Preparation and Solvolysis of 2-Alkynyl-, 2-Cyclopropyl-, and 2-Arylallyl Alcohol Tosylates. 3.[1] Relationship Among Allyl and Cyclopropyl Cations

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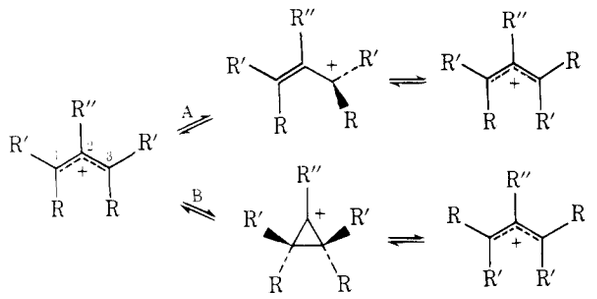
2-Phenylethynyl-, 2-cyclopropyl-, and 2-phenylallyl tosylates **3**, **4**, and **5** have been prepared. Their products of solvolysis in various solvents and their rates of ethanolysis were compared with those of 1-phenylethynyl-, 1-cyclopropyl-, and 1-phenylcyclopropyl tosylates **6**, **7**, and **8**, respectively. The theoretical expectations of the ring closure of 2-substituted allyl cations with efficient electron releasing groupings into stabilized cyclopropyl cations have not been proven experimentally by our results, but a limitation of the anchimeric assistance of the double bond in the solvolysis of allyl tosylates seems to result from the presence of such substituents. The solvolyses of 1-cyclopropyl- and 1-phenylcyclopropyl tosylates **7** and **8** have been reinvestigated.

The stereomutation of allyl cations can occur by two mechanisms involving either simple rotation about one of the C–C bonds (path A) or disrotatory closure to a cyclopropyl cation followed by disrotatory opening in the opposite sense (path B).[2]



Path A would be favored by carbocation stabilizing substitutents R, R′ at C_1 (or C_3), whereas path B would be favored by carbocation stabilizing substituents R″ at C_2.

Although all allyl cation stereomutations observed up to now have the substitution pattern required to proceed via path A and in fact have done so,[2-4] theoretical expectations however support path B.

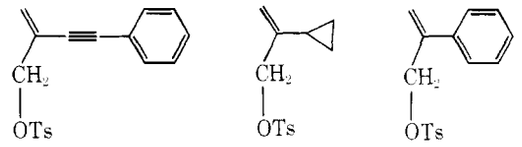
For example, calculations indicate that the 2-methylallyl cation (R = R′ = H; R″ = CH_3) should stereomutate through the 1-methylcyclopropyl cation since methyl substitution favors path B over path A by 18.5 kcal mol^{-1}.[4]

Thus, it can be expected that electron releasing substituents R″, which stabilize carbocations to a greater extent than methyl, might even render the 1-substituted cyclopropyl cations **1** more stable than their 2-substituted allyl counterparts **2**.[4]

1 **2**

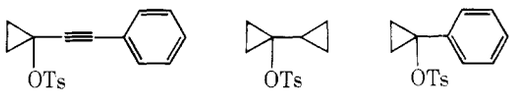
The reactions involving such stabilized cyclopropyl cations **1** (R″ = aryl,[5] cyclopropyl,[6,7] alkenyl,[8] alkynyl[1]) are known to proceed with only partial ring opening into allyl cations (**1** → **2**); however, no closure of 2-substituted allyl cations to 1-stabilized cyclopropyl cations has been reported yet (**2** → **1**).

We report here the solvolysis data of 2-substituted allyl tosylate derivatives **3** (R″ = –C≡CC_6H_5), **4** (R″ = cyclopropyl), and **5** (R″ = aryl) which have been investigated, in order to determine experimentally the effect of an efficient electron releasing substituent on the stabilization of the intermediate allyl cation **2**, and the eventual propensity of such 2-substituted allyl cations to undergo the ring closure into stabilized cyclopropyl cations **1**.



3 **4** **5**

The behavior of these 2-substituted allyl derivatives has been examined and compared to the behavior of their cyclopropyl counterparts **6**, **7**, and **8**, respectively.



6 **7** **8**

Results and Discussion

Preparation of the 2-(Phenylethynyl)allyl Tosylate 3. Despite several attempts, we did not succeed in obtaining the allylic halogenation[9-11] or oxidation[9] of 2-methyl-4-phenyl-1-buten-3-yne (readily available from phenylacetylenemagnesium bromide and acetone). Then, the enynol **9** was synthetized from the tetrahydropyranyl ether of the *n*-butylglycolic acid ester **10**. Heating at 100 °C with piperidine **10** gave the amide **11**; the addition of phenylethynylmagnesium bromide provided the ketone **12** which underwent the Wittig reaction with methylenephosphorane to give, after treatment in acidic methanol, the expected enynol **9**. The normal pyridine procedure[12] did not lead to the tosylate derivative of enynol **9**; upon treatment at 0 °C with an equivalent of *n*-BuLi followed by the addition at −40 °C of tosyl chloride, the enynol **9** was finally converted into the expected tosylate **3**.

The syntheses of the 1-(phenylethynyl)-1-cyclopropanol

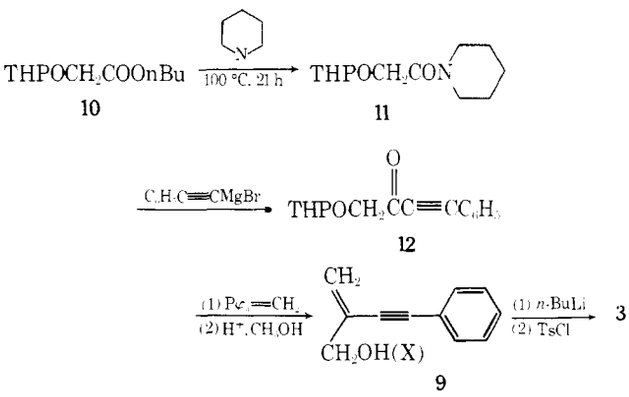


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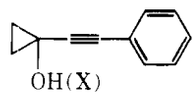
Table I. Solvolysis Products (%) of the Cyclopropyl Tosylates 6, 7, and 8 and Allyl Tosylates 3, 4, and 5, Comparatively[a]

