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SOLVOLYSIS OF 3-ALKENYL-2-CYCLOHEXENYL ESTERS

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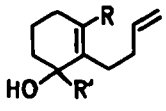
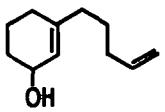
Abstract - In an attempt to study possible π-participation in allyl derivatives, 3-alkenyl-5,5-dimethyl-2-cyclohexenyl p-nitrobenzoates 4 and 2-alkenyl-3-methyl-2-cyclohexenyl p-nitrobenzoates 5 were solvolyzed in 97 wt % trifluoroethanol and 80 vol % ethanol. Water soluble 1-methyl-3-(3-alkenyl-5,5-dimethyl-2-cyclohexenyl)pyridinium iodides 6 were solvolyzed in water and in aqueous solvents, as well as under micellar conditions. All esters show in each of the solvents normal values of secondary α-deuterium isotope effects (k_H/k_D = 1.17 - 1.23). Also in comparison to saturated analogues the investigated esters show a lower solvolytic reactivity. On the basis of these results it was concluded that the solvolysis proceeds via a stepwise mechanism involving a resonance-stabilized cyclohexenyl cation as the reaction intermediate.

The 2-cyclohexenyl system with an alkenyl substituent at C-2 or C-3 is an excellent model for biomimetic polyene cyclizations.[1,2] The formolyses of 2-(3-butenyl)-2-cyclohexenol 1[3] and of 3-(4-pentenyl)-2-cyclohexenol 2[2] give bicyclic products in high yields and it was suggested that these cyclizations were initiated by the rate determining formation of the cyclohexenyl cation, but no decisive evidence for the stepwise nature of those cyclizations was provided.



1 ; R,R'=H or CH_3



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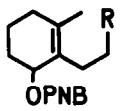
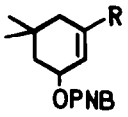


3a, R = $CH{=}CH_2$
b, R = CH_2CH_3

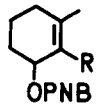
Our previous study[4] of the solvolysis of 2-alkenyl-2-cyclohexenyl p-nitrobenzoates showed that ester 3a solvolyzes in both 97% TFE and 80% EtOH slower than its 2-butyl analog 3b. It was also demonstrated that the cyclization of 1 in formic acid and the solvolysis of 3a proceeds by a stepwise mechanism which involves a resonance stabilized cyclohexenyl cation as reaction intermediate. Consequently, the side-chain C=C bond does not participate as a neighboring group in the ionization step.

In the present work we have further investigated the possible π-participation of a C-3 substituted alkenyl group in the solvolysis of p-nitrobenzoates 4. The solvolysis of esters 5 was also studied in order to compare the effects of C-2 substituted and C-3 substituted alkenyl groups on the solvolytic reactivity.

[a]undergraduate research trainee 1986/87



4a, R = $CH_2CH_2CH=CH_2$
b, R = $(CH_2)_3CH_3$
c, R = $(CH_2)_3CH=CH_2$
d, R = $(CH_2)_4CH_3$



5a, R = $CH_2CH=CH_2$
b, R = $CH_2CH_2CH_3$
c, R = $(CH_2)_3CH=CH_2$
d, R = $(CH_2)_4CH_3$

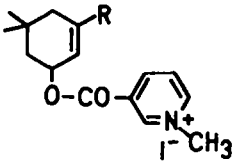
RESULTS AND DISCUSSION

p-Nitrobenzoates 4 and 5 were prepared following the published procedures (see Experimental Section). Solvolyses of these esters were accomplished in 97 wt % 2,2,2-trifluoroethanol (TFE) and in 80 vol % ethanol. The rates were measured potentiometrically at a constant pH. Clear first-order kinetic behavior was observed in all cases. The kinetic results are presented in Table 1. In both series studied, with esters 4 substituted at C-3 and with esters 3 and 5 substituted at C-2, and in both solvents studied, the solvolysis of each alkenyl-substituted ester (k_{un}) is slower than that of its alkyl-substituted counterpart (k_{sat}). This result can be explained by π-electron-withdrawing inductive effect of alkenyl groups at C-2 or C-3. The magnitude of rate-retardation (defined as k_{un}/k_{sat} ratio) is more pronounced in 97% TFE than in 80% EtOH for all esters studied (Table 1). The observed effect of solvent on rate retardation can be explained by a different degree of solvent participation in the rate-determining step of solvolyses,[4] as well as by hydrogen bonding between trifluoroethanol (acting as a proton donor) and the sterically unhindered side-chain C=C bond (acting as a base) which increases the electron-withdrawing effect of the alkenyl group.[5]

