7-norbornenyl tosylate (**2**) undergoes acetolysis 10^{11} times faster than 7-norbornyl tosylate (**1**).[2] In 1971, Hess[5] reported that the acetolysis of *endo*-bicyclo[3.2.1]oct-6-en-8-yl tosylate (**10**) was 1.9 $\times$ 10^5 times faster than that of *endo*-bicyclo[3.2.1]oct-8-yl tosylate (**9**).[8]



	9	10
rel rate:	1.0	1.9×10^5

In 1961, Winstein and Sonnenberg reported that cyclopent-3-en-1-yl tosylate (**12**) reacts 8.3 times slower than cyclopentyl tosylate (**11**) in acetic acid.[9]

	11	12
rel rate:	1.0	1.0/8.3

Clearly, the relative rates show a definite trend with the increase of the distance between the carbon-carbon double bond and the developing carbonium ion center. With increasing distance there is a marked decrease in the effectiveness of participation by the double bond.

Finally, in 1969 LeBel and Maxwell[10] reported that the acetolysis of *exo*-bicyclo[3.2.1]oct-6-en-3-yl tosylate (**14**) is slower than *exo*-bicyclo[3.2.1]octan-3-yl tosylate (**13**)[11] by a factor of 2.9.

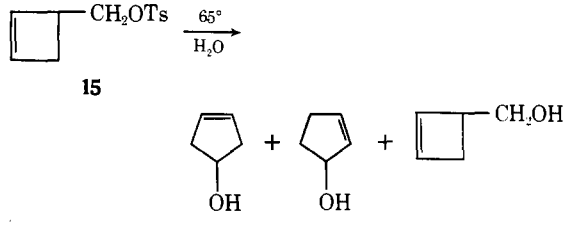
13 14

rel rate: 1.0 1.0/2.9

It was concluded that anchimeric assistance is not provided by the double bond in this system because the bond distance is too great for effective orbital overlap. Therefore, it is not surprising that Bartlett and Rice concluded that anchimeric assistance by the double bond in 4-bromocyclopentene is not significant.

Recently, however, Olah[12] has stated that the results of product studies and the interpretation of rate data in some recent works[13-15] do indeed support the presence of anchimeric assistance in the cyclopentenyl system.

For example, in 1967 Hanack and Riedlinger reported that Δ^2-cyclobutenylmethyl tosylate (**15**) undergoes hydrolysis to give cyclopent-3-en-1-ol (**16**) as the major product (eq 1).[13] Further, 4-bromocyclopentene (**5**) upon treatment

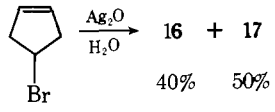


15

16 17

67% 17% 2% (1)

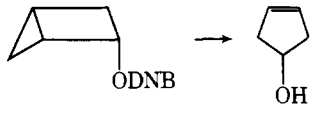
with silver oxide in water gives a mixture of cyclopent-3-en-1-ol (**16**) and cyclopent-2-en-1-ol (**17**)[14] (eq 2). Then in



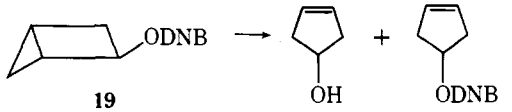
40% 50% (2)

5

1968, Wiberg and co-workers noted that the products produced in the solvolysis of bicyclo[2.1.0]pent-2-yl derivatives (**18, 19**) are only cyclopent-3-en-1-yl derivatives (eq 3, 4).[15]

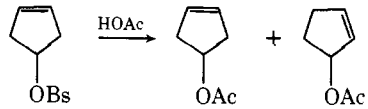


18 **16** (3)

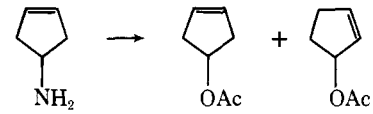


19 67% 33% (4)

Finally, in 1970, Allred and Flynn established the products of acetolysis of cyclopent-3-en-1-yl brosylate (**20**) and of the acetic acid deamination of 4-aminocyclopentene (eq 5, 6).[16] However, Olah and his co-workers were unable to observe the cations from cyclopent-3-en-1-ol and 1-methylcyclopent-3-en-1-ol in strong acid media.[12] Thus they were



20 40% 60% (5)



21 23% 77% (6)

unable to contribute to the resolution of the claim that there indeed is a 1,3 orbital interaction in the cyclopent-3-en-1-yl system.