	Registry no.		Temp, °C	Reaction time, h	 13. 22. 29	9. 21. 30	Others[d]
6[b]	57951-60-7	Acetone–H_2O	70.0	48	73.5	26.5	
		(60:40)	70.0	120	69	25	6
		EtOH–H_2O	70.0	40	85[c]	15[c]	
		(50:50)					
		Trifluoroethanol	70.0	8	52	48	
			70.0	19	50	50	
3	66303-62-6	Acetone–H_2O	70.0	1.5		60	40
		(60:40)	70.0	60		57	43
		EtOH–H_2O	70.0	40		58[c]	42
		(50:50)					
		Trifluoroethanol	70.0	6		36	64
			70.0	19		37	63
7	32364-40-2	Acetone–H_2O, CO_3Ca	25.0	24	50	26	24
		(50:50)					
		Acetone–H_2O[h]	25.0	26	67		33[e]
		(50:50)					
		EtOH–H_2O, CO_3Ca	25.0	24	68.5[c]	31.5[c]	
		(50:50)					
		Trifluoroethanol	25.0	48	42.5[g]	19.5[g]	38
4	66303-63-7	Acetone–H_2O, CO_3Ca	25.0	60		90	10[f]
		(50:50)					
		Acetone–H_2O[h]	25.0	60			100
		(50:50)					
		EtOH–H_2O, CO_3Ca	50.0	10		100[c]	
		Trifluoroethanol	50.0	48		60[g]	40
		Hexafluoro-2-propanol	50.0	48		45	55
8	4382-80-3	Acetone–H_2O, CO_3Ca	50.0		23.5	76.5	
		(50:50)					
		Acetone–H_2O[h]			22	63	15
		(50:50)					
		EtOH–H_2O, CO_3Ca			32[c]	68[c]	
		Hexafluoroisopropyl alcohol				49	51
5	66303-64-8	Acetone–H_2O, CO_3Ca	50.0	15		89	11
		(50:50)					
		Acetone–H_2O[h]	50.0	15		91	9
		(50:50)					
		EtOH–H_2O, CO_3Ca	50.0	15		100[c]	
		(50:50)					
		Hexafluoro-2-propanol	50.0	24		43	57

[a] If not specified, buffered with 1.1 equiv of triethylamine. [b] In part from ref 1. [c] As a mixture of the alcohol and its ethyl ether. [d] Mainly as nonidentified polymeric material. [e] With a trace (<5%) of cyclopropyl ethyl ketone. [f] Mainly as starting tosylate. [g] Low yield due to the formation of very volatile fluoro ethers. [h] Unbuffered.

(13) and 1-(phenylethynyl)-1-tosyloxycyclopropane (6) have been reported previously.[1]



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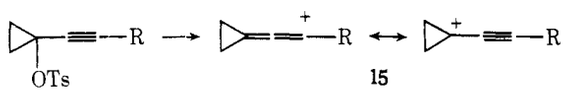
Solvolysis of 2-(Phenylethynyl)allyl Tosylate 3 and of 1-(Phenylethynyl)-1-tosyloxycyclopropane (6), Comparatively. Our investigation of the chemistry of the cyclopropyl cation 1 began with the solvolysis of 1-alkynylcyclopropyl tosylates 14; the results were clearly consistent with a S_Ni' ionization process involving anchimeric assistance of the triple bond and formation of the mesomeric cation 15,



14 15

highly stabilized by delocalization of the positive charge over the three-carbon system.[1]

However, as evidenced by product distribution and kinetic data, the formation of 15 as an intermediate in the solvolysis of 14 appeared to be strongly dependent upon the nature of the substituent R and entailed an efficient electron-releasing substituent at the allenyl (or propargyl) end.

Thus for instance, the only products of aqueous ethanolysis of 14 (R = CH_3) were allylic derivatives from total cyclopropane ring opening; while only partial or no ring opening at all was observed from 14 (R = cyclopropyl) and 14 (R = *p*-anisyl), yielding 90 and 100% of unrearranged cyclopropanols (or derivatives), respectively.[1]

In order to compare the data, the tosylates 3 and 6 were solvolyzed in solvents of different ionizing power and nucleophilicity, buffered with 1.1 equiv of triethylamine to avoid any acid-catalyzed rearrangement of the products[6] and at a temperature low enough (i.e., 70 °C) to avoid the subsequent homoketonization of the cyclopropanols.[1,13]

As shown by the product distribution listed in Table I, the allylic tosylate 3 did not undergo the expected ring closure into the cyclopropanol (or derivatives) 13 (R = $-C{\equiv}CC_6H_5$) but merely yielded, upon solvolysis, the unrearranged allylic alcohol 9 and undefined polymeric compounds. The lack of 13 (or of its derivatives) in the crude product of the solvolysis of 3 was carefully checked by GLC, TLC, and spectroscopic

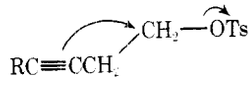
Table II. Solvolysis Rates of the Cyclopropyl Tosylates and Allyl Tosylates, Comparatively

	Solvent[a]	Temp, °C	$k^b \times 10^4$ s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	m
6[c]	50E	70.0	0.83 ± 0.02	19.67	−20.10	0.58
3	50E	70.0	9.91 ± 0.02	25.81	2.65	0.67
	50E	60.0	3.08 ± 0.05			
	60E	70.0	4.82 ± 0.02			
7[d]	50E	70.0	2915			
	80E	35.0	4.23 ± 0.01	21.08	−5.60	0.77
4	50E	70.0[f]	173.99			
	50E	60.0	56.02 ± 0.04	25.10	6.29	0.49
	50E	50.0	18.17 ± 0.02			
	60E	60.0	33.32 ± 0.03			
8	50E	70.0	86.55 ± 0.07	23.23	−0.53	0.37[g]
	50E	60.0	30.19 ± 0.05			
	60E	70.0	58.11 ± 0.08			
5	50E	70.0	37.84 ± 0.04	20.23	−10.93	0.30[g]
	50E	60.0	15.07 ± 0.04			
	60E	70.0	27.38 ± 0.03			
37[e]	100A[e]	100.1	0.13 ± 0.02	28.7	−4.6	
38[f]	70D[f]	50.0	1.06	19.3	−13.82	

[a] 50E refers to 50% aqueous ethanol v/v before mixing. [b] The errors reported were determined by means of a least-squares computer program. [c] From ref 1. [d] From ref 7. [e] From ref 26; 100A refers to 100% anhydrous acetic acid. [f] From ref 33; 70D refers to 70% aqueous dioxane. [g] The m values for allyl chloride and benzylic tosylate solvolysis are 0.40 and 0.39, respectively, in aqueous ethanol.[31]

analysis. Under the same conditions, however, the tosyloxycyclopropane **6** was reported to solvolyze with the formation of a mixture of the unrearranged cyclopropanol **13** and of the open ring allylic derivative **9**.[1] This result shows clearly that whatever the ionizing power and the nucleophilicity of the solvent the mesomeric carbocation **15** is not involved in the solvolysis of the allylic tosylate **3**.