The retardative effect of an alkenyl substituent at C-3 is more pronounced than the effect of the same substituent at the C-2 center (Table 1). The alkenyl substituent at C-3 with n methylene groups intervening between the side-chain double bond and the allylic double bond shows the retardative effect of similar magnitude as its C-2 substituted nor-analogue which has (n-1) methylene groups between the side-chain and allylic C=C bonds. For example, the retardative effect of 3-butenyl substituent at C-3 is similar to the effect of 2-propenyl substituent at C-2, while the retardative effect of 4-pentenyl substituent at C-3 is similar to the effect of 3-butenyl substituent at C-2. This result is in agreement with the known observation that in S_N1 reactions of allylic substrates electron-donating and electron-withdrawing substituents at C-1 and C-3 centers can greatly influence the solvolytic reactivity, while the effect of these substituents at C-2 is much weaker.[6]

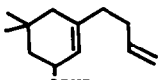
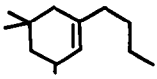
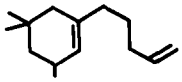
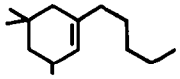
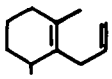
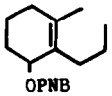
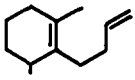
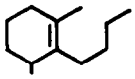
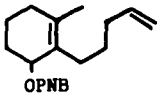
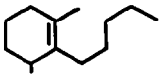
The specifically α-deuterated analogues of p-nitrobenzoates 4a and 4c were also synthesized and solvolyzed in 97% TFE at 50°C and in 80% EtOH at 70°C. Both esters show in each of these solvents the normal values of secondary α-deuterium isotope effects[7] (k_H/k_D = 1.18 - 1.23). All these results confirm the stepwise mechanism of solvolysis which includes the resonance-stabilized cyclohexenyl cation as reaction intermediate.

In order to further investigate the solvolysis of 3-alkenyl-2-cyclohexenyl substrates in water and in aqueous solvents, as well as under micellar conditions, esters 6 were prepared and solvolyzed in various solvents (Table 2). For these solvolyses the rate-retardative effect of the



6a, R = $(CH_2)_3CH=CH_2$
b, R = $(CH_2)_4CH_3$

Table 1. Solvolysis rate constants of substituted 2-cyclohexenyl p-nitrobenzoates

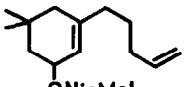
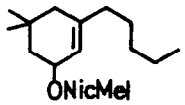
Ester	97% TFE			80% EtOH		
	temp. °C	$10^3 k$, [a] s^{-1}	k_{un}/k_{sat}	temp. °C	$10^3 k$, [a] s^{-1}	k_{un}/k_{sat}
4a  OPNB	50	1.181(2)		70	2.111(3)	
			0.355			0.503
4b  OPNB	50	3.329(7)		70	4.20(3)	
4c  OPNB	50	1.870(5)		70	2.64(2)	
			0.579			0.761
4d  OPNB	50	3.227(3)		70	3.47(1)	
5a  OPNB	25	0.552		50	1.49	
			0.298			0.452
5b  OPNB	25	1.854		50	3.30	
3a  OPNB	25	1.140(3)[b]		50	2.49(2)[b]	
			0.607			0.847
3b  OPNB	25	1.879(6)[b]		50	2.94(4)[b]	
5c  OPNB	25	1.524		50	2.615	
			0.814			0.878
5d  OPNB	25	1.873		50	2.98	

[a] Numbers in parentheses are standard deviations of the mean, e.g. 3.329(7) = 3.329 ± 0.007.
[b] Data from ref. 4.

alkenyl chain was again observed in all solvents studied, indicating the absence of the side-chain neighboring group participation during ionization. In the series of solvents that included water and various ethanol-water mixtures, both esters 6 show essentially the same m value (m = 0.840 and 0.845 for 6a and 6b, respectively[8]) which confirms that these two esters solvolyze via the same stepwise mechanism. Furthermore, 6a and 6b show normal values of secondary α-deuterium isotope effects (k_H/k_D = 1.17 - 1.20) in all solvents studied, and in each solvent the isotope effects for esters 6a and 6b have essentialy the same magnitude.

