Vinyl Cations. 30.[1] Preparation and Solvolysis of 1-Cyclobutenyl Nonaflates. Generation of Stabilized Vinyl Cation Species

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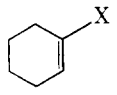
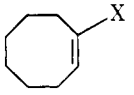
Abstract: 1-Cyclobutenyl nonaflate (**16**) and the series of 2- and 3-methyl- and aryl-substituted cyclobutenyl nonaflates **17, 18, 19, 21,** and **22** were synthesized by treatment of either the corresponding cyclobutanones directly with nonafluorobutanesulfonic acid anhydride or using the lithium enolates (e.g., **30a, 30b**) as starting compounds for a reaction with the anhydride. The solvolysis reactions of the cyclobutenyl nonaflates were studied in various solvents. All cyclobutenyl nonaflates solvolyze via a vinyl cation mechanism leading to rearranged cyclopropyl and homopropargyl compounds, the product composition being dependent upon the substituents in the 2 and 3 position. The same products as are formed in the solvolysis of the cyclobutenyl nonaflates are also found in the solvolysis reactions of cyclopropylidene methyl (**11**) and homopropargyl derivatives (**7**), pointing to the same cationic intermediates. The solvolysis products and the rates of the cyclobutenyl nonaflates are in agreement with the formation of stabilized bridged 1-cyclobutenyl cations (**14, 55, 67**).

Almost a decade has passed since vinyl cations were established as definite intermediates in the solvolyses reactions of many vinyl substrates.[3] In acyclic vinyl derivatives a variety of substituent groups have been successfully used to stabilize the cationic center formed during the solvolysis reactions.[4] However, in cyclic systems, the ease of formation of cyclic vinyl cations is dependent upon ring size.[5] This is due to the fact that the linear vinyl cation structure is energetically more favorable, as found by theoretical calculations.[6] Hence it could be expected that the rates of solvolyses of cyclic vinyl derivatives, e.g., vinyl triflates, should increase with increasing ring size, since the intermediate vinyl cation has the preferred linear geometry available as the ring becomes larger. This has been proven experimentally; 1-cyclooctenyl trifluoromethanesulfonate (**2a**), for example, solvolyzes 10^4 times faster than 1-cyclohexenyl triflate (**1a**)[5] with the maximum reaction rate being reached with 1-cyclononenyl triflate.



1a, X = OTf
b, X = ONf



2a, X = OTf
b, X = ONf

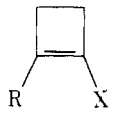
Tf = SO_2CF_3
Nf = $SO_2C_4F_9$

The same is true for the corresponding nonafluorobutanesulfonates (nonaflates):[7] 1-cyclooctenyl nonaflate (**2b**) solvolyzes 1.1×10^4 times faster than 1-cyclohexenyl nonaflate (**1b**).[7] 1-Cyclopentenyl triflate (**3a**) or 1-cyclopentenyl nonaflate (**3b**) solvolyzes with an even lower rate than the cyclohexenyl derivatives **1a** and **1b**, but no longer via a vinyl cation mechanism. In nucleophilic solvents like ethanol/water mixtures **3a** and **3b** solvolyze via a sulfur-oxygen cleavage,[8] thus avoiding the formation of the highly strained nonlinear vinyl cation (**4**). The cyclopentenyl cation **4**, which cannot be formed

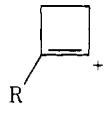
3a, X = OTf
b, X = ONf

4

via a solvolytic process, has been reported to form in a photochemical reaction.[9] Therefore, the solvolytic behavior of the next lower cyclic homologue, the cyclobutenyl triflate (**5a**, R = H) or cyclobutenyl nonaflate (**5b**, R = H) should be especially interesting. In this case one should expect an even smaller



5a, X = OTf
b, X = ONf



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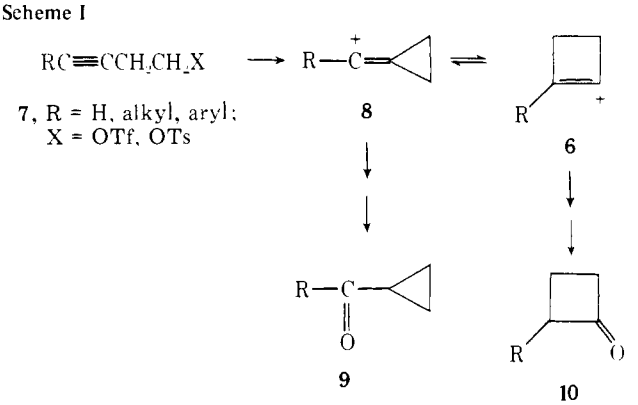
tendency to form the corresponding vinyl cation (**6**, R = H). Its formation seems unlikely, because a cyclobutenyl cation (**6**, R = H) should be even more strained than the cyclopentenyl cation **4**.

Nevertheless our earlier work on the homopropargyl rearrangement[10] led us to propose a cyclic four-membered vinyl cation intermediate in order to explain the formation of cyclobutanones. In this rearrangement reactive homopropargyl derivatives **7** can be solvolyzed with formation of cyclopropyl ketones **9** and cyclobutanones **10**, as shown in Scheme I. The rearrangement proceeds with participation of the triple bond via an unsymmetrical S_N2 transition state,[11] leading to the cyclopropylidenemethyl cation **8**, which is in equilibrium with the cyclobutenyl cation **6**.

The high stability of cyclopropylidenemethyl cations **8** is well documented by theoretical and experimental results,[4] e.g., through the extensive investigations on the reactivity of cyclopropylidenemethyl bromides (**11**).[4,12]

We have shown earlier that cyclopropylidenemethyl bromides (**11**), in contrast to other vinyl bromides, are highly reactive in solvolysis reactions, leading to products which are similar to the products obtained in the homopropargyl rearrangement of **7**, and thus pointing to the same intermediates.

Scheme I



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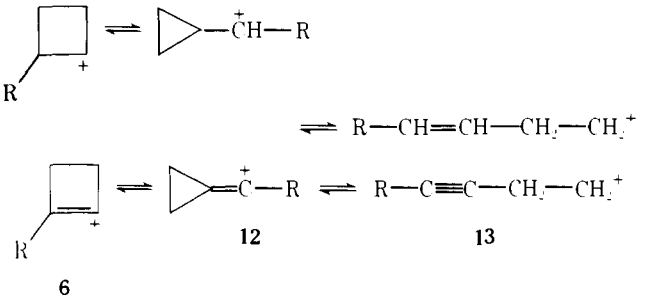
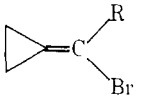
Scheme II



6 12 13

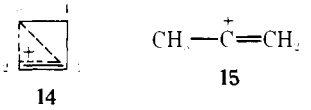
The high reactivity of cyclopropylidenemethyl bromides (**11**) resembles the solvolytic reactivity of cyclopropylmethyl halides. Therefore the observed rearrangement reactions of cyclopropylidenemethyl bromides **11** were discussed in similar



11, R = H, alkyl, aryl

terms according to Scheme II, where the cyclopropylidenemethyl (**12**), the cyclobutenyl (**6**), and the homopropargyl cations (**13**) are in equilibrium with each other.[4,12]

The proposed involvement of a cyclobutenyl cation (**6**) as a stable intermediate in the homopropargyl rearrangement was supported by MO calculations.[13] The positive charge in the cyclobutenyl cation was found to be delocalized over carbon atoms 2 and 3 due to the overlap of the vacant p orbital of the cation with the C_2-C_3 σ bond (**14**).



14 15

Recent ab initio calculations are also in agreement with a nonclassical structure **14** for the cyclobutenyl cation.[14] Accordingly C_3 in **14** acquires a bridging position with almost equal distances from C_1 and C_2. The calculations show that **14** and the linear 2-propenyl cation (**15**) have comparable stabilities.[14] This result is consistent with the similar solvolysis rates of 1-cyclobutenyl and 2-propenyl derivatives.

