Vinyl Cations. 41. Influence of 4-Aryl and 4-Alkyl Substituents on the π-Route Solvolyses of Homopropargyl Esters[1]

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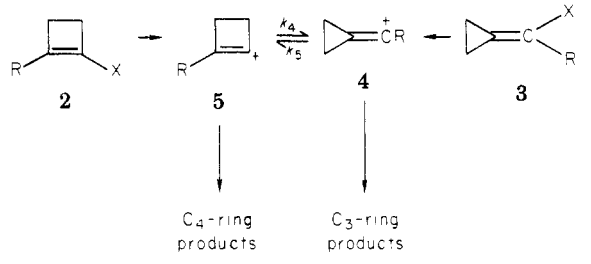
The four 4-substituted-homopropargyl tosylates and triflates **6b–e** (R = phenyl, *p*-tolyl, anisyl, and cyclopropyl) have been synthesized and solvolyzed under various conditions, as have 2-cyclopropyl-1-cyclobutenyl triflate (11-OTf) and nonaflate (11-ONf). In addition, the solvolyses of pent-3-yn-1-yl tosylate (**6a**-OTs, R = methyl) and triflate (prepared previously) are reported. The ratios of C-3 ring to C-4 ring [$R(C_3\ \text{ring}/C_4\ \text{ring})$] products are recorded for the reactions in various solvents. As expected, ring closure (k_Δ) increases and solvent displacement (k_s, S_N2) decreases with decreasing nucleophilicity of solvent. Temperature effects are noted for the solvolyses of tosylates **6a–e** in 100% TFE buffered with Na_2CO_3 in which k_Δ increases with increasing temperature. The result is explained by decomposition of the intimate ion pair with temperature, whereupon elimination to the enyne becomes smaller and ring closure (k_Δ) increases at the expense of elimination. The possibility of intervention of nonclassical vinyl cations is discussed, as are other mechanistic implications.

Introduction

In the solvolyses, through vinyl cations, of 1-cycloalkenyl triflates and nonaflates,[3–5] the rates (aqueous ethanol) decrease rapidly from C_9 to C_6, 1-cyclopentenyl triflate and nonaflate solvolyze most slowly of all (they do not form vinyl cations but undergo sulfur–oxygen cleavage), and 1-cyclobutenyl derivatives react nearly as rapidly as those of C_8 and C_9. The rate decrease from C_9 to C_6 is easily understood, since the sp-hybridized positively charged carbon of the vinyl cation prefers a linear structure, and this can be more easily accommodated by increasingly larger rings. The surprisingly fast rates of 1-cyclobutenyl triflate and nonaflate have been attributed[5,6] to intervention of the nonclassical cation **1** (R = H).

1, R = H

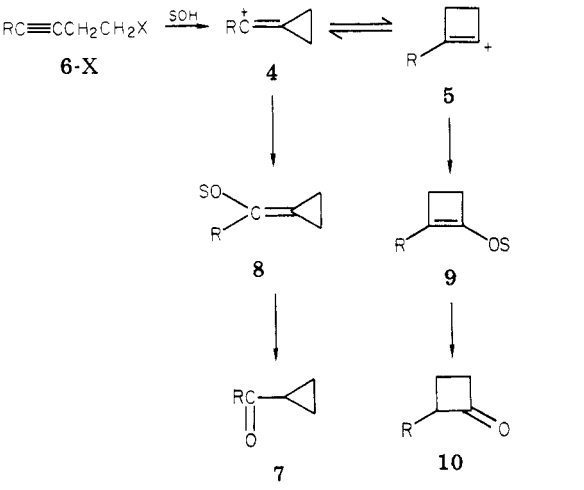
In earlier attempts to gain information about the nature of the cyclic vinyl cations **4** and **5**, a series of derivatives **2** and **3** (R = H, methyl, phenyl, *p*-tolyl, anisyl, and cyclopropyl) were prepared and solvolyzed.[4,7–13]



The yields of the products containing the four-carbon and three-carbon rings were determined in each case, and the results are summarized in Table I. Although leaving groups, solvents, and temperatures differ, there are enough data in Table I to demonstrate that, when R in **3** is *tert*-butyl or when R in **2** and **3** is H or CH_3, all solvolyze to yield almost exclusively products containing a four-carbon ring, whereas with R = phenyl, *p*-tolyl, or anisyl, both **2** and **3** solvolyze to products in which the three-carbon ring predominates.

The cyclopropyl group in **3** (R = cyclopropyl, X = Br) also leads to a 4:1 preference for the C_3-ring product. We conclude therefrom not only that **2** and **3** solvolyze through common intermediates but also that substituents (phenyl, *p*-tolyl, anisyl, cyclopropyl) that can exert mesomeric effects influence the solvolyses in such a way that products containing the C_3-ring are preferred.

The homopropargyl[14–16] rearrangement (**6** → **7** + **10**)



provides another solvolytic pathway for the generation of

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Table I. Ratio of C_3 Ring/C_4 Ring Products from Solvolyses of 2-Cyclobutenyl and Cyclopropylidene Derivatives

no.	R	leaving group X	solvent	T, °C	R(C_3 ring/C_4 ring) 2	3	ref
1	H	Nf[a]	50 EW[b]	100	0:100		7
		Br	50 MW[c]	140		0:100	8
2	Me	Nf	50 EW	50	1:99		9
		Br	60 EW	81		1:89	10
3	*t*-Bu	Br	80 EW	100		0:100	10
4	Ph	Nf	60 EW	75	31:17 (1.8)		11
		Br	80 EW	120	58:26 (2.2)		11
		Br	80 EW	80		52:*d*	11
5	An	Nf	80 EW	75	57:43 (1.3)		11
		Br	80 EW	80		54:4 (13.5)	12
6	*p*-Tol	Br	80 EW	80		49:8 (6.1)	12
7	cyclopropyl	Br	80 EW	60		65:15 (4.3)	13

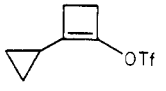
[a] Nf = nonaflate, nonafluorobutyl. [b] 50% ethanol/water. [c] 50% methanol/water. [d] C_4-ring ketone not stable.

vinyl cations. The linearity of the four carbons (CC≡CC) in and adjacent to the triple bond as well as its negative inductive effect[17,18] both contribute to a considerable deceleration of reaction rate that masks anchimeric assistance owing to triple-bond participation. We have been able, however, to demonstrate[19,20] anchimeric assistance in the trifluoroethanolysis, at 30.0 °C, of 1-pent-3-ynyl triflate (**6a**, R = CH_3, X = OSO_2CF_3) by measuring both carbon-14 and deuterium isotope effects during the solvolysis. The homopropargyl rearrangement is but one example of a larger class of reactions involving solvolytic participation of triple bonds.[21] During investigations of anchimeric assistance by the triple bond, it is necessary to insure that a second pathway—solvent addition followed by double-bond participation[22]—does not intervene.

Methods for measuring and suppressing solvent addition to triple bonds are well-known.[21,23] The purpose of the present investigation was (1) to synthesize the homopropargyl derivatives **6a–e** (R = CH_3, phenyl, *p*-tolyl, anisyl, cyclopropyl; X = OTf, OTs), carry out their solvolyses

$RC{\equiv}CCH_2CH_2OTs$	$RC{\equiv}CCH_2CH_2OTf$
6a-OTs, R = CH_3	**6a**-OTf, R = CH_3
6b-OTs, R = Ph	**6b**-OTf, R = Ph
6c-OTs, R = *p*-Tol	**6c**-OTf, R = *p*-Tol
6d-OTs, R = An	**6d**-OTf, R = An
6e-OTs, R = CP	**6e**-OTf, R = CP

in solvents of both high and low nucleophilicities and ionizing powers, and compare product analyses with those given in Table I (the synthesis of **6a**–OTf (R = methyl) has already been published[20]) and (2) to fill in one of the gaps in Table I by solvolyzing 2-cyclopropylcyclobutenyl triflate[24] (**11**-OTf) and nonaflate[24] (**11**-ONf).