On the other hand, these results can appear consistent with a triple bond participation. Indeed, such an anchimeric assistance has been previously reported for homopropargylic tosylates; thus, the cyclopropylidenemethylcation **17** was



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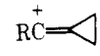
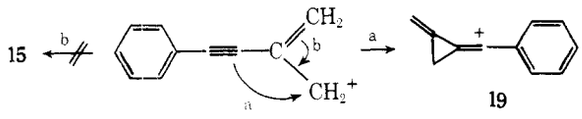


17

proposed as an intermediate in the homopropargylic rearrangement of the tosylate **16**.[14]

In this way, the triple bond participation in the solvolysis of the tosylate **3** would involve the intermediate vinyl cation **19**. As the parent 1,2-dimethylenecyclopropane itself was reported to be a very labile small ring compound which undergoes polymerization readily at −10 °C,[15] it does not appear unlikely that the homopropargyl rearrangement of **3** led, via cation **19**, to undefined polymeric compounds.



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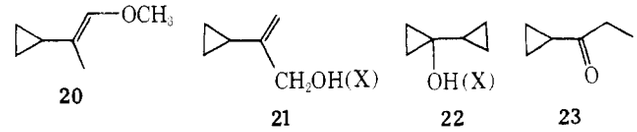
As shown in Table II the solvolysis rates of the tosylates **3** and **6** in aqueous ethanol were measured by automatic continuous titration at pH 7.0. It seems likely that the homopropargylic assistance of the triple bond (path a) reduces, in stabilizing by charge delocalization the intermediate carbocation **18**, the anchimeric assistance of the allylic double bond (path b) and thereby prevents the expected cyclization of ion **18** into the mesomeric carbocation **15**.

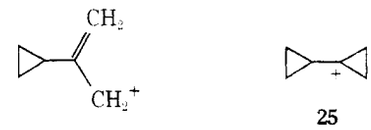
Preparation of the 2-Cyclopropylallyl Tosylate 4 and of the 1-Cyclopropylcyclopropyl Tosylate 7. The addition of the methoxymethylenetriphenylphosphorane on the cyclopropyl methyl ketone provided the enol ether **20**, which on addition of singlet oxygen[16] and hydride reduction led to the 2-cyclopropylallyl alcohol **21**. Inert to the normal pyridine procedure,[12] the allylic alcohol **21** was converted into the tosylate **4** upon treatment with n-BuLi and tosyl chloride at −40 °C.



20 21 22 23

The reaction of the hemiketal of cyclopropanone,[17] now readily available,[1] with 2 equiv of cyclopropylmagnesium bromide provided the 1-cyclopropylcyclopropanol (**22**) in high yield, which was converted into the tosylate **7** by the normal pyridine procedure.[12]

Solvolysis of 2-Cyclopropylallyl Tosylate 4 and of 1-Cyclopropyl-1-tosyloxycyclopropane (7), Comparatively. Taking into account the high effectiveness of the cyclopropane ring for stabilizing an adjacent carbocation,[18] the allyl tosylate **4** was solvolyzed in order to determine the propensity of the allyl cation **24** to undergo the ring closure (**24** → **25**).



24 25

Furthermore, an apparently facile acid-catalyzed rearrangement of the 2-cyclopropylallyl alcohol **21** into the cyclopropyl ethyl ketone **23** had been recently claimed by Howell and Jewett.[7] So, they have reported that the buffered ($CaCO_3$) solvolysis of **7** afforded a mixture of allylic and cyclopropyl alcohols **21** and **22**, while unbuffered (TsOH) solvolysis yielded a mixture of alcohol **22** and ketone **23**. But, when subjected to the conditions of the unbuffered solvolysis, by addition of TsOH, the mixture of alcohols **21** and **22** was converted to the same mixture of products (**22** + **23**), obtained directly from the unbuffered solvolysis.

To explain the acid rearrangement of the allylic alcohol **21** into the ketone **23**, the ring closure of carbocation **24** → **25** could then be envisaged.

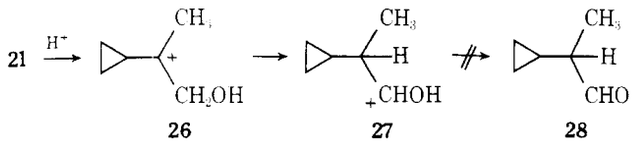
In view of this experimental fact and of the theoretical expectations[2-4] it appeared to us of interest to undertake this investigation. Thus, in order to compare the data, the tosylates **4** and **7** were solvolyzed in solvents of different ionizing power and nucleophilicity. As shown by the product distribution, listed in Table I, the allyl tosylate **4** solvolysis offered no detectable (GLC, NMR) amount of the product expected from the ring closure, i.e., 1-cyclopropylcyclopropanol (**22**) but only 2-cyclopropylallyl alcohol **21** (or its derivatives) even with a solvent of high ionizing power and low nucleophilicity such as 1,1,1,3,3,3-hexafluoroisopropyl alcohol.[19] Under the same conditions however, the cyclopropyl tosylate **7** solvolysis yielded a mixture of the unrearranged 1-cyclopropylcyclopropanol (**22**) and of the allylic alcohol **21** from ring opening.

The lack of cyclopropanol **22** in the solvolysis products of the allylic tosylate **4** shows clearly that, in spite of its very effective carbocation stabilizing power,[18] the cyclopropane ring, as substituent at C_2 of the allyl cation **2**, is not able to induce the expected ring closure **24** → **25**.

Moreover, we found the unbuffered solvolysis of the cyclopropyl tosylate **7** offers only a trace of ketone **23** (from IR and NMR spectroscopy of the crude solvolytic product). Furthermore, when subjected to the conditions of the unbuffered solvolysis, i.e., mixed with aqueous acetone containing either 0.1 or 1 equiv of *p*-toluenesulfonic acid, a pure sample of the 2-cyclopropylallylic alcohol **21** does not undergo the rearrangement into cyclopropyl ethyl ketone (**23**), as claimed by Howell and Jewett,[7] but yielded only undefined heavy alcoholic compounds, where cyclopropane rings are still present.

