Structural Effects in Solvolytic Reactions. 29. Solvolysis of Tertiary Allylic *p*-Nitrobenzoates. Effect of the Allylic Double Bond on the Rates of Solvolysis of Representative Tertiary *p*-Nitrobenzoates

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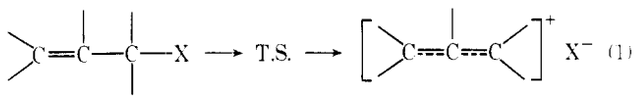
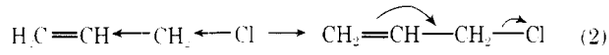
Representative cyclic and acyclic tertiary *p*-nitrobenzoates containing a double bond in the allylic position, together with the corresponding saturated derivatives, were solvolyzed in 80% aqueous acetone in order to establish the effect of the allylic double bond on the solvolysis rate. In all cases these allylic compounds exhibit rates that are considerably enhanced over the corresponding saturated derivatives. Thus, the simple α,α-dimethylallyl derivative solvolyzes at a rate that is 340 times faster than the saturated compound, *n*-propyldimethylcarbinyl. γ-Methyl substituents greatly enhance the rate of solvolysis. Thus, the rate for α,α,γ-trimethylallyl is 2.2×10^3 faster than α,α-dimethylallyl and 8.3×10^5 faster than the saturated derivative. Introduction of a double bond into the allylic position of cyclic systems also increases greatly the rate of solvolysis. Thus, 1-methylcyclohex-2-enyl and 1-methylcyclopent-2-enyl exhibit rates of solvolysis that are greater than those of the saturated derivatives by factors of 1.87 $\times 10^6$ and 5.4×10^8, respectively. The enhanced reactivity in these systems has been attributed to the combined effects of the allylic double bond and the γ substitution of the allylic double bond afforded by the ring system. The precise reason for the exceptionally high reactivity of the cyclopent-2-enyl system is still uncertain.

Allylic compounds containing an ionizable group in the allylic position exhibit considerably enhanced reactivities in solvolytic processes relative to the corresponding saturated derivatives.[2-6] Such rate enhancement in S_N1 reactions is recognized as being the result of tautomeric electron release from the allylic double bond, stabilizing the incipient allylic carbonium ion (expression 1).



(1)

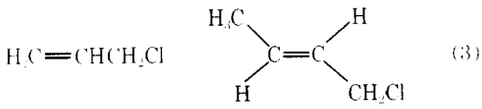
Often the observed rate enhancement is smaller than anticipated. For example, comparison of the solvolytic reactivities of allyl and *n*-propyl chlorides reveals that the allylic compound is more reactive, but the ratio of the rates of solvolysis is relatively small.[7] At one time the smallness of this effect was attributed to the operation of conflicting effects. It was proposed that the inductive effect of the double bond operates to strengthen the C–X bond, resisting the ionization[9] (expression 2).



(2)

However, at the present time this relatively small difference in reactivity is attributed to solvent participation in the solvolytic process.[10,11] Such solvent participation can seriously decrease the electron deficiency at the solvolytic center and reduce the electron release from the double bond.

The presence of a methyl group in the γ position causes a large enhancement in the solvolysis rate over that of the saturated compound and the parent allylic compound[9] (expression 3). A second methyl group has a similar effect. Thus, γ,γ-dimethylallyl chloride is more reactive than allyl chloride by a factor of 10^7 to 10^8.[9]



(3)

RR, 25 °C 1.00 3.44×10^3

A phenyl group in the γ position produces an effect intermediate in magnitude to that of one and two methyl groups.[9] On the other hand, a methyl group in the β position is without significant effect.[9]

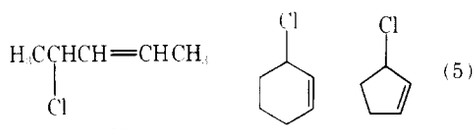
In these primary derivatives, there must be concern as to how seriously the relative reactivity values are distorted by solvent participation.[10,11]

The introduction of a double bond into a cyclic system enormously increases its reactivity over that of the corresponding saturated derivative. Thus, cyclohex-2-enyl chloride is 10^7 times more reactive[12] than its saturated analogue[13] (expression 4). This large increase in reactivity must be attributed to