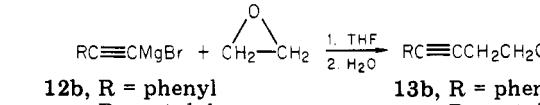


11-OTf

11-ONf

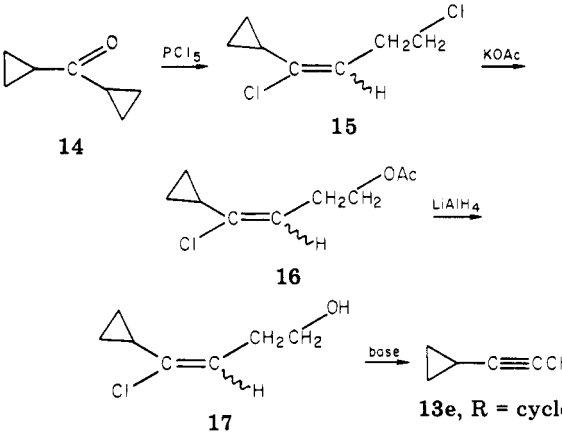
Methods and Results

A. Syntheses. The primary carbinols **13b–d** were prepared from the (arylethynyl)magnesium bromides (**12b–d**).[25–27] Carbinol **13e** (R = cyclopropyl) was synthesized from dicyclopropyl ketone (**14**)[28] through the sequence **14** → **15** → **16** → **17** → **13e**, as described in the Experimental Section. 2-Cyclopropylcyclobutenyl triflate



12b, R = phenyl
c, R = *p*-tolyl
d, R = anisyl

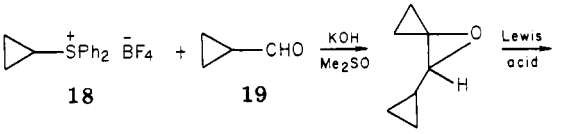
13b, R = phenyl
c, R = *p*-tolyl
d, R = anisyl



14 **15** **16** **17**

13e, R = cyclopropyl

(**11**-OTfe and nonaflate (**11**-ONf) were prepared[24] from the ketone **21**, which was synthesized as shown (**18** + **19** → **20** → **21**), starting with cyclopropyldiphenylsulfonium tetrafluoroborate (**18**)[29] and aldehyde **19**.[30]



18 **19** **20**

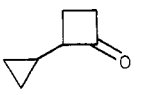


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Table II. Products[a] from Solvolyses of 6a-e Triflates and 6e Tosylate in Ethanol/Water

R	solvent	buffer	T, °C	t, days	22, %	10, %	7, %	23, %	13, %	% rearr	R(C₃ ring/C₄ ring)
CH₃	80 EW[b]	2,6-lutidine	25	1	5	1.3		74	18	1.3	0:1.3
6a-OTf	50 EW[b]	2,6-lutidine	25	1	1	2.8		50	46	2.8	0:2.8
Ph	80 EW	Na_2CO_3	25	1	<1	0.5	5	61	32	6	12.5
6b-OTf	80 EW	TEA	25	1	20	0.7	6	44	26	7	8.6
p-Tol	80 EW	Na_2CO_3	25	1	<1	1	13	63	19	14	13
6c-OTf	80 EW	TEA	25	1	<1	1	14	58	22	15	14
	80 EW	Na_2CO_3	30	5	1	1	17	54	24	18	17
6e-OTf	50 EW	Na_2CO_3	30	5	2	5	20	31	38	25	4
	80 EW	TEA	30	5	7	2	37	27	22	39	19
	50 EW	TEA	30	5	10	15	41	11	22	56	2.7
	80 EW	Na_2CO_3	60	5	52		1	23	11	1	1:0
6e-OTs	50 EW	Na_2CO_3	60	5	48		1	13	31	1	1:0
	80 EW	TEA	60	5	43			25	12	0	
	50 EW	TEA	60	5	76		2	11	10	2	2:0

[a] There were always some unidentified peaks (2-7% of product was normal, although in one case the unknowns were 20%). [b] Repeated from ref 20.

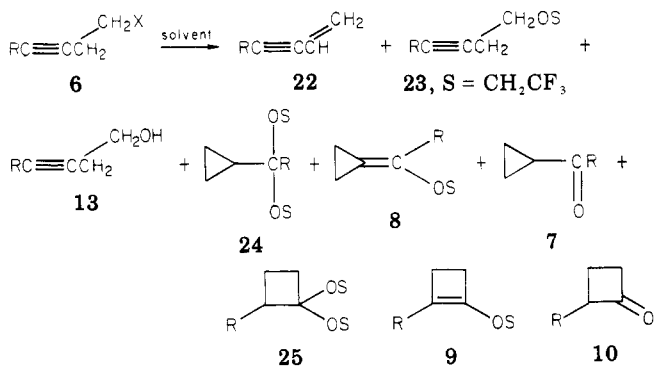
Table III. Variation of Percent Rearrangement and R(C₃ Ring/C₄ Ring) of 6a-e Tosylates with Temperature (100% TFE, Na_2CO_3, Buffer)

	R	T, °C	t, days	24, %	22, %	9, %	7, %	23, %	10, %	13, %	% rearr	R(C₃ ring/C₄ ring)
6a	Me	25	30[a]		42	0.5		57	0.2		1	0:1
		50	30		16	13	1	61	8	1	21	~0.04
		80	30		6	28	1	55	8	1	37	~0.03
6b	Ph	25	30[a]	4	57	1	5	32	1	2	11	4.5
		50	15	15	20	5	7	50	1	3	28	3.7
		80	12	21	12	5	9	42	6	4	41	2.7
6c	Tol	25	30[a]	7	39	0.4	10	41	1	1	18	17
		50	15	22	17	2	25	31	2	1	51	12
		80	9	23	10	2	31	28	3	3	59	11
6d	An	25	30	9	34		9	45		2	18	18:0
		50	6	35	10		30	21	1	3	66	65
		80	6	30	8		37	18	2	5	69	35
6e		40	7		52	3	16	22		1	20[b]	5.7
		60	5	44	13	10	4	20	1	1	60[b]	4.5
		80	5	41	7	23	8	16		2	72	2.1
		100	5	4	4	23	48	17	1	3	77[b]	2.2

[a] Some reactant still present after 30 days. [b] 1% 8 is also present.

B. Solvolyses. The homopropargyl esters **6b–e** (both tosylates and triflates) were solvolyzed in sealed-glass ampules in various solvents (and in the presence of appropriate buffers) at constant temperatures for 1–30 days. Solvolyses were carried out under the following conditions: starting material/buffer/solvent = 1:2:40. The time of reaction corresponded to at least 10 half-lives. A Colora thermostated bath type NB/05 was used for temperature control (±0.01 °C). The products (Scheme I) were identified by IR, ^1H NMR, preparative GC, liquid column chromatography, GC retention time, comparison with authentic samples on several different GC columns, or GC/MS analysis. Comprehensive studies of the effects of changing buffer during solvolysis, at 25 °C, of **6b**-OTf (R = phenyl) and **6c**-OTf (R = *p*-tolyl) in 100% TFE and in 80% TFE/H_2O were also performed. The buffers employed were Na_2CO_3, $CaCO_3$, 2,6-lutidine, K_2CO_3, and triethylamine (TEA). The results paralleled those already reported[20] for the solvolyses of **6a**-OTf (R = methyl), namely, that in the presence of the first three buffers, above, (1) the percent rearrangement is unchanged, and (2) the ratio R(C₃ ring/C₄ ring) is not appreciably affected. Potassium carbonate and TEA enhance the S_N2 (k_s) process at the expense of rearrangement (k_Δ), since they increase the nucleophilicity of the reaction medium by reacting with the solvent. As expected, there was less rearrangement in 80% TFE than in 100% TFE. Details[31] will not be presented here. More limited studies of buffer dependancy for **6e**-OTs and **6e**-OTf (R = cyclopropyl) were performed. Ethanol/water, pure TFE, and TFE/water mixtures were used, with results[32] similar to those already reported.[20]

Scheme I



Results of solvolyses of **6a–e** in ethanol/water (EW) mixtures at various temperatures (buffers Na_2CO_3 or TEA) are shown in Table II. The ratios R(C₃ ring/C₄ ring) shown in the last column illustrate the large preference for

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Table IV. Percent Rearrangement of 6a-e Triflates in 100% TFE (Na_2CO_3 Buffer Unless Otherwise Specified)

	R	T, °C	t, days	24	22	9	25	7	23	10	13	% rearr	R(C_3 ring/C_4 ring)
6a	Me	20	1		1	83	3	1	7	2		89	~0.01
		40	1		1	58	20	1	6	9	5	87	~0.01
		60	1		1.5	32	25	1	5	15	16	73	~0.015
		80	1		2	15	20	2	7	40	13	76	~0.03
6b	Ph	25	1	46	1	11		9	25	3	2	68	39
6c	*p*-Tol	25	1	66	1	3		11	14	1		81	20
6e		30	5	57[a]		10		24	2	3		94	6.4
		30	5[b]	32	6	4		8	30	5	9	49	4.4
		30	5[c]	28	1	9		44	2	2	4	83	6.5

[a] Included is 4% **8**. [b] NEt_3 buffer. [c] Pyridine buffer.