In the 2-norbornenyl system, 2-*exo*-norbornenyl tosylate (**23**) reacts slower by a factor of 2 than its saturated analogue (eq 7).[2,17] However, it has been estimated that a rate

22 **23** (7)

rel rate: 1.0 1.0/2

enhancing factor of 20, attributable to π-participation is also present in this system.[18] This rate decrease of 2 is comparable to those reported by Bartlett (1/4.7) and Winstein (1/8.3) for the cyclopent-3-en-1-yl system. Therefore, it was decided to investigate the solvolysis of 1-arylcyclopent-3-en-1-yl derivatives, utilizing the tool of increasing electron demand in order to determine the effect of the double bond and to resolve the question as to whether there is any measurable π-participation in the cyclopent-3-en-1-yl system.

Results and Discussion

Synthesis. The 1-arylcyclopent-3-en-1-yl derivatives (**25**) were prepared by the addition of the appropriate Grignard reagent to Δ^3-cyclopentenone (**24**), as shown in Scheme I. The Δ^3-cyclopentenone was prepared by the method of Hess and Brown.[19]

Kinetic Studies. Rates of solvolysis were determined in 80% aqueous acetone (v/v) and are summarized in Table I. Rate constants for the 1-arylcyclopentyl *p*-nitrobenzoates (Y = *p*-CH_3O, *p*-H, and *p*-CF_3) were similar to those of Takeuchi,[20] but with certain minor differences. To avoid

Scheme I. A Flow Diagram for the Synthesis of 1-Arylcyclopent-3-en-1-yl Derivatives

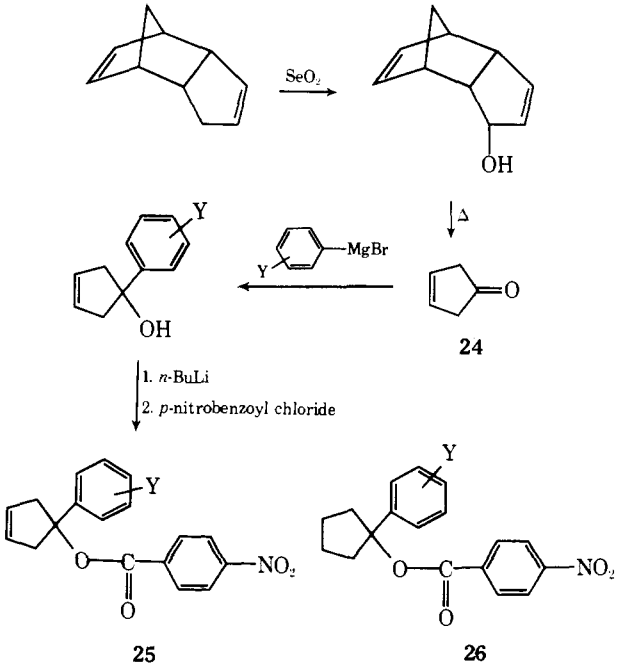


Table I. Rates of Solvolysis of 1-Arylcyclopent-3-en-1-yl (**25**) and 1-Arylcyclopentyl *p*-Nitrobenzoates (**26**) in 80% Acetone