(4)

RR, 25 °C 1.00 1.98×10^7

the combined effect of the allylic double bond, possibly enhanced in its effect by the cis conformation, and the presence of a γ-methylene substituent.[12,14] Cyclopent-2-enyl derivatives are much more reactive than both the corresponding cyclohexenyl and open-chain compounds. Thus, cyclopent-2-enyl chloride is more reactive than α,γ-dimethylallyl chloride by a factor of 151. It is more reactive than cyclohex-2-enyl chloride by a factor of 610[12,14] (expression 5). Similar results have been observed for the bromides.[15]



(5)

RR, 25 °C 1.00 0.25 151

The thermodynamic stability of the cyclopent-2-enyl cation has been shown experimentally to exceed that of the corresponding cyclohex-2-enyl and acyclic cations.[16] It has been shown by NMR that cyclopent-2-enyl cations are more stable than other allylic cations.[17]

As mentioned earlier, a major problem in interpreting such results has been the use of primary and secondary derivatives to explore the effects of the double bonds on reactivities. It is now recognized that the solvolysis of such derivatives in the usual solvolytic media often involves large solvent participation.[10,11] On the other hand, the solvolysis of tertiary derivatives appears to proceed by a process that is essentially k_c, essentially free of significant solvent participation.[18]

Accordingly, we decided to undertake an examination of the effects of such allylic double bonds by examining the solvolysis of tertiary derivatives only. In order to avoid rearrangement problems associated with the synthesis of allylic

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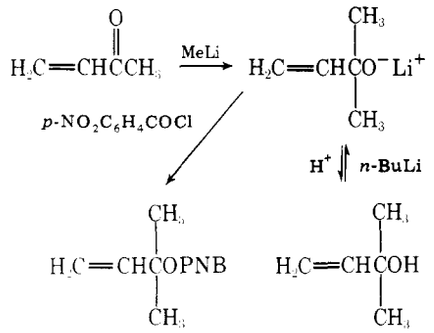
chlorides,[12,19] we utilized the *p*-nitrobenzoates, readily synthesized from allylic alcohols without detectable rearrangements. The rates of solvolysis were run in 80% aqueous acetone to provide data directly comparable with other systems we have been examining. Finally, we examined a number of saturated derivatives to make possible a direct estimation of the effect of the allylic double bond.

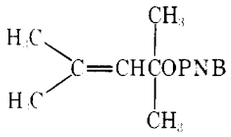
Results

Synthesis. The α,α-dimethylallyl alcohols were prepared by addition of the appropriate ketone to methyllithium at 0 °C[20] (expression 6). The *p*-nitrobenzoates were prepared by



(6)

treating the purified alcohols with *n*-butyllithium to form the alkoxides, followed by treatment with *p*-nitrobenzoyl chloride in THF[21] (expression 6). The properties of the *p*-nitrobenzoates are summarized in the Experimental Section. $\alpha,\alpha,\gamma,\gamma$-Tetramethylallyl *p*-nitrobenzoate could not be isolated owing to its exceptionally high reactivity. Accordingly, the benzoate was prepared and utilized.



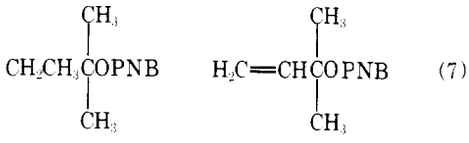
Neither 1-methylcyclopent-2-enyl *p*-nitrobenzoate nor the benzoate could be isolated because of their enormous reactivities. Accordingly, a special procedure was adopted to prepare the *p*-nitrobenzoate and to measure its rate of solvolysis without isolating the ester. A molar equivalent of methyllithium was added to 2-cyclopentenone in ether at low temperatures. To the resulting lithium alkoxide of 1-methylcyclopent-2-enol at −78 °C was added *p*-nitrobenzoyl chloride in ether. The reaction mixture was stirred as the temperature was allowed to rise to 0 °C and the solvent removed under vacuum. The crude ester, maintained at low temperature, was used as such for the determination of the rates of solvolysis.