Table V. Product Distribution on Solvolysis of 11-OTf, 11-ONf, and 6e-OTs

no.	reactant	solvent	buffer	T, °C	time	24, %	7, %	9, %	10, %	22, %	23, %	13, %	% rearr	R(C_3 ring/C_4 ring)
1	11-OTf	80 EW	TEA	70	24 h		92		?[a]		4	4	92	92:0[a]
2	11-OTf	100 TFE	TEA	70	24 h	69	11	8			12	1	80	10
3	11-ONf	100 TFE	DTBMP[b]	25	5 days	82[e]	3[e]	11			4		85	7.7
4	*c*	*c*	*c*	80	20 h	83[e]	3[e]	11			3		86	7.8
5	11-ONf	100 TFE	DTBMP[b]	80	5 h	68[e]	2[e]	25			5		70	2.8
6	11-ONf	100 TFE	TEA	25	5 days	77[e]	7[e]	11			5		84	7.6
7	*c*	*d*	*d*	80	20 h	83[e]	2[e]	10			5		85	8.5
8	11-ONf	100 TFE	TEA	80	2 h	71[e]	2[e]	15			12		73	4.9
9	6e-OTs	100 TFE	Py	60	5 days	2	48	12		5	18	2	57	4.2
10	6e-OTs	100 TFE	TEA	60	5 days	4	1	1	1	56	37		5	2.5

[a] A further experiment with 11-ONf indicates ca. 6% 2-cyclopropyl-1-cyclobutanone (**10**) was produced vs. dicyclopropyl ketone (**7**). Nf = nonaflate, nonafluorobutyl. [b] DTBMP= 2,6-di-*tert*-butyl-4-methylpyridine. [c] Product from run 3 heated to 80 °C for 20 h. [d] Product from run 6 heated to 80 °C for 20 h. [e] The ratio **24/7** changes with GC conditions, although the sum **24** + **7** is always constant. It is possible that **7** is produced from **24** during GC analysis.

the formation of 1) four-carbon-ring product from **6a** (R = methyl) and (2) three-carbon ring products from **6b–e**, even in cases where the total percent rearrangement is quite small. The **6a–e** tosylates were also solvolyzed in 100% TFE/Na_2CO_3 at temperatures between 25 and 100 °C. The conditions and product analyses are given in Table III together with the total percent rearrangement and the R(C_3 ring/C_4 ring).

Given in Table IV are product data for solvolyses of triflates **6a–c** and **6e** in 100% TFE/Na_2CO_3, together with additional results for triflate **6e**, for which the buffers were TEA and pyridine.

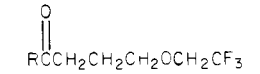
2-Cyclopropylcyclobutenyl triflate (**11**-OTf) and nonaflate (**11**-ONf) were solvolyzed in 80% ethanol/water (EW) and in 100% TFE. Triethylamine (TEA) and DTBMP (2,6-di-*tert*-butyl-4-methylpyridine)[24] were used as buffers. The results are given in Table V, together with data for the solvolyses (100% TFE, TEA, or pyridine buffers, 60 °C) of **6e**-OTs. That the products of solvolysis are sufficiently stable to the reaction conditions that no rearrangement of C_3-ring to C_4-ring product takes place can be seen by comparing run 3 with run 4 and run 6 with run 7 (Table V). In each case (runs 3 and 6) the reaction was allowed to proceed for 5 days at 25 °C; the products were then analyzed. The reaction products (runs 4 and 7) were then heated at 80 °C for 20 h (same solvent and buffer as in runs 3 and 6, respectively) and reanalyzed. The total yields of C_3-ring and C_4-ring product remained constant, within experimental error. The effect of temperature upon C_3 ring/C_4 ring has already been demonstrated (Table III) and is once again obvious by comparing runs 3 with 5 and 6 with 8 (Table V).

The data of Table V are not strictly comparable with those given in Tables III and IV for solvolysis in 100% TFE because the buffers (Na_2CO_3 vs. TEA or DTBMP) are different.

Since the buffer activity of TEA differs from that of Na_2CO_3 primarily in that it increases nucleophilicity by reacting with solvent[20] and since **11** does not undergo a normal S_N2 reactions,[3,4] the use of TEA should not seriously affect the results. (Note the last three entries in Table IV and the last two in Table V). The comparison of R(C_3 ring/C_4 ring) for solvolyses using TEA and DTBMP (runs 3, 5, and 6, Table V) supports the foregoing conclusion.

Under the standard solvolysis conditions employed, the enynes **22b–d**, acetylene alcohols **13b–d**, and esters **23b–d**, are stable, although after 30 days at 80 °C some polymerization takes place. At 25 °C the acetylene alcohols **13b–d** could be reisolated after being dissolved in TFE with buffer and added $NaSO_3CF_3$ under the appropriate concentrations of the solvolyses.

Another important criterion for the stability of the reaction products is to compare the results of solvolyses with and without buffers and in underbuffered media. From the unbuffered solvolyses (more than 50% polymerization) we were able to separate by GC only very small quantities of known compounds. For example, in the case of phenyl and *p*-tolyl triflates **6b** and **6c**, the main, nonpolymeric products were **26b** and **26c**. There were also two or three



26b, R = phenyl
c, R = *p*-tolyl

minor components (unidentified) that were not formed in the presence of buffer, plus 5% each of the C_3-ring ketone **7** and the C_4-ring ketone **10**. Neither **26b** nor **26c** were produced in measurable amounts during completely buffered trifluoroethanolyses. With decreasing concentrations of buffer, however, **26b** and **26c** appeared in ever increasing quantities. Polymerization occurred concurrently, and the ratio of **10/7** increased. When the alcohols **13b** and **13c** were treated in TFE with trifluoromethanesulfonic acid in the ratio 1:40:1, **26b** and **26c** were produced

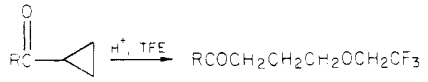
Table VI. Products from Rearrangement of 6b-OTf, 6c-OTf, 6e-OTs, and 6e-OTf in TFE/water Solutions (Reactant/Buffer/Solvent = 1:2:20)

R	T, °C	t, days	24, %	22, %	9, %	7, %	23, %	10, %	13, %	% rearr	R(C3 ring/C4 ring)
Ph (6b-OTf)	25[a,b]	1	8	14	1	14	47	1	14	24	11
p-Tol (6c-OTf)	25[a,b]	1	19	11	3	9	46	1	8	32	7
(6e-OTf)	30[a,b]	5	9	5	2	34	39	3		48	6.6
6e-OTs	60[a,b]	5		41		4	49	1	5	5	4
	60[c,b]	5		23		4	53	1	18	5	4
	60[a,d]	5		75		1	23		1	1	1:0
	60[a,e]	5		6		27	6		26	27	27:0

[a] 80% TFE/H_2O. [b] Na_2CO_3 buffer. [c] 50% TFE/H_2O. [d] NEt_3 buffer. [e] Pyridine buffer.

(30% yield) together with the ethers **23b** and **23c**, some unconverted alcohol and polymer.[33] Increasing the acid concentration (0.5 mL of **13**, 0.5 mL of trifluoromethanesulfonic acid, 3 mL of TFE) lead to the ketones **26b** and **26c** as the sole products.

The products **26b** and **26c** are completely stable in both buffered and acidic TFE. The aryl cyclopropyl ketones **7b** and **7c**, however, are converted to **26b** and **26c** under acid conditions. With increasing time (without buffer)



7b, R = phenyl
c, R = *p*-tolyl

26b, R = phenyl
c, R = *p*-tolyl

the content of **7b** and **7c** decreased, whereas the concentrations of **26b** and **26c** rose, although it is certain that no more of the starting materials (triflates **6b**, **6c**) were present. The keto ethers **26b** and **26c** therefore originate not only through acid cleavage of the cyclopropane rings of **7b** and **7c** but also by solvent addition to the triple bond. In underbuffered solutions, through which it was shown that as buffer increased so did the concentration of cyclization product, polymer product decreased and so did the concentrations of the 4-arylbutynyl trifluoroethyl ethers **23b** and **23c** (S = CH_2CF_3).

