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SOLVOLYSIS OF MEDIUM RING SIZE CYCLOALKENYL TRIFLATES

A COMPARISON OF RELATIVE RATES VS RING SIZE[1]

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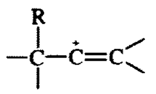
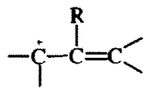
Abstract—Cyclononenyl (**5**), cycloundecenyl (**6**) and cyclododecenyl (**7**) triflates were solvolyzed in 70% aqueous trifluoroethanol. A comparison of the relative rates of these and other previously reported solvolytic studies were made from the cyclopentenyl system to the cyclododecenyl system. A "saw tooth" effect analogous to that found in the cycloalkyl system was observed. Furthermore product studies to determine the possibility of transannular hydride migration resulted in no evidence of rearrangement in the cyclododecenyl system and very small amounts in the cyclononeyl system.

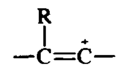
Vinyl cations have been reported as undergoing two types of rearrangements, i.e. rearrangement to the double bond (**1a**→**1b**), and rearrangement across the double bond (**2a**→**2b**). These rearrangements have been extensively investigated.[2]



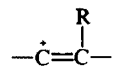
1a



1b

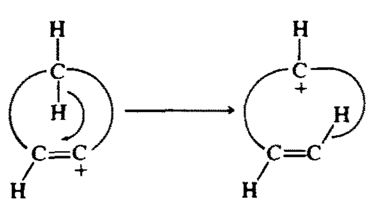


2a



2b

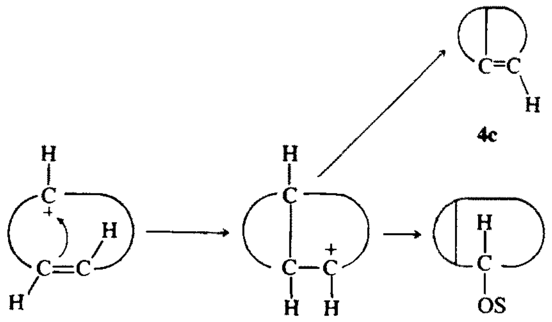
A third type of rearrangement in vinyl cations, that of transannular hydride migration to the double bond (**3a**→**3b**) was the objective of this endeavor together with a study of the relative rates vs ring size for cyclic vinyl cations. Transannular hydride migration in saturated carbonium ions has been extensively investigated.[3]



3a **3b**

Since unsaturated cations behave analogous to saturated carboniums in many instances, we sought to obtain evidence for such hydride migration in vinyl cations. Lamparter and Hanack[4] alluded to its existence when they reported some 12% of bicyclic products in the solvolysis of cyclononenyl triflate in 60% aqueous ethanol. The bicyclic products might result from a subsequent ring closure by double bond participation (**4a**→**4b**). Proton elimination or solvent capture would result in either a bicyclic alkene (**4c**), alcohol or ether (**4d**).

We studied three medium size ring cycloalkenyl triflates; i.e. cyclonenyl triflate (**5**), cycloundecenyl triflate (**6**), and cyclododecenyl triflate (**7**).



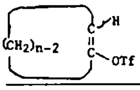
4a **4b** **4c** **4d**

70% Aqueous trifluoroethanol (TFE) was the solvent of choice for solvolysis because it has nearly the same Y[5] value as 50% aqueous ethanol (EtOH) to allow the rate data to be compared to that for other cycloalkenyl triflate solvolysis,[6] and because of its relatively low nucleophilicity,[7] which should enhance the amount of rearrangement. The kinetic data of the buffered solvolysis is summarized in Table 1.

This study extends the solvolysis data of cycloalkenyl triflates to the C-12 system. As a result we thought it might be instructive to compare all the known cyclic systems (C-5 to C-12) by extrapolating kinetic data to one temperature using one or two solvents. The temperature of choice was 75° because more data was experimentally available at that temperature. The solvents, 70% TFE and 60% EtOH, were chosen because our data was obtained in the former and most other data was in the latter.

Using the data in the literature[4,6,8] calculated rates at 75° were obtained from the activation parameters and are summarized in Table 2. Three solvent ratios were calculated using cycloheptenyl and cyclooctenyl triflate data. An average of those ratios are as follows: 70% TFE/60% EtOH, 2·2; 50% EtOH/60% EtOH, 2·3; 70% TFE/50% EtOH, 1·0. One can, with these ratios, estimate the rate of reaction of each of the nine compounds in both 70% TFE and 60% EtOH. *cis*-2-Butenyl triflate was chosen as the reference system, because of its uncon-

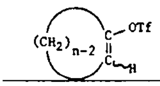
Table 1. Rates of solvolysis of medium size ring cycloalkenyl triflates in 70% aqueous trifluoroethanol buffered with 1.1 equivalents of pyridine

	k (sec^{-1})	No. of Determinations	Temperature (°C)	$\Delta H^{\ddagger b}$ (kcal/mole)	$\Delta S^{\ddagger b}$ (e.u)
n = 9	$2.48 \pm .084 \times 10^{-4}$	6	34.97		
	1.53×10^{-3a}		50.00	23.4 ± 0.9	0.7 ± 1.2
5	$1.55 \pm .045 \times 10^{-3}$	5	50.12		
n = 11	4.31×10^{-4a}		50.00	27.9 ± 2.0	12.4 ± 6.2
	$4.37 \pm .119 \times 10^{-4}$	6	50.09		
6	$1.05 \pm .194 \times 10^{-2}$	5	74.94		
n = 12	3.69×10^{-4a}		50.00	25.0 ± 0.8	2.8 ± 2.2
	$3.73 \pm .191 \times 10^{-4}$	4	50.07		
7	$7.82 \pm .294 \times 10^{-3}$	7	76.79		

[a] extrapolated from other temperatures.