The reaction was easily followed by NMR, using a mixture of D_2O–deuterioacetone as solvent, containing 1 equiv of TsOH; after 45 min at 25 °C the signals of the olefinic protons of **21** around δ 4.60–4.82 ppm nearly vanished while the expected characteristic signals of the protons of the ketone **23** (i.e., a quartet around δ 2.30–2.67 ppm and a triplet around δ 0.87–1.15 ppm) were not detected. It must be emphasized that the cyclopropyl ethyl ketone (**23**) is really stable in acidic medium;[6] so, treated under the same conditions, a sample of ketone **23** was recovered unaltered and no measurable H–D exchange was detected.

Thus, contrary to the claim of Howell and Jewett[7] a revision of the generally accepted mechanism for the homoketonization of cyclopropanols[13] does not seem to be required. On the other hand, Mc Kinney and So have reported that the protonation, in acid solution, of the double bond of the 2-phenylallyl alcohol led to 2-phenylpropionaldehyde;[20] in the same way, the protonation of the double bond of **21** would lead, via carbocations **26** and **27**, to 2-cyclopropylpropionaldehyde (**28**).

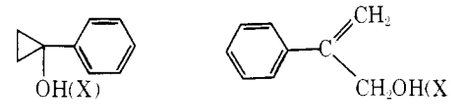


26 27 28

The lack of aldehyde **28** was readily checked (NMR, IR) either in the acid solution of allylic alcohol **21** or in the unbuffered solvolysis products of the tosylates **4** and **7**.

The solvolysis rates of the tosylates **4** and **7** in aqueous ethanol were measured by automatic continuous titration at pH 7.0, and the activation parameters were calculated as shown in Table II. These results confirm that the 1-cyclopropylcyclopropyl cation **25** is not involved in the solvolysis of the allyl tosylate **4**, i.e., the expected ring closure **24** → **25** did not occur, and provide a straightforward demonstration of the higher efficiency of the cyclopropane ring over the double bond to stabilize an adjacent electron deficiency.

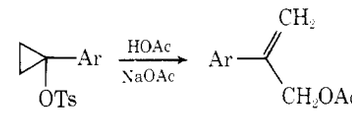
Preparations of the 1-Phenylcyclopropyl Tosylate 8 and of the 2-Phenylallyl Tosylate 5. The reaction of the hemiketal of cyclopropanone[1,17] with 2 equiv of phenylmagnesium bromide provided the 1-phenylcyclopropanol **29** in high yield. The oxidation of α-methylstyrene with selenium dioxide in acetic acid–acetic anhydride and reduction of the acetate ester with lithium aluminum hydride led to the 2-phenylallyl alcohol **30**.[20,21]



29 30

The cyclopropanol **29** was converted into the tosylate **8** by the normal pyridine procedure;[12] while the allylic alcohol **30** was converted into the tosylate **5** upon treatment with *n*-BuLi and tosyl chloride at −40 °C.

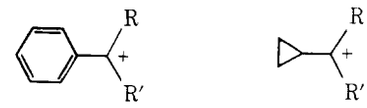
Solvolysis of 2-Phenylallyl Tosylate 5 and of 1-Phenyl-1-tosyloxycyclopropane (8), Comparatively. It has been reported by Depuy et al. that 1-arylcyclopropyl *p*-toluenesulfonates **31** readily undergo solvolysis in dry acetic acid–sodium acetate solution.[22]



31 32

The products of the solvolysis were allyl acetates **32** and no 1-arylcyclopropyl acetates were detected, although stable to the reaction conditions. A concerted process, with disrotatory ring opening occurring in the transition state of the reaction, was put forward to take into account these solvolysis data.[13,22] Steric or direct conjugative interactions were invoked to explain the few examples of limited ring opening reported in the solvolysis of 1-arylcyclopropyl tosylates.[5]

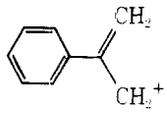
Disparity in the relative abilities of phenyl and cyclopropyl groups to stabilize an empty p orbital on an adjacent carbocation center were reported in the literature. Thus, for example, from ^{13}C shielding measurements Olah has concluded that the aromatic grouping is far superior to the cyclopropane ring in stabilizing a carbocation.[23] This stipulation is however at odds with the formation rates of the tertiary carbocations **33** and **34** determined by Brown from solvolysis data.[24]



33 34

In fact, recent combined experimental and theoretical investigatons have clearly depicted, in the lack of steric inhibition of conjugation, the phenyl group as the more effective stabilizing substituent by 20 kcal/mol for a primary carbocation (R = R′ = H) and roughly by 10 kcal/mol for a secondary cation (R = H; R′ = CH_3), while in reverse the Walsh orbitals of cyclopropane are slightly superior (0.8 kcal) to the phenyl π system in stabilizing a tertiary carbocation center (R = R′ = CH_3).[25]

In view of these results and within the framework of our investigation it appears to us of interest to reexamine the solvolytic behavior of 1-phenylcyclopropyl tosylate (**8**) in other solvents than acetic acid, in order to compare the stabilizing effect of the phenyl and cyclopropane rings to the cyclopropyl carbocations **36** and **25**, respectively. On the other hand, the solvolytic behavior of 2-phenylallyl tosylate **5** was investigated in order to determine the propensity of the carbocation ring closure (**35** → **36**).



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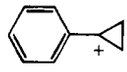

36

As shown by the product distribution, listed in Table I, the 1-phenylcyclopropyl tosylate (**8**) solvolyzes with the formation of a mixture of the unrearranged cyclopropanol (or ether derivatives) **29** (R = C_6H_5) and of the open ring allylic derivatives **30.** As expected, the electron donating effect of the phenyl ring is effective in stabilizing the electron deficiency of the cyclopropyl carbocation **36** and, as a matter of fact, in limiting the opening of the cyclopropane ring.

On the other hand, the lack of cyclopropanol **29** in the solvolysis products of the 2-phenylallyl tosylate **5** confirms our previous findings that neither the σ bonds of the cyclopropane ring itself (vide supra) nor the electron-donating power of the π phenyl system are efficient enough to favor the expected ring closure: allyl cation **35** → cyclopropyl cation **36.**

The comparison of the solvolysis product ratios of unrearranged cyclopropanols/open ring allyl derivatives (e.g., 68.5/31.5 and 32/68 in aqueous ethanol, respectively) listed in Table I shows clearly that the cyclopropane ring is more effective than the phenyl group in stabilizing the cyclopropyl cation. These results are confirmed by the kinetic data listed in Table II. Thus, the 1-phenylcyclopropyl tosylate reacted 3×10^{-2} times slower than the 1-cyclopropylcyclopropyl tosylate (**7**).