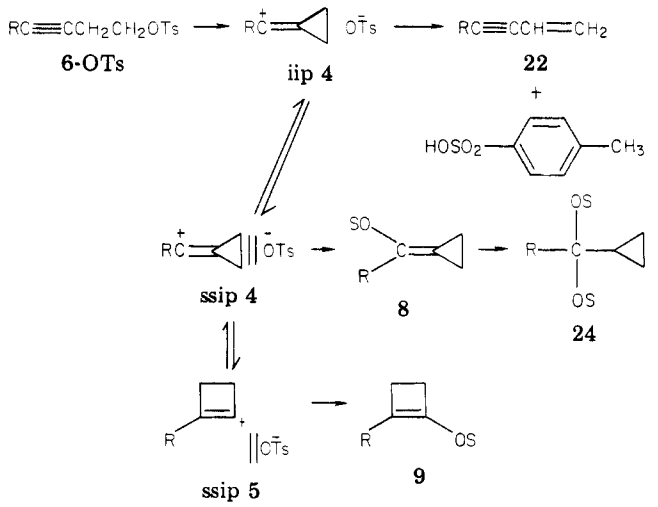
Kinetics for the reactions of the triflates of **6a**,[19,20] **6b**, and **6c** were determined for various TFE/water solutions at pH 4. At 20 °C, in 97% TFE/H_2O the specific reaction rate constants (10^5k) were as follows: **6a** (R CH_3), 1.62; **6b** (Ph), 3.5; **6c** (*p*-Tol), 240. At 30 °C, the rate constants for **6a** and **6b** were 4.87 and 14, respectively. The corresponding value for amyl triflate was 12.3. The triflates of **6a** and **6b** were solvolyzed at pH 3.1 and 5.0 with no change in rate constant.

Finally, in Table VI we present the results of product determination, percent rearrangement, and R(C3 ring/C4 ring) for solvolyses of **6b**-OTf, **6c**-OTf, **6e**-OTs, and **6e**-OTf (R = cyclopropyl) in TFE/water solutions.

Discussion

In Tables II and III we observe the expected[35] increase in percent rearrangement (k_Δ process) with decreasing nucleophilicity and increasing ionizing power of the solvent. In all of the examples shown, when R = methyl (and where rearrangement occurs) the homopropargyl ester (**6a**-OTs or **6a**-OTf) produces almost exclusively the four-carbon-ring product. Of five examples, only two (TFE at 50 and 80 °C) exhibited traces of methyl cyclopropyl ketone (**7**). In the solvolyses of all other tosylates and triflates (**6b–e**, R = phenyl, *p*-tolyl, anisyl, or cyclopropyl) either in ethanol/water solutions or in TFE, the three-carbon-ring products predominated. These results coincide with prior data[4,7-13] (Table I) wherein vinyl cations were generated from the cyclic vinylic starting materials **2** and **3**. Further, at the same temperature the percent rearrangement (and thus k_Δ) increases as R in the **6a–e** tosylates varies in the order methyl, phenyl, *p*-tolyl, cyclopropyl, and/or anisyl (in the latter two cases the choice is not clear). During solvolyses of the triflates (Table IV), the various substituents have a less important effect on the percent rearrangement because triflate is a much better leaving group than tosylate, and in all cases k_Δ is favored over k_s.[35]

Scheme II[a]



[a] iip = intimate ion pair, ssip = solvent-separated ion pair.

Increasing temperature (Table III) increases the percent rearrangement of the **6a–e** tosylates. This effect is consistent with Scheme II, in which at higher temperatures the equilibrium iip 4 ⇌ ssip 4 is displaced toward the solvent-separated ion pair, since in iip 4 the tosylate anion is better situated to abstract a proton from cation **4**, leading to the enyne **22**. From Table II it is clear that in each case the increase in percent rearrangement with increasing temperature takes place at the expense of the elimination product **22**. The foregoing explanation gains credence with the results of Table IV, portraying the trifluoroethanolyses of the **6a–c** and **6e** triflates. Here elimination to the enyne **22** is minimal, because triflate is a much weaker base than tosylate and is therefore less able to abstract a proton from cation **4**. This almost complete lack of elimination reverses the effect of temperature on

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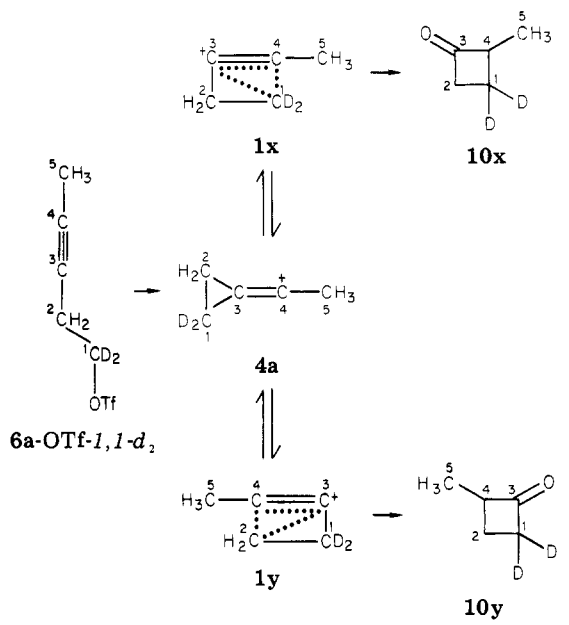
(35) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466 and references given therein. Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *Ibid.* **1976**, *98*, 7667.

Scheme III



percent rearrangement in the case of **6a**-OTf (R = methyl, the only triflate for which we have observed product yields vs. temperature). Here (Table IV), in contrast to experience (Table III) with the tosylates, the percent rearrangement decreases with increasing temperature. Elimination is not an important factor with the weaker base (triflate anion) as the leaving group, because the intimate ion pair (corresponding to iip **4**) must be dissociated very strongly in favor of the solvent-separated ion pair (corresponding to iip **4**). The increase in nucleophilicity of the solvent with rising temperature then favors the S_N2 reaction (k_s), which results in a decrease in the percent rearrangement.

There is another effect of temperature on the trifluoroethanolysis of the tosylates **6b–6e** (Table III), namely, the displacement of $R(C_3$ ring/C_4 ring) in favor of the four-carbon-ring product [$R(C_3$ ring/C_4 ring) decreases with increasing temperature]. For reasons that we will explain later, we prefer to write the equilibrium between the cation **4** and the cation **1**. With increasing temperature the constant K for the equilibrium **4** $\rightleftharpoons$ **1** must be displaced in favor of the least abundant cation **1**. In addition, the nucleophilicity of the solvent increases. Both of these factors favor an increase in yield of products containing the four-carbon ring. A similar decrease in $R(C_3$ ring/C_4 ring) with increasing temperature is observed (Table V) during trifluoroethanolysis of **11**-ONf and is explained in the same way.

The question now arises of how to characterize the intermediate carbocations in the rearrangements of the various esters of **6a–e** and of **11**. The nonclassical character of the parent cation **1** (R = H) seems well-documented[3-6] and was referred to in the Introduction. In addition (Scheme III), **6a**-OTf (R = CH_3), labeled in C-1 with two deuteriums,[19,20] on trifluoroethanolysis yields a 50:50 mixture of the isotope position isomers **10x** and **10y** (the numbers surrounding the structure in Scheme III identify the original carbons in **6a**-OTf-*1,1*-d_2). Nonclassical ion **1** (R = CH_3) can exist in two forms, **1x** and **1y**, which can conceivably interconvert without going through **4a**, provided they are nonplanar. The planar form, however, seems to be considerably more stable,[6] and it is difficult to visualize how planar **1x** and **1y** can equilibrate without passing through the classical ion **4a**. Further, there is experimental evidence that two different, stable $C_5H_5^+$ vinyl cations, to which the structures of the parent ions **1** and **4** (R = H) have been assigned, can exist in the gas phase.[36]

For the foregoing reasons, we propose Scheme III as an explanation for the deuterium scrambling during the solvolyses of **6a**-OTf-*1,1*-d_2.[19,20] As the R group in **1** or **4** is better able to stabilize positive charge (Me < Ph < *p*-Tol < An ≃ cyclopropyl), the fraction of C_3-ring product increases (we assume the electrophilicities of the two ions are not vastly different). As R varies from methyl through anisyl, the C_3 vinyl cation (**4**) becomes more important, and the proportion of C_3 product increases. The cation (**4d**), in which R is anisyl, is reminiscent of the cation formed on solvolysis of 3-anisyl-2-butyl brosylate,[37] which is itself an example of a nonclassical phenonium ion.[38]

