Solvolysis of 2-Alkenyl-2-cyclohexenyl *p*-Nitrobenzoates

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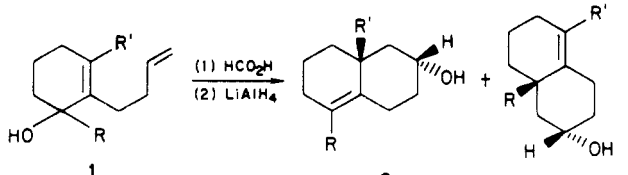
In an attempt to study possible π-participation in allyl derivatives, 2-alkenyl-3-methyl-2-cyclohexenyl *p*-nitrobenzoates **6** and **7** were solvolyzed in 97 wt % trifluoroethanol and 80 vol % ethanol. These esters show in both solvents a solvolysis rate retardation in comparison with the saturated analogue and normal values of secondary α-deuterium isotope effects (k_H/k_D = 1.17–1.22). The solvolysis products from the trifluoroethanolysis and ethanolysis of the unlabeled esters **6H** and **7H** were also determined. On the basis of these results it was concluded that the solvolysis proceeds via a stepwise mechanism involving an allylic cation and a bicyclic cation as reactive intermediates in the first and second reaction step, respectively.

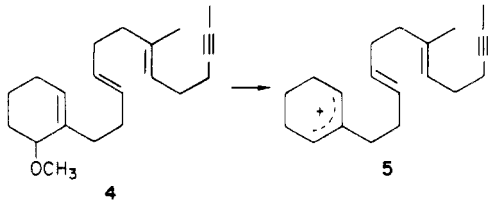
Allylic cations play a significant role in a number of biochemically important cyclization and condensation reactions.[1] The cationic cyclizations of allylic substrates with the appropriately juxtaposed olefinic bond(s) can give polycyclic steroid-type compounds in high yields. Although such cyclizations represent a good synthetic approach to these compounds, the question of mechanism of stereospecific cationic polyene cyclizations, be it enzymatic or biomimetic, is still open to debate.[1a]

Suitable systems for such investigations are 2-alkenyl derivatives of 2-cyclopentenol and 2-cyclohexenol. It was shown[2-6] that the solvolysis of alcohols **1** in formic acid gave, after reduction of the resulting mixture with $LiAlH_4$, preferentially *syn*-octalinols **2** and **3** (except in the case of **1c**, where none of **3c** was found[3]).



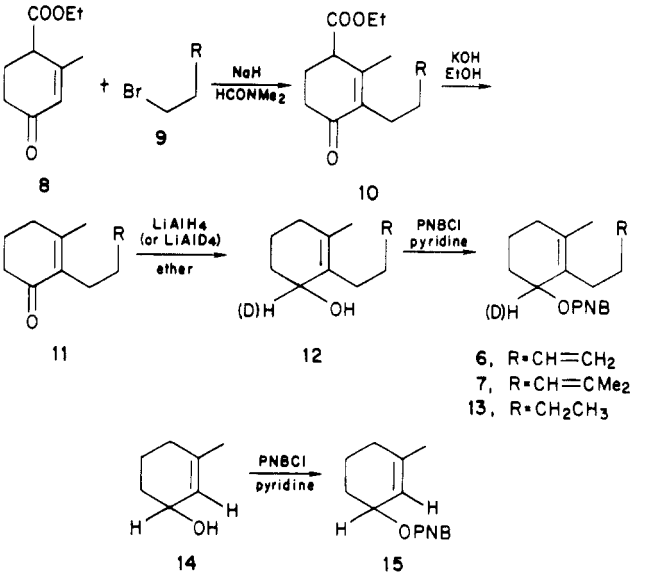
a, R=R'=H; **b**, R=D, R'=H **c**, R=H, R'=CH_3; **d**, R=R'=CH_3; **e**, R=CD_3, R'=CH_3

Johnson studied the solvolysis of alcohols **1a**, **1c**, and **1d** and obtained evidence that suggested (but did not prove) that the ionization step preceded cyclization.[2] A similar conclusion was reached in the study of cationic cyclization of methoxy trienyne **4**.[7] The obtained results



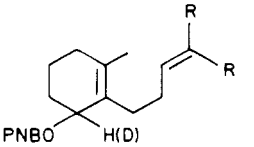
suggest that cyclization proceeds via the allylic cation **5**, but they do not rule out completely the less likely alternative that two concerted mechanisms (S_N2 and S_N2' reactions) occur at the same time, giving the same stereochemical result.