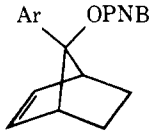
OPNB	Substituent	Rate constant ($10^6 k_1$), sec^{-1}				
		T_1	T_2	25°[a]	$\Delta H^{\ddagger}$[c]	$\Delta S^{\ddagger}$[d]
1-Arylcyclopentyl[22]	*p*-OCH_3			3980[b]		
	p-H	926 (75°)	61.6 (50°)	2.6	23.7	−4.8
	p-CF_3	98.1 (100°)	7.54 (75°)	0.012	25.9	−7.9
	3,5-$(CF_3)_2$	76.2 (125°)	7.02 (100°)	4.97×10^{-4}	27.6	−8.2
1-Arylcyclopent-3-en-1-yl	*p*-OCH_3			1780[b]		
	p-H	307 (75°)	19.7 (50°)	0.798	24.0	−6.1
	p-CF_3	371 (125°)	35.8 (100°)	3.07×10^{-3}	26.9	−7.3
	3,5-$(CF_3)_2$	337 (150°)	37.8 (125°)	1.53×10^{-4}	28.7	−7.2

[a] Extrapolated from data at higher temperatures, except where otherwise indicated. [b] Estimated by multiplying the rate constant for the benzoate by the factor 20.8.[21] [c] Units of kcal mol^{-1}. [d] Units of eu.

confusion, only the rate constants determined in the present study will be used, especially since they were determined with the 1-arylcyclopent-3-en-1-yl derivatives in the same solvent batches and should provide more precise values of the relative rates. The rate constants for the *p*-anisyl *p*-nitrobenzoates were determined by multiplying the rate constant for the benzoate by the factor 20.8.[21]

The data reveal excellent linear correlations with σ^+ constants. The 1-arylcyclopentyl system (**26**) yields a ρ^+ value of −3.82[22] (correlation coefficient 0.999), while the 1-arylcyclopent-3-en-1-yl system (**25**) yields one of −3.92 (correlation coefficient 0.999).

The tool of increasing electron demand, varying the electron demand by the introduction of appropriate substituents in the meta and para positions of the aryl group while maintaining the steric requirements essentially constant, is proving of major value in providing an objective answer to the importance of π- or σ-participation in many systems. Thus the tool has confirmed the large π-participation postulated for the *anti*-7-norbornenyl system (**2, 27**).[23] It has also confirmed the large σ-contribution in stabilizing cyclopropylcarbinyl cations (**28**).[24]



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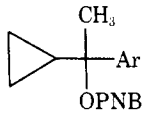

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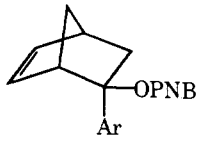
It has been established that π-participation is negligible in the 2-aryl-2-norbornenyl system (**29**), becoming important only in the corresponding secondary derivative.[25] On the other hand, in the 5-methyl-2-aryl-2-norbornenyl system, with its more activated double bond (**30**), major π-participation is clearly revealed by the tool of increasing electron demand.[26]



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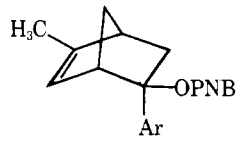

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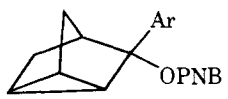
It has provided a definite answer to the importance of σ-contributions in the 3-nortricyclyl system (**31**).[27] Finally, it proved capable of detecting electronic contributions as small as a factor of 2 in the 1-(*p*-cyclopropylphenyl)-1-aryl ethyl system (**32**).[28]



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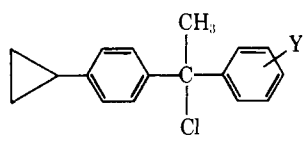

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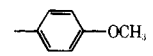
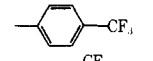
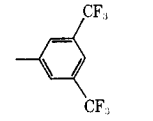
Table II. Comparison of the Rates of Solvolysis of Cyclopentyl and Cyclopent-3-en-1-yl Derivatives

R	X	Rel rate	
			
	OPNB	1.0	1/2.24[a]
	OPNB	1.0	1/3.26[a]
	OPNB	1.0	1/4.0[a]
	OPNB	1.0	1/3.24[a]
H	Br	1.0	1/4.7[b]
H	OTs	1.0	1/8.3[c]

[a] This study. [b] Reference 4. [c] Reference 9.