Solvolytic Studies. The rates of the *p*-nitrobenzoates were determined in 80% aqueous acetone.[21] The rate for $\alpha,\alpha,\gamma,\gamma$-tetramethylallyl benzoate was converted to that for the *p*-nitrobenzoate by using the factor 20.8.[22] The rate data, together with the activation parameters, are summarized in Table I. The rates at other temperatures were used to calculate the rates at 25 °C for determination of the relative reactivities: RR, 25 °C.

Solvolytic Products. In representative cases the solvolyses were run in 80% aqueous acetone containing 10 mol % excess sodium acetate. Following dilution, the reaction products were extracted with ether, the ether removed under reduced pressure, and the products analyzed by NMR and GC.

Discussion

The rate of solvolysis of α,α-dimethylallyl *p*-nitrobenzoate (**7B**) is faster than that of its saturated analogue, ethyldimethylcarbinyl *p*-nitrobenzoate (**7A**), by a factor of 340 (expression 7).

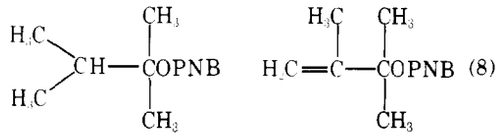


(7)

	7A	7B
RR, 25 °C	1.00	340

This factor of 340 is considerably larger than the factor observed for the primary derivatives (36 for the benzene sulfonates[8] and 25 for the chlorides[9]). The electron demand by a developing tertiary cationic center should be enormously smaller than that by a developing primary cationic center. We can only conclude that solvent participation in the primary derivatives is distorting the data, so that the value of 340 better represents the stabilizing effect of a simple allylic double bond.

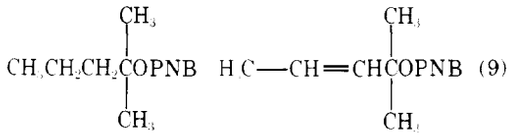
Introduction of a methyl group into the β position has no significant effect upon the solvolysis rate. Indeed, a slight decrease is observed. Thus, α,α,β-trimethylallyl *p*-nitrobenzoate (**8B**) undergoes solvolysis only 101 times faster than isopropyldimethylcarbinyl *p*-nitrobenzoate (**8A**) (expression 8).



(8)

	8A	8B
RR, 25 °C	1.00	101

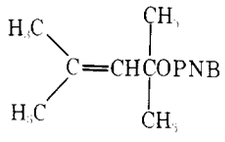
In contrast, the introduction of a methyl group at the γ position increases the rate of solvolysis by a large factor. Thus, the rate constant for α,α,γ-trimethylallyl *p*-nitrobenzoate (**9B**) is 8.3×10^5 larger than that for *n*-propyldimethylcarbinyl *p*-nitrobenzoate (**9A**) (expression 9).



(9)

	9A	9B
RR, 25 °C	1.00	8.3×10^5

Introduction of a second methyl group in the γ position increases the rate further. Thus, $\alpha,\alpha,\gamma,\gamma$-tetramethylallyl *p*-nitrobenzoate (**10A**) undergoes solvolysis at a rate that is 8.7×10^6 greater than that of the saturated compound (**9A**) (expression 10).



(10)

	10A
RR, 25 °C	8.7×10^6

This large increase in rate accompanying the introduction of methyl groups in the γ position has been attributed to hyperconjugative stabilization of the developing cationic center. In **10A** the cationic intermediate is symmetrical. Since the transition state must closely resemble the cationic intermediate,[23,24] it is not surprising that the effects of methyl substituents in the γ position approach in magnitude their effects in the α position.

In Table II, the effects of each methyl substituent are compared directly. Thus, the γ,γ-dimethyl compound undergoes solvolysis at a rate 2.3×10^4 times faster than the parent allylic derivative.