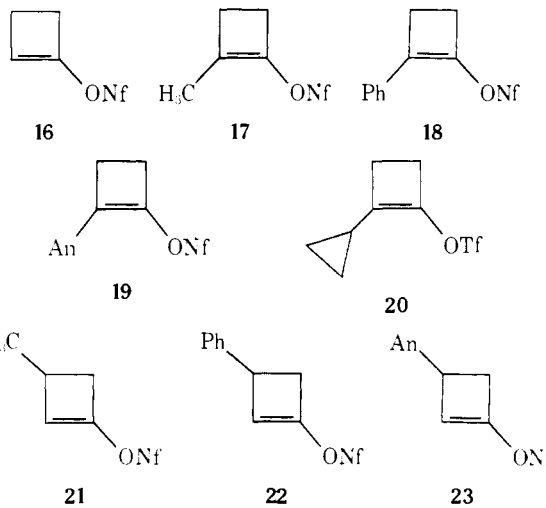
The unusually high solvolysis rate of 1-cyclobutenyl derivatives reflecting the stabilization of the intermediate cyclobutenyl cation **14** is best demonstrated by a comparison of the relative rates of a series of cyclic vinyl nonaflates. Going from 1-cyclohexenyl nonaflate (**1b**) to cyclobutenyl nonaflate (**16**) one indeed observes a dramatic rate increase of 3723 as shown in Table I.

In order to assess in more detail the behavior and nature of such cyclobutenyl cations we report in this paper the syntheses and solvolyses of a series of cyclobutenyl nonaflates and triflates **16-23.**

Synthesis of the 1-Cyclobutenyl Nonaflates. Vinyl triflates are usually prepared from the corresponding ketones by treatment with trifluoromethanesulfonic acid anhydride and a base to neutralize the triflic acid formed.[5] When this reaction was applied to cyclobutanone (**24**) it gave only negligible amounts of 1-cyclobutenyl triflate and large amounts of starting material and polymer. As the usual aqueous workup gave no indication of the triflate product, this led us to suspect that 1-cyclobutenyl triflate once formed is very reactive and solvolyzes to the ketone **24** during workup. A nonaqueous workup also produced problems in that the triflic anhydride itself is low boiling and therefore could not be easily removed from the reaction mixture without affecting the volatile 1-cyclobutenyl triflate. Therefore the homologous nonaflates were prepared.

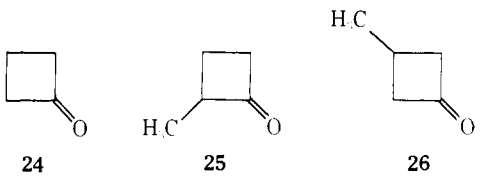
Table I. Rate Constants for Cyclic Vinyl Nonaflates in 50% Ethanol at 100 °C[7,15]

nonaflate	k, s^{-1}	k^{rel}
cyclobutenyl (**16**)	3.5×10^{-3}	3723
cyclohexenyl (**1b**)	9.4×10^{-7}	1
cyclooctenyl (**2b**)	10.5×10^{-3}	11 170



16 17 18 19 20 21 22 23

Nonafluorobutanesulfonic acid anhydride is higher boiling than triflic anhydride[7] and therefore we could pump out the cyclobutenyl nonaflate **16** formed from the polymeric reaction mixture and excess anhydride. This method worked well for all low-boiling cyclobutanones such as **24, 25,** and **26.** The yield



24 25 26

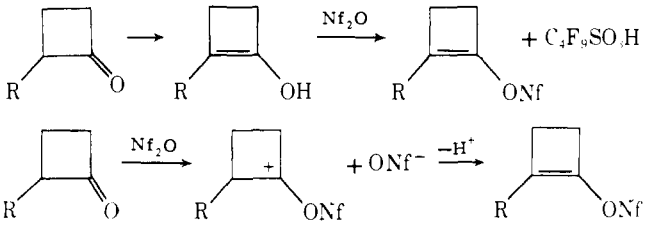
of nonaflates **16** and **17** was 15% in the case of **24** and **25,** respectively, and much less (ca. 5%) for **26** to form the 3-methylcyclobutenyl nonaflate (**21**). For the syntheses of nonaflates **18** and **19** 2-phenylcyclobutanone (**29a**) and 2-anisylcyclobutanone (**29b**) were required. Both ketones were prepared according to the method of Salaün and Conia.[16] In this method the cyclopropylidenemethanes **27a** and **27b,** which we synthesized earlier,[17,18] were treated with *p*-nitroperbenzoic acid in methylene chloride. The thereby formed intermediate epoxides **28a** and **28b** rearranged quantitatively with formation of the ketones **29a** and **29b,** respectively.

The same method, which was applied to prepare the nonaflates **16** and **17,** namely, reacting the ketones with nonafluorobutanesulfonic acid anhydride in the presence of a base, could not be applied to the synthesis of nonaflates **18** and **19;** only products not containing the four-membered ring and polymers were isolated.

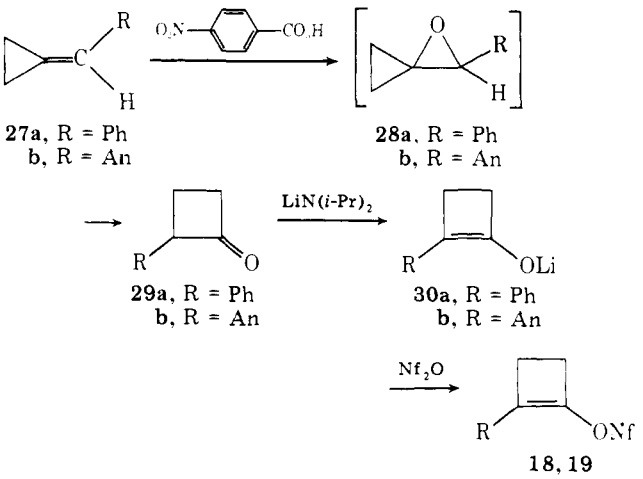
The reaction of cyclobutanones with either triflic anhydride or nonafluorobutanesulfonic acid anhydride to form the vinyl triflates or nonaflates has not been studied from a mechanistic point of view. It is not clear whether or not reaction of the cyclobutanone with anhydride proceeds via an enolization of the ketone with subsequent formation of the sulfonate or via direct O-acylation of the cyclobutanone generating a positive charge on the carbonyl carbon and subsequent deprotonation to give the cyclobutenyl sulfonate according to Scheme III.

In the latter case 2 substituents with a high stabilizing ability on a positive charge, like phenyl or anisyl, would induce a rearrangement reaction instead of the necessary deprotonation,

Scheme III

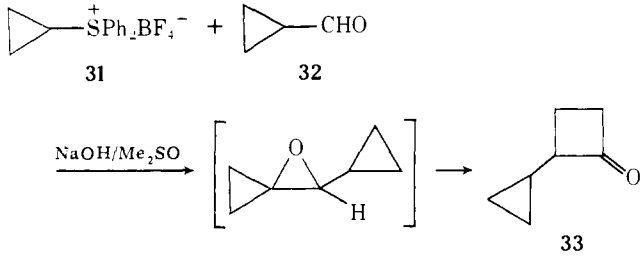


leading to the required cyclobutenyl sulfonate.[19] To avoid rearrangement reactions of this type the ketones **29a** and **29b** were first converted with lithium diisopropylamine in glyme to the corresponding lithium enolates **30a** and **30b,** which were



subsequently treated with the anhydride. The nonaflates **18** and **19** could be isolated using this method in yields of 40–50%.

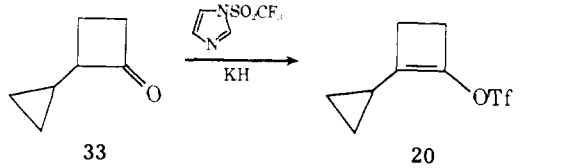
As starting material for the preparation of the 2-cyclopropylcyclobutenyl triflate (**20**) again the corresponding ketone **33** was chosen. For the synthesis of 2-cyclopropylcyclobutanone **33** the method of Trost was applied.[20] Cyclopropyldiphenylsulfonium tetrafluoroborate (**31**) was reacted with cyclopropylcarboxaldehyde (**32**) for 5 min under basic conditions forming 2-cyclopropylcyclobutanone (**33**). Despite the fact that



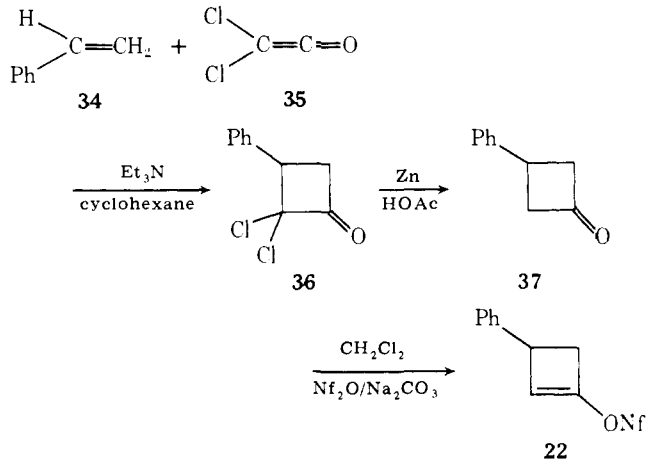
aldehyde **32** was used in excess, the desired ketone **33** could not be isolated in yields higher than 40% based upon the sulfonium salt **31** used. This is due to the low stability of the cyclopropanecarboxaldehyde (**32**) under the strongly basic conditions. Increasing yields up to 55% were obtained with an inverse addition technique (see Experimental Section).