Experimental Section

Synthesis of Carbinols 13a–d. The synthesis of 1-pent-3-yn-1-ol (**13a**) has been described previously[20] in detail. The three carbinols **13b–d** were obtained by treatment of phenylacetylene,[25] *p*-tolylacetylene,[26] and anisylacetylene[27] with ethylene oxide. The general procedure was as follows: into a 1-L, three-neck, round-bottom flask fitted with dropping funnel, stirrer, and reflux condenser and containing 24 g (1 mol) of magnesium turning was added (under N_2) 120 g of ethyl bromide (1.1 mol) in 250 mL of dry THF. The addition was controlled so that the reaction proceeded with gentle boiling. After the magnesium had completely disappeared, 1 mol of arylacetylene in 250 mL of dry THF was added dropwise, and the mixture then was heated for 1 h under reflux. The reaction mixture was then cooled to −20 °C, and ethylene oxide (53 g, 1.2 mol) was added dropwise from a cooled dropping funnel. The reaction mixture was allowed to stand 6 h at 0 °C and then was stirred for 12 h at room temperature, after which it was poured into a solution of 200 g of NH_4Cl in 1 L of H_2O. The organic phase was separated, after which the aqueous phase was extracted three times each with 50-mL portions of ether. The organic fractions were combined and dried over sodium sulfate, the solvent was removed, and the residue was distilled through a 20 cm long Vigreux column.

4-Phenylbut-3-yn-1-ol (13b): bp 130 °C (1200 Pa); yield, 85 g (58%); NMR (CCl_4) δ 2.68 (t, 2 H, $CCCH_2$, J = 6.5 Hz), 3.42 (s, 1 H, OH), 3.70 (t, 2 H, OCH_2, J = 6.5 Hz), 7.1–7.5 (m, 5 H, aryl). Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 81.8; H, 6.93.

4-*p*-Tolylbut-3-yn-1-ol (13c): bp 119–121 °C (300 Pa); yield, 82 g (51%); NMR (CCl_4) δ 2.33 (s, 3 H, CH_3), 2.62 (t, 2 H, $CCCH_2$, J = 6.5 Hz), 3.45 (s, 1 H, OH), 3.75 (t, 2 H, OCH_2, J = 6.5 Hz), 6.9–7.4 (q, 4 H, aryl). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 83.0; H, 7.64.

4-Anisylbut-3-yn-1-ol (13d): bp 131 °C (100 Pa); mp 61 °C; yield, 76 g (43%); NMR (CCl_4) δ 2.58 (t, 2 H, $CCCH_2$, J = 6.5 Hz), 2.80 (s, 1 H, OH), 3.71 (t, 2 H, OCH_2, J = 6.5 Hz), 3.75 (s, 3 H, OCH_3), 6.6–7.4 (m, 4 H, aryl). Anal. Calcd for $C_{11}H_{12}O_2$: C, 75.00; H, 6.82. Found: C, 75.47; H, 6.99.

Synthesis of 4-Cyclopropylbut-3-yn-1-ol (13e). a. 1-Cyclopropyl-1,4-dichloro-1-butene (15). A suspension of 61 g (0.3 mol) of pure PCl_5 in 300 mL of absolute CCl_4 was cooled to 5–10 °C in a three-neck, 500-mL, round-bottom flask fitted with stirrer, reflux condenser, and dropping funnel. After dropwise addition of 27.5 g (0.25 mol) of dicyclopropyl ketone (**14**), the mixture was boiled under reflux for 18 h (**caution**, HCl). After being cooled, the mixture was transferred to a separatory funnel and slowly added, dropwise, to about double its volume of ice. The ensuing suspension was stirred for 2 h after which the aqueous phase was saturated with NaCl and then extracted five times with 100-mL portions of ether. The combined organic phases were neutralized carefully with $NaHCO_3$ and dried over Na_2SO_4, and after removal of the solvent, the residue was fractionally distilled

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through a 15-cm Vigreux column. The fraction boiling at 50–62 °C (266 Pa) was a cis–trans mixture of dichloride **15**: yield, 32.2 g (72%); NMR (CCl_4) δ 0.59–0.90 (m, 4 H, cyclopropyl CH_2), 1.45–2.10 (m, 1 H, cyclopropyl *t*-CH), 2.64 (q, 2 H, $=CCH_2$), 3.53 (t, 2 H, CH_2Cl, J = 6.5 Hz), 5.67 (t, 1 H, C=CH, J = 6.5 Hz); IR 1635, 3095 (C=C) cm^{-1}.

b. 4-Chloro-4-cyclopropylbut-3-en-1-yl Acetate (16). Dry potassium acetate (130 g, 1.25 mol) was dissolved in 400 mL of absolute acetic acid in a 1-L, three-neck, round-bottom flask fitted with reflux condenser, drying tube, stirrer, and dropping funnel. After being cooled to about 10 °C, 25 g of the isomeric mixture **15** was added dropwise. The mixture was then boiled gently for 48 h under moderate reflux. The reaction mixture was cooled and then poured slowly into a mixture of 200 mL of ether and 1.5 kg of ice with swirling. After separation of the organic phase, the aqueous layer was saturated with NaCl and extracted several times with ether. The combined organic phases were carefully neutralized with dilute $NaHCO_3$ solution, dried with $MgSO_4$, concentrated, and fractionally distilled. The isomeric mixture **16** boiled in the region of 54–61 °C (33 Pa): yield, 20 g (70)%; NMR (CCl_4) δ 0.55–0.95 (m, 4 H, cyclopropyl CH_2), 1.45–1.85 (m, 1 H, cyclopropyl *t*-CH), 2.00 (s, 3 H, CH_3), 2.27–2.72 (m, 2 H, $C=CCH_2$), 4.07 (dt, 2 H, OCH_2, J = 7 Hz), 5.42–5.78 (m, 1 H, C=CH); IR 1040 1223 (COC), 1650, 3100 (C=C), 1752 (C=O), 825 (cyclopropane) cm^{-1}.

c. 4-Chloro-4-cyclopropyl-3-buten-1-ol (17). Lithium aluminum hydride (4.56 g, 0.12 mol) was placed in a 250-mL, round-bottom flask (three-neck, etc.) with 250 mL of absolute ether. With vigorous stirring there was added 37.4 g of acetate **16** in 100 mL of dry ether at such a rate that the mixture gently boiled. After this the mixture was heated 3 h under reflux and then hydrolyzed.[39] After removal of the solvent, the mixture of alcohols **17** was obtained as a colorless liquid, which boiled over the range 112–116 °C (2260 Pa): yield, 22.8 g, 85%; NMR (CCl_4) δ 0.46–0.90 (m, 4 H, cyclopropyl CH_2), 1.46–2.06 (m, 1 H, cyclopropyl *t*-CH), 2.34 (s, 1 H, OH), 2.47 (tm, 2 H, $C=CCH_2$), 3.63 (tm, 2 H, CH_2O), 5.63 (tm, 1 H, C=CH); IR 818 (COC), 1645, 3050 (C=C), 3290 (OH) cm^{-1}.

d. 4-Cyclopropylbut-3-yn-1-ol (13e). For preparation of the triton B reagent (benzyltrimethylammonium hydroxide), 1 L of benzene was added to 1 mol of triton B (40% by weight) in methanol, and a rotary evaporator was used to concentrate to half-volume.[40] Then 4.0 g of cyclopropylchlorobutenol (**17**, 17.5 mmol) was treated with 30 mL of benzene, and to the solution was added all at once 30 mmol of freshly prepared triton B reagent at room temperature. The resulting solution was stirred 1 h at 50 °C. After acidification with acetic acid, the organic phase was neutralized with dilute $NaHCO_3$; the benzene–water mixture was then directly distilled to remove solvent. Almost pure **13e** was obtained: 2.7 g, 90% of theory; bp 67–68 °C (266 Pa); NMR (CCl_4) δ 0.50–0.81 (m, 4 H, cyclopropyl CH_2), 0.81–1.32 (m, 1 H, cyclopropyl *t*-CH), 1.90 (s, 1 H, OH), 2.32 (dt, 2 H, $CCCH_2$, J = Hz), 3.58 (t, 2 H, OCH_2, J = 6.5 Hz); IR 813, 3080 (cyclopropane), 1050 (CO), 2240 (CC), 3320 (OH) cm^{-1}; MS, *m/e* 110 (65, M^+), 109 (17-H), 95 (9), 82 (10), 81 (21), 79 (42, $-HOCH_2$), 77 (15), 73 (8), 69 (100, $-C_3H_5$), 68 (20), 67 (10).