[b] calculated at 50.0°C.

Table 2. A summary of solvolysis data for *cis*-2-butenyl and cycloalkenyl triflates extrapolated to 75°

	Solvent	k (sec^{-1})	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Reference
cis-$CH_3CH = C(CH_3)OTf$	60% ETOH	8.15×10^{-5}	26.4	-1.8	8
Cyclic					
n = 5	60% ETOH	4.61×10^{-10}	33.1	-6.4	6
n = 6	60% ETOH	5.14×10^{-9}	34.0	0.9	6
n = 7	60% ETOH	1.70×10^{-5}	27.4	-2.1	6
n = 8	60% ETOH	2.21×10^{-4}	25.3	-30	6
cis-$CH_3CH = C(CH_3)OTf$	50% ETOH	1.75×10^{-4}			8
Cyclic					
n = 7	50% ETOH	4.22×10^{-5}	26.2	-3.6	6
n = 8	50% ETOH	4.52×10^{-4}	27.1	3.6	6
n = 9	50% ETOH	1.13×10^{-2}	21.7	-5.4	4
n = 10	50% ETOH	3.29×10^{-3}	24.2	-0.7	4
n = 7	70% ETOH	3.31×10^{-5}	26.8	-2.3	6
n = 8	70% ETOH	5.48×10^{-4}	25.4	-8.1	6
n = 9	70% TFE	2.24×10^{-2}	24.0	0.5	This Work
n = 11	70% TFE	1.06×10^{-2}	27.9	12.2	This Work
n = 12	70% TFE	6.47×10^{-3}	24.9	2.7	This Work

strained geometry. Table 3 contains this estimated data along with calculated rates relative to the acyclic *cis*-2-butenyl triflate.

If one plots the logarithm of the relative rates vs ring size (Fig. 1), one obtains an interesting plot demonstrating two important concepts—(a) there appears to be only minor differences between the two solvents and (b) one can postulate that cycloheptenyl and larger cyclic vinyl cations possess a similar linear geometry to that of the *cis*-2-butenyl cation, which is geometrically unconstrained. Furthermore, the lower membered rings are less reactive than the acyclic model compounds due to Baeyer and Pitzer[9] strain, whereas the higher membered ring compounds are more reactive.

A statement, qualitative in nature, can be made concerning the relative strain energies of the medium size ring, 8–12, cycloalkenyl cations. An analogous "saw toothed" plot was obtained by Brown and Borkowski[10] when they compared the rates of solvolysis of 1-methylcycloalkyl chlorides relative to t-butyl chloride. This trend is further observed when comparing the heats of hydrogenation of cycloalkenes in acetic acid.[9] This phenomenon in medium size rings has been attributed to the higher strain energy of odd member rings relative to their next nearest even membered rings.[9]

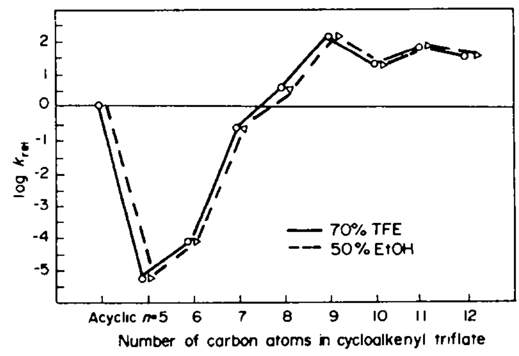
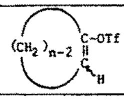


Fig. 1. Plot of logarithm of relative rates of solvolysis vs number of carbon atoms in cycloalkenyl triflates.

In order to determine the amount of transannular hydride migration, product studies were completed for

Table 3. Extrapolated rate of solvolysis of *cis*-2-butenyl and cycloalkenyl triflates in 70% aqueous trifluoroethanol and 50% aqueous ethanol at 75°

	70% TFE		50% ETOH	
	k (sec^{-1})	k_{rel}	k (sec^{-1})	k_{rel}
cis-$CH_3CH = C(CH_3)OTf$	1.8×10^{-4}	1	1.7×10^{-4}	1
Cyclic				
n = 5	1.0×10^{-9}	5.6×10^{-6}	1.0×10^{-9}	5.9×10^{-6}
n = 6	1.1×10^{-8}	6.1×10^{-5}	1.2×10^{-8}	7.1×10^{-5}
n = 7	3.3×10^{-5}	1.8×10^{-1}	4.2×10^{-5}	2.5×10^{-1}
n = 8	5.5×10^{-4}	3.1	4.5×10^{-4}	2.6
n = 9	2.2×10^{-2}	120	2.3×10^{-2}	135
n = 10	3.3×10^{-3}	18	3.3×10^{-3}	19
n = 11	1.1×10^{-2}	61	1.1×10^{-2}	65
n = 12	6.5×10^{-3}	36	6.8×10^{-3}	40

two of the three cycloalkenyl triflates. Cyclododecenyl triflate (7) was solvolyzed both buffered and unbuffered and cyclononenyl triflate (5) was solvolyzed only buffered in 70% TFE. Products were isolated using preparative gas chromatography and amounts were determined using internal standards. Products were identified by spectral means and the results are given in Table 4.