Scheme I



In our previous investigations of such cyclizations[6] deuterium labeling was used to introduce a convenient perturbation of symmetry. The solvolysis of alcohols **1b** and **1e** in formic acid resulted in a mixture of equal parts of **2** and **3**, proving that the resonance-stabilized allylic cation is the first formed intermediate. It is sufficiently stable to permit rotation of the butenylic side chain and a subsequent indiscriminate attack of the double bond on either one of the equivalent carbon atoms of the allylic system. It is interesting to note that in this respect the less substituted cation derived from **1b** behaves identically as the tertiary allyl cation derived from **1e**. These results rule out the alternative concerted mechanism for the solvolysis of these alcohols in formic acid.

In this work we studied the solvolysis of esters **6** and **7** under the mild, nonacidic conditions, in order to investigate the possible effect of π-participation of the side chain on the solvolysis rate.[8]



6, R=H
7, R=CH_3
PNB = *p*-nitrobenzoyl

(1) For review, see: (a) Johnson, W. S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 9. (b) Johnson, W. S. *Bioorg. Chem.* **1976**, *5*, 51. (c) Johnson, W. S. *Acc. Chem. Res.* **1968**, *1*, 1.
(2) Johnson, W. S.; Lunn, W. H.; Fitzi, K. *J. Am. Chem. Soc.* **1964**, *86*, 1972.
(3) Johnson, W. S.; Neustaedter, P. J.; Schmiegel, K. K. *J. Am. Chem. Soc.* **1965**, *87*, 5148.
(4) Marshall, J. A.; Cohen, N.; Hochstetler, A. R. *J. Am. Chem. Soc.* **1966**, 88, 3408.
(5) Johnson, W. S.; Marshall, J. A.; Keana, J. F. W.; Franck, R. W.; Martin, D. G.; Bauer, V. J. *Tetrahedron, Suppl.* **1966**, *No. 8*, 541.
(6) Ladika, M.; Bregovec, I.; Sunko, D. E. *J. Am. Chem. Soc.* **1981**, *103*, 1285.
(7) Peters, J. A. M.; Posthumus, T. A. P.; van Vliet, N. P.; Zeelen, F. J.; Johnson, W. S. *J. Org. Chem.* **1980**, *45*, 2208.

0022-3263/85/1950-4544$01.50/0

Table I. Rates and Secondary α-Deuterium Kinetic Isotope Effects in Solvolysis of 2-Substituted 3-Methyl-2-cyclohexenyl *p*-Nitrobenzoates

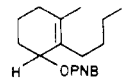
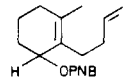
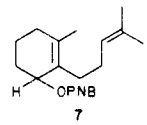
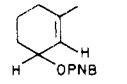
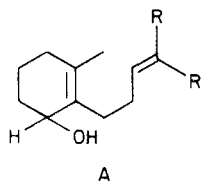
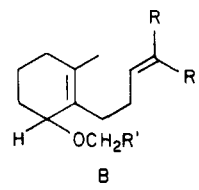
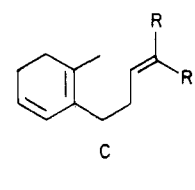
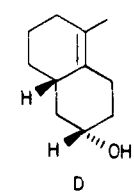
ester	80% EtOH; 50 °C			97% TFE; 25 °C		
	10^4k, s^{-1}	k_{rel}	k_H/k_D	10^4k, s^{-1}	k_{rel}	k_H/k_D
 13	2.94 ± 0.04	1.000	1.19 ± 0.02	18.79 ± 0.06	1.000	1.190 ± 0.008
 6	2.49 ± 0.02	0.847	1.19 ± 0.01	11.40 ± 0.03	0.607	1.204 ± 0.005
 7	2.45 ± 0.02	0.833	1.17 ± 0.01	17.38 ± 0.07	0.925	1.218 ± 0.006
 15	1.023 ± 0.007	0.348		2.25 ± 0.03	0.120	