Synthesis of Tosylates 6a-e. The procedures for the preparation of all tosylates were identical except for one feature; in the preparation of **6e** the temperature was kept at −5 to 0 °C. To a solution of 20 mmol of alcohol **13 (a–e)** in 2 mL of dry pyridine was added 4 g of *p*-toluenesulfonyl chloride (21 mmol) in 4 mL of pyridine (with cooling), and the ensuing mixture was stirred 1 h at room temperature and then left in the refrigerator for 24 h. The reaction mixture was then poured on to ice, the oil was taken up in ether, and the ether solution was washed with dilute HCl and NaCl solutions. After drying with $MgSO_4$ and removal of the solvent, white crystals were obtained in each case (after repeated crystallization).

Pent-3-yn-1-yl tosylate (6a-OTs):[20] mp 39 °C; yield, 3.4 g (69%); NMR (CCl_4) δ 1.7 (t, 3 H, $CCCH_3$, J = 2 Hz), 2.45 (s, 3 H, aryl CH_3), 2.50 (m, 2 H, $CCCH_2$), 4.02 (t, 2 H, OCH_2, J = 7 Hz), 7.2–7.9 (m, 4 H, aryl). Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.48; H, 5.92; S, 13.46. Found: C, 60.6; H, 6.04; S, 13.0.

4-Phenylbut-3-yn-1-yl tosylate (6b-OTs): mp 41 °C; yield, 4.1 g (65%); NMR (CCl_4) δ 2.46 (s, 3 H, CH_3), 2.70 (t, 2 H, $CCCH_2$, J = 7 Hz), 4.18 (t, 2 H, OCH_2, J = 7 Hz), 7.30 (m, 5 H, phenyl), 7.46 (m, 4 H, aryl in tosyl). Anal. Calcd for $C_{17}H_{16}O_3S$: C, 67.98; H, 5.37; S, 9.81. Found: C, 69.0; H, 5.77; S, 10.1.

4-*p*-Tolylbut-3-yn-1-yl tosylate (6c-OTs): mp 47 °C; yield, 3.7 g (59%); NMR (CCl_4) δ 2.38 (s, 3 H, CH_3), 2.46 (s, 3 H, CH_3), 2.77 (t, 2 H, $CCCH_2$, J = 7 Hz), 4.13 (t, 2 H, OCH_2, J = 7 Hz), 7.15 (m, 4 H, aryl in tolyl), 7.46 (m, 4 H, aryl in tosyl). Anal. Calcd for $C_{18}H_{18}O_3S$: C, 68.77; H, 5.77; S, 9.81. Found: C, 69.0; H, 5.77; S, 10.1.

4-Anisylbut-3-yn-1-yl tosylate (6d-OTs): mp 50 °C; yield, 3.79 g (56%); NMR (CCl_4) δ 2.42 (s, 3 H, CH_3), 2.73 (t, 2 H, $CCCH_2$, J = 7 Hz), 3.80 (s, 3 H, OCH_3), 4.11 (t, 2 H, OCH_2, J = 7 Hz), 7.10 (m, 4 H, aryl in anisyl), 7.46 (m, 4 H, aryl in tosyl). Anal. Calcd for $C_{18}H_{18}O_4S$: C, 65.44; H, 5.49; S, 9.70. Found: C, 65.9; H, 5.51; S, 10.02.

4-Cyclopropylbut-3-yn-1-yl tosylate (6e-OTs): mp 55 °C; yield, 3.0 g (60%); NMR (CCl_4) δ 0.40–0.75 (m, 4 H, cyclopropyl CH_2), 0.75–1.40 (m, 1 H, cyclopropyl *t*-CH), 2.45, (dt, 2 H, CCH_2, J = 2 Hz), 2.47 (s, 3 H, Ar CH_3), 4.01 (t, 2 H, OCH_2, J = 7.2 Hz), 7.20–7.90 (m, 4 H, arom CH); IR (KBR) 1018 (cyclopropane), 1178, 1355 (SO_2O), 1598 (arom) cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.61; H, 6.10. Found: C, 63.9; H, 6.15.

Syntheses of Triflates 6a–e. The general procedure for preparation of the triflates has been published,[20,24] as have the physical constants for **6a**-OTf.[20] The yields of all triflates (from 20 mmol carbinol) were acceptable (49–92%) except that for the **6e** triflate (R = An), which could only be prepared in less than 10% yield; it was necessary to filter the crude product through Kieselgel in a solution (1:10) of CH_2Cl_2 and Freon 11.

4-Phenylbut-3-yn-1-yl triflate (6b-OTf): yield, 3.0 g, 62%; NMR (CCl_4) δ 2.99 (t, 2 H, $CCCH_2$, J = 6.5 Hz), 4.60 (t, 2 H, OCH_2, J = 6.5 Hz), 7.35 (m, 5 H, Ph). Test for purity: GC, 2 m, 10% UCC W982, 170 °C, 95–99%. Small impurity due to enyne.

4-*p*-Tolylbut-3-yn-1-yl triflate (6c-OTf): yield, 2.5 g, 49%; NMR (CCl_4) δ 2.36 (s, 3 H, CH_3), 2.88 (t, 2 H, $CCCH_2$, J = 6.5 Hz), 4.58 (t, 2 H, OCH_2, J = 6.5 Hz), 6.95–7.4 (m, 4 H, aryl). Test for purity; GC, 2 m, 10% UCC W982, 190 °C, 84–97%. Impurity due to enyne.

4-Cyclopropylbut-3-yn-1-yl triflate (6e-OTf): yield, 2.4 g, 60%; NMR (CCl_4) δ 0.50–0.90 (m, 4 H, cyclopropyl CH_2), 1.70–2.10 (m, 1 H, cyclopropyl *t*-CH), 2.67 (dt, 2 H, CCH_2, J = 2 Hz), 4.50 (t, 2 H, OCH_2, J = 7.4 Hz); IR 820, 1151, 1210, 1255, 1240 (triflate), 2280 (arom) cm^{-1}. Anal. Calcd for $C_8H_9O_3SF_3$: C, 39.66; H, 3.74. Found: C, 39.6; H, 3.65.

Synthesis of 2-Cyclopropyl-1-cyclobutanone (21). a. Cyclopropanecarbaldehyde (19) was obtained by oxidation (Ce^{4+}) of cyclopropylmethanol in aqueous solution as described by Young and Trahanovsky:[30] yield, 62% of theory; NMR (CCl_4) δ 0.9–1.15 (m, 4 H, cyclopropyl CH_2), 1.58–2.18 (m, 1 H, cyclopropyl *t*-CH), 9.10 (d, 1 H, CHO, J = 2.1 Hz).

b. Cyclopropyldiphenylsulfonium Tetrafluoroborate (18). The sulfonium salt **18** was prepared in three steps from 1-bromo-3-chloropropane and diphenyl sulfide:[29] colorless crystals; mp 139 °C; yield, 25% of theory.

c. 2-Cyclopropyl-1-cyclobutanone (21). In a modification of the usual method,[41] 8.0 g of the sulfonium salt **18** (25 mmol) and 1.8 g of aldehyde **19** were placed in a 250-mL, three-neck, round-bottom flask (fitted with a drying tube) containing 150 mL of absolute Me_2SO. The operation was carried out under N_2 with stirring, and 2.0 g of finely divided NaOH was added in ca. 0.5-g portions at room temperature over a 30-min period. The clear, weak-orange solution was treated with 1 mL of acetic acid, whereupon the color changed to weak yellow. The mixture was then diluted 5-fold with water and saturated with NH_4Cl. After at least 10 extractions with 1:1 ether/benzene, there was no more ketone in the aqueous phase (GC analysis). The combined organic phases were neutralized with saturated $NaHCO_3$ solution. After drying with $MgSO_4$ the solvent was removed and the residue was subjected to liquid column chromatography (SiO_2; ether/CH_2Cl_2,

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2:1). 2-Cyclopropylbutanone [21; 1.45 g (54%)] was obtained, which was pure according to GC and NMR analyses. The product was a slightly yellow liquid: bp 168 °C; NMR (CCl_4) δ 0.17–0.60 (m, 4 H, cyclopropyl CH_2), 0.60–1.15 (m, 1 H, cyclopropyl *t*-CH), 1.34–2.43 (m, 2 H, CCH_2C), 2.70–3.38 (m, 3 H, $COCH_2$ and COCH); IR 815, 1020, 3070 (cyclopropane), 1078, 1787 (C=O) cm^{-1}. Anal. Calcd for $C_{10}H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.2; H, 9.10. The mass spectrum was also compatible with structure 21.