Consequently, it appeared appropriate to apply this tool to the cyclopent-3-en-1-yl system (**25**) to test the position that π-participation may indeed be a factor in that system.[12]

It is evident from an examination of the effect of increasing electron demand (Table II) that there is no significant increase in the relative rates as the demand is increased in the tertiary derivatives. If the examination is extended to the much more electron demanding secondary derivatives, a hazardous procedure because of the altered steric requirement, the relative rate reveals not an increase in the relative rates but an actual decrease. It was previously noted that the rate-retarding inductive effect of a double bond is somewhat larger in secondary than in tertiary derivatives.[25]

In conclusion, the rate data reveal the absence of any significant amount of 1,3-interaction between the π-electrons and the cationic center. The 1-arylcyclopent-3-en-1-yl derivatives undergo solvolysis at a rate about three times slower than their saturated derivatives. The small rate retardation is in the direction anticipated for the inductive effect of the double bond on the rates of solvolysis, with no evidence for a trend which could be attributed to π-participation.

Experimental Section

Melting points (taken in capillary tubes) and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 137 or 700 spectrometer. NMR spectra were recorded on a Varian T-60 spectrometer.

1-Dicyclopentadienol was prepared following the procedure of Rosenblum:[29] bp 83–85° (2.8 mm).

Δ^3-Cyclopentenone was obtained by the method of Hess and Brown:[19] bp 28° (17 mm) [lit.[19] bp 28° (17 mm)]; NMR (CCl_4) δ 2.77 (s, 2 H, methylene) and 6.08 (s, 1 H, olefinic).

1-*p*-Anisylcyclopent-3-en-1-ol. Addition of *p*-anisylmagnesium bromide to Δ^3-cyclopentenone gave a clear oil. Distillation gave the desired alcohol (87% yield): bp 118–119° (0.7 mm).

1-Phenylcyclopent-3-en-1-ol. This alcohol was prepared by the addition of phenylmagnesium bromide to Δ^3-cyclopentenone and worked up in the normal manner. Distillation gave the desired alcohol (95.5% yield): bp 76–78° (2.6 mm);[30] NMR (CCl_4) δ 2.69 (s, 4 H, methylenes), 5.68 (s, 2 H, olefinic), and 7.27 (broad, m, 5 H, aromatic).

1-(*p*-Trifluoromethyl)phenylcyclopent-3-en-1-ol. Addition of *p*-trifluoromethylphenylmagnesium bromide to Δ^3-cyclopentenone and work-up in the normal manner resulted in a pale yellow oil which solidified on standing. Recrystallization from hexane gave the alcohol (81% yield): mp 49.5–50.8°; NMR ($CDCl_3$) δ 2.82 (broad s, 4 H, methylene), 5.80 (s, 2 H, olefinic), and 7.60 (s, 4 H, aromatic).

1-[3,5-Bis(trifluoromethyl)phenyl]cyclopent-3-en-1-ol. Addition of 3,5-bis(trifluoromethyl)phenylmagnesium bromide to Δ^3-cyclopentenone and work-up in the normal manner gave a yellow oil which solidified on standing. Recrystallization from hexane gave the desired alcohol (75% yield): mp 49–50°; NMR ($CDCl_3$) δ 2.87 (s, 4 H, methylene), 5.83 (s, 2 H, olefinic), 7.77. (s, 1 H, para H), and 7.98 (s, 2 H, ortho H's).