Conclusion. The m values listed in Table II, which are a measure of the sensitivity of the substrates to changes in solvent ionizing power Y,[27] fall in the range normally found for k_s and k_Δ processes.[28] From the low propensity of the parent cyclopropyl tosylate itself to changes in solvent nucleophilicity, it has been reported that the solvolyses of cyclopropyl derivatives are mainly k_Δ processes (m = 0.508) where the electrons from the breaking cyclopropane bond take the place of the attacking nucleophile.[26] Such an anchimeric assistance can be provided, however, by an efficient electron releasing substituent and thereby the ring opening of the cyclopropyl moiety is reduced, or even suppressed totally.[1,6,7]

The anchimeric assistance of the substituent seems to be effective too in the solvolysis of the allyl tosylates **3, 4,** and **5** but, unfortunately, this k_Δ process has the effect of limiting by further charge delocalization the assistance of the allylic double bond and thereby the expected ring closure in stabilizing the intermediate carbocations **18** by homopropargylic type assistance,[14] **24** by homocyclopropylcarbinyl type assistance,[29] and **35** by phenonium type assistance.[30]

Although the formation of stabilized cyclopropyl cations has been proved to occur in the solvolysis of suitably substituted cyclopropyl derivatives and the ^{13}C shielding measurements of a cyclopropyl cation have even been reported recently by Olah et al.,[32] the theoretical expectations of the 2-substituted allyl cation ring closure **2** → **1** have not been proven experimentally.

Experimental Section

2-Tetrahydropyranyl Ether Glycolamide (11). A solution of 10.8 g (0.05 mol) of n-butyltetrahydropyranyl glycolate and 16 mL of piperidine was heated at 100 °C. The reaction was followed by IR; after 21 h at 100 °C the ester carbonyl stretching at 1760 cm^{-1} completely disappeared and the amide band appeared at 1655 cm^{-1}. The piperidine excess was removed under vacuum; distillation at reduced pressure of the crude product gave 7.5 g (70%) of **11:** bp 110 °C (0.035 mm); IR (neat) $\nu_{C=O}$ 1655 cm^{-1}; NMR (CCl_4) δ 1.65 (m, 12 H), 3.45 (m, 6 H), 4.10 (d, 2 H), and 4.62 (m, 1 H).

4-Phenyl 1-Tetrahydropyranyl Ether 3-Butyn-2-one (12). To 12.31 g (0.06 mol) of phenylacetylenemagnesium bromide[34] in 50 mL of tetrahydrofuran was added with stirring at room temperature a solution of 7.5 g (0.033 mol) of glycolamide **11** in 20 mL of tetrahydrofuran. The mixture was stirred for 1 h at room temperature and heated under reflux for 2 h. The cold mixture was poured on a mixture of 60 mL of sulfuric acid (1 N) and 100 g of crushed ice and extracted with ether. The organic layer was washed with water, dried over magnesium sulfate, and concentrated to yield a light yellow oil. Distillation at reduced pressure gave a mixture of piperidine and phenylacetylene [bp 30–40 °C (10 mm)] and 2.9 g of glycolamide **11** [bp 110 °C (0.035 mm)]. The residue (8 g) was dissolved in a minimum amount of diethyl ether and placed on a silica gel column (200 g of silica gel 70–230 mesh) and eluted with 25 vol % diethyl ether in pentane, giving 1 g of unidentified product, 0.6 g of glycolamide **11,** 1.1 g of 4-phenyl-2-oxo-3-propynol, 0.6 g of N-(2-hydroxyacetyl)-piperidine, and 3.7 g (46%) of 4-phenyl 1-tetrahydropyranyl ether 3-butyn-2-one (**12**): IR (neat) 2210 ($\nu_{C\equiv C}$) and 1690 cm^{-1} ($\nu_{C=O}$); NMR (CCl_4) δ 1.15 (m, 6 H), 3.55 (m, 2 H), 4.30 (s, 2 H), 4.80 (m, 1 H), and 7.50 (m, 5 H).

2-(Phenylethynyl)allyl Alcohol 9. To 2.93 g (8.2 mmol) of methyltriphenylphosphonium bromide suspended in 60 mL of dry benzene was added with stirring 0.92 g (8.2 mmol) of potassium *tert*-butylate, at room temperature, under dry N_2. The mixture was refluxed for 1 h. The yellow solution was then cooled to 0 °C and a solution of 1 g (4.1 mmol) of butynone **12** in 10 mL of benzene was added. The yellow color was discharged and the solution was allowed to warm to room temperature and stirred for a further 2 h and then refluxed for 30 mn. The resulting deep-red mixture was washed with water, dried over magnesium sulfate, and concentrated. The residue was chromatographed on silica gel eluting with ether–light petroleum (20:80) to give an enyne (850 mg, 86%): IR (neat) 2220 ($\nu_{C\equiv C}$) and 1673 cm^{-1} ($\nu_{C=C}$); NMR (CCl_4) δ 1.60 (m, 6 H), 3.60 (m, 2 H), 4.15 (m, 1 H), 4.80 (m, 1 H), 5.60 (m, 1 H), and 7.30 (m, 5 H).

A solution of 800 mg of the enyne in 5 mL of methanol containing 2 drops of 1 N sulfuric acid was stirred at room temperature for 15 min. The solution is then washed with sodium bicarbonate and water and dried over magnesium sulfate, and the methanol was removed under vacuum. Fractional distillation of the crude material yielded 0.5 g (97%) of the 2-(phenylethynyl)allyl alcohol **9:** bp 96–98 °C (0.008 mm); IR (CCl_4) 3630 and 3350 (ν_{OH}), 2210 ($\nu_{C\equiv C}$), and 1620 cm^{-1} ($\nu_{C=C}$); NMR (CCl_4) δ 2.80 (m, 1 H), 4.15 (m, 2 H), 5.60 (m, 2 H), and 7.33 (m, 5 H); MS M^+ m/e (rel intensity) 158 (8.5), 153 (10), 152 (12.5), 141 (8), 127 (12.5), 119 (99), 117 (100), 105 (10), 94 (14), 84 (10), 82 (14), 47 (15).