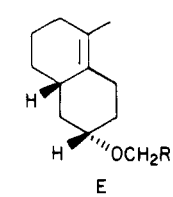
Table II. Solvolysis Products of 2-(3-Butenyl)-3-methyl-2-cyclohexenyl *p*-Nitrobenzoate (6H) and 2-(4-Methyl-3-pentenyl)-3-methyl-2-cyclohexenyl *p*-Nitrobenzoate (7H)

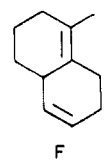

A

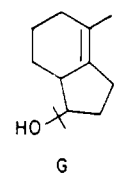

B

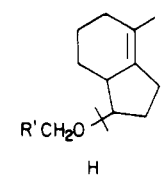

C

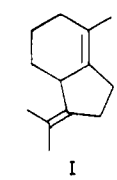

D

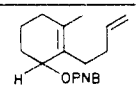
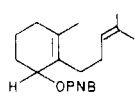

E


F


G


H


I

ester	reacn conditions[a]	% bicyclic products	products, % A	B	C	D	E	F	G	H	I
 6H	97T; 25 °C	34	41[b]	20[b,d]	5[b]	10	23[d]	1			
	80E; 50 °C	0	56[b]	36[b,e]	8[b]						
 7H	97T; 25 °C	88	3[c]	5[c,d]	4[c]				27	57[d]	4
	80E; 50 °C	40	39[c]	13[c,e]	8[c]				34	2[e]	4

[a] 80E is 80 vol % aqueous ethanol and 97T is 97 wt % aqueous 2,2,2-trifluoroethanol. [b] R = H. [c] R = CH_3. [d] R' = CF_3. [e] R' = CH_3.

Results

p-Nitrobenzoates **6H**, **7H**, **13H**, and **15**, as well as their α-deuterated analogues **6D**, **7D**, and **13D** were prepared by appropriate modifications[6] of published procedures[3,4] according to Scheme I. Details are given in the Experimental Section.

Solvolyses of esters **6**, **7**, **13**, and **15** were accomplished in 97 wt % 2,2,2-trifluoroethanol (TFE) at 25 °C and in 80 vol % ethanol at 50 °C. The rates were measured potentiometrically[9] at a constant pH. Clear first-order kinetic behavior was observed in all cases. The kinetic results are presented in Table I.

For product studies esters **6H** and **7H** were also solvolyzed under identical conditions as for the rate measurements. After removal of the solvent the products were separated by chromatography on silica gel. The structures of products were determined by IR, ^1H NMR and mass spectrometry, as well as by comparison with previously identified compounds. The results are summarized in Table II and details are given in the Experimental Section.

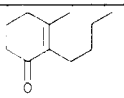
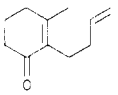
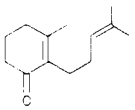
Discussion

The results obtained in the course of this work show that the neighboring group π-participation of the 2-substituted side chain is not revealed in the studied solvolyses of esters **6** and **7**.

The observed differences in reaction rate constants (Table I) of the compounds **6**, **7**, **13**, and **15** are small, showing that the structural changes in the side chain

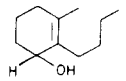
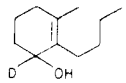
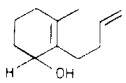
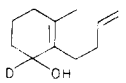
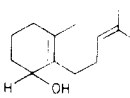
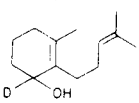
(8) For a preliminary communication, see: Ladika, M.; Sunko, D. E. *Croat. Chem. Acta* **1984**, *57*, 179.
(9) Hiršl-Starčević, S.; Majerski, Z.; Sunko, D. E. *J. Org. Chem.* **1980**, *45*, 3388.