All attempts to prepare the 2-cyclopropylcyclobutenyl nonaflate using the above-mentioned method via the lithium enolate were unsuccessful; only unidentified and polymeric products were isolated.

In contrast to the nonaflate the 2-cyclopropylcyclobutenyl triflate (**20**) was synthesized in low yield by treating ketone **33**



Scheme IV

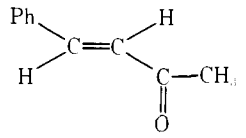


with potassium hydride[21] and trifluoromethanesulfonic acid imidazolide[22] with very short reaction times. Triflate **20** is not very stable; it decomposes within 24 h even at lower temperatures.

To study the influence of 3 substituents on the formation of a cyclobutenyl cation, attempts were made to synthesize the phenyl- and anisyl-substituted nonaflates **22** and **23**. For the synthesis of 3-phenylcyclobutenyl nonaflate (**22**) the prerequisite, 3-phenylcyclobutanone (**37**), was prepared according to the sequence in Scheme IV. This differs from the syntheses described in the literature,[23] containing fewer and experimentally less demanding steps.

As shown in Scheme IV first the 2,2-dichloro-3-phenylcyclobutanone (**36**) is prepared from styrene (**34**) and dichloroketene (**35**).[24] Ketone **36** can be reduced either by triphenyltin hydride or zinc powder in acetic acid in very high yields. The latter procedure was used.

The synthesis of 3-phenylcyclobutenyl nonaflate (**22**) from ketone **37** turned out to be very difficult. All reactions with ketone **37** can only be done at room temperature or even better at 0 °C. Heating the ketone, for example, with trimethylchlorosilane in triethylamine, in an attempt to prepare the corresponding enol trimethylsilyl ether,[25] gave the thermally rearranged product **38**. Attempts to enolize ketone **37** by using



lithium diisopropylamine in glyme at 0 °C followed by reaction with either nonafluorobutanesulfonic imidazolide or nonafluorobutanesulfonyl chloride gave only very small amounts of the nonaflate **22** along with unidentified polymers. Also, the reaction of **37** with sodium hydride in glyme at room temperature, followed by treatment with nonafluorobutanesulfonyl fluoride, did not yield the required nonaflate **22.** Finally 3-phenylcyclobutanone (**37**) was reacted with nonafluorobutanesulfonic acid anhydride in methylene chloride in the presence of sodium carbonate at 0 °C, using the original method of preparing nonaflates and triflates.[5] Careful chromatographic purification allowed the isolation of **22** in low yield.

Scheme V shows the synthesis of 3-anisylcyclobutanone (**40**), which was prepared from the dichlorocarbene adduct **39.** The nonaflate **23** could not be obtained in pure state despite many attempts.

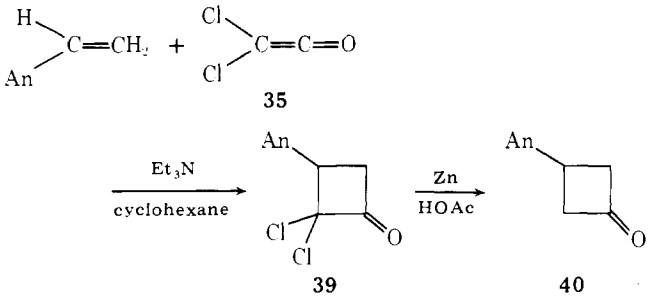
Results and Discussion

The high solvolytic reactivity of 1-cyclobutenyl nonaflate

Table II. Solvolysis Rates of Cyclobutenyl Nonaflates in Aqueous Ethanol Mixtures

nonaflate	solvent	temp, °C	k, s^{-1}	k_{rel}	$\Delta H^{\ddagger}$, kcal/mol
16	50% EtOH	51.2	$2.57 \times 10^{-5} \pm 0.021$	1	23.6
	50% EtOH	74.8	$3.27 \times 10^{-4} \pm 0.08$		
	80% EtOH	74.8	$3.23 \times 10^{-5} \pm 0.04$		
17	50% EtOH	28.8	$3.01 \times 10^{-4} \pm 0.08$	130	20.2
	50% EtOH	50.8	$3.20 \times 10^{-3} \pm 0.06$		
	80% EtOH	28.8	$2.38 \times 10^{-5} \pm 0.1$		
	80% EtOH	50.8	$3.50 \times 10^{-4} \pm 0.04$		
18	50% EtOH	51.8	$2.61 \times 10^{-5} \pm 0.04$	1	25.3
	50% EtOH	75.2	$3.90 \times 10^{-4} \pm 0.02$		
	80% EtOH	75.2	$6.10 \times 10^{-5} \pm 0.1$		
19	50% EtOH	51.8	$9.50 \times 10^{-5} \pm 0.33$	3.7	22.4
	50% EtOH	75.2	$1.01 \times 10^{-3} \pm 0.1$		
	80% EtOH	75.2	$3.48 \times 10^{-4} \pm 0.01$		
21	50% EtOH	50.5	$5.92 \times 10^{-5} \pm 0.09$	2.3	23.2
	50% EtOH	75.0	$7.60 \times 10^{-4} \pm 0.1$		
	80% EtOH	75.0	$1.54 \times 10^{-4} \pm 0.08$		

Scheme V



(**16**) with respect to other cyclic vinyl nonaflates (vide supra) points to a stabilized intermediate vinyl cation. Cyclobutanone (**24**), the major solvolysis product in 50% ethanol/water, however, could also have been formed by an alternate mechanism, e.g., a sulfur-oxygen cleavage of the nonaflate. The main task therefore was to prove a vinyl cation mechanism in the solvolysis of **16** and to exclude other competing mechanisms.[3]

Cyclobutenyl nonaflate (**16**) was solvolyzed in solvents of different nucleophilicity and ionizing power, the resulting reaction products were identified, and the solvolysis rates were measured. The solvolysis of **16** in 50% ethanol/water containing triethylamine as a base at 100 °C gave cyclobutanone (**24**) as the main product, thus leading mostly to a nonrearranged compound. Of the expected rearranged products, namely, cyclopropanecarboxaldehyde (**32**) and 3-butyn-1-ol (**41**), only 3-butyn-1-ol (**41**) was detected. The product composition therefore is in accordance with the results obtained in the solvolysis of the two other "homopropargyl isomers", leading to the vinyl cations given in Scheme II: cyclopropylidenemethyl bromide (**11**, R = H) in 50% aqueous methanol solvolyzes with complete rearrangement to form cyclobutanone (**24**).[12] The solvolysis of 3-butyn-1-yl triflate (**7**, R = H) in trifluoroacetic acid yields exclusively cyclobutanone (**10**, R = H, in Scheme I).

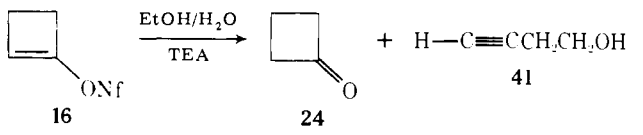


Table III. Rate Constants for **16** at Different pH in 50% EtOH-H_2O at 52.2 °C

pH	$k \times 10^5$, s^{-1} [a]	pH	$k \times 10^5$, s^{-1} [a]
3.2	2.66	7.2	2.74
4.2	2.55	8.2	2.86
5.2	2.69	9.2	2.83
6.2	2.57		

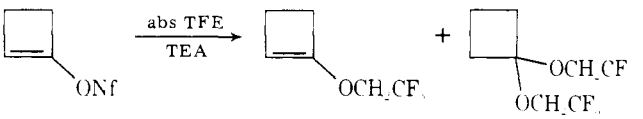
[a] Average error 1.7%.

The predominant formation of cyclobutanone from these three diverse precursors is in agreement with recent ab initio calculations about the relative stabilities of the unsubstituted cyclopropylidenemethyl cation **12** (R = H) (Scheme II) vs. the cyclobutenyl cation **6** (R = H). According to these calculations one can safely predict that the cyclobutenyl cation (**12**, R = H)[14] is more stable than the cyclopropylidenemethyl cation (**6**, R = H).

