Bridgehead Carbocations: A Solvolytic Study of 1-Bromobicyclo[1.1.1]pentane and Its Bridgehead-Substituted Derivatives

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Abstract: The rate constants (k) for solvolysis of a range of 3-X-substituted bicyclo[1.1.1]pentyl bromides in 80% aqueous ethanol have been measured and a linear relationship found to exist between log k and the inductive/field constant σ_I. These observations, together with the results of isotope and solvent effect studies described below, have been interpreted as evidence for the formation of 1-bicyclo[1.1.1]pentyl cations in the ionization step in preference to mechanisms in which either ring-opening is concerted with ionization to give 3-methylenecyclobutyl cations or ionization is accompanied by ring-contraction to give bicyclo[1.1.0]butyl-1-carbinyl cations. The latter mechanisms would have been expected to show the effects of strong π-donor substituent participation, a phenomenon which was not observed. A comparison of the rates of solvolysis of the parent bromide and its 3-deuterated analog is characterized by a large deuterium-isotope effect (k_H/k_D = 1.30) which, combined with the observation that 1-bromobicyclo[1.1.1]pentane solvolyses with enhanced rates in solvents which are strong hydrogen bonding acceptors, lends support to the view that the 1-bicyclo[1.1.1]pentyl cation derives substantial stabilization from σ-hyperconjugative interactions.

Introduction

With the exception of several notable examples such as the larger bicyclic systems exemplified by manxyl chloride (**1**)[1] and other specially designed substrates incorporating judiciously placed cyclopropyl rings, e.g., 1-chlorotrishomobarrelene (**2**),[2] the solvolysis of tertiary bridgehead derivatives generally occurs much more slowly than that of their acyclic counterparts. At the same time, the solvolytic rates of bridgehead systems also span an enormous range compared with those of the open-chain analogs.[3] The sluggish behavior displayed by the majority of bridgehead systems toward solvolysis is a manifestation of their reluctance to accommodate the developing positive charge at the bridgehead in accordance with the degree of nonplanarity required to be sustained at the cationic site. Thus those substrates with the greatest accumulation of strain during formation of the transition state react the slowest.

Some time ago, Schleyer and his associates[1,4] observed the existence of a linear correlation between the rates of solvolysis of bridgehead derivatives and the strain-energy difference between precursor and carbocation as computed by molecular mechanics calculations. More recently, Müller[5] has enjoyed considerable success in extending the strain–reactivity relationship and by employing modified, updated force-field parameters, for example, he has found that cyclobutyl-containing compounds of unexpected reactivity such as the cubyl system[6] can be accommodated readily. It is noteworthy, however, that these correlations fail[7] when applied to another group of cyclobutyl-containing substrates, viz., the 1-bicyclo[n.1.1]alkyl halides (**3–5**), which undergo solvolysis far more rapidly than anticipated on the basis of the strain engendered upon formation of the corresponding cations. The enhanced rates of solvolysis of both the 1-bicyclo[1.1.1]pentyl halides (**3**)[8] and (**4**)[9] and 1-bicyclo[3.1.1]heptyl bromide (**5**)[10] are quite extraordinary because simple ionization in each case would lead to a cation which possesses a large amount of strain, yet each system reacts faster than the classic acyclic example, *tert*-butyl bromide. Interestingly, whereas **5** has been shown unequivocally to react via the intermediacy of the 1-bicyclo[3.1.1]heptyl cation (**6**),[10,11] the situation with its smaller homologs **3** and **4** is ambiguous.

The rapid rate of solvolysis of 1-chlorobicyclo[1.1.1]pentane (**3**) was reported many years ago by Wiberg and Williams.[8] However, in view of the nature of the product, which consisted exclusively of ring-opened material, a definite mechanistic description of the reaction could not be presented. Thus, of the two mechanisms under consideration at the time, it was impossible to distinguish between, on the one hand, a process involving the 3-methylenecyclobutyl cation (**7**) as the primary intermediate, i.e., a reaction in which ionization and ring-fragmentation are concerted (Scheme 1, pathway a) and, on the other hand, a simple ionization of **3** to yield the 1-bicyclo[1.1.1]pentyl cation (**8**) which

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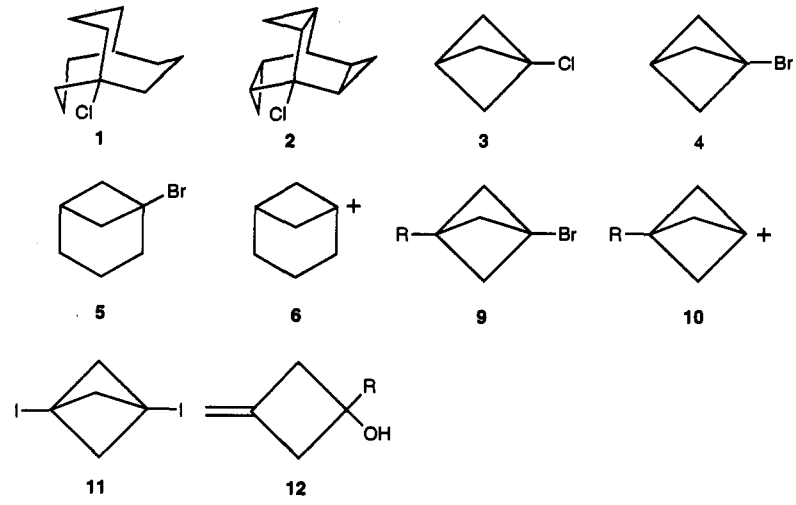
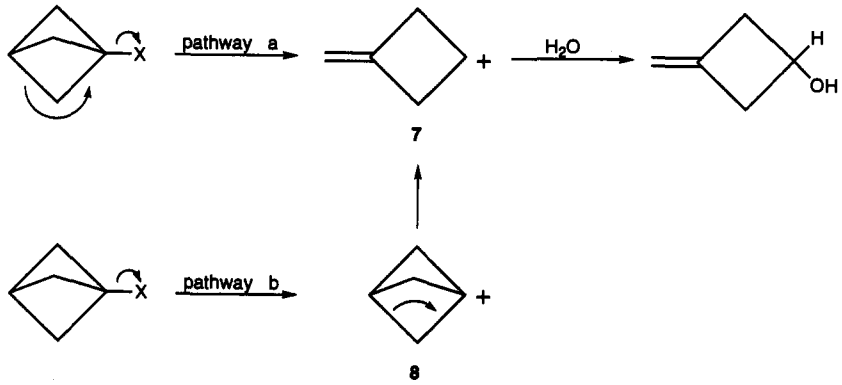
Chart 1



Scheme 1

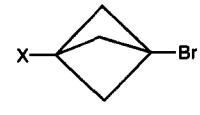


avoided detection by rapidly rearranging to **7** before it could be intercepted by solvent (Scheme 1, pathway b). With the available evidence at that stage, Wiberg and Williams[8] favored the former pathway. A more recent attempt[9] to detect the intermediate **8** during solvolysis of bromide **4** by trapping it prior to ring-opening also proved to be unsuccessful. It should be borne in mind that if the stepwise mechanism operates, then the 1-bicyclo[1.1.1]-pentyl cation (**8**) must possess unusually high thermodynamic stability. In fact, *ab initio* calculations[12] all point to considerable thermodynamic stabilization of **8** as a result of cross-ring orbital interactions.