Table I. Rates of Solvolyses of Tertiary Acyclic and Cyclic *p*-Nitrobenzoates in 80% Aqueous Acetone

p-nitrobenzoate	registry no.	$10^6 k_1$, s^{-1} T_1, °C	T_2, °C	25 °C[a]	rel rate	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
ethyldimethylcarbinyl[b] (**7A**)	55705-62-9	460 (150)	45.6 (125)	9.13×10^{-5}	1.00	30.4	−2.6
ethenyldimethylcarbinyl (**7B**)	35945-67-6	83.8 (100)	8.78 (75)	3.1×10^{-2}	340	22.7	−16.8
isopropyldimethylcarbinyl[c,d] (**8A**)	55705-64-1			2.2×10^{-4}	1.00		
β-methylethenyldimethylcarbinyl (**8B**)	68001-65-0	165 (100)	12.9 (75)	2.23×10^{-2}	101	25.7	−7.4
n-propyldimethylcarbinyl (**9A**)	68001-66-1	451.7 (150)	44.1 (125)	8.16×10^{-5}	1.00	30.6	−2.3
γ-methylethenyldimethylcarbinyl (**9B**)	68001-67-2			68.2	8.33×10^5		
γ,γ-dimethylethenyldimethylcarbinyl (**10A**)	68001-68-3			707[e]	8.7×10^6		
cyclohexyldimethylcarbinyl (**11A**)	68001-69-4	1000 (150)	105 (125)	2.91×10^{-4}	1.00	29.6	−2.9
cyclohex-1-enyldimethylcarbinyl (**11B**)	68001-70-7			57.3	1.96×10^5		
cyclohex-2-enyldimethylcarbinyl (**12A**)	68001-71-8	436 (150)	43.4 (125)	8.89×10^{-5}	0.30	30.9	−2.9
cyclopentyldimethylcarbinyl[f] (**13A**)	68001-72-9	1240 (150)	129 (125)	3.4×10^{-4}	1.00	29.7	−2.2
cyclopent-1-enyldimethylcarbinyl (**13B**)	68001-73-0			36.8	1.08×10^5		
1-methylcyclohexyl[g] (**14A**)	31058-46-5	247 (150)	24.9 (125)	5.48×10^{-5}	1.00	30.1	−4.4
1-ethenylcyclohexyl (**14B**)	68001-74-1	39.1 (100)	4.17 (75)	1.54×10^{-2}	234	22.5	−18.8
1-methylcyclohex-2-enyl (**15A**)	38313-13-2			103.1			
1-methylcyclopentyl[g] (**16A**)	19013-42-4	236 (125)	23.0 (100)	2.11×10^{-3}	1.00		
1-methylcyclopent-2-enyl[h] (**16B**)	68001-75-2	1.68×10^4 (−25)	1.0×10^4 (−30)	1.15×10^6	5.4×10^8	11.4	−20.4

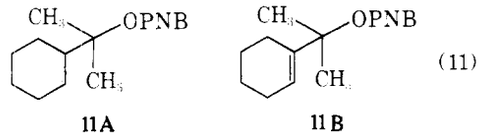
[a] Extrapolated from data at higher temperatures. [b] $k_1^{100\ °C}$ 2.3×10^{-5} s^{-1}, in 60% dioxane–water as reported by W. Duismann and C. Rüchardt, *Tetrahedron Lett.*, 4517 (1974). [c] E. N. Peters, Final Report, Purdue University. [d] $k_1^{100\ °C}$ 3.47×10^{-5} in 60% dioxane–water. [e] Calculated by multiplying the rate of the benzoate by the factor 20.8. [f] H. C. Brown and M. Ravindranathan, *J. Am. Chem. Soc.*, **100**, 1865 (1978). [g] E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **97**, 2892 (1975). [h] Value reported in H. M. Hess, Ph.D. Thesis, Purdue University, 1969, is $k_1^{25\ °C}$ 9.2×10^{-1} s^{-1}.

Table II. Effect of Methyl Substitution on the Relative Rates of Solvolysis of Allylic Systems in 80% Aqueous Acetone at 25 °C

p-nitrobenzoate	R–CMe_2OPNB	rel rate at 25 °C
ethenyldimethylcarbinyl	$H_2C{=}CHCMe_2OPNB$	1.00
β-methylethenyldimethylcarbinyl	$H_2C{=}C(CH_3)CMe_2OPNB$	0.72
γ-methylethenyldimethylcarbinyl	$H_3CCH{=}CHCMe_2OPNB$	2.2×10^3
γ,γ-dimethylethenyldimethylcarbinyl	$(H_3C)_2C{=}CHCMe_2OPNB$	2.3×10^4

We wished to examine the effect of a double bond on the rates of solvolysis of alicyclic derivatives. Three situations were examined: compounds in which the double bond is in the ring, allylic to the cationic center outside the ring; compounds in which the double bond is outside the ring, allylic to the cationic center in the ring; and compounds in which the double bond and the cationic center are both in the ring.