2-(Phenylethynyl)allyl Tosylate 3. A solution of 0.316 g (2 mmol) of the enynol **9** in 5 mL of tetrahydrofuran was placed in a 50-mL reaction flask, flushed with argon, and fitted with a side arm with a rubber serum cap. At 0 °C was added dropwise 2 mmol (1.27 mL of a 1.575 N solution in hexane) of n-butyllithium. The reaction mixture was stirred for 2 h and then cooled to −40 °C (dry ice + acetonitrile bath). Next, a solution of 0.382 g (2 mmol) of p-toluenesulfonyl chloride in 2 mL of tetrahydrofuran was added and stirred for 15 min at −40 °C. The reaction mixture was allowed to warm to room temperature and stirred for an additional 2 h. The reaction mixture was cooled to 0 °C and then placed in a separatory funnel and washed rapidly with cold 5% sodium bicarbonate solution. The organic layer was decanted and dried over anhydrous magnesium sulfate and the solvent was removed. The residue was chromatographed on silica gel eluting with ether–light petroleum (5:95) to give 0.540 g (87%) of the pure 2-(phenylethynyl)allyl tosylate **3** as a pale yellow oil: NMR (CCl_4) δ 2.35 (s, 3 H), 4.55 (s, 2 H), 5.55 (s, 2 H), 7.30 (s, 5 H), and 7.20–7.87 (q, 4 H). Anal. Calcd for $C_{18}H_{16}O_3S$: C, 69.21; H, 5.16; S, 10.26. Found: C, 68.94; H, 5.25; S, 9.97.

1-Cyclopropylcyclopropanol (22). The preparation and description of **22** have been previously reported.[7,35,36] More conveniently, **22** has been obtained by the addition at room temperature of 16.83 g (0.16 mol) of cyclopropanone hemiketal[1] to 48.52 g (0.33 mol) of cyclopropylmagnesium bromide in 150 mL of tetrahydrofuran. The reaction mixture was stirred for 2 h at room temperature and heated under reflux for 4 h. After the usual workup the cyclopropanol **22** was obtained in 88% yield.

1-Cyclopropyl-1-tosyloxycyclopropane (7). The tosylate **7** was obtained in 74% yield by conventional means through the reaction of the alcohol **22** with tosylchloride in pyridine at 0 °C.[12] Two recrystallizations from pentane gave the pure 1-cyclopropyl-1-tosyloxycyclopropane (**7**): mp 39 °C; NMR (CCl_4) δ 0.15–1.40 (m, 8 H), 1.70 (m, 1 H), 2.53 (s, 3 H), and 7.30–7.90 (q, 4 H). Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.89; H, 6.39; S, 12.43. Found: C, 62.04; H, 6.56; S, 12.42.

2-Cyclopropylallyl Alcohol 21. Method A.[7] A solution of 9 g (35.7 mmol) of the tosylate **7** in 60 mL of acetic acid buffered with 3.22 g (39.3 mmol) of sodium acetate was stirred at room temperature for 60 h. The mixture was concentrated by removing acetic acid under

vacuum and extracting with ether. The extract was washed with two 75-mL solutions of 1 N sodium hydroxyde and twice with water and then dried over magnesium sulfate. The solvent was evaporated and the NMR spectrum of the crude product (3.6 g, 72%) showed the formation of two products: 1-cyclopropyl-1-acetoxycyclopropane (28%) and 2-cyclopropylallyl acetate (72%). The acetates were converted to the alcohols with lithium aluminum hydride, and the alcohols separated by preparative liquid chromatography to yield cyclopropanol **22** and 2-cyclopropylallyl alcohol **21**: IR (CCl_4) 3620 and 3450 (ν_{OH}), 3090 (ν_{CH}), and 1645 cm^{-1} ($\nu_{C=C}$); NMR (CCl_4) δ 0.5 (m, 4 H), 1.20 (m, 1 H), 2.10 (s, 1 H), 4.00 (s, 2 H), 4.65 (m, 1 H), and 4.85 (m 1 H); MS M^+ *m/e* (rel intensity) 98.2 (26.8), 83.2 (20.6), 79.1 (91.7), 69.1 (34.5), 57.1 (39.5), 39.2 (100).

Method B.[16] The enol ether **20** has been prepared in 90% yield from cyclopropyl methyl ketone and methoxymethylenetriphenylphosphorane by the procedure of Corey.[37] A solution of 0.08 mol of enol ether **20** in 60 mL of benzene containing 15 mg of *meso*-tetraphenylporphine was irradiated in a current of oxygen for 15 min, following a recently reported procedure.[38] The benzene was removed on a rotary evaporator and the residue was dissolved in 20 mL of ether. To the etheral solution were added at −5 °C 2 equiv of lithium aluminum hydride with stirring. After the usual workup 2-cyclopropylallyl alcohol **21** was isolated by preparative GLC in 60% yield.

2-Cyclopropylallyl tosylate 4 was prepared analogously to the tosylate **3** by the reaction of 262 mg (2.7 mmol) of the allyl alcohol **21** with 1 equiv of *n*-BuLi at 0 °C followed by the addition of 500 mg (2.68 mmol) of tosyl chloride at −40 °C. After workup (excess of alcohol **21** can be removed under vacuum, 0.05 mm), 500 mg (72%) of practically pure tosylate **4** was yielded as a pale yellow oil: NMR (CCl_4) δ 0.55 (m, 4 H), 1.20 (m, 1 H), 2.48 (s, 3 H), 4.55 (s, 2 H), 4.90 (s, 1 H), 5.05 (m, 1 H), 7.45–8.05 (q 4 H). Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.89; H, 6.39; S, 12.43. Found: C, 62.17; H, 6.54; S, 12.31.

1-Phenylcyclopropanol 29. To phenylmagnesium bromide prepared from 31.4 g (0.2 mol) of bromobenzene and 4.86 g (0.2 mol) of magnesium metal in 150 mL of anhydrous tetrahydrofuran was added dropwise a solution of 10.2 g (0.1 mol) of cyclopropanone hemiketal.[1] The reacting mixture was stirred at room temperature overnight. After the usual workup, 13.4 g (100%) of pratically pure 1-phenylcyclopropanol was obtained: NMR δ 0.85 (m, 2 H), 1.05 (m, 2 H), 4.10 (m, 1 H), and 7.15 (m, 5 H).

1-Phenyl-1-tosyloxycyclopropane (8) was prepared by the normal pyridine procedure.[12] Two recrystallizations from pentane at −60 °C gave the pure 1-phenyl-1-tosyloxycyclopropane (**8**): mp 73.1 °C; NMR (CCl_4) δ 1.10 (m, 2 H), 1.60 (m, 2 H), 2.32 (s, 3 H), 7.18 (m, 5 H), and 6.98–7.50 (q, 4 H). Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59; S, 11.12. Found: C, 66.82; H, 5.72; S, 10.83.