Several years ago we embarked on a substituent-effect study of the solvolytic behavior of a series of 3-substituted bicyclo-[1.1.1]pentyl bromides (**9**). The purpose of the investigation was to determine whether a linear correlation exists between the values of log k for solvolysis of the derivatives **9** and the substituent inductive/field parameter, σ_I. The occurrence of such a relationship would be interpreted as strong evidence against a concerted ring-opening ionization process, i.e., mechanism (a) above, inasmuch as substituents which are π donors would be expected to provide anchimeric assistance to ionization by mesomeric stabilization of the developing positive charge at C3 in the transition state leading to the ring-opened cation **7**. Absence of such a rate enhancement coupled with a linear (log k *vs* σ_I) Hammett plot would, we believed, be compelling evidence for mechanism (b), viz., production of the 1-bicyclo[1.1.1]pentyl cation (**10**) as the primary intermediate.

The results described in the preliminary report[13] lent strong support to the view that the bicyclic cation **10** is produced in the rate-determining ionization step. Corroborative evidence for these observations has been provided by the results of recent experiments conducted by Wiberg and McMurdie[12a] and Adcock and Gakh[14] on S_N1 reactions of 1,3-diiodobicyclo[1.1.1]pentane (**11**). 3-Iodobicyclo[1.1.1]pentyl derivatives were produced in each case demonstrating that the reactions are, indeed, mediated by the 3-iodobicyclo[1.1.1]pentyl cation (**10**, R = I).

We now wish to disclose the detailed results of the substituent-effect investigation, which in addition has revealed some new and unexpected observations.



13 : X = CH_3
14 : X = t-Bu
15 : X = CO_2^-
16 : X = C_6H_5
17 : X = p-$O_2NC_6H_4$
18 : X = p-$MeOC_6H_4$
19 : X = CH_2OH
20 : X = CH_2OAc
21 : X = CH_2OTs
22 : X = CH_2Cl
23 : X = $COOCH_3$
24 : X = $COCH_3$
25 : X = $OCOCH_3$
26 : X = Br
27 : X = Cl
28 : X = CN
29 : X = F
30 : X = $SiMe_3$
31 : X = $SnMe_3$
32 : X = OCH_3

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Table 1. First-Order Rate Constants for Solvolysis[a] of the 3-X-Substituted Bicyclo[1.1.1]pentyl Bromides **4** and **13–25**

substrate	substituent	σ_I[b]	temp, °C	$k \times 10^4$, s^{-1}
4	H	0.00	5	1.19
			15	5.01
			25	16.5
			70	2080[c]
13	CH_3	–0.01	30	1.34
			40	4.73
			50	13.6
			70	108[c]
14	*t*-Bu	–0.01	40	1.77
			50	5.29
			60	14.6
			70	39.3[c]
15	CO_2^-	–0.19	15	0.73
			25	3.89
			35	15.0
			70	133[c]
16	C_6H_5	0.12	55	1.32
			65	3.90
			75	10.1
			70	6.17[c]
17	*p*-$O_2NC_6H_4$	0.23	90	2.70
			100	5.91
			110	13.1
			70	0.46[c]
18	*p*-$MeOC_6H_4$	0.11	70	18.6
19	CH_2OH	0.11	50	4.77
			60	13.7
			70	38.4
			70	37.9[c]
20	CH_2OAc	0.15	90	4.48
			100	12.6
			110	25.1
			70	0.655[c]
21	CH_2OTs	0.23	100	2.17
			110	4.92
			120	11.1
			70	0.131[c]
22	CH_2Cl	0.17	85	0.72
			95	1.62
			105	2.85
			70	0.237[c]
23	$COOCH_3$	0.32	120	1.17
			130	2.52
			140	5.74
			70	0.0096[c]
24	$COCH_3$	0.30	100	4.05
			110	9.51
			120	20.4
			70	0.254[c]
25	$OCOCH_3$	0.38	130	0.475
			135	0.653
			140	0.893
			70	0.0055[c]

[a] In 80% aqueous ethanol buffered with 1.2 equiv of triethylamine; averaged values of triplicate determinations. [b] Taken from ref 18. [c] Extrapolated value.

Results and Discussion

In order to be confident of the validity of the substituent-effect study, it was essential to include a variety of substituents with as wide a range of electronic effects as possible. Of the 20 bromides **13–32** selected to provide the required range of σ_I values (see Table 1) only two, 3-phenylbicyclo[1.1.1]pentyl bromide (**16**)[15] and 3-carbomethoxybicyclo[1.1.1]pentyl bromide (**23**),[16] had previously been reported. Synthesis of the required substrates, with the exception of the fluoride **29**, the silane **30**, the stannane **31**, and the ether **32**, is reported separately.[17] Our attempts to prepare **29–32** were unsuccessful, which was most disappointing particularly in the case of the metalloidal substituents because these represent the only groups which are inductively electron-releasing.

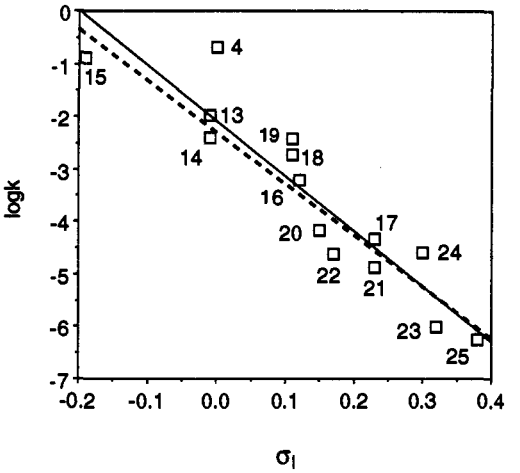

Figure 1. Plot of log k for solvolysis of the 3-X-substituted bicyclo-[1.1.1]pentyl bromides **4** and **13–25** in 80% aqueous ethanol against σ_I at 70 °C (solid line, $r = 0.93$); identical plot minus data for the parent bromide **4** (broken line, $r = 0.95$).