Table II lists the solvolysis rates of cyclobutenyl nonaflates in different aqueous ethanol mixtures.

To exclude an addition-elimination mechanism in the solvolysis of **16**, the rate of **16** was measured at different pH. As the data in Table III show the solvolysis rate was constant in the pH range of 3.2–9.2 in 50% ethanol, ruling out an electrophilic addition to the double bond of **16**.[3]

To obtain further insight into the mechanism of the solvolysis of **16** an attempt was made to capture the intermediate cyclobutenyl cation by use of other solvents. Reaction of the nonaflate **16** in absolute trifluoroethanol (TFE), buffered with triethylamine (TEA), at 75 °C for 10 days gave cyclobuten-1-yl trifluoroethyl ether (**42**) and ketal **43** in a ratio of 10:1. The

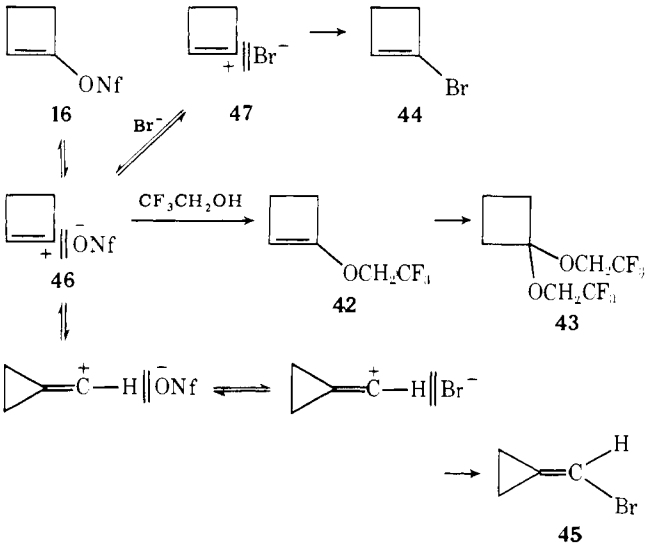


formation of the enol ether **42** can be explained only by postulating an intermediate cyclobuten-1-yl cation. The ketal **43** is formed by the addition of TFE to the enol ether **42**. An addition-elimination mechanism for the solvolysis of cyclobutenyl nonaflate (**16**) in TFE was excluded by carrying out the reaction in absolute CF_3CH_2OD under the conditions mentioned above. The enol ether **42** obtained did not contain any deuterium, thus unequivocally ruling out such a mechanism.[26]

Conclusive evidence for the intermediate formation of a four-membered cyclic vinyl cation was obtained by solvolyzing **16** in absolute TFE buffered with TEA containing a tenfold excess of tetraethylammonium bromide at 75 °C for 10 days. The product analysis showed that cyclobuten-1-yl bromide (**44**) and cyclopropylidenemethyl bromide (**45**) were formed in a ratio of 85:15 along with enol ether **42** and ketal **43**.

The formation of the cyclobutenyl bromide **44** and the rearranged cyclopropylidenemethyl bromide **45** along with **42** and **43** could be explained via ion pairs as shown in Scheme VI. In the solvolysis reaction the solvation of the leaving group leads to the solvent separated ion pair **46**. The enol ether **42** and

Scheme VI

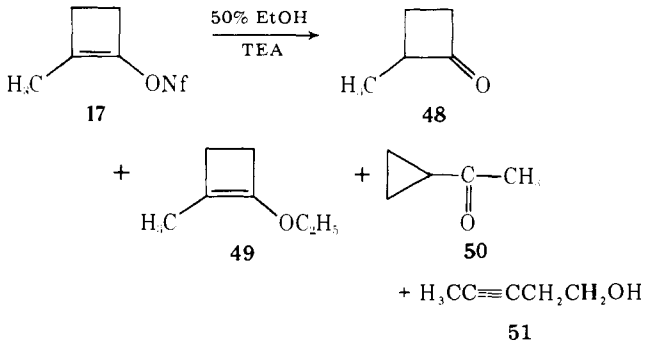


the intermediate ion pair **47** are formed from the ion pair **46**. The rearrangement to form the cyclopropylidenemethyl bromide **45** occurs in the solvent separated ion pair **46**. The addition of excess tetraethylammonium bromide made the special salt effect possible and the cation **46** had enough time to rearrange and capture the more nucleophilic bromide.[26]

These results are in agreement with our earlier work on the solvolysis reactions of other substituted cyclopropylidenemethyl bromides and homopropargyl sulfonates. The bromides **44** and **45** are stable under the conditions of solvolysis (75 °C). To bring them to solvolysis, higher temperatures than 75 °C are required.[12]

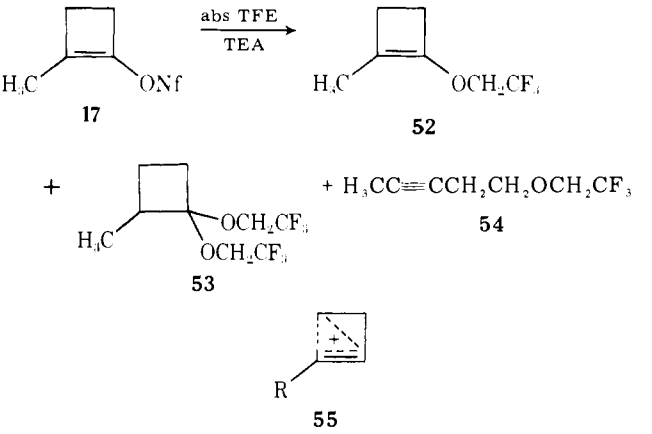
2-Methylcyclobutenyl nonaflate (**17**) was found to solvolyze 130 times faster than the parent compound in 50% EtOH (Table I).[27] The Winstein-Grunwald *m* value was found to be $m = 0.67$ (at 29 °C), which is in good agreement with a vinyl cation mechanism.[3]

The solvolysis products obtained were mostly formed without rearrangement and consisted of 90% 2-methylcyclobutanone (**48**), 4% enol ether **49**, and 5% of 3-pentyn-1-ol (**51**).



Only a small amount (1%) of the rearranged cyclopropyl methyl ketone (**50**) was found in the product mixture. Therewith the product composition is again qualitatively the same as obtained in the solvolysis of the corresponding cyclopropylidenemethyl bromide **11** (R = CH_3)[12] and the homopropargyl derivatives **7**, R = CH_3; X = OTs, OTf.[28] Solvolysis of **17** in absolute TFE gave the corresponding enol ether **52** and the ketal **53** and a small amount of the propargyl ether (**54**), as expected for a vinyl cation mechanism. **53** is formed from the enol ether **52** by addition of TFE to the double bond.

The higher reaction rate of 2-methylcyclobutenyl nonaflate (**17**) compared to the parent cyclobutenyl nonaflate (**16**) is another indication for the formation of a bridged vinyl cation (**55**, R = CH_3) which is additionally stabilized by the methyl group in the 2 position.



When one compares the rate of 2-methylcyclohexenyl triflate (**56**) with the rate of cyclohexenyl triflate (**57**) under the

same conditions the former solvolyzes only ten times faster than the latter.[5] Relief of steric strain in the transition state can therefore only in part be made responsible for the high increase in the rate of 2-methylcyclobutenyl nonaflate (**17**) over cyclobutenyl nonaflate (**16**).

As shown in Table II, 2-phenylcyclobutenyl nonaflate (**18**) in contrast to the 2-methyl derivative **17** solvolyzes approximately at the same rate as the parent compound **16**. To exclude an addition-elimination mechanism[3] for the solvolysis of 2-phenylcyclobutenyl nonaflate (**18**) the solvolysis rates were measured in a pH range of 4-10. As shown in Table IV the reaction rates are practically independent of the pH, which establishes that the solvolysis does not proceed via an addition-elimination process to the double bond. The *m* value for this system was found to be 0.49, which is low, but still indicative for a S_N1 process for vinyl derivatives.[3]

2-Anisylcyclobutenyl nonaflate (**19**), as shown in Table II, also does not show a large rate acceleration. It only reacts 3.7 times faster than cyclobutenyl nonaflate (**16**).

The small influence of the phenyl and the anisyl group in the 2 position of the cyclobutenyl system on the solvolysis rate in comparison with the methyl group in **17** can be explained with the negative inductive effect of the aryl groups. A mesomeric stabilization of the intermediate bridged vinyl cation **55** (R = Ph) would require a rotation of the phenyl group. In the starting nonaflates **18** and **19** the phenyl group is in the same plane as the cyclobutenyl ring, thus allowing maximum conjugation with the double bond.