The effect of cationic and anionic surfactants on hydrolysis rates of esters 6a and 6b (which are structurally similar to cationic surfactants) was also investigated. Our previous study[10] showed that for substrates which hydrolyze by the S_N1 mechanism and which are structurally related to cationic surfactants the addition of an anionic surfactant (SDS) resulted in a very pronounced

Table 2. Solvolysis rate constants of esters 6a and 6b at 20°C

Solvent[a]	 ONicMel 6a	 ONicMel 6b	k_{un}/k^{b}_{sat}
97T	$4.81(5) \times 10^{-2}$[c]	$7.21(5) \times 10^{-2}$	0.67
90E	$1.07(3) \times 10^{-5}$	$1.28(5) \times 10^{-5}$	0.84
80E	$3.81(4) \times 10^{-5}$	$4.79(4) \times 10^{-5}$	0.80
60E	$2.36(1) \times 10^{-4}$	$2.97(2) \times 10^{-4}$	0.79
40E	$1.72(1) \times 10^{-3}$	$2.17(2) \times 10^{-3}$	0.79
20E	$2.33(4) \times 10^{-2}$	$3.26(4) \times 10^{-2}$	0.71
H_2O	$0.97(8) \times 10^{-1}$	$1.18(9) \times 10^{-1}$	0.82
0.1M CTAB	$0.97(7) \times 10^{-1}$	$1.20(9) \times 10^{-1}$	0.81
0.1M SDS	$8.45(8) \times 10^{-5}$	$9.59(9) \times 10^{-5}$	0.88

[a]97T is 97 wt % aqueous 2,2,2-trifluoroethanol; 90E is 90 vol % aqueous ethanol; 80E, 60E, 40E, and 20E similarly; 0.1M CTAB is 0.1 M aqueous solution of cetyltrimethylammonium bromide; 0.1M SDS is 0.1M aqueous solution of sodium dodecyl sulfate. [b]Ratio of rate constants for esters 6a and 6b. [c]All reported rate constants are in s^{-1}.

inhibition of hydrolysis rates. On the contrary, the hydrolysis rates of substrates which contain internal nucleophile and solvolyze under anchimeric assistance are relatively unaffected by the presence of SDS. In the present work it was shown that cetyltrimethylammonium bromide (CTAB) as cationic surfactant does not affect the rate of hydrolysis of either 6a or 6b even when it is present in high concentration (0.1M CTAB, comparing with 2mM 6). On the contrary, SDS in the same concentration drastically reduces the hydrolysis rate of both esters 6 by virtually the same factor [$k(0.1M\ SDS)/k(H_2O) = 8.7 \times 10^{-4}$ and 8.1×10^{-4} for esters 6a and 6b, respectively]. This result, as well as all other results presented in this work, confirm that the neighboring group participation of the C-3 substituted alkenyl chain in 2-cyclohexenyl esters 4 and 6 is not revealed in any of the solvolyses studied.

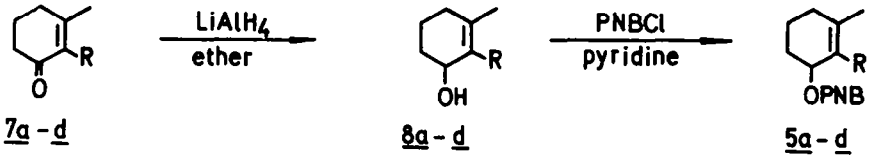
EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer. ^1H NMR spectra were recorded on a JEOL FX-90Q spectrometer. Signal positions are given in δ units, with tetramethylsilane as internal standard. All new compounds gave IR and ^1H NMR spectra which are fully consistent with their structure. In some cases the compounds were also characterized by elemental analysis.

The synthesis of ketones 7a,[11] 7b,[11], 7d[11], and 10b[13], and alcohol 8a[14] was previosuly described.