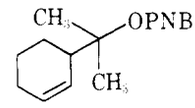
The first situation is contained in the system cyclohex-1-enyldimethylcarbinyl *p*-nitrobenzoate (**11B**). This compound undergoes solvolysis at a rate 1.96×10^5 times faster than the corresponding saturated compound, cyclohexyldimethylcarbinyl *p*-nitrobenzoate (**11A**) (expression 11). This rate increase is comparable to that observed for the acyclic analogue (**9B**). The large rate enhancement reflects the combined effect of the allylic double bond and the γ-methylene substituent.



(11)

	11A	**11B**
RR, 25 °C	1.00	1.96×10^5

Although not pertinent to the present discussion, it is worthy of note that a shift of the double bond to the homoallylic position (**12A**) results in an actual decrease in rate relative to the saturated derivative (**11A**) (expression 12).

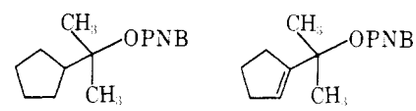


(12)

12A

RR, 25 °C	1.00/3.2

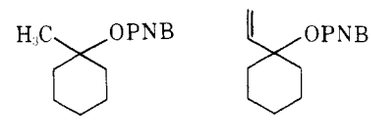
A change of the ring system from six to five has no significant effect upon the influence of the allylic double bond on the rate of solvolysis. Thus, cyclopent-1-enyldimethylcarbinyl *p*-nitrobenzoate (**13B**) undergoes solvolysis at a rate 1.08×10^5 faster than the saturated derivative, cyclopentyldimethylcarbinyl *p*-nitrobenzoate (**13A**).



(13)

	13A	**13B**
RR, 25 °C	1.00	1.08×10^5

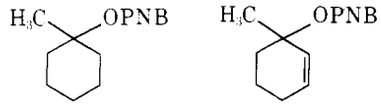
A simple allylic structure, without γ substitution, exerts an effect comparable to that observed for the parent system (**7B**). Thus, the rate enhancement exhibited by 1-ethenylcyclohexyl *p*-nitrobenzoate (**14B**) over the related saturated derivative, 1-methylcyclohexyl *p*-nitrobenzoate (**14A**), is a factor of 234 (expression 14), as compared to the factor of 340 realized in the acyclic case (expression 7).



(14)

	14A	**14B**
RR, 25 °C	1.00	234

The largest effects of the double bond are realized in systems where both the double bond and the allylic cationic center are in the ring. Thus, 1-methylcyclohex-2-enyl *p*-nitrobenzoate (**15A**) solvolyzes 1.87×10^6 times faster than its saturated analogue (**14A**) (expression 15).

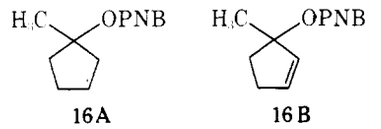


(15)

	14A	**15A**
RR, 25 °C	1.00	1.87×10^6

How can we account for the increase by a factor of 10 over the effect of the double bond in **11B**? One might be tempted to ascribe the effect to a greater ability of the cis arrangement of the allylic system in **15A** over the trans arrangement in **11B** to supply electrons to the developing cationic center. Unfortunately, we did not include a cis derivative of **9B** in our studies.

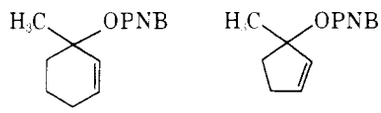
A much larger effect is observed in the corresponding cyclopentyl derivative. Thus, 1-methylcyclopent-2-enyl *p*-nitrobenzoate (**16B**) solvolyzes 5.4×10^8 times faster than 1-methylcyclopentyl *p*-nitrobenzoate (**16A**) (expression 16).