The solvolysis products of **18** and **19** in 50 and 80% aqueous ethanol were formed with rearrangement. Thereby a vinyl cation mechanism and the influence of the substituent in the 2 position on the product composition according to Scheme II is demonstrated. The solvolysis of 2-phenylcyclobutenyl nonaflate (**18**) in 50% EtOH yields phenyl cyclopropyl ketone (**58**), 2-phenylbutanone (**59**), and the homopropargyl deriv-

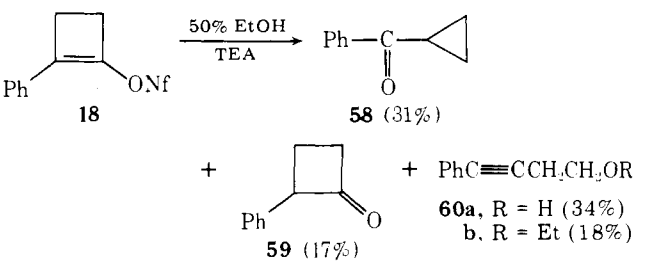
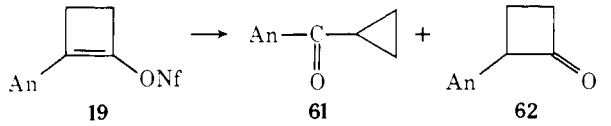


Table IV. Solvolysis Rates of 2-Phenylcyclobutenyl Nonaflate (**18**) in 50% EtOH at Different pH Values, 75.2 °C

pH	$k \times 10^4$, s^{-1}	pH	$k \times 10^4$, s^{-1}
4	3.92 ± 0.06	8	3.86 ± 0.06
5	3.84 ± 0.01	9	3.82 ± 0.06
6	3.89 ± 0.04	10	3.88 ± 0.04
7	3.90 ± 0.02		

atives **60a** and **60b.** In 80% EtOH the product composition is only slightly different.

In the solvolysis of 2-anisylcyclobutenyl nonaflate (**19**) in 80% aqueous ethanol (buffered with TEA) anisyl cyclopropyl ketone (**61**) and 2-anisylcyclobutanone (**62**) were found in a ratio of 1.3:1.

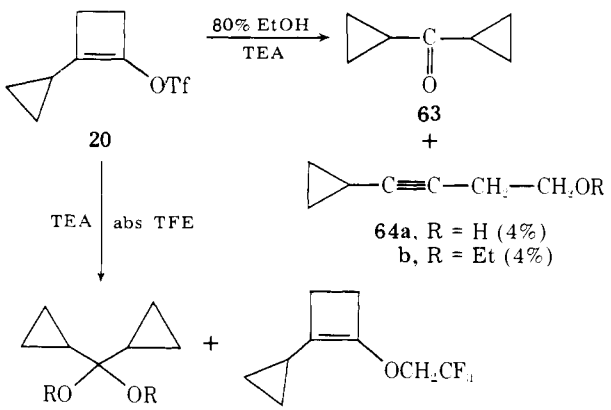


19 **61** **62**

The products formed in the solvolysis of **18** and **19** compare well with the solvolysis products of cyclopropylidenemethyl bromides (**11**, R = Ph, An)[17,18] under the same conditions. In both cases the cyclopropyl ketones **58** and **61,** respectively, were formed in comparatively high yield demonstrating the stabilizing effect of a phenyl and anisyl group, respectively, on the corresponding cyclopropylidenemethyl cations **12** (Scheme II). The vinyl cations **12** can be formed either directly from the cyclopropylidenemethyl bromides (**11**, R = Ph and R = An) or by rearrangement according to Scheme II from the cyclobutenyl nonaflates **18** and **19,** respectively, via the cyclobutenyl cations **6** (Scheme II).

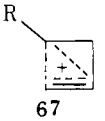
As shown earlier the stabilizing effect of a cyclopropane ring on a vinyl cation is especially large. Cyclopropylcyclopropylidenemethyl bromide (**11**, R = cyclopropyl) is one of the fastest solvolyzing vinyl bromides. Depending upon the solvent, nonrearranged products like dicyclopropyl ketone (**63**) via the highly stabilized cyclopropylcyclopropylidenemethyl cation (**12**, R = cyclopropyl) (Scheme II) are formed.[12] As expected therefore in the solvolysis of 2-cyclopropylcyclobutenyl triflate (**20**) in 80% EtOH dicyclopropyl ketone (**63**) was found to be the main product (86%) beside small amounts of the homopropargyl alcohol **64a,** the ether **64b,** and two unidentified products.

2-Cyclopropylcyclobutenyl triflate (**20**) gave on solvolysis in absolute TFE major amounts (67%) of the rearranged ketal (**65**) besides the enol ether (**66,** 7%), the homopropargyl ether



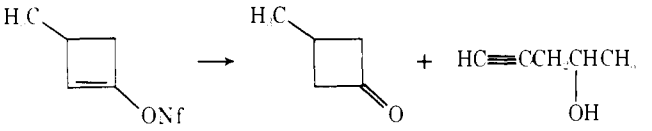
(**64c**, R = CH_2CF_3, 11%), and the alcohol (**64a,** 1%). Ketal **65** was formed by addition of TFE to the initially obtained trifluoroethyl enol ether of **63.**[28]

The effect of a methyl group in the 3 position of the cyclobutenyl system is comparatively small. 3-Methylcyclobutenyl nonaflate (**21**) only solvolyzes 2.3 times faster than the parent compound, but this still indicates a rate enhancement and therefore a stabilizing effect of the 3-methyl group on the positive charge in the bridged cyclobutenyl cation **67** (R = CH_3).



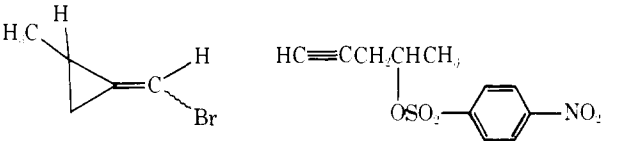
67

Owing to the difficulties in synthesizing the 3-methylcyclobutenyl nonaflate (**21**) only the major solvolysis products of **21** in 50% aqueous ethanol were identified. Beside minor unidentified products, 3-methylcyclobutanone (**26**) and the secondary homopropargyl alcohol (**68**) were formed, demon-



21 **26** **68**

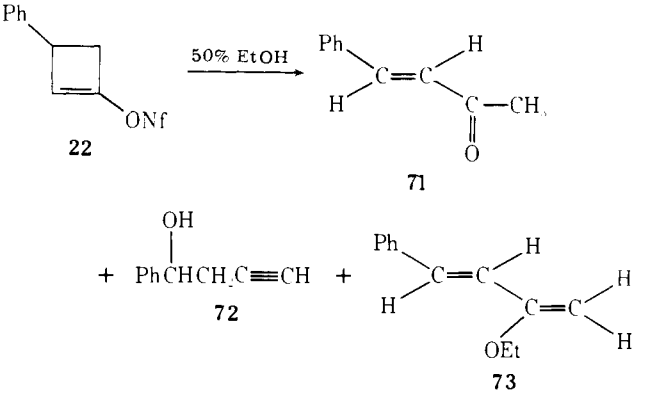
strating a vinyl cation mechanism. As described above for the 2-substituted cyclobutenyl derivatives, also in the case of 3-methylcyclobutenyl triflate (**21**) the solvolysis products can be generated, starting with the corresponding two other "homopropargyl isomers": 3-methylcyclobutanone (**26**) as well as 1-pentyn-4-ol (**68**) are found in the solvolysis of the stereoisomeric 2-methylcyclopropylidenemethyl bromides (**69**)[29] (50% EtOH). 3-Methylcyclobutanone (**26**) and the alcohol **68** are formed in the trifluoroacetolysis of 1-pentyn-4-yl *p*-nitrobenzenesulfonate (**70**).[30] The results are in agreement with the generation of the same cationic intermediates, starting either from **21, 69,** or **70.**



69 **70**

The solvolysis of 3-phenylcyclobutenyl nonaflate (**22**) followed a more complicated reaction path and was mostly controlled not by a solvolysis reaction but by a thermal rearrangement to form open-chain compounds. In spite of the fact that strongly ionizing solvents like TFE and hexafluoro-2-propanol (HFIP) were used, the rate of thermal ring opening of **22** was faster than the solvolysis rate.