The rates of solvolysis of the 1-bicyclo[1.1.1]pentyl bromides **4** and **13–25** were measured conductimetrically[18] in 80% v/v aqueous ethanol buffered with 1.2 equiv of triethylamine. All substrates showed clean first-order kinetics. The products of solvolysis of eight of the bromides in either aqueous dioxane or tetrahydrofuran were isolated and analyzed by GC, GCMS, and NMR spectroscopy. Contrary to our expectations, in all cases only ring-opened methylenecyclobutanols **12** were isolated; their identities were established by standard procedures.

The rates of solvolysis determined for the bromides **4** and **12–25** are collected in Table 1. Inspection of the data reveals a large range of reactivity, and, in order to provide direct comparisons between them, rates were generally measured over several temperatures. All rate constants were averaged over at least three determinations at each temperature, and extrapolation of the kinetic data so derived allowed the rate constant at 70 °C to be evaluated for each bromide. Table 1 shows that the solvolysis rates of the extreme systems **4** and **25**, corresponding to the substituents H and OAc, differ by more than five orders of magnitude. It is noteworthy that the reactivities of the bromides **26–28**, which involve the substitutents Br, Cl, and CN, were so depressed, even at the maximum temperature of 140 °C at which the reactions could be followed conductimetrically, that rate data for these compounds could not be obtained, and they had to be omitted from the analyses.

In accordance with the procedure described above, the logarithms of the rate constants (log k) for the remaining 14 bromides were plotted against the relevant inductive/field constant, σ_I, for each substituent. Values of the latter were extracted from the comprehensive list collated by Charton.[19] The plot, which is displayed in Figure 1 (solid line), illustrates that there is a linear relationship ($r = 0.93$) between log k and σ_I. If the log k values are plotted against the σ_I^q values derived by Grob[20] from pK_a data of the 4-substituted quinuclidine perchlorates, a linear correlation is again observed and a value of –2.30 is obtained for the reaction constant.[21] This represents the largest recorded ρ-value to date in the solvolysis of γ-substituted

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(21) The Charton data were preferred because several σ_I^q values which were required are unavailable.

substrates[22] and is believed to be a reflection of the extent to which the cross-ring interaction is affected by the substituent.

The correlation observed in Figure 1 is seen to be satisfactory if the point for the parent bromide **4** is omitted. Compound **4** is found to react at an exalted rate, an aspect which is discussed in some detail below. These observations are consistent with the view that ionization of the series of compounds **13–25** is essentially controlled by the inductive/field effect of the substituent. The corollary is that solvolysis of the bromides most likely proceeds via the intermediacy of the 1-bicyclo[1.1.1]pentyl cations (**10**), i.e., by mechanism (b). If the alternative mechanism (a) were operating the 3-phenyl-, 3-(*p*-methoxyphenyl)-, and 3-acetoxybicyclo[1.1.1]-pentyl bromides (**16**, **18**, and **25**) should show deviant behavior in Figure 1 because these substituents are π-donors and should provide a strong stabilizing influence on the transition leading to the cyclobutyl cation **7**. The points for **16**, **18**, and **25** would, therefore, have been expected to fall well off the correlation line. In fact, these substrates behave precisely in accordance with their inductive/field effect as defined by their σ_I values. We attribute the driving force for the enhanced rate of solvolysis of the 1-bromobicyclo[1.1.1]pentanes to the formation of the thermodynamically stable bicyclic cation **8** in the same way as the cation **6** has been shown[10,11] to mediate the solvolysis of the homologous 1-bromobicyclo[3.1.1]heptanes. Formation of cation **8** (**10**) is also consistent with *ab initio* calculations[12d,23] which show that C3 in **8** bears little, if any, positive charge, and, therefore, the transition state associated with formation of **8** would also be expected to possess a similar charge distribution. As predicted by the calculations, the cations **8** and **10** evade detection by rearranging rapidly to the corresponding methylenecyclobutyl ions **7** which are the species ultimately trapped by solvent.

Of considerable importance and relevance to this study is the very recent disclosure by Wiberg and McMurdie[24] that ionization of 1-iodobicyclo[1.1.1]pentane (**33**) in the prescence of azide ion leads to bicyclo[1.1.0]butyl-1-carbinyl azide (**34**). Formation of the rearranged azide is attributed to interaction of azide ion with the bicyclo[1.1.0]butyl-1-carbinyl cation intermediate (**35**) which is formed directly from (**33**), in preference to the 1-bicyclo[1.1.1]-pentyl cation (**8**). Interestingly, *ab initio* calculations at the MP2/6-31G* theoretical level[12d,23] predict cation **8** to be a transition state on the reaction surface on the way to the rearranged cation **35**[25] although similar calculations on several of the 3-X-substituted bicyclo[1.1.1]pentyl derivatives predict[24] that the corresponding substituted 1-bicyclo-[1.1.1]pentyl cation **10** is a minimum on the potential surface.

Inasmuch as both calculation and experiment support the intermediacy of the 3-X-substituted bicyclo[1.1.1]pentyl cation (**10**) in the solvolysis of at least several of the substituted bicyclo-[1.1.1]pentyl bromides, the essential point of difference between our conclusions and those of Wiberg and McMurdie[24] is that whereas we believe the solvolysis of bromide **4** is mediated by the carbocation **8**, Wiberg and McMurdie regard **8** as the transition state in the ionization of iodide **33**. It would appear to us, however, that a contribution from a species such as the bicyclo[1.1.0]butyl-1-carbinyl cation (**35**) to the transition state for ionization of the 1-halobicyclo[1.1.1]pentanes is unlikely because calculations[24] place considerable positive charge at C3 in this carbocation a feature which, as discussed above in connection with cation **7**, would surely have been evident in the kinetics of those bromides with π-donor substituents.