1-[3,5-Bis(trifluoromethyl)phenyl]cyclopentanol. Addition of bis(3,5-trifluoromethyl)phenylmagnesium bromide to cyclopentanone and work-up in the normal manner gave a solid which was recrystallized from hexane to give the desired alcohol (79% yield): mp 80.6–81.5°; NMR ($CDCl_3$) δ 2.03 (broad s, 8 H, methylenes), 7.77 (s, 1 H, para H), and 7.97 (s, 2 H, ortho H's).

1-*p*-Anisylcyclopent-3-en-1-yl Benzoate. This ester was prepared from the lithium alkoxide. The ester would not solidify. Crystallization at −80° failed. The NMR indicated that the ester was about 90% pure.

1-Phenylcyclopent-3-en-1-yl *p*-Nitrobenzoate. This *p*-nitrobenzoate was prepared in the usual way[27] from the lithium alkoxide (81% yield) and recrystallized from hexane to constant melting point: mp 90.5–91.4°;[30] NMR (CCl_4) δ 3.25 (s, 4 H, methylenes), 5.85 (s, 2 H, olefinic), 7.38 (s, 5 H, phenyl), and 8.28 (s, 4 H, *p*-nitrobenzoate).

Anal. Calcd for $C_{18}H_{15}NO_3$: C, 69.89; H, 4.89; N, 4.53. Found: C, 69.82; H, 4.86; N, 4.53.

1-(*p*-Trifluoromethyl)phenylcyclopent-3-en-1-yl *p*-Nitrobenzoate. This *p*-nitrobenzoate was prepared in the usual way[27] from the lithium alkoxide (92% yield) and recrystallized from hexane to constant melting point: mp 117–118°; NMR ($CDCl_3$) δ 3.27 (s, 4 H, methylenes), 5.86 (s, 2 H, olefinic), 7.58 (s, 4 H, phenyl), and 8.29 (s, 4 H, *p*-nitrobenzoate).

Anal. Calcd for $C_{19}H_{14}O_4F_3N$: C, 60.48; H, 3.74; N, 3.71; F, 15.11. Found: C, 60.44; H, 3.81; N, 3.71; F, 15.20.

1-[3,5-Bis(trifluoromethyl)phenyl]cyclopent-3-en-1-yl *p*-Nitrobenzoate. This *p*-nitrobenzoate was prepared from the lithium alkoxide[27] (82% yield), and recrystallized from hexane to constant melting point: mp 87.8–88.5°; NMR ($CDCl_3$) δ 3.27 (broad s, 4 H, methylenes), 5.87 (s, 2 H, olefinic), 7.81 (s, 3 H, phenyl), and 8.27 (s, 4 H, *p*-nitrobenzoate).

Anal. Calcd for $C_{20}H_{13}NF_6O_4$: C, 53.94; H, 2.94; N, 3.14; F, 25.60. Found: C, 53.96; H, 3.11; N, 3.21; F, 25.54.

1-[3,5-Bis(trifluoromethyl)phenyl]cyclopentyl *p*-Nitrobenzoate. This *p*-nitrobenzoate was prepared from the lithium alkoxide[27] (84% yield) and recrystallized from hexane to constant melting point: mp 85.7–86.8°; NMR ($CDCl_3$) δ 2.02 (m, 4 H, 3,4-methylene), 2.35 and 2.62 (broad m, 4 H, 2,5-methylene), 7.78 (s, 1 H, para H), 7.90 (s, 2 H, ortho H's) and 8.20 (d, 4 H, *p*-nitrobenzoate).

Anal. Calcd for $C_{20}H_{15}NF_6O_4$: C, 53.70; H, 3.38; N, 3.13; F, 25.49. Found: C, 53.84; H, 3.30; N, 3.14; F, 25.39.

Kinetic Procedure. The procedure utilized for the determination of rate constants was similar to that previously reported by Brown and Peters.[27]

References and Notes

(1) Postdoctoral research associate, 1972–1973, on a grant (GP 31385) supported by the National Science Foundation.
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