Synthesis of Compounds

The p-nitrobenzoates 5 were prepared from ethyl 4-keto-2-methyl-2-cyclohexenecarboxylate and the appropriate alkyl bromide or alkenyl bromide via 2-cyclohexenones 7 and 2-cyclohexenols 8 following the literature procedures.[4,11]

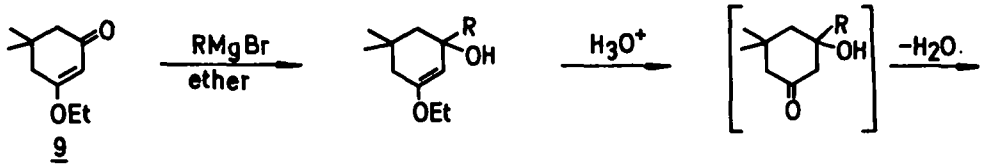


7a-d 8a-d 5a-d

a, R = $CH_2CH{=}CH_2$ c, R = $(CH_2)_3CH{=}CH_2$

b, R = $CH_2CH_2CH_3$ d, R = $(CH_2)_4CH_3$

The p-nitrobenzoates 4 were prepared from 5,5-dimethyl-3-ethoxy-2-cyclohexenone 9[12] and the appropriate Grignard reagent via 2-cyclohexenones 10 and 2-cyclohexenols 11 according to the published procedures.[4,13]



9

10a - d

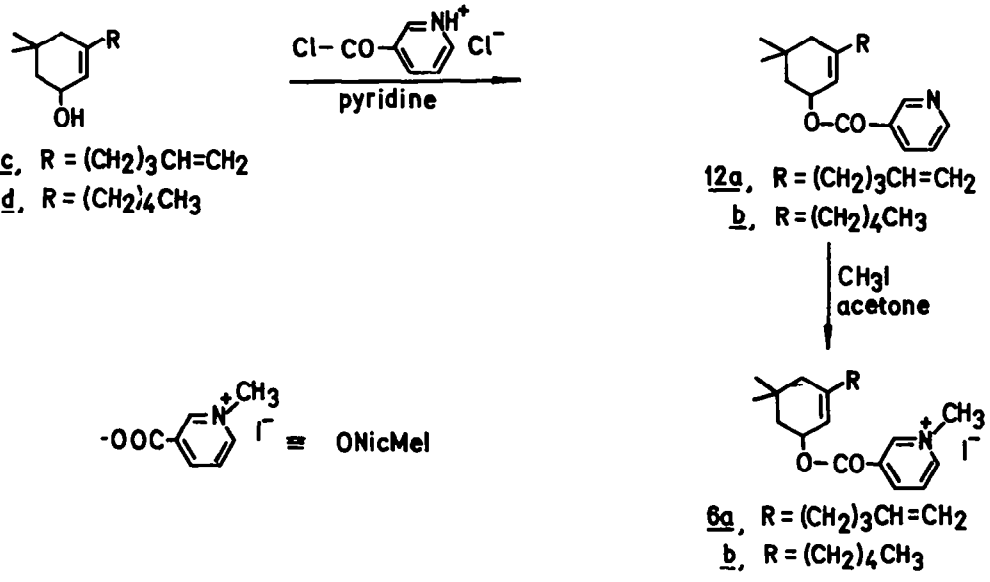
11a - d

4a - d

a, R = $CH_2CH_2CH=CH_2$ c, R = $(CH_2)_3CH=CH_2$

b, R = $(CH_2)_3CH_3$ d, R = $(CH_2)_4CH_3$

Alcohols 11c and 11d were converted into esters 6a and 6b following our published procedure.[10]



11c, R = $(CH_2)_3CH=CH_2$

d, R = $(CH_2)_4CH_3$

12a, R = $(CH_2)_3CH=CH_2$

b, R = $(CH_2)_4CH_3$

6a, R = $(CH_2)_3CH=CH_2$

b, R = $(CH_2)_4CH_3$

3-Methyl-2-(4-pentenyl)-2-cyclohexenone (7c)

Yield = 34%; IR (neat) 3080 (C=C-H), 1665 and 1630 (C=C), 917 cm^{-1} (C=C); ^1H NMR (CCl_4) δ 5.57+5.03-4.80 (3H, 3m, $CH=CH_2$), 2.27 (8H), 1.90 (3H, s, CH_3), 1.43 (4H).