In 50% aqueous ethanol at 54 °C (buffered with TEA) **22** was completely rearranged after 53 h with formation of **71, 72,** and **73.**



22 **71**

72 **73**

The formation of the homopropargyl alcohol **72** is an indication for a solvolytic process in which the 3-phenylcyclobu-

tenyl cation (**67**, R = Ph), as one should expect, rearranges to the more stable secondary homopropargyl cation **74**, stabilized by the neighboring phenyl group. However, **72** is formed only in low yields, the ratio of **71** and **73** to **72** being 14:1, as shown by gas chromatography.

$$PhC^{+}HCH_2C{\equiv}CH$$

74

We surmised that at the employed reaction temperature of 54 °C most of the 3-phenylcyclobutenyl nonaflate (**22**) rearranged to the open-chain nonaflate **75**, which then subsequently solvolyzed to **71** and **73**. In fact the thermal rearrangement of **22** was followed by NMR spectroscopy in CCl_4 solution with cyclohexane as an internal standard at 54 °C. After 30 h the starting nonaflate **22** was no longer detectable and a compound which was assigned structure **75** was the only product (other than cyclohexane) in the spectrum. The half-life of the rearrangement **22** → **75** (54 °C) was 10 h, giving a rate constant of 2.0×10^{-5} s^{-1}, and therewith quite close to the rate of the thermal rearrangement of 3-phenylcyclobutene.[31]

22 **75**

To avoid the thermal rearrangement, two alternatives were tried, lowering the reaction temperature and changing the solvent to one with greater ionizing power. When compound **22** was solvolyzed in 20% aqueous EtOH for 109 h at 30 °C, beside a very small amount of the homopropargyl alcohol **72** only unreacted nonaflate **22** and ketone **71** were observed in a ratio of 3:1. When using either TFE or HFIP as a solvent at room temperature 3-phenylcyclobutenyl nonaflate (**22**) was recovered in both cases unchanged after 13 days. Therefore the temperature was raised again and **22** solvolyzed in 97% HFIP at 48 °C for 29 h.

In principle the product composition did not change in comparison with the results obtained in 50% EtOH: **71** and **72** were formed in a ratio of 2:1 beside the ether **76**.

22 **76** + **71** + **72**

X = $CH(CF_3)_2$

The results of the solvolysis reactions of the perfluorosulfonates **16**–**21** are summarized as follows. 1-Cyclobutenyl nonaflates (and triflates) solvolyze in aqueous ethanol/water, aqueous trifluoroethanol, and absolute trifluoroethanol via a vinyl cation mechanism. In spite of their small ring size the 1-cyclobutenyl nonaflates solvolyze with rates which are in the same range as that of the fast-reacting 1-cyclooctenyl nonaflate (**2b**) and 10^3 times faster than the 1-cyclohexenyl nonaflate (**1b**) though the energetically favorable linear arrangement for a vinyl cation cannot be reached in a 1-cyclobutenyl system.

To explain the high solvolytic reactivity of the 1-cyclobutenyl nonaflates stabilized bridged cyclobutenyl cations, e.g., **14**, **55**, or **67**, are proposed as intermediates. 1-Cyclobutenyl nonaflates substituted in the 2 and 3 positions show characteristic substituent effects on the solvolysis rate, e.g., 2-methylcyclobutenyl nonaflate (**17**) solvolyzes 130 times faster than the parent 1-cyclobutenyl nonaflate (**16**), thereby also pointing to the charge delocalization in the 1-cyclobutenyl cations.

The vinyl cation mechanism for 1-cyclobutenyl nonaflates is also proven by its rearrangement reactions during solvolysis: all 1-cyclobutenyl nonaflates solvolyze with formation of cyclobutenyl, cyclopropylidenemethyl, and homopropargyl derivatives, the exact product composition being dependent upon the substituent pattern in the starting 1-cyclobutenyl nonaflates. The rearrangement products are formed via the cyclobutenyl, cyclopropylidenemethyl, and homopropargyl cations according to Scheme II.

The same solvolysis products which are obtained from 1-cyclobutenyl nonaflates and triflates are also formed in the solvolysis of either cyclopropylidenemethyl (**11**) or homopropargyl derivatives (**7**), thereby indicating that the solvolysis of **11** and **7** proceeds through the same intermediate vinyl cations as those generated from the 1-cyclobutenyl nonaflates.

Experimental Section

General. The boiling points given are all uncorrected. Infrared spectra were obtained from films on NaCl plates using Beckman IR 4, Perkin-Elmer Model 21, or PYE Unicam SP 1000 spectrophotometers. ^{1}H NMR spectra were recorded on Varian A-60, Varian EM 360, and Bruker HX 90 instruments with pulse Fourier transform mode and chemical shifts are reported in parts per million downfield from internal Me_4Si. ^{13}C and ^{19}F NMR spectra were taken on a Bruker HX 90 instrument with Me_4Si and $CFCl_3$ as internal standard, respectively. Mass spectra were obtained from a Varian MAT 311 and MS9 of AEI Manchester. GC–MS were recorded on a LKB 900 instrument.

Analytical GC was carried out on Hewlett-Packard 5750 and 5720 instruments with flame ionization detector. Preparative GC was performed on a Varian P90 and Hewlett-Packard 5750 and 5720 equipped with a thermal conductivity detector and using helium as carrier gas. The columns mostly used are (A) 4 mm × 3 m copper column packed with 1% DEGS on Chromosorb P (60/80 mesh); (B) 2 mm × 3 m steel column packed with 10% Carbowax 20M-TPA on Varaport (80/100 mesh); (C) 4 mm × 3 m glass column packed with 10% Carbowax 20M on Chromosorb P (80/100 mesh).

A. Synthesis of Cyclobutanones (25, 26, 29a, 29b, 33, 37, and 40). The syntheses of 2- and 3-methylcyclobutanones (**25** and **26**) were carried out according to the multistep procedure of Conia.[32] The physical and spectral properties were identical with the reported data.[32]

2-Phenyl- and 2-anisylcyclobutanone (**29a** and **29b**) were prepared by the epoxidation of the corresponding (arylcyclopropylidene)-methanes.[18] The physical and spectral properties of 2-phenylcyclobutanone were similar to those of the one prepared by Trost.[33] The experimental details are demonstrated below for the example of 2-anisylcyclobutanone.

2-Anisylcyclobutanone (29b). To a stirred suspension of *p*-nitroperbenzoic acid (15 g, 82 mmol) in CH_2Cl_2 (40 mL) cooled in an ice bath was added (*p*-anisylcyclopropylidene)methane[18] (7 g, 44 mmol) dissolved in CH_2Cl_2 (40 mL) slowly. After 1 h the reaction mixture was filtered, and the CH_2Cl_2 layer was washed twice with sodium hydroxide solution (1 mol) and three times with water and dried over $MgSO_4$. Evaporation of CH_2Cl_2 and column chromatography over silica gel (benzene–hexane, 1:10) gave 1 g (13%) of ketone **29b**: bp 80 °C (bath temperature) (0.006 Torr); IR 1790 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.85–2.75 (m, 2 H), 2.9–3.35 (m, 2 H), 3.7 (s, 3 H), 4.3 (m, 1 H), 6.9 (m, 4 H). Anal. ($C_{11}H_{12}O_2$) C, H.

2-Cyclopropylcyclobutanone (33). To a mixture of 1.8 g (30 mmol) of cyclopropylcarboxaldehyde and 8.0 g (25 mmol) of cyclopropyldiphenylsulfonium tetrafluoroborate[20] in 150 mL of absolute Me_2SO was added 2.0 g (50 mmol) of finely powdered NaOH in 0.5-g portions within 30 min at room temperature and under N_2 atmosphere. The clear, pale orange solution was treated with 1 mL of acetic acid. The reaction mixture was then poured into water, saturated with NH_4Cl, and extracted several times with ether–benzene (1:1). After neutralization of the organic phase with saturated $NaHCO_3$ and drying over Na_2SO_4, the solvent was distilled off and the product chromatographed over silica gel (eluant ether–methylene chloride, 2:1) to give 1.45 g (54% based on the sulfonium salt) of the ketone **33**: bp 168 °C (690 Torr); IR 3070, 1787, 1020, 815 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.17–0.6 (m, 4 H), 0.6–1.15 (m, 1 H), 1.34–2.43 (m, 2 H), 2.7–3.38

(m, 3 H); mass spectrum *m/e* (rel intensity) 110 (molecular ion, absent), 82 (14), 68 (86), 67 (100). Anal. ($C_7H_{10}O$) C, H.