(22) See, e.g.: Grob, C. A.; Sawlewicz, P. *Helv. Chim. Acta* **1984**, *67*, 1906. Grob, C. A.; Wittwer, G.; RamaRao, K. *Helv. Chim. Acta* **1985**, *68*, 651. Bielman, R.; Fuso, F.; Grob, C. A. *Helv. Chim. Acta* **1998**, *71*, 57.
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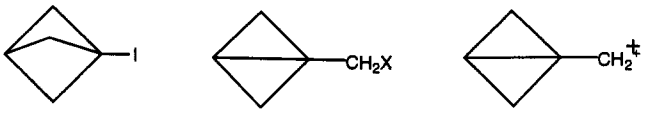
(24) Wiberg, K. B.; McMurdie, N. *J. Org. Chem.* **1993**, *58*, 5603.
(25) A salient feature of the computations is that, despite exhaustive efforts, MP2/6-31G* calculations are unable to locate the 1-bicyclo[3.1.1]heptyl cation (**6**) at an energy minimum either. Professor Paul Müller (University of Geneva) has made a similar observation (private communication). Yet **6** clearly exists with a sufficiently long lifetime to be trapped.



33 **34,X=N3** **36,X=I** **35**

In fact, we believe that the behavior of the halides **4** and **33** reported in the two studies cannot be strictly compared because the conditions under which the ionization processes are conducted are significantly different. It seems likely that a different mechanism of reaction is operating in the two cases, and we present the following rationale in support of this suggestion.

The work described herein is concerned with the solvolysis of 1-bromobicyclo[1.1.1]pentane (**4**) in 80% aqueous ethanol, a solvent which promotes S_N1 processes very effectively, and so ionization of **4** to **8** is facilitated by the powerful stabilizing effect associated with solvation of the incipient ions by the protic solvent. On the other hand, Wiberg and McMurdie monitored the reaction of 1-iodobicyclo[1.1.1]pentane (**33**) in a range of *aprotic* solvents (e.g., CH_2Cl_2, DMF, and CHCl=CHCl), none of which is conducive to S_N1 reactions. Accordingly, in these solvents, the highly reactive iodide **33** could also be converted slowly to its isomer **36** via formation of a tight ion pair, [**7**]·[I^-], which, in the aprotic media, is precluded from proceeding further to solvent-separated ions, followed by rearrangement/internal return. We envisage that production of the rearranged azide **34** from **36** then occurs by an S_N2 displacement of iodide by azide. We suspect that this sequence would occur relatively slowly because our experience[26] is that in the absence of nucleophiles the iodide **33** can be handled conveniently, without deterioration, in solvents such as CH_2Cl_2. We propose as a modification to the process, therefore, that strong nucleophiles, e.g., the azide ion, facilitate bond-making and -breaking such that ionization and rearrangement proceed in concerted fashion, as depicted in Figure 2. When the halide is dissolved in protic solvents anchimeric assistance of this kind is not required and presumably does not occur. Finally, because solvent effects are necessarily ignored in the *ab initio* calculations, the theoretical results are more likely to mimic the reactions conducted in the aprotic media.

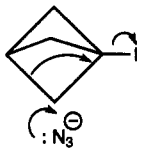


Figure 2. A representation of the concerted formation of bicyclo[1.1.0]-butyl-1-carbinyl azide (**34**) from 1-iodobicyclo[1.1.1]pentane (**33**) promoted by azide ion (see ref 24).

To summarize the position, it is clear that in the absence of other supporting data the question of the nature of the cationic intermediate produced in the solvolysis of 1-bromobicyclo[1.1.1]-pentane (**4**) remains unresolved. On the basis of the observations reported herein, we are inclined to the view that in protic solvents the unrearranged cation **8** is favored over both the rearranged cations **7** and **35**.

Deuterium Isotope and Solvent Effect Studies. As alluded to above, a closer scrutiny of the Hammett plot displayed in Figure 1 (solid line) reveals that the point for the parent bromide **4** actually deviates distinctly from the correlation line. Indeed, if the parent is excluded from the correlation, the fit (broken line, Figure 1) shows a definite improvement (r = 0.95), indicating something unusual about the solvolysis of the bromide **4** compared with its derivatives. We suggest that the aberrant behavior of **4** can be ascribed to the unique nature of the cation **8** compared with its 3-substituted relatives **10**.

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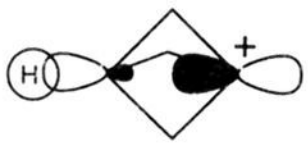
Table 2. First-Order Rate Constants and k_H/K_D Values for Solvolysis of **4** and **9**, R = D in Various Binary Mixtures[a,b]

solvent	temp, °C	$k_H \times 10^3$, s^{-1}	$k_D \times 10^3$, s^{-1}	k_H/k_D
80E	25	1.65	1.27	1.30
	15	0.4995[c]	0.3849[c]	1.30
70	25	6.49	4.95	1.31
60E	25	24.2	18.3	1.32
	20	12.61		
	15	61.8	4.73	1.31
	5	1.57	1.21	1.30
	−10	0.151		
100M	25	0.129		
97T	25	22.6[d]	16.5[d]	1.37
	5	2.36	1.72	1.37
	−5	0.58	0.427	1.36
	−15	0.165	0.120	1.37
	−16	0.137[d]	0.010	1.37

[a] Buffered with 1.2 equiv of triethylamine. [b] 80E = 80% aqueous ethanol, etc., 100M = 100% methanol; 97T = 97% aqueous trifluoroethanol. [c] Averaged value of six determinations. [d] Extrapolated values.

As indicated earlier, the rationale for the unexpected production of the 1-bicyclo[3.1.1]heptyl cation (**6**) as the primary intermediate in the solvolysis of the highly reactive bromide **5** is that the cation is endowed with exceptional stability. We hypothesized[10,11] that **6** derives favorable thermodynamic stabilization from cross-ring σ-hyperconjugation involving overlap of the empty p orbital on the charged carbon atom with the with back-lobe of the C–H bonding orbital of the other bridgehead carbon atom. Extension of this phenomenon to the 1-bicyclo[1.1.1]pentyl cation **8** is particularly attractive because *ab initio* calculations[23] predict the bridgehead carbons to be much closer in **8** than they are in **6**. Additionally, the orbitals involved are perfectly aligned (180°) for overlap as illustrated in structure **37**.[27] In simple valence-bond terminology, this kind of interaction can be depicted by the resonance contributors **38** ↔ **39**, a phenomenon unique to the parent 1-bicyclo[1.1.1]pentyl cation among the family of related cations **10**.