(16)

	16A	**16B**
RR, 25 °C	1.00	5.4×10^8

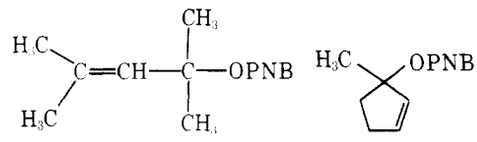
The enormous reactivity of 1-methylcyclopent-2-enyl *p*-nitrobenzoate is indicated by comparing it directly with the corresponding cyclohexyl derivative (expression 17), and with



(17)

RR, 25 °C 1.00 1.12×10^4

the fastest of the acyclic derivatives examined, $\alpha,\alpha,\gamma,\gamma$-tetramethylallyl *p*-nitrobenzoate (expression 18).



(18)

RR, 25 °C 1.00 1.6×10^3

Even after correcting for a factor of approximately 10^2 attributed to the greater reactivity of cyclopentyl derivatives, I strain,[25,26] there remains a significant residual enhancement accompanying the presence of the double bond in the cyclopentyl ring system (**16B**).

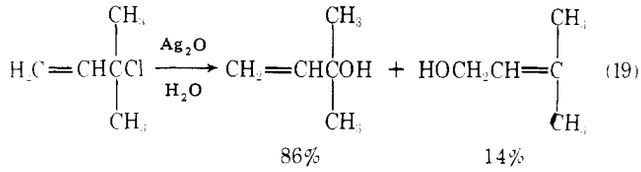
An electronic cross-ring interaction between the orbitals of the 1 and 3 positions in the cyclopent-2-enyl cation has been proposed to explain the enhanced reactivity of the cyclopent-2-enyl derivatives in ionization reactions.[15] It was suggested that the smaller ring size of the cyclopent-2-enyl cation brings the two terminal allylic carbon atoms closer together and facilitates dispersal of the positive charge.

This effect would be less in the cyclohex-2-enyl system, nicely accounting for the difference in the behavior of the two systems.

In recent years considerable information on the structure of cycloalk-2-enyl cations has been obtained from NMR studies of the cations generated in either aqueous sulfuric acid or in the stronger acid systems now available.[27-30] From his ^{13}C NMR studies of cyclohex-2-enyl and cyclopent-2-enyl cations, Olah has concluded that "they show little or no evidence of C1–C3 interactions". He argues that such C1–C3 interactions are of importance only in cyclobutenyl cations.[28,31]

Sorensen has offered an alternative explanation.[32] He suggests that delocalization could occur in 2-cyclopentenyl cations by invoking both methylene groups (C4 and C5) in a hyperconjugative delocalization, giving a cyclic 6π-electron system. With the staggered configuration of the three methylene groups in the 2-cyclohexenyl cation, the stabilization would be considerably less.[33] At the present time this appears to be the preferred explanation for the exceptionally high reactivity of the cyclopent-2-enyl cations.

Solvolysis Products. It was early established that the saturated tertiary acyclic and cyclic chlorides undergo solvolysis in aqueous systems without rearrangements.[34-36] However, the products from allylic derivatives can be more complex. Thus, W. G. Young established that the products formed in the solvolysis of α,α-dimethylallyl chloride in the presence of silver oxide and water contained two isomeric alcohols (expression 19).[37]



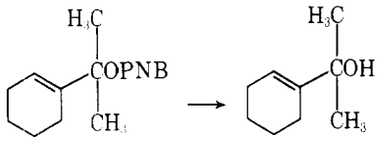
(19)

86% 14%

In the present work, we observed both solvolyses without allylic rearrangement and solvolyses with allylic rearrangement. For example, cyclohex-1-enyldimethylcarbinyl *p*-nitrobenzoate underwent solvolysis without detectable allylic rearrangement (expression 20).