2-Cyclopropylcyclobutenyl Triflate (11-OTf) and Nonaflate (11-ONf). Both of these esters were prepared by the improved method referred to earlier.[24] **11-OTf**: NMR (CCl_4) δ 0.5–1.05 (m, 5 H, cyclopropyl CH_2 and CH), 1.96 (t, 2 H, $=CCH_2$, J = 2.8 Hz), 2.78 (t, 2 H, $OCCH_2$); IR 820, 1016 (cyclopropane), 1150, 1215, 1235 (triflate), 1430 cm^{-1}. Physical constants for 11-ONf have been reported earlier.[24]

Independent Syntheses of Solvolysis Products. a. Pent-1-en-3-yne (22a). Potassium hydroxide (34 g, 0.66 mol) was dissolved in 150 mL of triethylene glycol in a 500-mL, three-neck, round-bottom flask fitted with stirrer, dropping funnel, and a condenser for distillation. The mixture was heated to 130 °C, and over a period of 10 min, 20 g (0.14 mol) of 2,5-dichloropent-2-ene[42] was added. The material that distilled was fractionated: bp 57–59 °C; yield, 4.5 g (49%); NMR (CCl_4) δ 1.9 (d, 3 H, CH_3, J = 2 Hz), 5.1–5.8 (m, 3 H, $C=CH_2$); IR (CCl_4) 2250 (triple bond), 1613 (conjugated double bond); MS, *m/e* 66 (100, M^+), 40 (42, $-C_2H_2$).

1-Arylbut-3-en-1-ynes 22b–d (R = phenyl, *p*-tolyl, anisyl). Two millimoles of the appropriate alcohol **13b-d** was placed in a 20-mL flask containing 13 mL of HMPT. The mixture was stirred rapidly (magnetic stirrer) at an oil-bath temperature of about 250 °C.[43] Upon cooling, the mixture was poured into water and extracted 3 times with petroleum ether (30–50 °C), the organic phase was washed 5 times with water and dried with sodium sulfate, and the solvent was removed by distillation. The residue was purified by liquid column chromatography on Kieselgel with petroleum ether (30–50 °C). The yields were 210 mg (82%) of **13b** (R = phenyl), 200 mg (71%) of **13c** (R = *p*-tolyl), and 180 mg (57%) of **13d** (R = anisyl). The NMR, IR, and mass spectra[31] were all consistent with the expected enynes.

1-Cyclopropylbut-3-en-1-yne (22, R = Cyclopropyl). Freshly prepared sodium acetate (2.2 mol) was dissolved in 100 mL of absolute Me_2SO in a 250-mL, three-neck, round-bottom flask (drying tube, room temperature, under N_2) and treated with 46.2 g (0.3 mol) of 1-cyclopropyl-1,4-dichlorobut-1-ene (**15**, vide supra). The temperature was gradually (magnetic stirring) raised to 70–80 °C, whereupon the suspension turned yellow. The reaction was followed by taking probes and subjecting them to GC. After ca. 3 h all the dichloride had disappeared. After addition of 400 mL of H_2O, the mixture was extracted 10 times with 50 mL each of ether. The organic phase was neutralized with dilute acetic acid and dried with Na_2SO_4. Distillation through a 20-cm Vigreux column yielded 14 g (60% of theory) of the butenyne **22** (R = cyclopropyl) as a colorless, relatively volatile liquid: bp 60 °C (10 640 Pa). The NMR, IR, and mass spectra were all consistent with the assigned structure.[32]

4-Substituted-but-3-yn-1-yl 2,2,2-Trifluoroethyl Ethers (13a–d, R = Me, Ph, *p*-Tolyl, Anisyl). Triflates **6a–c** and tosylate **6d** (5 mmol) were dissolved in 1 mL of water-free methylene chloride and treated with 1 mL of a saturated solution of K_2CO_3 in TFE.[44] After being stirred for 24 h, the reaction mixture was poured into water and extracted with methylene chloride, and the solvent was removed. The residues were purified by LC on Kieselgel columns with petroleum ether (30–50 °C). Triflates **6a–c** were stirred at room temperature, whereas **6d**-OTs (R = anisyl) was heated under reflux. The yields were as follows: **23a**, 89%; **23b**, 78%; **23c**, 80%; **23d**, 61%. The NMR, IR, and mass spectra[44] were consistent with the assigned structures.

2-*p*-Tolyl- and 2-Anisylcyclobutanone (10c and 10d). 2-Methylcyclobutanone (**10a**)[3] and 2-phenylcyclobutanone (**10b**)[45] have been described previously. 3-(Bromopropyl)triphenylphosphonium bromide[46] (0.56 g, 0.12 mol) was stirred under nitrogen, with 250 mL of water-free glyme in a 1-L, three-neck, round-bottom flask fitted with reflux condenser, drying tube, dropping funnel, and stirrer; 8 g (a. 0.24 mol) of 80% NaH–mineral oil suspension and a few drops of ethanol were added, and the mixture was stirred 6 h at 70 °C. The previously grey suspension turns reddish brown after addition, dropwise, of 0.12 mol of *p*-tolualdehyde (or anisaldehyde); the mixture was stirred for 12 h at 80 °C, then poured into ice water, and extracted thrice with 50 mL of petroleum ether (30). The solution was dried over $MgSO_3$ after being washed with saturated NaCl solution. *p*-Tolylmethylenecyclopropane, bp 41 °C (26.6 Pa), 7 g (40% yield). Anisylmethylenecyclopropane, bp 70 °C (26.6 Pa), 7.5 g (39% yield).

The 2-arylcyclobutanones[47] were then prepared as follows: 40 mmol of arylmethylenecyclopropane was placed in 50 mL of absolute methylene chloride and stirred magnetically at 0 °C while 7.3 g (40 mmol) of *p*-nitrobenzoic acid was added portionwise. (The flask was fitted with a reflux condenser and drying tube.) The mixture was stirred further for 1 h at room temperature and 1 h under reflux, filtered (vacuum), washed thrice each with 10% NaOH and water, and then dried over $MgSO_4$. The products were purified on Kieselgel columns with 30–50 °C petroleum ether. 2-*p*-Tolylcyclobutanone (**10c**): 4.8 g (75%); NMR (CCl_4) δ 1.65–3.4 (m, 4 H, CH_2 in C_4 ring), 2.30 (s, 3 H, CH_3), 4.35 (t, 1 H, CH), 7.04 (m, 4 H, aryl); IR 3010 (s), 1790 (s, C=O), 1545 (m), 1300 (m), 1095 (m) cm^{-1}. 2-Anisylcyclobutanone (**10d**): NMR (CCl_4) δ 1.85–2.75 (m, 2 H, CH_2), 2.90–3.35 (m, 2 H, CH_2 adjacent to C=O), 3.75 (s, 3 H, OCH_3), 4.32 (m, 1 H, CH), 7.1–8.0 (m, 4 H, aryl); IR 2960 (m), 1780 (s, C=O), 1540 (m), 1292 (m), 1070 (m) cm^{-1}.