3-Phenyl- and 3-anisylcyclobutanone (**37, 40**) were obtained by the dichloroketene addition[24] to styrene and *p*-methoxystyrene and subsequent dechlorination with Zn-HOAc.[34] The spectral properties of 3-phenylcyclobutanone were identical with the reported values.[24] 3-Anisylcyclobutanone (**40**): bp 96-99 °C (0.005 Torr); IR 1780 cm^{-1}; ^1H NMR (CCl_4) δ 3.23 (m, 4 H), 3.52 (m, 1 H), 3.7 (s, 3 H), 6.93 (q, 4 H, J = 4 Hz).

B. Preparation of Cyclobutenyl Nonaflates. Cyclobutenyl Nonaflate (16). A mixture of cyclobutanone (1.75 g, 25 mmol) and tri-*n*-butylamine (9.25 g, 50 mmol) was added to nonafluorobutanesulfonic acid anhydride (17.5 g, 30 mmol) cooled in an ice-salt bath while stirring under nitrogen atmosphere. After the reaction mixture was allowed to come to room temperature overnight it was stirred for 24 h. The nonaflate formed was then condensed into a cold trap at −78 °C at 0.1 Torr. The condensate (stench!) consisting of two layers was chromatographed over silica gel with petroleum ether (bp 40-60 °C) as eluant. After the petroleum ether was distilled off, the residue was purified by short-path distillation to give 1.3-1.7 g (13-17%) of pure **16**: bp 82-88 °C (bath temperature, 22 Torr); IR 1645, 1440, 1250, 1150 cm^{-1}; ^1H NMR (CCl_4) δ 2.25 (m, 4 H), 2.95 (m, 4 H), 5.4 (m, 1 H); ^{13}C NMR ($CDCl_3$) 138.3, 116.7, 34.08, 21.3 ppm; ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) Φ 81.6, 110.38, 121.87, 126.6; mass spectrum *m/e* (rel intensity) 352 (molecular ion, 6), 219 (7), 69 (88), 53 (100). Anal. ($C_8H_5SO_3F_9$) C, H.

2-Methylcyclobutenyl Nonaflate (17). This nonaflate was also prepared in a similar way to yield 10-12% of a liquid, **17**: bp 90-95 °C (bath temperature, 18 Torr); IR 1640, 1250, 1215, 1150 cm^{-1}; ^1H NMR (CCl_4) δ 1.8 (m, 3 H), 2.2 (m, 2 H), 2.8 (m, 2 H). Anal. ($C_9H_7SO_3F_9$) C, H.

3-Methylcyclobutenyl nonaflate (21) was also prepared in analogous manner. **21**: IR 1630, 1250, 1210, 1150 cm^{-1}; ^1H NMR (CCl_4) δ 1.2 (d, 3 H), 2.2-3.4 (m, 3 H), 5.5 (br s, 1 H).

2-Phenylcyclobutenyl Nonaflate (18). Because the normal procedure of treating the ketone with anhydride in CH_2Cl_2 in the presence of Na_2CO_3 yielded only traces of nonaflate, the following modification was used in this case. Methyllithium (2 M solution in ether, 3.4 mL, 6.8 mmol) was stripped of ether and glyme (15 mL) was added. The flask was cooled in an ice bath and diisopropylamine (0.84 mL, 6.0 mmol) was added under N_2. The mixture was stirred at ice bath temperature for 40 min. Then the flask was cooled in a dry ice-methanol bath and a solution of 2-phenylcyclobutanone (0.66 g, 4.52 mmol) in glyme (5 mL) was injected into the flask very slowly. The reaction mixture was then stirred at −78 °C for 1.5 h and in an ice bath for another 10 min. Then the flask was cooled to −78 °C and nonafluorobutanesulfonic acid anhydride (3.5 g, 6.0 mmol) was added very slowly. After the addition, the reaction mixture was stirred while the dry ice in the bath gradually melted (about 2 h) and then at ambient temperature for 14 h. After the solvent was removed on a rotary evaporator, the residual yellow liquid was chromatographed over silica gel and eluted with petroleum ether (bp 40-60 °C)-benzene (12:1) mixture. The first 200 mL of eluate contained the required nonaflate **18**: bp 90-95 °C (bath temperature) (0.001 Torr); 0.748 g (38.6%); IR 1265, 1175 cm^{-1}; ^1H NMR (CCl_4) δ 2.5 (t, 2 H, J = 3 Hz), 3.04 (t, 2 H, J = 3 Hz), 7.38 (m, 5 H). Anal. ($C_{14}H_9SO_3F_9$) C, H, S, F.

2-Anisylcyclobutenyl Nonaflate (19). This was prepared by the same method as for **18**, yield 24%. **19**: ^1H NMR (CCl_4) δ 2.46 (m, 2 H), 3.0 (m, 2 H), 3.75 (s, 3 H), 7.06 (m, 4 H).

2-Cyclopropylcyclobutenyl Triflate (20). KH (330 mg, 25% in mineral oil, 8.5 mmol) was washed with THF to remove the mineral oil and suspended in 5 mL of absolute THF. This suspension was cooled to 0 °C and treated with 550 mg of cyclopropylcyclobutanone (5.5 mmol). The reaction mixture was cooled to −75 °C and imidazolide triflate[22] (1.15 g, 6 mmol) was added. It was then allowed to come to room temperature and stirred for 2 days. Pentane (15 mL) was added, the mixture filtered, and the solvent removed. Chromatography over silica gel with benzene-ether gave the triflate (30 mg, 2%). **20**: IR 1430, 1235, 1215, 1150, 1016, 820 cm^{-1}; ^1H NMR (CCl_4) δ 0.5-1.05 (m, 5 H), 1.96 (t, 2 H, J = 2.8 Hz), 2.78 (t, 2 H).

3-Phenylcyclobutenyl Nonaflate (22). To a cooled (ice bath) and stirred suspension of nonafluorobutanesulfonic acid anhydride (9.9 g, 17 mmol) and dry Na_2CO_3 (4 g, 37.7 mmol) in CH_2Cl_2 (25 mL) was added 3-phenylcyclobutanone (2.0 g, 13.7 mmol) in 5 mL of CH_2Cl_2 under N_2. The reaction mixture was stirred at room temperature for 45 h after the ice was allowed to melt away. It was then filtered and the solvent removed. Two phases were formed; the lower phase consisting of excess anhydride was removed and the upper layer chromatographed over silica gel. Elution with petroleum ether (bp 40-60 °C)-benzene in the ratio of 12:1 gave a liquid which was distilled to give 83 mg (1.4% yield) of the required nonaflate. More than 90% of the starting material was recovered from the column by elution with benzene. **22**: (83 mg, 1.4%): bp 90 °C (bath temperature, 0.001 Torr); IR 1610, 1430, 1245, 1175 cm^{-1}; ^1H NMR (CCl_4) δ 2.5-3.9 (m, 3 H), 5.68 (br s, 1 H), 7.25 (m, 5 H).

3-Anisylcyclobutenyl Nonaflate (23). This nonaflate was prepared in the same way as **22**, 64 mg (impure, 1.4%). **23**: bp 100 °C (bath temperature, 0.005 Torr); ^1H NMR (CCl_4) δ 2.0-3.0 (m, 3 H), 3.74 (s, 3 H), 5.05 (br s, 1 H), 6.98 (q, 4 H).

C. Kinetics. The rates of solvolysis of the sulfonate esters were measured by a continuous automatic titration method using a combititrator as described previously.[35] The rate of reaction was evaluated from the curve by the Guggenheim method and by a least-squares computer program for first-order reactions. The rates of reaction are given in Table II.

D. Product Analysis. The nonaflates were solvolyzed in appropriate solvents (30-40 fold) containing triethylamine as buffer (one- to twofold) at the given temperature in a sealed ampule with stirring. They were then directly analyzed by GC or worked up as described for individual cases.

Cyclobutenyl Nonaflate (16). A. 50% EtOH, 100 °C, 2 Days. Only cyclobutanone was detected by GC using column A. With column B butyn-1-ol (**41**) was detected to an extent of 30%.

B. Absolute TFE, 75 °C, 10 Days. The enol ether (**42**) and the ketal (**43**) were detected by GC (column B, 90 °C) in 82 and 8.3% yield, respectively, besides 9.7% of cyclobutanone. They were separated by preparative GC using column B.

42: ^1H NMR ($CDCl_3$) δ 2.15 (m, 2 H), 2.64 (m, 2 H), 4.18 (q, 2 H, J = 4 Hz), 4.61 (s, 1 H); mass spectrum *m/e* (rel intensity) 153 (5.5), 152 (61.4, M^+), 53 (74.3, cyclobutenium ion), 39 (base peak, cyclopropenium ion).