Table III. Summary of Properties of Ketones 11

ketone	% yield[a]	IR[b] λ_{max}, μm	^{1}H NMR[c] δ (H's, mult)
	16.0	6.00 (C=O), 6.13 (C=C)	1.89 (3 H, s, C=CCH$_3$), 0.70-2.40 (15 H)
	50.7	3.20 (C=C—H), 6.00 (C=O), 6.12 (C=C), 10.01, 10.92 (HC=CH$_2$)	5.40-6.12 (1 H, m, C=CH), 4.69-5.13 (2 H, m, C=CH$_2$), 1.89 (3 H, s, C=CCH$_3$), 1.71-2.50 (10 H)
	24.3	6.00 (C=O), 6.12 (C=C)	4.83-5.30 (1 H, m, C=CH), 1.93 (3 H, s, C=CCH$_3$), 1.67 (3 H, s, C=CCH$_3$), 1.59 (3 H, s, C=CCH$_3$), 1.46-3.0 (10 H)

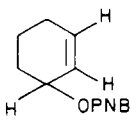
[a] All isolated yields from keto ester **8**. [b] Neat. [c] CCl_4; internal standard, Me_4Si.

Table IV. Summary of Properties of Alcohols 12

alcohol	% yield[a]	IR[b] λ_{max}, μm	^{1}H NMR[c] δ (H's, mult)
	91.5	2.94 (O—H)	3.77-4.00 (1 H, br s, O-CH), 1.60 (3 H, s, C=CCH$_3$), 0.80-2.20 (16 H)
	91.6	2.93 (O—H), 4.66 (C—D)	1.60 (3 H, s, C=CCH$_3$), 0.80-2.35 (16 H)
	89.6	2.93 (O—H), 3.22 (C=C—H), 6.11 (C=C), 10.43, 10.97 (HC=CH$_2$)	5.41-6.19 (1 H, m, C=CH), 4.70-5.17 (2 H, m, C=CH$_2$), 3.77-4.07 (1 H, br s, O-CH), 2.28-2.50 (1 H, br s, OH), 1.63 (3 H, s, C=CCH$_3$), 1.40-2.28 (10 H)
	88.4	2.94 (O—H), 3.22 (C=C—H), 4.66 (C—D), 6.10 (C=C), 10.62, 10.93 (HC=CH$_2$)	5.42-6.11 (1 H, m, C=CH), 4.77-5.23 (2 H, m, C=CH$_2$), 2.62 (1 H, s, OH), 1.63 (3 H, s, C=CCH$_3$), 1.38-2.35 (10 H)
	93.9	2.98 (O—H), 11.95 (C=C—H)	4.87-5.33 (1 H, m, C=CH), 3.77-4.05 (1 H, br s, O-CH), 1.64 (9 H, s, C=CCH$_3$), 1.34-2.30 (11 H)
	93.3	2.94 (O—H), 4.70 (C—D), 11.98 (C=CH)	4.87-5.30 (1 H, m, C=CH), 2.52-2.95 (1 H, br s, OH), 1.66 (9 H, s, C=CCH$_3$), 1.32-2.40 (10 H)

[a] All isolated yields. [b] Neat. [c] CCl_4; internal standard, Me_4Si.

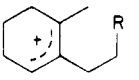
substituted at position 2 of the allylic moiety do not influence the rate-determining ionization step.[10] Even in the case of ester **15** without a C-2 substituent, the rate of solvolysis is depressed only 8 and 3 times in 97% TFE and 80% EtOH, respectively, compared with the solvolysis rate of reference ester **13H**. On the contrary, it is known that substitution at C-3 center of allylic substrates can drastically change the reactivity of such compounds.[10] For example, ester **15** solvolyzes in CF_3CH_2OH about 5×10^3 times faster than its C-3 nor analogue **16**.[11]



16

Our results also show that the solvolyses of 2-alkenylic esters **6** and **7** are slower than the solvolysis of reference 2-butyl ester **13** in both solvents (97% TFE and 80% EtOH). This result can be explained[12] by π-electron-withdrawing inductive effects of alkenylic groups at C-2.