3-(3-Butenyl)-5,5-dimethyl-2-cyclohexenone (10a)

Yield 57%; IR (neat) 3080 (C=C-H), 1670 (C=O), 1650 and 1630 (C=C), 907 cm^{-1} ($C=CH_2$); ^1H NMR (CCl_4) δ 5.80 (1H, s, C=C-H, in ring), 5.30 (1H, m, C=C-H, butenyl), 4.90 (2H, m, $C=CH_2$), 2.20-1.15 (8H), 1.04 (6H, s, $C(CH_3)_2$).

5,5-Dimethyl-3-(4-pentenyl)-2-cyclohexenone (10c)

Yield 64%; IR (neat) 3080 (C=C-H), 1670 (C=O), 1650 and 1630 (C=C), 920 cm^{-1} ($C=CH_2$); ^1H NMR ($CDCl_3$) δ 5.87 (1H, s, C=C-H, in ring), 5.40 (1H, m, C=CH, pentenyl), 4.93 (2H, m, $C=CH_2$), 2.18-1.20 (10H), 1.04 (6H, s, $C(CH_3)_2$).

5,5-Dimethyl-3-pentyl-2-cyclohexenone (10d)

Yield 46%; IR (neat) 1670 (C=O), 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 5.87 (1H,s, C=CH), 2.18 (6H, m), 1.40-1.10 (6H) 1.03 (6H, s, $C(CH_3)_2$), 0.94 (3H, t, J=6Hz, CH_3).

3-Methyl-2-propyl-2-cyclohexenol (8b)
Yield 95%; IR (neat) 3330 (O-H), 1605 cm^{-1} (C=C); ^1H NMR (CCl_4) δ 3.93 (1H, s, CHOH), 3.60 (1H, s, OH), 2.20-1.70 (6H), 1.62 (3H,s, CH_3), 1.33-0.73 (7H).

3-Methyl-2-(4-pentenyl)-2-cyclohexenol (8c)

Yield 92%; IR (neat) 3340 (O-H), 1645 and 1612 (C=C), 912 cm^{-1} ($C=CH_2$); ^1H NMR (CCl_4) δ 5.47 (1H, m, C=CH, pentenyl), 4.80 (2H, m, $C=CH_2$), 3.85 (1H, s, CHOH), 2.97 (1H, s, OH), 2.20-1.80 (8H), 1.62 (3H, s, CH_3), 1.50-1.10 (4H).

3-Methyl-2-pentyl-2-cyclohexenol (8d)

Yield 93%; IR (neat) 3350 (O-H), 1612 cm^{-1} (C=C); ^1H NMR (CCl_4) δ 3.92 (1H, s, CHOH), 3.58 (1H, s, OH), 2.23-1.70 (6H), 1.62 (3H, s, CH_3), 1.40-0.83 (11H).

3-(3-Butenyl)-5,5-dimethyl-2-cyclohexenol (11a)

Yield 95%; IR (neat) 3360 (O-H), 3080 (C=C-H), 1670 and 1630 (C=C), 915 cm^{-1} ($C=CH_2$); ^1H NMR (CCl_4) δ 5.57 (1H, m, C=CH, butenyl), 5.37 (1H, s, C=CH, in ring), 4.50 (2H, m, $C=CH_2$), 3.70 (1H, s, CHOH), 3.43 (1H, s, OH), 2.20-1.14 (8H), 0.90 (6H, d. J = 12Hz, $C(CH_3)_2$).

3-Butyl-5,5-dimethyl-2-cyclohexenol (11b)

Yield 93%; IR (neat) 3360 (O-H), 1670 cm^{-1}(C=C); ^1H NMR (CCl_4) δ 5.37 (1H, s, C=CH), 3.98 (1H, s, CHOH), 3.40 (1H, s, OH), 2.10-1.10 (13H), 0.93 (6H, d, J = 12 Hz, $C(CH_3)_2$).