43: IR (CCl_4) 1072, 1140, 1170, 1280 cm^{-1}; ^1H NMR (CCl_4) δ 1.6-2.5 (m, 6 H), 3.78 (q, 4 H); mass spectrum *m/e* (rel intensity) 240 (32), 224 (81), 153 (55), 57 (100), 53 (50).

C. Absolute TFE with Tenfold Excess of Tetramethylammonium Bromide, 75 °C, 10 Days. The enol ether (**42**, 34%), the ketal (**43**, 0.9%), cyclobutenyl bromide (**44**, 45%), cyclopropylidenemethyl bromide (**45**, 8.3%), and cyclobutanone (11.8%) were detected by GC (column B, 60 °C) directly after the solvolysis. For separating the components, the solvolysis mixture was extracted with ether. Most of the ether was distilled off and the residue was used for preparative GC (column B). The spectral properties of the separated bromides were identical with the literature values.[12] They were also identified by combined GC/MS technique.

D. 80% TFE with Tenfold Excess of Tetramethylammonium Bromide, 75 °C, 10 Days. The following products were identified by GC (column B, 60 °C, 90 °C), the enol ether (**42**, 19%), cyclobutenyl bromide (**44**, 39%), cyclopropylidenemethyl bromide (**45**, 6.5%), cyclobutanone (25.5%), and butyn-1-ol (**41**, 10%).

E. Absolute CF_3CH_2OD, 75 °C, 10 Days. Similar product distribution as in the case of CF_3CH_2OH was found. The enol ether obtained was separated by preparative GC (column B, 90 °C) and analyzed by NMR. Careful integration showed no incorporation of deuterium in the enol ether (**42**) obtained from the solvolysis. Moreover, mass spectra of the enol ether obtained also indicated that no deuterium was incorporated.

F. 50% EtOH-$H_2{}^{18}O$ (6.25% Enriched in ^{18}O), 100 °C, 2 Days. The cyclobutanone obtained was analyzed by GC/MS, which indicated the presence of ^{18}O. From a control experiment it was observed that cyclobutanone itself underwent the isotope exchange reaction.

2-Methylcyclobutenyl Nonaflate (17). A. 50% EtOH, 50 °C, 62 h. After the reaction mixture was cooled, it was saturated with NaCl and extracted several times with small portions of ether. The ether phase was dried over $CaCl_2$ and the solvent distilled. The residue was investigated by GC (3 m × 4 mm 10% Carbowax 20M on Chromosorb P, acid washed, 60-80 mesh, oven temperature 90 °C) whereby 94.5% of 2-methylcyclobutanone (**48**) and 1% of methyl cyclopropyl ketone (**50**) were identified. A third peak which was present to an extent of 4.5% disappeared on treatment with 1 mL of 1 N HCl for 24 h. This peak is therefore assigned to the enol ether (**49**). On repetition of the

solvolysis at 75 °C for 3 days and analyzing the solvolysis mixture by GC using column B and a higher oven temperature (130 °C), an additional product, the 3-pentyn-1-ol (**51**, 5%), could also be detected.

B. Absolute TFE, 80 °C, 10 Days. The mixture obtained was analyzed by GC using column B (90 °C) and column C (100 °C). The following products were identified by comparing with authentic specimens:[28] the enol ether (**52**, 48%), the ketal (**53**, 47%), and 3-pentyn-1-trifluoroethyl ether (**54**, 5%). **52** and **53** were also separated by preparative GC and identified unequivocally by ^{1}H NMR spectra.

2-Phenylcyclobutenyl Nonaflate (18). A. 50% EtOH, 75 °C, 6 h. After solvolysis the ethanol was removed by a rotary evaporator and the product was extracted with ether and dried over $MgSO_4$. The residue after removing the ether was separated into two fractions by preparative TLC (silica gel, benzene). One fraction was identified as the homopropargyl alcohol (**60a**, 34%). **60a**: IR 2240 cm^{-1}; ^{1}H NMR (CCl_4) δ 2.6 (m, 2 H), 3.02 (s, 1 H), 3.72 (m, 2 H), 7.3 (m, 5 H).

The second portion was separated by preparative GC and identified as the ether (**60b**, 18%) [IR 2240 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.2 (m, 3 H), 2.62 (m, 2 H), 3.5 (m, 4 H), 7.3 (m, 5 H)], phenylcyclopropyl ketone (**58**, 31%), and 2-phenylcyclobutanone (**59**, 17%).

B. 80% EtOH, 75 °C, 6 h. The solvolysis product was worked up as given above for the 50% EtOH solvolysis and the following compounds were separated by preparative TLC and GC and identified: **58**, 26%; **59**, 14%; **60a**, 13%; **60b**, 47%.

2-Anisylcyclobutenyl Nonaflate (19). 80% EtOH, 75 °C, 6 h. The products could not be separated by preparative TLC and GC. From the IR and NMR spectra of the mixture two products were identified, anisyl cyclopropyl ketone (**61**, 57%) IR 1670 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.6–1.5 (m, 4 H), 3.86 (s, 3 H), 4.6 (m, 1 H), 7.5 (m, 4 H) and 2-anisylcyclobutanone (**62**, 43%).

2-Cyclopropylcyclobutenyl Triflate (20). A. 80% EtOH, 70 °C, 1 Day. After the solvolysis the reaction products were identified by comparison with authentic samples[36] in GC (column C). Dicyclopropyl ketone (**63**, 86%), the homopropargyl alcohol (**64a**, 4%), and the corresponding ether (**64b**, 4%) were found.

B. Absolute TFE, 70 °C, 1 Day. Here the known products were identified by comparing with authentic samples in GC and the new products were separated by preparative GC and identified by their spectral properties. The ketal (**65**, 67%): ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.42–0.71 (m, 8 H), 0.84–1.11 (m, 2 H), 3.97 (q, 4 H, J = 8.6 Hz); mass spectrum *m/e* (rel intensity) 292 (1), 264 (40), 251 (100), 193 (51), 181 (21), 165 (20), 153 (16), 139 (24), 83 (44), 81 (26), 77 (26), 69 (39). The enol ether (**66**, 7%): ^{1}H NMR (90 MHz, CCl_4–$CDCl_3$) 0.42–0.73 (m, 4 H), 0.8–1.11 (m, 1 H), 1.73–1.87 (m, 2 H), 2.37–2.51 (m, 2 H), 4.2 (q, 2 H, J = 8 Hz); mass spectrum *m/e* (rel intensity) 192 (molecular ion), 191 (8), 177 (100), 109 (17), 93 (27), 79 (83). Dicyclopropyl ketone (10%), the homopropargyl ether (**64c**, R = CH_2CF_3, 11%), and the alcohol (**64a**, 1%) were also obtained.

3-Methylcyclobutenyl Nonaflate (21). 50% EtOH, 75 °C, 4 Days. From the solvolysis product 3-methylcyclobutanone (42%) and the secondary homopropargyl alcohol (**68**, 58%) were identified by comparing with authentic specimens[29] in GC (column B).

3-Phenylcyclobutenyl Nonaflate (22). 50% EtOH, 54 °C, 53 h. From the reaction mixture the homopropargyl alcohol (**72**) and the ring-opened products **71** and **73** were identified by GC (column C, 180 °C) by comparing the retention times with those of authentic samples. Solvolysis at lower temperature (30–34 °C) in 20% EtOH with Na_2CO_3 as buffer gave the starting nonaflate and the ketone (**71**) in 3:1 ratio. In 97% hexafluoro-2-propanol at room temperature for 13 days no reaction occurred. But at 48 °C, the products **71**, **72**, and **76** were detected by GC (column C, 180 °C), the compounds **71** and **72** being present in the ratio of 2:1.

Thermal Rearrangement of 22. A solution of 3-phenylcyclobutenyl nonaflate in CCl_4 with cyclohexane as an internal standard was put in a tightly capped NMR tube and heated in an oil bath maintained at 54 °C. The thermal rearrangement was followed by NMR. After 30 h, peaks due to the starting material were no longer detectable and a compound which was assigned structure **75** was the only product other than the cyclohexane in the spectrum: ^{1}H NMR δ 5.23 (q, 2 H, J = 3.2 Hz), 6.77 (q, 2 H, J = 16 Hz), 7.37 (m, 5 H). The half-life of this rearrangement was estimated to be 10 h, the rate constant for the thermal rearrangement being 2.0×10^{-5} s^{-1}.

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