The extent of the rate retardation in the solvolysis of esters **6** and **7** relative to the reference ester **13** depends on the solvent. Solvolysis of these esters in 97% TFE, a solvent of large ionization power and low nucleophilicity,[13] includes the formation of the corresponding cations **17** as reaction intermediates.



17a, R=CH_2CH_3
b, R=CH=CH_2
c, R=CH=CMe_2

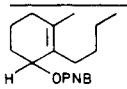
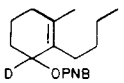
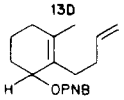
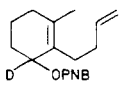
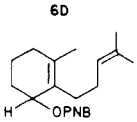
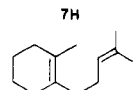
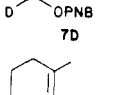
Substituents R in the C-2 side chain have influence on the stability and rate of formation of these cations. In our previous paper[14] it was shown that inductive effects of these substituents are linearly correlated with the inductive influence of the same substituents on pK_a values of carboxylic acids **18a–c**.

RCH_2CO_2H

18a, R=CH_2CH_3
b, R=CH=CH_2
c, R=CH=CMe_2

(10) De Wolfe, R. H.; Young, W. G. *Chem. Rev.* **1956**, *56*, 753.
(11) Uebel, J. J.; Milaszewski, R. F.; Arlt, R. E. *J. Org. Chem.* **1977**, *42*, 585.
(12) Peterson, P. E.; Casey, C.; Tao, E. V. P.; Agtarap, A.; Thompson, G. *J. Am. Chem. Soc.* **1965**, *87*, 5163.
(13) Scott, F. L. *Chem. Ind. (London)* **1959**, 224.
(14) Ladika, M.; Borčić, S.; Sunko, D. E. *Croat. Chem. Acta* **1984**, *57*, 331.

Table V. Summary of Properties of *p*-Nitrobenzoates

ester	% yield[a]	IR[b] λ_{max}, μm	^{1}H NMR[c] δ (H's, mult)
 13H	97.8	3.18 (C=C—H), 5.82 (CO—O—C), 6.22 (C=C), 6.54, 7.43 (NO_2), 9.07 (C—O), 13.82 (Ar H)	8.25 (4 H, s, *p*-O_2N—C_6H_4), 5.40-5.77 (1 H, m, OCH), 1.75 (3 H, s, C=CCH_3), 0.60-2.30 (15 H)
 13D	97.3	5.81 (CO—O—C), 6.21 (C=C), 6.53, 7.43 (NO_2), 9.07 (C—O), 13.82 (Ar H)	8.20 (4 H, s, *p*-$O_2NC_6H_4$), 1.73 (3 H, s, C=CCH_3), 0.60-2.40 (15 H)
 6H	97.6	3.20 (C=C—H), 5.84 (CO—O—C), 6.13 (C=C), 6.54, 7.44 (NO_2), 9.07 (C—O), 10.62, 10.92 ($HC=CH_2$), 13.90 (Ar H)	8.18 (4 H, s, $C_6H_4NO_2$-*p*), 5.38-6.03 (1 H, m, C=CH), 5.42-5.66 (1 H, m, O-CH), 4.71-5.14 (2 H, m, $C=CH_2$), 1.73 (3 H, s, C=CCH_3), 1.46-2.44 (10 H)
 6D	97.2	3.20 (C=C—H), 5.84 (CO—O—C), 6.10 (C=C), 6.57, 7.42 (NO_2), 9.05 (C—O), 10.61, 10.88 ($HC=CH_2$), 13.90 (Ar H)	8.18 (4 H, s, $C_6H_4NO_2$-*p*), 5.32-6.03 (1 H, m, C=CH), 4.73-5.15 (2 H, m, $C=CH_2$), 1.73 (3 H, s, C=CCH_3), 1.41-2.43 (10 H)
 7H	97.7	3.15 (C=C—H), 5.80 (CO—O—C), 6.20 (C=C), 6.53, 7.41 (NO_2), 9.04 (C—O), 13.80 (Ar H)	8.23 (4 H, s, $C_6H_4NO_2$-*p*), 5.38-5.70 (1 H, br s, O-CH), 4.83-5.28 (1 H, m, C=CH), 1.75, 1.63, and 1.53 (9 H, 3 s, C=CCH_3), 1.33-2.50 (10 H)
 7D	97.7	3.20 (C=C—H), 5.80 (CO—O—C), 6.20 (C=C), 6.53, 7.40 (NO_2), 9.02 (C—O), 13.80 (Ar H)	8.20 (4 H, s, $C_6H_4NO_2$-*p*), 4.75-5.27 (1 H, m, C=CH), 1.75, 1.64, and 1.54 (9 H, 3 s, C=CCH_3), 1.40-2.45 (10 H)
 15	95.2[d]	3.18 (C=C—H), 5.81 (CO—O—C), 6.22 (C=C), 6.53, 7.42 (NO_2), 9.04 (C—O), 13.82 (Ar H)	8.00 (4 H, s, $C_6H_4NO_2$-*p*), 5.20-5.50 (1 H, br s, O-CH), 5.35-5.45 (1 H, br s, C=CH), 1.70 (3 H, s, C=CCH_3), 1.55-2.20 (6 H)