5,5-Dimethyl-3-(4-pentenyl)-2-cyclohexenol (11c)

Yield 90%; IR (neat) 3350 (O-H), 3080 (C=C-H), 1670 and 1640 (C=C) and 912 cm^{-1} ($C=CH_2$); ^1H NMR ($CDCl_3$) δ 5.60 (1H, m, C=CH, pentenyl), 5.42 (1H, s, C=CH, in ring), 5.00 (2H, m, $C=CH_2$), 4.23 (1H, s, CHOH), 2.17-1.11 (11H), 0.94 (6H, d, J = 12Hz, $C(CH_3)_2$).

5,5-Dimethyl-3-pentyl-2-cyclohexenol (11d)

Yield 90%; IR (neat) 3340 (O-H), 1675 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 5.43 (1H, s, C=CH), 4.20 (1H, m, CHOH), 1.94-1.21 (16H), 0.94 (6H, d, J = 12Hz, $C(CH_3)_2$).

3-Methyl-2-propenyl-2-cyclohexenyl p-Nitrobenzoate (5a)

Yield 85%; IR (neat) 3110, 3075, and 3055 (Ar-H), 1720 (CO-O-C), 1635 (C=C), 1530 and 1350 (NO_2), 1275 (CO-OC), 915 ($C=CH_2$), 722 cm^{-1} (Ar-H); ^1H NMR (CCl_4) δ 8.22 (4H, s, p-O_2N-C_6H_4), 5.57 (1H, s, CHOPNB), 5.60 (1H, m, C=CH), 4.90 (2H, m, $C=CH_2$), 2.85 (2H, d, J = 6Hz, $CH_2CH=CH_2$), 2.10-1.80 (6H), 1.77 (3H, s, CH_3).

Anal. Calcd. (%) for $C_{17}H_{19}NO_2$: C, 67.76; H, 6.36; N, 4.65
Found (%): C, 67.85; H, 6,57; N, 4.47

3-Methyl-3-propyl-2-cyclohexenyl p-Nitrobenzoate (5b)

Yield 93%; IR (neat) 3110, 3080, and 3050 (Ar-H), 1720 (CO-O-C), 1535 and 1350 (NO_2), 1275 (CO-OC), 725 cm^{-1} (Ar-H); ^1H NMR (CCl_4) δ 8.15 (4H, s, p-O_2N-C_6H_4), 5.42 (1H, s, CHOPNB), 2.05-1.73 (6H), 1.62 (3H, s, CH_3), 1.37-0.85(7H).

3-Methyl-3-(4-pentenyl)-2-cyclohexenyl p-Nitrobenzoate (5c)

Yield 91%; IR (neat) 3110, 3090, and 3040 (Ar-H), 1720 (CO-O-C), 1530 and 1350 (NO_2), 1280 (CO-OC), 915 ($C=CH_2$), 725 cm^{-1} (Ar-H); ^1H NMR (CCl_4) δ 8.15 (4H, s, p-O_2N-C_6H_4), 5.48 (1H, s, CHOPNB), 5.33 (1H, m, C=CH), 4.80 (2H, m, $C=CH_2$), 2.20-1.83 (8H), 1.73 (3H, s, CH_3), 1.60-0.90(4H).

3-Methyl-3-pentyl-2-cyclohexenyl p-Nitrobenzoate (5d)

Yield 87%; IR (neat) 3110, 3080, and 3040 (Ar-H), 1720 (CO-O-C), 1535 and 1350 (NO_2), 1275 (CO-OC), 725 cm^{-1} (Ar-H); ^1H NMR (CCl_4) δ 8.10 (4H, s, p-O_2N-C_6H_4), 5.49 (1H, s, CHOPNB), 2.18-1.70 (6H), 1.62 (3H, s, CH_3), 1.30-0.70 (11H).

3-(3-Butenyl)-5,5-dimethyl-2-cyclohexenyl p-Nitrobenzoate (4a)

Yield 90%; IR (neat) 3110, 3090, and 3050 (Ar-H), 1720 (CO-O-C), 1640 (C=C), 1530 and 1350 (NO_2), 1280 (CO-OC), 722 cm^{-1} (Ar-H); ^1H NMR (CCl_4) δ 8.23 (4H, s, p-O_2N-C_6H_4), 5.91 (1H, s, C=C-H, in ring), 5.50 (1H, s, CHOPNB), 5.10 (1H, m, C=C-H, butenyl), 4.91 (2H, m, $C=CH_2$), 2.30-1.20 (8H), 1.05 (6H, d, J = 10Hz, $C(CH_3)_2$).