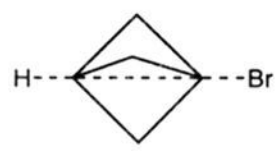


37

38 **39**

Evidence to support the unique character of the cation **8** was provided by the results of an isotope effect study conducted on the parent bromide **4** and its deuterated analog **9**, R = D. The kinetic data are reproduced in Table 2. Secondary β-deuterium isotope effects have been used extensively to probe hyperconjugative electron demand in solvolysis reactions,[28] and the magnitude of k_H/k_D is found to vary from 1.1–1.4 depending upon the position of the transition along the reaction coordinate. In contrast, comparable studies at the γ-position are rare,[29] and those which have been reported show that the k_H/k_D ratio is very small; e.g., the ratio observed in the solvolysis of 1-bromobicyclo[3.1.1]-heptane (**5**) was 1.044,[11] and in the 1-substituted adamantyl system 1.041.[29]

As revealed in Table 2 the value of 1.30–1.37 for the γ-isotope effect in the 1-bicyclo[1.1.1]pentyl system is surprisingly large, comparable in magnitude with the largest of the β-isotope effects. We believe that these data confirm the presence of a strong transannular orbital interaction in the 1-bicyclo[1.1.1]pentyl cation and that they are a manifestation of the phenomenon described by structures **37**–**39**. The very large deuterium isotope effect can best be accounted for by invoking a species such as **40** for the transition state for solvolysis of **4**. If this view is correct, and if σ-hyperconjugation does play an important role in stabilizing the transition state for solvolysis of 1-bromobicyclo[1.1.1]pentane, then the rate of reaction of **4**, unlike that of its derivatives **9**, should be dependent upon the nature of the solvent employed. For example, strongly basic solvents have strong hydrogen bonding acceptor properties and would, therefore, be expected to have a stabilizing effect on **40** through electrostatic interactions as depicted in structure **41**. Solvents which are poor hydrogen bonding acceptors, on the other hand, would be incapable of interacting in a similar way and would not be expected to be associated with any significant stabilization. An examination of the role of solvent was, therefore, clearly warranted.



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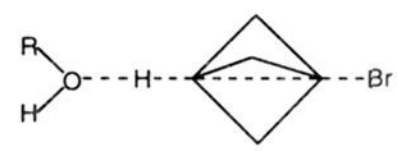


41

Many years ago Grunwald and Winstein[30] noted that *tert*-butyl bromide, the classic substrate used to describe S_N1 reactions, actually has an exalted solvolytic rate in nucleophilic solvents because of a contribution arising from solvent-assisted backside displacement of the leaving group. Over the intervening years, Winstein[30] and others[31] have proposed that caged systems such as the 1- and 2-adamantyl derivatives, in which it is impossible for the solvent to promote backside substitution, are to be preferred as model systems for illustrating true S_N1 processes. The simple expedient that has evolved from these investigations for establishing the mechanism of solvolysis of a particular substance is to plot its solvolysis rate in a range of solvents of varying nucleophilic power against that of the model substance (such as 1-bromoadamantane). If a linear plot is observed it can confidently be assumed that the compound under investigation reacts by a limiting S_N1 mechanism. A dislocation in the plot corresponding to the use of nonnucleophilic solvents, however, would indicate that the compound ionizes with solvent assistance.

In order to test these hypotheses, we have examined the role of solvent in the solvolysis of three of the bromides under investigation, viz., the parent, **4**, as well as 3-*tert*-butyl- and 3-phenylbicyclo[1.1.1]-pentyl bromide (**14** and **16**). The rates of solvolysis of **14** and **16** were measured in 80%, 70%, and 60% aqueous ethanol as well as 70% and 97% aqueous trifluoroethanol. Unlike the other binary solvent mixtures, 97% trifluoroethanol is regarded as having little nucleophilic power. The data are collated in Table 3. Figures 3 and 4 depict the correlations obtained for the bromides **14** and **16**, respectively. The excellent linear plots observed confirm that, in agreement with expectation,

(27) While the enhanced stability of the 1-bicyclo[1.1.1]pentyl cation **8** is not in dispute, the factors responsible for its stabilization are still to be resolved. σ-Hyperconjugation is certainly a strong possibility, as discussed, although C–C hyperconjugation should not be discounted (see ref 12f).

(28) See, e.g.: Shiner, V. J. In *Isotope Effects in Chemical Reactions*; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand-Reinhold: Princeton, 1970; pp 90–159. Sunko, D. E.; Hehre, W. J. *Prog. Phys. Org. Chem.* **1983**, *14*, 205.

(29) Sunko, D. E.; Hirsl-Starcevic, S.; Pollack, S. K.; Heyre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 6163, and references therein.

(30) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846.

(31) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1955**, *78*, 1955. Shiner, V. J.; Dowd, W.; Fisher, R. D.; Hartshorn, S. R.; Kessick, M. A.; Milakofsky, L.; Rapp, M. W. *J. Am. Chem. Soc.* **1969**, *91*, 4838. Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 5741. Raber, D. J.; Neil, W. C.; Dukes, M. D.; Hams, J. M.; Mount, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 8137. Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v R. *J. Am. Chem. Soc.* **1981**, *103*, 5466. Schadt, F. L.; Bentley, T. W.; Schleyer, P. v R. *J. Am. Chem. Soc.* **1976**, *98*, 7667. Harris, J. M.; Mount, D. L.; Smith, M. R.; Neil, W. C.; Dukes, M. D.; Raber, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 8147. Brown, H. C.; Pavindranathan, M.; Chloupek, F. J.; Rothberg, I. *J. Am. Chem. Soc.* **1978**, *100*, 3143. Fry, J. L.; Lancelot, C. J.; Lamlk, M.; Harris, J. M.; Bingham, R. C.; Raber, D. J.; Hall, J. E.; Schleyer, P. v R. *J. Am. Chem. Soc.* **1970**, *92*, 2538.

Table 3. First-Order Rate Constants for Solvolysis of **14**, **16**, **19**, and **23** in Various Binary Mixtures[a]

substrate	solvent	temp, °C	$k \times 10^4$, s^{-1}
14	80E	25	0.297
	70E	25	0.990
	60E	25	2.71
	97T	25	31.0
	70T	25	39.0
16	80E	25	0.037[b]
	70E	25	0.080[b]
	70E	45	0.990
	70E	60	5.35
	60E	25	1.64[b]
	60E	45	2.15
	60E	60	12.1
	97T	25	0.980
	70T	25	1.60
19	97T	25	0.953
23	97T	25	0.000176[b]
		100	0.461
		110	0.934
		121	2.42

[a] Buffered with 1.2 equiv of triethylamine. [b] Extrapolated.