Phenyl Cyclopropyl Ketone (7b). (The syntheses of the methyl cyclopropyl ketone (**7a**) and *p*-tolyl cyclopropyl ketones (**7c**) have been reported previously.[48] Anisyl cyclopropyl ketone (**7c**) is available from Aldrich.) The Grignard reagent from 12 g (0.5 mol) of Mg in 50 mL of dry ether and bromobenzene (0.5 mol) was prepared and to it was added 41.2 g (0.4 mol) of 3-chlorobutyronitrile in 200 mL of dry ether (dropwise) while the flask was cooled with ice. After 4 h the viscous mixture was poured on to ice–HCl. The imine hydrochloride that was formed remained in aqueous solution. After separation of the aqueous phase, it was washed twice with 100-mL portions of ether. After 24 h at room temperature, the imine was completely hydrolyzed to the aryl cyclopropyl ketone (**7b**, R = phenyl, or **7c**, R = *p*-tolyl) and precipitated as an oil or solid. The ketone was taken up in ether, the aqueous phase was washed with ether, and the combined organic phases were dried over Na_2SO_4. After removal of the solvent, the residue was dissolved in 50 mL of water-free methanol and slowly added to a solution of 22.6 g (0.4 mol) of KOH in 250 mL of methanol. After 12 h of stirring, the greater portion of solvent was distilled, and the residue was treated with water and thrice extracted with 50-mL portions of ether. After being dried over Na_2SO_4 and removal of solvent, the product was vacuum distilled. **7b** (R = phenyl): bp 113 °C (1729 Pa); NMR (CCl_4) δ 0.70–1.32 (m, 4 H, CH_2 in C_3 ring), 2.40–2.83 (m, 1 H, CH), 7.30–7.55 (m, 3 H, aryl), 7.83–8.11 (m, 2 H, aryl); IR 1660 (C=O), 1597, 1577 (C=C), 1042 (C_3 ring) cm^{-1}.

Addition to the Triple Bonds of 13b and 13c. Synthesis of 1-Phenyl- and 1-*p*-Tolyl-1-oxobut-4-yl 2,2,2-Trifluoroethyl Ether (26b and 26c). Trifluoromethanesulfonic acid (0.5 mL, water free) was added carefully to a solution of 0.5 mL of **13b** or **13c** in 0.5 mL of absolute TFE, contained in a 10-mL, round-bottom flask fitted with reflux condenser and drying tube. After being stirred for 3 h, the contents were poured on to ice, and the mixture was neutralized with $NaHCO_3$ and then extracted with ether. The ether layer was dried over $MgSO_4$ and the solvent was removed by distillation. The residue was shown by GC to consist in each case of 90% of a single product, which was purified by column chromatography on Kieselgel with petroleum ether (30–40

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°C)/methylene chloride (5:1). On the basis of their NMR spectra, the products are the two keto ethers **26b** and **26c**. NMR for (a) **26b** (R = Ph), (b) **26c** (R = Tol): δ (CCl_4) (a) 1.75–2.25, (b) 1.75–2.3, (m, 2 H, $CH_2CH_2CH_2$); (b) 2.42, (s, 3 H, CH_3); (a) 3.10, (b) 3.00, (t, 2 H, CH_2CO, J = 6 Hz); (a) 3.70, (b) 3.67, (t, 2 H, CH_2O, J = 6.5 Hz); (a) 3.78, (b) 3.78, (q, 2 H, CH_2CF_3, J = 8.5 Hz); (a) 7.25–7.60 (5 H), (b) 7.00–8.00, (4 H, m, aryl).

Acid Ring Opening of Aryl Propyl Ketones 7b and 7c. To a solution of 0.5 g of aryl cyclopropyl ketone (**7b**, R = Ph; **7c**, R = Tol) in 10 mL of TFE was added 1 drop of trifluoromethanesulfonic acid (in a 50-mL, round-bottom flask with condenser). *p*-Xylene (100 μL) was added to serve as a GC standard. The reaction was followed by taking aliquots for GC analysis, which showed a steady decline in the concentration of **7b** or **7c** and a corresponding increase in the concentration of ether **26b** or **26c**. After 3 h the content of keto ether **26** was about 30%.

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Registry No. **6a**-OTf, 54106-83-1; **6a**-OTs, 3329-88-2; **6b**-OTf, 87639-40-5; **6b**-OTs, 85375-43-5; **6c**-OTf, 87639-41-6; **6c**-OTs, 87639-42-7; **6d**-OTs, 87639-43-8; **6e**-OTf, 87639-44-9; **6e**-OTs, 87639-45-0; **7b**, 3481-02-5; **7c**, 7143-76-2; **10c**, 87639-46-1; **10d**, 70106-27-3; 11-OTf, 70106-33-1; 11-ONf, 83961-10-8; **13b**, 10229-11-5; **13c**, 31208-53-4; **13d**, 52999-15-2; **13e**, 87639-47-2; **14**, 1121-37-5; (*E*)-**15**, 83313-95-5; (*Z*)-**15**, 87639-48-3; (*E*)-**16**, 87639-49-4; (*Z*)-**16**, 87639-50-7; (*E*)-**17**, 87639-51-8; (*Z*)-**17**, 87639-52-9; **18**, 33462-81-6; **19**, 1489-69-6; **20**, 87639-53-0; **21**, 70106-28-4; **22a**, 646-05-9; **22b**, 13633-26-6; **22c**, 30011-66-6; **22d**, 55088-86-3; **22e**, 71452-17-0; **26b**, 87639-54-1; **26c**, 87639-55-2; EtMgBr, 925-90-6; triton B, 100-85-6; phenylacetylene, 536-74-3; *p*-tolylacetylene, 766-97-2; anisylacetylene, 768-60-5; ethylene oxide, 75-21-8; 1-bromo-3-chloropropane, 109-70-6; diphenyl sulfide, 139-66-2; 2,5-dichloropent-2-ene, 20177-02-0; 3-bromopropyltriphenylphosphonium bromide, 3607-17-8; *p*-tolualdehyde, 104-87-0; anisaldehyde, 123-11-5; (*p*-tolylmethylene)cyclopropane, 55088-80-7; (anisylmethylene)cyclopropane, 55088-84-1; *p*-nitrobenzoic acid, 62-23-7; bromobenzene, 108-86-1; 3-chlorobutyronitrile, 53778-71-5; α-cyclopropylbenzylidenimine hydrochloride, 20127-69-9.

Kinetic Study of the Reaction of 2,4,6-Triphenylpyrylium Ion with Amines. Base-Catalyzed Ring-Opening Reaction of 2*H*-Pyran Intermediates

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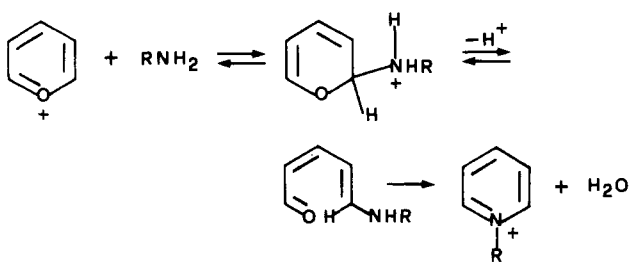
The kinetics of reaction of 2,4,6-triphenylpyrylium ion with butylamine, cyclohexylamine, pyrrolidine, piperidine, and morpholine to yield the corresponding ring-opened divinylogous amides have been studied in methanol at 25 °C. The reactions with the secondary amines are base-catalyzed, whereas those with the primary amines are not. The results are consistent with the formation of a charged 2*H*-pyran as a reaction intermediate. With the primary amines the formation of the intermediate is the rate-determining step, whereas for the secondary amines it is the decomposition of the intermediate toward the ring-opened product that is the slow process. In particular, the sensitivity of the base-catalyzed step to the nature of the secondary amine is shown to indicate that the rate-controlling step is the proton transfer from the charged 2*H*-pyran to the amine to yield the corresponding neutral 2*H*-pyran.

The reaction of primary amines with pyrylium salts is an important route to the synthesis of N-substituted pyridinium salts.[1] A ring-opened divinylogous amide is generally observed as an intermediate in this process. It is presumably formed from the 2*H*-pyran isomer that should be a primary product of the nucleophilic attachment of the amine (see Scheme I). 2*H*-Pyrans are observed in several reactions between pyrylium salts and nucleophiles,[1a] but in the reaction with amines they can be detected only in a few cases.[2]

The synthetic importance of this reaction, in conjunction with our continuing interest in the study of interactions between nucleophiles and heteroaromatic organic cations[3] has led us to investigate the kinetic influence of several primary and secondary amines with varying structural features such as butylamine, cyclohexylamine, pyrrolidine, piperidine, and morpholine on the early stages of the reaction of 2,4,6-triphenylpyrylium ion (**1**) in methanol, i.e., up to the formation of the divinylogous amide. This was a convenient substrate to deal with because of its low tendency to decompose otherwise under the reaction conditions and because of the availability of the rate data for the reaction with MeO^- in the same solvent from previous work.[3]

Scheme I



Experimental Section

Materials. 2,4,6-Triphenylpyrylium perchlorate was available from previous work.[3] All the amines were distilled from sodium and potassium and kept under argon in the dark. Methanol and

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