Anal. Calcd. (%) for $C_{19}H_{23}NO_2$: C, 69.28; H, 7.04; N, 4.25
Found (%): C, 69.51; H, 7.05; N, 4.24

3-Butyl-5,5-dimethyl-2-cyclohexenyl p-Nitrobenzoate (4b)

Yield 95%: IR (neat) 3110, 3090, and 3060 (Ar-H), 1720 (CO-O-C), 1530 and 1355 (NO_2), 1280 (CO-OC), 720 cm^{-1} (Ar-H); ^1H NMR (CCl_4) δ 8.20 (4H, s, p-O_2N-C_6H_4), 5.80 (1H, s, C=C-H), 5.40 (1H, s, CHOPNB), 2.10-1.70 (13H), 1.03 (6H, d, J = 10Hz, $C(CH_3)_2$).

5,5-Dimethyl-3-(4-pentenyl)-2-cyclohexenyl p-Nitrobenzoate (4c)

Yield 92%; IR (neat) 3110, 3080, and 3040 (Ar-H), 1730 (CO-O-C), 1610 (C=C), 1535 and 1355 (NO_2), 1282 (CO-OC), 730 and 690 cm^{-1} (Ar-H); ^1H NMR ($CDCl_3$) δ 8.21 (4H, s, p-O_2N-C_6H_4), 5.88 (1H, s, C=C-H, in ring), 5.60 (1H, m, C=C-H, pentenyl), 5.50 (1H, s, CHOPNB), 4.95 (2H, m, $C=CH_2$), 2.35-1.20 (10H), 1.03 (6H, d, J = 12Hz, $C(CH_3)_2$).

5,5-Dimethyl-3-pentyl-2-cyclohexenyl p-Nitrobenzoate (4d)

Yield 88%; IR (neat) 3100, 3080, and 3040 (Ar-H), 1730 (CO-O-C), 1536 and 1355 (NO_2), 1280 (CO-OC), 730 and 690 cm^{-1} (Ar-H); ^1H NMR ($CDCl_3$) δ 8.23 (4H, s, p-O_2N-C_6H_4), 5.81 (1H, s, C=C-H), 5.60 (1H, s, CHOPNB), 2.00-1.25 (15H), 1.04 (6H, d, J = 12Hz, $C(CH_3)_2$).

5,5-Dimethyl-3-(4-pentenyl)-2-cyclohexenyl Nicotinate (12a)

Yield 96%; IR (neat) 3090, 3060, and 3040 (Ar-H), 1725 (CO-O-C), 1670, 1650, and 1598 (C=C), 1290 (CO-OC), 760 and 710 cm^{-1} (Ar-H); ^1H NMR ($CDCl_3$) δ 9.22, 8.75, 8.35, and 7.35 (4H, four m, nicotinyl), 5.80 (1H, s, C=C-H, in ring), 5.70 (1H, m, C=C-H, pentenyl), 5.60 (1H, s, CHONic), 4.95 (2H, m, $C=CH_2$), 2.10-1.25 (10H), 1.04 (6H, d, J = 12Hz, $C(CH_3)_2$).

5,5-Dimethyl-3-pentyl-2-cyclohexenyl Nicotinate (12b)

Yield 95%; IR (neat) 3090, 3060, and 3040 (Ar-H), 1720 (CO-O-C), 1640 and 1593 (C=C), 1285 (CO-OC), 750 and 708 cm^{-1} (Ar-H); ^1H NMR ($CDCl_3$) δ 9.22, 8.75, 8.28, and 7.35 (4H, four m, nicotinyl), 5.70 (1H, s, C=C-H), 5.53 (1H, s, CHONic), 2.30-1.25 (12H), 1.04 (6H, d, J = 12H, $C(CH_3)_2$). 0.83 (3H, t, J = 8Hz).