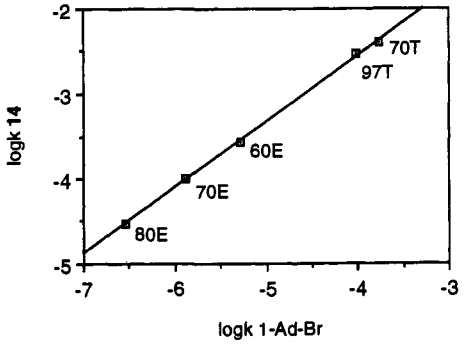


Figure 3. Plot of log k for solvolysis of 3-*tert*-butylbicyclo[1.1.1]pentyl bromide (**14**) against log k for solvolysis of 1-bromoadamantane in various binary mixtures.

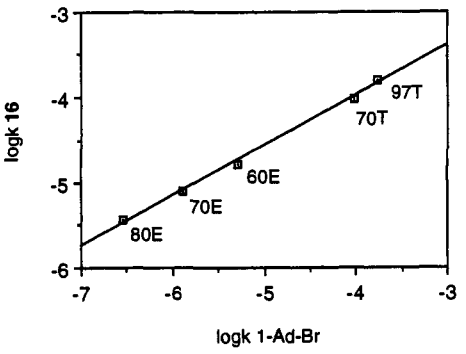


Figure 4. Plot of log k for solvolysis of 3-phenylbicyclo[1.1.1]pentyl bromide (**16**) against log k for solvolysis of 1-bromoadamantane in various binary mixtures.

these bromides solvolyze by the same mechanism as 1-bromoadamantane, i.e., they react by unassisted S_N1 processes.

In contrast, the corresponding plot between 1-bromobicyclo[1.1.1]pentane **4** and 1-bromoadamantane, shown in Figure 5, displays a dislocation similar to that found for *tert*-butyl bromide. This is indicative of an exalted rate of solvolysis of **4** in the nucleophilic/basic solvents, and it supports our contention above that the enhanced rate of **4** can be ascribed to stabilization of the transition state by dispersal of the positive charge in **40** through favorable hydrogen bonding as shown in **41**. This interaction occurs with the better hydrogen bonding acceptors such as aqueous ethanol and is essentially absent in the case of trifluoroethanol.

If this view is correct, then a determination of the Hammett plot of all the bromides (Figure 1, solid line) employing 97% trifluoroethanol as solvent should show a much improved linear fit. In order to limit the investigation to one of manageable but significant scale, we undertook the measurement of the rates of solvolysis of two additional bromides, 3-hydroxymethylbicyclo[1.1.1]pentyl bromide (**19**) and 3-carbomethoxybicyclo[1.1.1]pentyl bromide (**23**), in 97% trifluoroethanol. These substrates were chosen to provide an acceptable extension of the range of σ_I values. The plot of log k versus σ_I for the five bromides, presented in Figure 6, demonstrates that an excellent fit is indeed observed. The linear correlation displayed in Figure 6 lends support to the prediction that the parent bromide **4** does not behave irregularly and that it undergoes an unassisted ionization in the nonnucleophilic solvent. Some years ago we observed[32] an accelerating role of hydrogen in the solvolysis of a series of 4-substituted-bicyclo[2.2.2]octyl sulfonates and attributed this to the effects of dative transannular interaction. A more recent study[33] into the solvolysis of a series of 3-X-substituted bicyclo[3.1.1]heptanes has also revealed that the parent bromide **5** displays deviant behavior in the Hammett plot when dissolved in nucleophilic solvents but that it behaves regularly in trifluoroethanol.

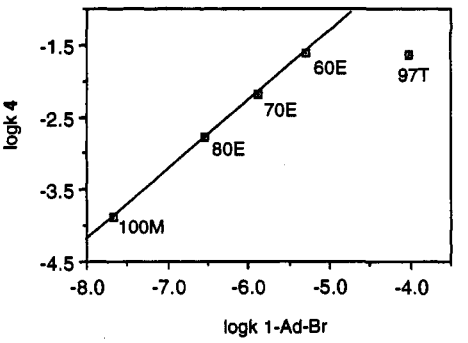


Figure 5. Plot of log k for solvolysis of 1-bromobicyclo[1.1.1]pentane (**4**) against log k for solvolysis of 1-bromoadamantane in various binary mixtures.

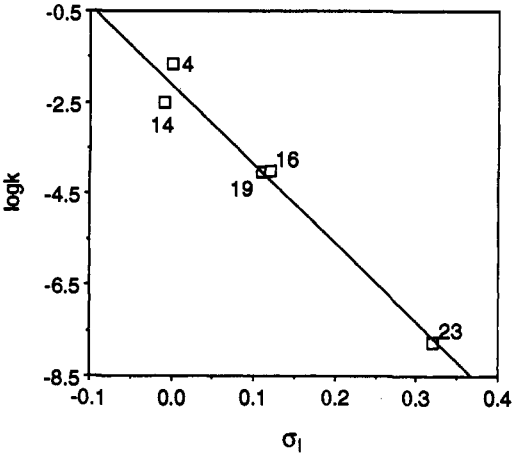


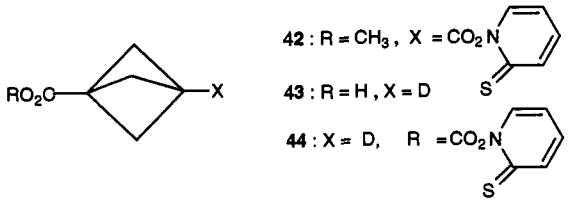
Figure 6. Plot of log k for solvolysis of the bromides **4**, **14**, **16**, **19**, and **23** in 97% trifluoroethanol against σ_I at 25 °C (r = 0.99).