Table III. Summary of Physical and Microanalytical Data for *p*-Nitrobenzoates

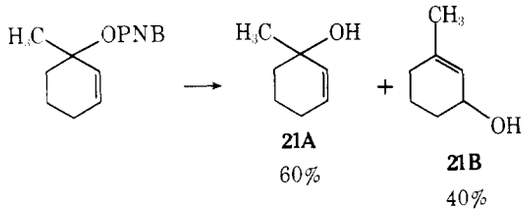
p-nitrobenzoate	mp, °C	mol formula	anal. calcd C	calcd H	calcd N	found C	found H	found N
ethyldimethylcarbinyl (**7A**)	84–85	$C_{12}H_{15}O_4N$	60.75	6.32	5.90	60.70	6.32	5.88
ethenyldimethylcarbinyl (**7B**)	115–116	$C_{12}H_{13}O_4N$	61.27	5.53	5.95	61.23	5.52	5.94
n-propyldimethylcarbinyl (**9A**)	68–69	$C_{13}H_{17}O_4N$	62.15	6.77	5.57	61.93	7.00	5.65
β-methylethenyldimethylcarbinyl (**8B**)	91–92	$C_{13}H_{15}O_4N$	62.65	6.02	5.62	62.87	6.25	5.44
γ-methylethenyldimethylcarbinyl (**9B**)	65–66	$C_{13}H_{15}O_4N$	62.65	6.02	5.62	62.72	6.17	5.58
cyclohexyldimethylcarbinyl (**11A**)	103–104	$C_{16}H_{21}O_4N$	65.97	7.21	4.81	65.76	6.94	4.84
cyclohex-1-enyldimethylcarbinyl (**11B**)	103–104 dec	$C_{16}H_{19}O_4N$	66.43	6.57	4.84	66.65	6.85	4.64
cyclohex-2-enyldimethylcarbinyl (**12A**)	91–92	$C_{16}H_{19}O_4N$	66.43	6.57	4.84	66.64	6.65	4.63
cyclopentyldimethylcarbinyl (**13A**)	97–98	$C_{15}H_{19}O_4N$	64.98	6.86	5.05	64.88	6.76	5.17
cyclopent-1-enyldimethylcarbinyl (**13B**)	101–102	$C_{15}H_{17}O_4N$	65.45	6.18	5.09	65.55	6.42	4.88
1-ethenylcyclohexyl (**14B**)	104–105	$C_{15}H_{17}O_4N$	65.45	6.18	5.09	65.62	6.30	5.12
1-methylcyclohex-2-enyl (**15A**)	100–101	$C_{14}H_{15}O_4N$	64.36	5.74	5.36	64.22	5.79	5.40



(20)

>88%

On the other hand, 1-methylcyclohex-2-enyl *p*-nitrobenzoate underwent solvolysis to give 60% of the unrearranged alcohol (**21A**) and 40% of the rearranged allylic product (**21B**) (expression 21).



(21)

21A 60%

21B 40%

Experimental Section

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

Preparation of *p*-Nitrobenzoates. The tertiary allyl alcohols were prepared by the addition of the appropriate ketone to methyllithium in ether.[20] The saturated tertiary alcohols were made by the addition of the appropriate ketone to methyl magnesium iodide in ether. α,α,β-Trimethylallyl alcohol and 1-ethenylcyclohexanol were available from earlier studies in this laboratory. The alcohols from these sources were converted into the corresponding lithium salts in THF by treatment with *n*-butyllithium and then converted into the *p*-nitrobenzoate by treatment with *p*-nitrobenzoyl chloride in THF.[21] The physical and analytical data are listed in Table III.

Kinetic Procedure. The procedure followed in determining the rate constants is essentially the same as described earlier.[21] But, a special procedure was used to determine the rate of solvolysis of the highly reactive 1-methylcyclopent-2-enyl *p*-nitrobenzoate. The method used was similar to that of Roberts.[15] Weighed samples of the ester, prepared at low temperature, were dissolved in 100 mL of 80% aqueous acetone that had been thermostated at the required temperature, in a 500-mL, three-necked, round-bottom flask, fitted with a calibrated low-temperature thermometer and a sealed stirrer. The reaction was followed by intermittent titration with freshly prepared standard (0.02 N) sodium hydroxide in 80% aqueous acetone.

Products of Solvolysis. The solvolysis products were established for representative cases. The esters were solvolyzed in 80% aqueous acetone containing 10 mol % excess sodium acetate. Acetone was removed under reduced pressure, diluted with water, and worked up in the usual way. After removal of solvent (ether), the products were analyzed by NMR and GC.

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