1-Methyl-3-[5,5-dimethyl-3-(4-pentenyl)-2-cyclohexenyl]pyridinium Iodide (6a)

Yield 95%; IR (KBr) 3090, 3060, and 3030 (Ar-H), 1728 (CO-O-C), 1670, 1650, 1640, and 1595 (C=C), 1295 (CO-OC), 750 and 680 cm^{-1} (pyridinium); ^1H NMR (DMSO-d_6) δ 9.50, 9.20, 8.94, and 8.21 (4H, four m, yridinium), 6.38 (1H, m, C=C-H, pentenyl), 5.94 (1H, s, C=C-H, in ring), 5.80 (1H, s, CHONicMeI), 5.00 (2H, m, $C=CH_2$), 4.43 (3H, s, N-CH_3), 1.80-1.20 (10H), 1.04 (6H, J = 12Hz, $C(CH_3)_2$).

1-Methyl-3-(5,5-dimethyl-3-pentyl-2-cyclohexenyl)pyridinium Iodide (6b)

Yield 84%; IR (KBr) 3090,, 3060, and 3030 (Ar-H), 1730 (CO-O-C), 1670, 1645, 1640, and 1595 (C=C), 1296 (CO-OC), 750 and 680 cm^{-1} (pyridinium); ^1H NMR (DMSO-d_6) δ 9.40, 9.13, 8.85, and 8.20 (4H, four m, pyridinium), 5.80 (1H, s, C=C-H), 5.72 (1H, s, CHONicMeI), 4.45 (3H, s, N-CH_3), 2.00-1.10 (15H), 0.98 (6H, d, J = 12Hz, $C(CH_3)_2$).

Kinetic Measurements

Reaction rates were measured by continuous automatic potentiometric titration of the released acids by means of a pH-stat (Radiometer, Copenhagen). In each measurement ca. 0.03 mmol of the substrate was dissolved in 15 mL of solvent and the liberated acid titrated with 0.025M NaOH solution in the same solvent. The data were evaluated by an on-line Apple-II computer using a non-linear least squares program. The solvolyses were followed up to two half-lives. Uncertainties are standard deviations of the mean for five to ten separate runs for each compound.

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REFERENCES

1. For review, see: W.S. Johnson, Angew. Chem., Int. Ed. Engl., 15, 9 (1976).
2. K.E. Harding, J.L. Cooper, and P.M. Puckett, J. Org. Chem., 44, 2834 (1979).
3. a) W.S. Johnson, W.H. Lunn, and K. Fitzi, J. Am. Chem. Soc., 86, 1972 (1964).
   b) W.S. Johnson, P.J. Neustaedter, and K.K. Schmiegel, J.Am. Chem. Soc., 87, 5148 (1965).
4. M. Ladika and D.E. Sunko, J. Org. Chem., 50, 4544 (1985).
5. M. Ladika, B. Jurišić, and D.E. Sunko, Spectrochim. Acta, 42A, 1397 (1986).
6. R.H. De Wolfe and W.G. Young, Chem. Rev., 56, 753 (1956).
7. D.E. Sunko and S. Borčić, "Isotope Effects in Chemical Reactions", ed. by C.J. Collins and N.S. Bowman, American Chemical Society, Washington, D.C., 1970, ACS Monograph No. 167, pp. 160-209.
8. The reported m values were calculated using the equation[9] $\log (k/k_o) = mY_{OTs}$. The correlation coefficients are 0.9992 and 0.9987 for esters 6a and 6b, respectively.
9. a) T.W. Bentley and P.v.R. Schleyer, J. Am. Chem. Soc. 98, 7658 (1976).
   b) F.L. Schadt, T.W. Bentley, and P.v.R. Schleyer, J. Am. Chem. Soc., 98, 7667 (1976).
10. B. Jurišić, M. Ladika, and D.E. Sunko, Tetrahedron, 43, 1955 (1987).
11. A.J.B. Edgar, S.H. Harper, and M.A. Kazi, J. Chem. Soc. 1083 (1957).
12. R.L. Frank, and H.K. Hall, Jr., J. Am. Chem. Soc., 72, 1645 (1950).
13. R.N. Lacey, J. Chem. Soc., 1639 (1960).
14. C.J. Reichel and T.A. Bryson, Heterocycl., 18, 277 (1982).