2-Phenylallyl Alcohol 30. The oxidation of α-methylstyrene with selenium dioxide in acetic acid–acetic anhydride yielded 36% of 3-acetoxy-2-phenyl-1-propane: bp 60–61 °C (0.085 mm) [lit.[21] bp 112–113 °C (5 mm)]; NMR (CCl_4) δ 1.95 (s, 3 H), 4.90 (s, 2 H), 5.30 (m, 1 H), 5.47 (m, 1 H), and 7.30 ppm (m, 5 H). The acetate was reduced with lithium aluminum hydride as usual and the crude product was distilled: bp 73 °C (0.25 mm); IR (neat) 3350 (ν_{OH}) and 1632 cm^{-1} ($\nu_{C=C}$); NMR (CCl_4) δ 3.20 (m, 1 H), 4.32 (s, 2 H), 5.25 (m, 1 H), 5.35 (m, 1 H), and 7.25 (m, 5 H); MS M^+ *m/e* (rel intensity) 134.2 (73.2), 115.1 (26.5), 104.1 (13.8), 103.1 (97.9), 102.2 (20.4), 92.1 (81.8), 91.1 (60.8), 77.1 (100.0).

2-Phenylallyl tosylate 5 was prepared analogously to the tosylate **3** by the reaction of 1.5 (11.25 mmol) of the alcohol **30** with 1 equiv of *n*-BuLi at 0 °C, followed by the addition of 2.15 g (11.30 mmol) of tosyl chloride at −40 °C in tetrahydrofuran. After workup was obtained 2 g of a mixture containing only 30% of tosylate **5.** The mixture was chromatographed on silica gel eluting with ether–light petroleum (5:95) to give 500 mg (16%) of the pure 2-phenylallyl tosylate **5:** NMR (CCl_4) δ 2.40 (s, 3 H), 4.82 (s, 2 H), 5.32 (s, 1 H), 5.48 (s, 1 H), 7.22 (s, 5 H), and 7.20–7.78 (q, 4 H). Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.64: H, 5.59; S, 11.12. Found: C, 65.89; H, 5.69; S, 11.21.

Description of a Typical Comparative Product Analysis. The tosylates **4** and **7** (125 mg, ~0.5 mmol) were dissolved in 2.5 mL of acetone–H_2O (50:50) containing 1.1 equiv of calcium carbonate as buffer, respectively. The solvolysis mixtures were heated in sealed tubes at 25 °C for 40 h. After cooling the tubes were opened and the mixture was poured into 100 mL of ether. The etheral extract was washed with 5 mL of aqueous NaCl solution and with water and then dried with water and then dried over anhydrous magnesium sulfate. The solvent was removed by a short-path distillation. The crude solvolysis mixtures were worked up by preparative gas chromatography or thin layer chromatography, and the products of each solvolysis were identified comparatively by combined GC and MS analysis and from their IR and NMR spectra.

The other solvolysis reactions were run in the same way, under the conditions reported in Table I.

1-(Phenylethynyl)cyclopropanol 13 (R = $-C{\equiv}CC_6H_5$) has been described.[1]

1-Ethoxy-1-(phenylethynyl)cyclopropane 13 (R = $-C{\equiv}CC_6H_5$; X = $-CH_2CH_3$) has been described.[1]

1-(2′,2′,2′-Trifluoroethoxy)-1-(phenylethynyl)cyclopropane 13 (R = $-C{\equiv}CC_6H_5$, X = $-CH_2CF_3$) has been described.[1]

1-Ethoxy-3-methylene-4-phenyl-3-butyne 9 (R = $-C{\equiv}CC_6H_5$; X = $-CH_2CH_3$) has been described.[1]

1-(2′,2′,2′-Trifluoroethoxy)-2-methylene-4-phenyl-3-butyne 9 (R = $-C{\equiv}CC_6H_5$; X = $-CH_2CF_3$) has been described.[1]

2-Cyclopropyl-3-ethoxy-1-propene 21 (X = CH_2CH_3): NMR (CCl_4) δ 0.35–0.75 (m, 4 H), 1.10 (m, 1 H), 1.20 (t, 3 H, J = 7.10 Hz), 3.60 (q, 2 H, J = 7.10 Hz), 3.85 (m, 2 H), 4.68 (m, 1 H), and 4.82 (m, 1 H); MS M^+ *m/e* (rel intensity) 126.1 (0.3), 111.3 (0.8), 98.3 (14.1), 67.2 (32.3), 39.2 (100.0).

2-Cyclopropyl-3-(2′,2′,2′-trifluoroethoxy)-1-propene 21 (X = CH_2CF_3): NMR (CCl_4) δ 0.40–0.90 (m, 4 H), 1.30 (m, 1 H), 3.80 (q, 2 H, J = 8.65 Hz), 4.05 (m, 2 H), 4.82 (m, 1 H), and 4.90 (m, 1 H); MS M^+ *m/e* (rel intensity) 180.1 (26.5), 165.0 (37.0), 139.1 (45.9), 80.1 (46.1), 79.0 (100.0), 67.1 (36.3), 41.1 (53.8).

2-Cyclopropyl-3-(1′,1′,1′,3′,3′,3′-hexafluoroisopropoxy)-1-propene 21 (X = $CH(CF_3)_2$): NMR (CCl_4) δ 0.40–0.90 (m, 4 H), 1.40 (m, 1 H), 4.25 (h, 1 H, J = 6 Hz), 4.35 (s, 2 H), 4.98 (m, 1 H), and 5.05 (m, 1 H); MS M^+ *m/e* (rel intensity) 248.1 (21.6), 233.2 (29.6), 207.0 (23.6), 82.1 (15.8), 81.1 (34.0), 80.1 (36.5), 79.1 (100.0), 69.0 (53.2), 67.1 (30.1).

1-Cyclopropyl-1-(2′,2′,2′-trifluoroethyl)cyclopropane 22 (X = CH_2CF_3): NMR (CCl_4) δ 0.25–1.50 (m, 9 H) and 3.80 (q, 2 H, J = 8.65 Hz); MS M^+ *m/e* (rel intensity) 180.1 (25.1), 165.0 (30.6), 139.0 (42.2), 80.1 (44.9), 79.0 (100.0), 41.1 (49.4).

Addition of *p*-Toluenesulfonic acid to 2-Cyclopropylallyl Alcohol 21. (a) One equivalent of TsOH. To a solution of 98 mg (1 mmol) of alcohol **21** in 2 mL of aqueous acetone (50:50) was added 190.2 mg (1 mmol) of *p*-toluenesulfonic acid monohydrate. The mixture was stirred at 25 °C for 24 h and then poured into 100 mL of ether. The extract was washed with water and dried over magnesium sulfate and the ether was removed by a short-path distillation to yield 98 mg (100%) of residue.