[a] All isolated yields. [b] 6H and 6D in KBr, others neat. [c] CCl_4; internal standard, Me_4Si. [d] The precursor alcohol was prepared according to ref 19.

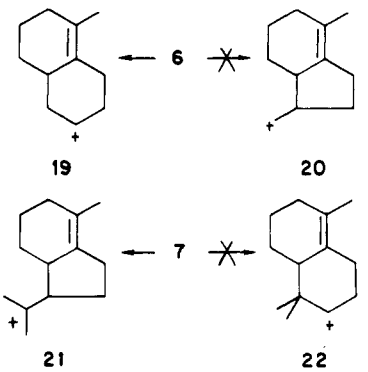
Solvolyses of esters **6**, **7**, and **13** in 80% EtOH involve the stronger participation of solvent in the rate-determining step[15] compared with the solvolyses in 97% TFE, resulting in smaller rate retardations.

The obtained normal values of secondary α-deuterium isotope effects[16] for esters **6**, **7**, and **13** (1.19–1.22 in 97% TFE and 1.17–1.19 in 80% EtOH; Table I) are also in keeping with the proposed mechanism according to which π-participation is not revealed in these solvolytic reactions. The slightly reduced isotope effect of k_H/k_D = 1.17 for the solvolysis of ester **6** in 80% EtOH could be explained by a rate-determining formation of the tight ion pair and subsequent exclusive formation of unrearranged products.

The composition of solvolysis products of esters **6H** and **7H** (Table II) is also fully consistent with the proposed stepwise mechanism of solvolysis. In the solvolysis of ester **6H** in 80% EtOH the nucleophilicity of the side chain double bond is apparently too low either to participate in ionization or even to compete with the more nucleophilic solvent for the allyl cation formed in the rate-determining step. Thus only simple substitution and elimination products are formed, while bicyclic products are not observed.

In the less nucleophilic and more ionizing solvent (97% TFE vs. 80% EtOH) in which the allylic cations **17** are formed, the side chain double bond in ester **6H** can efficiently compete with solvent for the allyl cation **17b**. As the result ester **6H** gives 34% bicyclic products in 97% TFE. The trisubstituted side chain double bond in ester **7** is significantly more nucleophilic than the monosubstituted double bond in ester **6**, resulting in a higher percentage of bicyclic products in both solvents from ester **7H** (88% in 97% TFE and 40% in 80% EtOH; Table II) than from **6H**.