Conclusions

We believe that the results of the substituent effect, the solvent effect, and the deuterium isotopic effect studies presented above provide strong evidence that the mechanism of solvolysis of the series of 1-bromobicyclo[1.1.1]pentanes (**13**–**25**) in protic solvents involves a simple ionization to give the corresponding bridgehead carbocation **10**. Although there is some ambiguity concerning the nature of the primary intermediate produced in the solvolysis

(32) Bielmann, R.; Grob, C. A.; Küry, D.; Yao, G. W. *Helv. Chim. Acta* **1985**, *68*, 2158.
(33) Della, E. W.; Elsey, G. M., unpublished observations.

of the parent bromide **4**, on balance, we believe that the evidence is still in favor of the unrearranged cation **8**. The possibility that either the ring-opened 3-methylenecyclobutyl cation (**7**) or the rearranged bicyclo[1.1.0]butyl-1-carbinyl cation (**35**) is the intermediate produced during ionization of the bromide **4** is less likely because calculations place some fractional positive charge on C3 in each cation, a property which would also be featured in the transition state preceding the cation. If this were extended to the substituted species, then a linear $\log k/\sigma_1$ correlation would not have been observed. Although the 1-bicyclo[1.1.1]pentyl cations (**8** and **10**) possess enhanced thermodynamic stability, they undergo ring-opening to the isomeric cyclobutyl cations before they can be intercepted; as a result the products of solvolysis are found to consist of cyclobutyl derivatives only, arising from solvent capture of the rearranged cation.



Experimental Section

The water, ethanol, methanol, and trifluoroethanol employed for the solvolyses were purified by standard techniques.[34] The solvent mixtures used for the kinetic measurements are designated as follows: 60E, 70E, and 80E refer to aqueous ethanol solvents and were prepared by mixing 60, 70, and 80 vol % ethanol with 40, 30, and 20 vol % water, respectively; 70T and 97T represent 70 and 97 wt % trifluoroethanol mixed with 30 and 3 wt % water, respectively. 100M consists of pure methanol only. Rates of solvolysis of the bromides were measured conductimetrically[18] employing a Philips PW9501 conductivity cell (cell constant 0.79 cm^{-1}). The conductance of solutions was measured with a Philips PW9512/00 conductance bridge and recorded on a BBC SE120 variable speed chart recorder. At least 20 data points were collected for each half-life, and the progress of the solvolyses was followed for 2 half-lives in each case. The first-order rate constants were calculated by a least-squares linear regression analysis of the raw data. Temperature control was maintained (±0.05 °C) with a Julabo PC F18 temperature thermostatted bath. Synthesis of the bromides **13–28** was accomplished as described.[17]

2-Thioxo-1,2-dihydropyridin-1-yl 3-(Methoxycarbonyl)bicyclo[1.1.1]-pentane-1-carboxylate (42). The general method of Barton and his colleagues[35] was employed in this preparation. 3-(Methoxycarbonyl)-bicyclo[1.1.1]pentane-1-carboxylic acid (2.5 g, 14.7 mmol) and 1-hydroxypyridine-2(1H)-thione (1.87 g, 14.7 mmol) were dissolved in dry dichloromethane (40 mL), and the solution cooled to 0 °C under nitrogen. The solution was shielded from light with aluminum foil. Dicyclohexylcarbodiimide (DCC) (3.1 g, 15.0 mmol) was introduced in one portion, and the solution was stirred for 1.5–2 h. Dicyclohexylurea (DCU) was then filtered off and washed with dichloromethane (10 mL). The combined organic solutions were concentrated in vacuo at room temperature yielding the thiohydroxamic ester **42** in high purity and yield (>95%) as a pale yellow-green solid. This could be used directly or further purified by flash chromatography (benzene/dichloromethane 1:1): mp 138–140 °C dec; IR (Nujol) 1799 (CO_2N), 1734 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.78–6.56 (m, 4H), 3.72 (s, 3H), 2.57 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 174.44, 168.86, 164.64, 137.71, 136.90, 135.59, 113.17, 53.63, 51.95, 38.52, 36.24; mass spectrum *m/z* (rel intensity) 279 (M^+, 12.0), 264 (4.0), 220 (6.0), 163 (14), 150 (15.2), 127 (36), 111(100), 78 (50), 67 (95), 55 (65).

3-Deuteriobicyclo[1.1.1]pentane-1-carboxylic acid (43). Decarboxylation of the thiohydroxamic ester **42** (2.0 g,7.2 mmol) dissolved in dry benzene (30 mL) containing Bu_3SnD was effected[36] by heating for 1 h at 60 °C under nitrogen, whilst irradiating with a tungsten lamp (300 W). After carbon dioxide evolution had ceased, the solution was cooled and washed successively with concentrated HCl (2 × 20 mL) and water (20 mL), then dried ($MgSO_4$), and concentrated. Alkaline hydrolysis and standard workup provided the acid **43** (0.59 g, 73%): mp 56–57.5 °C which had spectral properties consistent with those of the protio analog; ^1H NMR ($CDCl_3$) δ 10.4 (brs, 1H (exch D_2O)), 2.15 (s, 6H).

1-Bromo-3-deuteriobicyclo[1.1.1]pentane (9, R = D). The procedure described above was used to convert the acid **43** (2.0 g, 17.7 mmol) into the hydroxamic ester **44** (3.77 g, 96%) [^1H NMR ($CDCl_3$) δ 7.75–6.50 (m, 4H), 2.34 (s, 6H)]. The ester **44** (3.0 g, 13.5 mmol) was dissolved in 1-bromo-1-chloro-2,2,2-trifluoroethane (20 mL), and the solution was subjected to irradiation from a tungsten lamp (300 W) under a nitrogen atmosphere for 1 h.[36] The solution was then cooled, washed successively with cold concentrated HCl (10 mL) and saturated sodium bicarbonate solution (10 mL), and then dried ($MgSO_4$), and the solvent was carefully removed by distillation through a Vigreux column. Distillation (Kugelrohr, 100 °C) of the residue afforded the deuterated bromide **9**, X = D (1.2 g, 60%), which had spectral properties in agreement with those[9] of the unlabeled isomer (**4**): ^1H NMR ($CDCl_3$) δ 2.25 (s).

General Procedure for Product Analyses. The bromide **9** was dissolved in the appropriate solvent buffered with triethylamine (1.2 equiv) and heated at the temperature indicated in Table 4 for the time designated. The solution was then cooled to ambient temperature and extracted with ether (5 × 15 mL) and then dried ($MgSO_4$). Careful removal of the solvent in vacuo afforded the crude product which was purified by distillation and analyzed by GC, NMR, and GCMS. The yields of the products **12** are displayed in Table 4.