The ^1H NMR spectrum of the crude product was quite complex and showed three multiplets at 0.40, 1.0, and 3.60 ppm and two singlets at 1.15 and 3.48 ppm; the IR (CCl_4) showed a very strong ν_{OH} at 3400 and a very sharp ν_{CH} (cyclopropane) at 3092 cm^{-1}. The lack of cyclopropyl ethyl ketone[35] [IR (neat) 1696 cm^{-1} $\nu_{C=O}$; NMR (CCl_4) δ 0.90 (m, 4 H), 1.10 (t, 3 H, J = 8.25 Hz), 1,80 (m, 1 H), and 2.55 (q, 2 H, J = 8.25 Hz); MS M^+ *m/e* (rel intensity) 98 (16.5), 69 (100), 57 (7.8), 41 (54), 39 (31.4)] was clearly established and confirmed by TLC and GC analysis.

(b) One-Tenth Equivalent of TsOH. In the same manner, to a solution of 98 mg (1 mmol) of **21** in 2 mL of H_2O–acetone (50:50) was added 19 mg (0.1 equiv) of TsOH, H_2O. The mixture was stirred for 24 h at 25 °C and yielded, after workup, the same polymeric mixture containing ~15% of allylic alcohol **21.**

(c) Into D_2O–CD_3COCD_3. A solution of 49 mg (0.5 mmol) of **21** in 0.4 mL of D_2O–hexadeuterio acetone (50:50) was placed in a NMR tube and the ^1H NMR spectrum was recorded: δ 0.4 (m, 4 H), 1.15 (m, 1 H), 3.90 (s, 2 H), 4.55 (s, 1 H), and 4.75 (m, 1 H). Then, 95 mg (0.5 mmol) of *p*-toluenesulfonic acid monohydrate was added to the NMR tube and the spectra were recorded, showing for the allylic + methylenic protons of **21** vs. the aromatic protons of TsOH a ratio equal to 61.5% after 3 min and roughly to 10% after 45 min, at 36 °C. But the characteristic signals of the cyclopropyl ethyl ketone (**23**) were not recognized in the spectra.

Addition of *p*-Toluenesulfonic Acid to Cyclopropyl Ethyl Ketone (23). A solution of 49 mg (0.5 mmol) of ketone **23** in 0.4 mL of D_2O–hexadeuterio acetone (50:50) was placed in a NMR tube and the ^1H NMR spectrum was recorded: δ 0.90–1.0 (m 4 H), 1.05 (t, 3 H, J = 7.35 Hz), 2.10 (m, 1 H), and 2.65 (q, 2 H, j = 7.35 Hz). Then 95 mg (0.5 mmol) of *p*-toluenesulfonic acid monohydrate was added to the NMR tube and the spectra were recorded every 15 min at 36 °C. After 45 min, the ^1H NMR spectra showed the presence of unaltered ketone **23,** with a ratio of 2/3 for the signals of the protons of the ethyl group.

3-Ethoxy-2-phenyl-1-propene 30 (X = CH_2CH_3): NMR (CCl_4) δ 1.20 (t, 3 H, J = 6.66 Hz), 3.45 (q, 2 H, J = 6.66 Hz), 4.20 (m, 2 H), 5.35 (m, 2 H), and 7.30 (m, 5 H); MS M^+ *m/e* (rel intensity) 162.2 (1.6), 119.1 (10.5), 118.1 (100), 117.1 (41.3), 105.1 (44.4), 103.1 (31.6), 91.1 (19.4), 77.1 (29.5).

1-Ethoxy-1-phenylcyclopropane 29 (X = CH_2CH_3): NMR

(CCl_4) δ 0.92 (m, 4 H), 1.15 (t, 3 H, J = 6.66 Hz), 3.45 (q, 2 H, J = 6.66 Hz), and 7.30 (m, 5 H); MS M^+ m/e (rel intensity) 162.2 (32.8), 161.1 (97.5), 133.1 (71.9), 117.1 (55.3), 115.1 (25.2), 105.1 (100.0), 91.1 (26.6), 77.1 (85.5).

3-(1′,1′,1′,3′,3′,3′-Hexafluoroisopropoxy)-2-phenyl-1-propene 30 (X = $CH(CF_3)_2$): NMR δ 4.15 (h, 1 H, J = 6 Hz), 4.72 (s, 2 H), 5.40 (m, 1 H), 5.68 (s, 1 H), and 7.35 (m, 5 H); MS M^+ m/e 284.1 (76.3), 118.1 (46.6), 117 (100), 116.0 (23.9), 115 (52.4), 105 (84.5), 104 (18), 103 (92.7), 102 (14.2), 92.1 (38.7), 91 (92.8), 77.0 (51.1).

Addition of *p*-Toluenesulfonic Acid to 2-Phenylallyl Alcohol 30. To a solution of 134 mg (1 mmol) of alcohol **30** in 2 mL of aqueous acetone (50:50) was added 190 mg (1 equiv) of *p*-toluenesulfonic acid monohydrate. The mixture was stirred at 25 °C for 24 h and worked up anagously to alcohol **21**; the ^1H NMR spectrum of the crude residue showed unchanged allylic alcohol **30**. Again, treated by *p*-toluenesulfonic acid at 50 °C for 15 h, **30** was recovered with 90% of purity.

Kinetic procedures have been described previously.[1]

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Registry No.—**9,** 57951-69-6; **10,** 37952-37-7; **11,** 66303-65-9; **12,** 66303-66-0; **20,** 66303-67-1; **21,** 66303-68-2; **21** (X = Et), 66303-69-3; **21** (X = CH_2CF_3), 66303-70-6; **21** (X = $CH(CF_3)_2$), 66303-71-7; **22,** 54251-80-8; **29,** 29526-96-3; **29** (X = Et), 66303-72-8; **30,** 6006-81-8; **30** (X = Et), 7534-41-0; **30** (X = $CH(CF_3)_2$), 66303-73-9; cyclopropanone ethylhemiketal, 13837-45-1; cyclopropyl bromide, 4333-56-6; α-methylstyrene, 98-83-9; 3-acetoxy-2-phenylpropane, 10402-52-5; 4-phenyl-2-methylene-1-butanal, THP ether, 66303-74-0; 1-cyclopropyl-1-(2′,2′,2′,trifluoroethyl)cyclopropane, 66303-75-1.

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