It is interesting to note the difference in the size of rings (six- and five-membered) formed during cyclization of esters **6** and **7**. This result shows that the studied reactions include formation of bicyclic cations as reaction intermediates prior to attack of solvent as nucleophile. Ester **6** cyclizes via secondary carbocation **19** with the six-membered new ring and not via primary cation **20** with the five-membered new ring. On the contrary, ester **7** cyclizes via tertiary carbocation **21** with the five-membered new ring and not via secondary cation **22** with the six-membered new ring. The alternative formation of products



with five-membered and six-membered rings from esters **6** and **7**, respectively would be possible only in the concerted process which excludes developing of a positive

(15) For an excellent discussion of the S_N1–S_N2 spectrum of mechanisms, see: Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7658.

(16) Sunko, D. E.; Borčić, S. "Isotope Effects in Chemical Reactions"; Collins, C. J., Bowman, N. S., Ed.; American Chemical Society: Washington, DC, 1970; ACS Monogr. No. 167, pp 160–209.

charge in bicyclic structures. This mechanism requires concertedness of two reactions: nucleophilic attack of a solvent on the alkenylic side chain of allyl cation **17b** or **17c** and the ring closure. Our results prove that esters **6** and **7** do not cyclize via such concerted mechanism.

Finally, the bicyclic alcohol and ether formed from ester **6H** in 97% TFE have syn stereochemistry as indicated by their ^{1}H NMR characteristics. The same stereoselectivity was observed in previous cyclizations of such substrates.[3]

Experimental Section

All compounds were identified by IR, ^{1}H NMR, and MS. The following instruments were used: a Perkin-Elmer 167 IR spectrometer, Varian T-60 and JEOL 100 NMR spectrometers, and a Varian CH7 mass spectrometer. Satisfactory elemental analyses were obtained for all new compounds.

General Procedure for the Preparation of Ketones 11. These compounds were prepared by a modification[6] of the published procedures.[3,4] All reactions were performed in an atmosphere of dry nitrogen. To a suspension of NaH (4.06 g, 0.169 mol) in anhydrous *N,N*-dimethylformamide (140 mL) was added ethyl 2-methyl-4-keto-2-cyclohexenecarboxylate (**8**)[17] (30.6 g, 0.168 mol). During the addition the temperature of the reaction mixture was kept below 0 °C. Subsequently, the mixture was refluxed with stirring for 12 h. After the mixture was again cooled to 0 °C, bromide **9**[18] (0.168 mol) was slowly added, and then the mixture was refluxed for additional 12 h.

The cooled mixture was diluted with water and extracted with ether (3 × 70 mL). After the combined extracts were dried over Na_2SO_4 and the solvent was evaporated, the residual crude oily product **10** was subjected to hydrolysis and decarboxylation without further purification. It was added slowly to a stirred solution of KOH (16.65 g, 0.3 mol) in anhydrous ethanol (110 mL). Stirring and refluxing was continued for 20 h. Ethanol was removed in vacuo and the remaining dark oil dissolved in water and taken up in ether (3 × 70 mL). The dried (Na_2SO_4) ethereal solution was evaporated in vacuo and the residue dissolved in a mixture of benzene and ether (4:1). It was purified on a silica gel column using the same solvent mixture as eluent to give the desired ketone **11** (Table IIII).

General Procedure for the Preparation of Alcohols 12. Ketones **11** (1.46 mmol) were reduced with $LiAlH_4$ (7 mmol) or $LiAlD_4$ (7 mmol) in anhydrous ether (16 mL) by using a previously described procedure[3] to give alcohols **12H** or their deuterated analogues **12D** (Table IV).

General Procedure for the Preparation of *p*-Nitrobenzoates. A solution of alcohol **12** (18.6 mmol) and *p*-nitrobenzoylchloride (73 mmol) in dry pyridine (175 mL) was stirred for 3 days at room temperature. The mixture was then poured on ice and extracted with pentane. The dried (Na_2SO_4) pentane solution was evaporated in vacuo, and the residual material was purified on a silica gel column using mixture of pentane and benzene (9:1) as eluent. By this procedure oily crystals of ester **6**, **7**, **13**, or **15** (97–98% yield; see Table V) were obtained. Esters **6H** and **6D** were recrystallized from CCl_4 to give yellow crystals in 69% and 65% yield, respectively, with mp 42–43 °C and 41–42 °C, respectively.