Table 4. Solvolysis Products of Some 3-X-Substituted Bicyclo[1.1.1]pentyl Bromides in 50% Aqueous Mixtures[a]

substrate	solvent	temp, °C	time	product (yield)
4	THF/H_2O	35	2 h	**12**: R = H (90%)
14	THF/H_2O	70	3 h	**12**: R = *t*-Bu (83%)
15	$dioxane/H_2O$	100	2 days	**12**: R = COOH (82%)
16	$dioxane/H_2O$	100	1 day	**12**: R = C_6H_5 (77%)
19	THF/H_2O	70	3 h	**12**: R = CH_2OH (92%)
20	THF/H_2O	70	1 day	**12**: R = CH_2OAc (80%)
22	THF/H_2O	70	5 days	**12**: R = CH_2Cl (91%)
23	$dioxane/H_2O$	100	3 days	**12**: R = $COOCH_3$ (92%)

[a] Buffered with 1.2 equiv. of triethylamine.

Physical Data for the Products 12. 3-Methylene-1-cyclobutanol (12, R = H). Physical properties were in agreement with those reported for the known compound:[37] ^1H NMR ($CDCl_3$) δ 5.1 (brs, 1H (exch D_2O)), 4.93–4.74 (q, 2H 0, 4.37–4.18 (q, 1H, *J* = 6.7 Hz), 3.16–2.44 (m, 4H).

1-*tert*-Butyl-3-methylene-1-cyclobutanol (12, R = *t*-Bu): bp (Kugelrohr) 110 °C/ 20 mm; IR (neat) 3600–3100 (OH), 1677 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.93–4.74 (q, 2H), 3.23–2.10 (m, 4H), 1.70 (brs, 1H (exch D_2O)), 0.92 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 141.67, 107.48, 77.63, 41.61, 35.97, 24.11; mass spectrum *m/z* (rel intensity) 140 (M^+, 15), 125 (90), 97 (30), 83 (28), 67 (33), 57 (55), 55 (100); HRMS calcd for $C_9H_{16}O$ 140.1201, found 140.1207. Anal. Calcd for $C_9H_{16}O$: C, 77.1; H, 11.5. Found: C, 77.2; H, 11.8.

1-Phenyl-3-methylene-1-cyclobutanol (12, R = Ph): bp (Kugelrohr) 120 °C/1 mm; IR (neat) 3600–3100 (OH), 1681 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.60–7.20 (m, 5H), 5.0–4.82 (q, 2H), 3.15–2.97 (m, 4H), 2.80–2.67 (m, 1H (exch D_2O)); ^{13}C NMR ($CDCl_3$) δ 145.95, 140.80 (C_3), 128.29, 127.04, 124.60, 107.97, 72.92, 47.67; mass spectrum *m/z* (rel intensity) 160 (M^+, 5), 159 (10), 145 (10), 115 (12), 105 (100), 91 (12), 77 (60); HRMS calcd for $C_{11}H_{12}O$ 160.0888, found 160.0886. Anal. Calcd for $C_{11}H_{12}O$: C, 82.5; H, 7.5. Found: C, 82.4; H, 7.4.

1-(Hydroxymethyl)-3-methylene-1-cyclobutanol (12, R = CH_2OH): bp (Kugelrohr) 130 °C/1 mm; IR (neat) 3600–3100 (OH), 1683 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.0–4.78 (q, 2H), 3.80–3.50 (bs, 2H (exch D_2O)), 3.60 (s, 2H), 2.78–2.66 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 139.99, 108.29, 71.40, 67.56, 42.74; mass spectrum *m/z* (rel intensity) 114 (M^+, 2), 95 (13), 83 (70), 67 (25), 55 (100); HRMS calcd for $C_6H_{10}O_2$ 114.0681, found 114.0674. Anal. Calcd for $C_6H_{10}O_2$: C, 63.1; H, 8.8. Found: C, 63.0; H, 8.5.

1-(Acetoxymethyl)-3-methylene-1-cyclobutanol (12, R = CH_2OAc): bp (Kugelrohr) 105 °C/10 mm; IR (neat) 3600–3100 (OH), 1735 (C=O), 1681 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.99–4.81 (q, 2H), 4.14 (s, 2H), 2.88 (brs, 1H (exch D_2O)), 2.80–2.72 (m, 4H) 2.10 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 171.62, 139.17, 108.51, 70.16, 69.29, 43.18, 20.81; mass

(34) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: U.K., 1983.
(35) Barton, D. H. R.; Ozbalik, N.; Vacher, B. *Tetrahedron* **1988**, *44*, 7385.
(36) Della, E. W.; Tsanaktsidis, J. *Aust. J. Chem.* **1986**, *39*, 2061.
(37) Applequist, D. E.; Nickel, G. W. *J. Org. Chem.* **1979**, *44*, 321.

spectrum *m/z* (rel intensity) 125 (20), 114 (14), 101 (84), 83 (77), 73 (81), 55 (100). Anal. Calcd for $C_8H_{12}O_2$: C, 61.5; H, 7.7. Found: C, 61.4; H, 7.7.

1-(Chloromethyl)-3-methylene-1-cyclobutanol (12, R = CH_2Cl): bp (Kugelrohr) 120 °C/20 mm; IR (neat) 3600–3100 (OH), 1675 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.0–4.78 (q, 2H), 3.70 (s, 2H), 2.90–2.64 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 138.74, 108.84, 70.97, 52.77, 43.56; mass spectrum *m/z* (rel intensity) 132 (M^+, 3), 111 (12), 96 (29), 83 (30), 71 (32), 57(32), 55 (100); HRMS calcd for C_6H_9OCl 132.0342, found 132.0351. Anal. Calcd for C_6H_9OCl: C, 54.3; H, 6.8. Found: C, 54.1; H, 6.9.

1-(Methoxycarbonyl)-3-methylene-1-cyclobutanol (12, R = CO_2Me): Physical properties were in agreement with those reported for the known compound:[16] mp 39–40 °C (lit.[16] mp 38.5–39.5 °C); ^1H NMR ($CDCl_3$) δ 5.01–4.92 (q, 2H), 3.69 (s, 3H) 3.27 (bs, 1H (exch D_2O)), 3.20–2.83 (m, 4H).

1-Hydroxy-3-methylenecyclobutane-1-carboxylic acid (12, R = CO_2H): ^1H NMR ($CDCl_3$) δ 6.20–5.60 (brs, 2H (exch D_2O)), 5.04–4.90 (q, 2H), 3.52–2.74 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 179.91, 138.85, 108.35, 70.86, 44.91. Conversion of the product into the corresponding ester with diazomethane gave **12**, X = CO_2CH_3 (82%), which had physical properties consistent with those of the known compound.[16]

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