Kinetic Measurements. Reaction rates were measured by continuous automatic potentiometric titration of the liberated *p*-nitrobenzoic acid by means of a pH-stat (Radiometer, Copenhagen). In each measurement ca. 0.03 mmol of the *p*-nitrobenzoate was dissolved in 15 mL of solvent and the liberated acid titrated with 0.025 M NaOH solution in the same solvent.

Product Studies. In a typical experiment 6.1 mmol of ester **6H** or **7H** was solvolyzed in nitrogen atmosphere in 170 mL of 97 wt % trifluoroethanol at 25.0 ± 0.1 °C or 80 vol % ethanol at 50.0 ± 0.1 °C under the same conditions as in the kinetic runs for about 10 half-lives. The products were extracted with pentane or diethyl ether, and the solvent was evaporated under reduced pressure. The separation of the obtained product mixture on the column of silica gel[20] gave three fractions which contained alkenic products (eluted with mixtures of pentane and benzene), ethereal products (eluted with benzene), and alcoholic products (eluted with diethyl ether). The further separation and purification of products was performed by TLC using pentane as eluent for alkenic products, mixtures of pentane and benzene for ethereal products, and mixtures of benzene and diethyl ether (8:2–19:1) for alcoholic products.

Acknowledgment. This work was supported by Grant 02-011-1 (PL 480) from the National Institutes of Health and by Grant II-21/0119 from the Research Council of Croatia (SIZ-II).

Registry No. **6**, 90740-17-3; **6-*d***, 98361-52-5; **7**, 90740-18-4; **7-*d***, 98361-53-6; **8**, 487-51-4; **9** (R = CH=CH_2), 5162-44-7; **9** (R = CH=$C(CH_3)_2$), 2270-59-9; **9** (R = Et), 109-65-9; **10** (R = CH=CH_2), 4994-08-5; **10** (R = CH=$C(CH_3)_2$), 59841-28-0; **10** (R = Et), 17161-13-6; **11** (R = CH=CH_2), 2658-92-6; **11** (R = CH=$C(CH_3)_2$), 59841-29-1; **11** (R = Et), 13679-29-3; **12** (R = CH=CH_2), 4505-58-2; **12** (R = CH=$C(CH_3)_2$), 98361-38-7; **12** (R = Et), 98361-39-8; **12-*d*** (R = CH_2CH_3), 98361-48-9; **12-*d*** (R = CH=CH_2), 98361-49-0; **12-*d*** (R = CH=$C(CH_3)_2$), 98361-50-3; **13**, 90740-16-2; **13-*d***, 98361-51-4; **14**, 21378-21-2; **15**, 38313-03-0; A (R = H), 90740-17-3; A (R = CH_3), 98361-38-7; B (R = H, R′ = CF_3), 98361-40-1; B (R = CH_3, R′ = CF_3), 98361-43-4; C (R = H), 98361-41-2; C (R = CH_3), 98361-44-5; D, 4505-59-3; E (R′ = CF_3), 98361-42-3; G, 98361-45-6; H (R′ = CF_3), 98361-46-7; I, 98361-47-8; D_2, 7782-39-0.

Supplementary Material Available: Separation and spectral characterization data for solvolysis products A–I (5 pages). Ordering information is given on any current masthead page.

(17) Smith, L. I.; Rouault, G. F. *J. Am. Chem. Soc.* **1943**, *65*, 631.
(18) Julia, M.; Julia, S.; Guégan, R. *Bull. Soc. Chim. Fr.* **1960**, 1072.
(19) Bowman, M. I.; Ketterer, C. C.; Dinga, G. *J. Org. Chem.* **1952**, *17*, 563.

(20) Products of this type are known[3] to be unstable under conditions for separation by gas chromatography.