The amount of possible rearranged products was disappointingly low. None was observed with compound (7) and less than 5% with compound (5). The latter result was surprising relative to the results of Lamparter and Hanack.[4] Our use of 70% TFE, a highly ionizing but low nucleophilic solvent, had not increased the amount of rearranged products expected. Perhaps more transannular rearrangements might be observed in solvents of even lower nucleophilicity such as pure TFE or trifluoroacetic acid.

In conclusion, our findings did not substantiate transannular hydride migrations in cycloalkenyl cations but did provide for an extension of the cyclic vinyl solvolysis data up through the C-12 system and allow for an interesting correlation of the relative solvolysis rates with ring size that parallels the chemistry of the cycloalkanes.

EXPERIMENTAL

B.ps are uncorrected. Spectra were recorded on the following instruments: NMR, Varian A-60 spectrometer using TMS as internal standard; IR, Beckman IR-5 spectrometer and mass spec, AEI MS-30 spectrometer. Gas-liquid chromatography was performed on a Varian Aerograph Model 90-P using a 10 × 0·25 in. 10% SF-96 on 60/80 mesh Chromosorb W.

Preparation of cyclononeyl triflate (5). Cyclononanone (Aldrich Chemical Co) (1·0 g, 7·14 mmole) was added to a serum-stoppered 50 ml Erlenmeyer flask containing pyridine (0·58 g, 7·34 mmole) and 10 ml of dry CCl_4. After this soln was cooled to −50°, triflic anhydride (2·02 g, 7·16 mmole) was added dropwise over a period of 5 min with a cold syringe.

The soln was swirled and allowed to react for 1 hr. The reaction was warmed to −20° for 24 hr and then warmed to 25°. After 8 days the soln contained approx. 2% starting material by GLC. The mixture was diluted with 30 ml CCl_4, and washed with 15 ml ice water. The organic layer was dried with $MgSO_4$ and the solvent was removed by Rotovap. Distillation of the brown-purple residue gave 0·80 g (41·2%) of the desired product (b.p. 45–46° (0·07 mm)); NMR (neat), δ5·25 (t, 1H, C=C–H), 2·02 (m, 4H, C=C–CH_2), 1·20 (bd. s, 10H, –CH_2); IR (thin film), 2941 (CH), 1683 (C=C), 1412 (S=O), 1208, 1144, 901 cm^{-1}.

Attempts to separate the peaks of *cis*- and *trans*-isomers in the NMR as for 6 and 7 by adding deuteriobenzene were unsuccessful. A study of models indicated that the transannular H, would be directly over or possibly in the π cloud of the double bond in the *trans*-isomer. This would indicate that the product may be the pure *cis*-isomer.

Attempts to synthesize cyclononeyl triflate by addition of triflic acid to 1,2-cyclononadiene were unsuccessful. NMR analysis indicated no vinylic protons. Acid-catalyzed polymerization was the probable reaction.

Preparation of cycloundecenyl triflate (6). Cycloundecanone (Aldrich Chemical Co) (1·68 g, 0·01 mole) was placed in a 50 ml

Table 4. Product study of cyclononenyl (5) and cyclododecenyl triflate (7) in 70% aqueous trifluoroethanol at 75°

Compound	Reaction Time (% Reaction)	Equivalents of Pyridine	% Acetylene[a]	% Allene[a]	% Ketone[a]	% Other[a]
5	6 min, (98)	1.1	47.1	21.6	3.5	27.8[b]
7	8 min, (95)	1.1	17.1	80.0	2.9	0
7	8 min, (95)	0	7.6	87.6	4.8	0

[a] All percentages corrected for unreacted triflate.

[b] Five other products of which two have been identified as cyclononenyl trifluoroethyl ether, 4.1% and a cyclic unsaturated alcohol or bicyclic alcohol, 3.1%. Preparative gas chromatography of the other three products, 11.1%, 6.2%, 3.3% did not yield enough material to analyze.

Erlenmeyer flask fitted with a serum cap containing pyridine (0·869 g, 0·011 mole) and 15 ml CCl_4. This soln was cooled to −78°. Cold triflic anhydride (2·82 g, 0·01 mole) was added dropwise with swirling over a period of 10 min. The mixture was allowed to warm to −20°. Analysis by GLC determined that the product eliminates on the column. The reaction was followed by means of TLC by spotting the mixture and the authentic starting ketone on Polygram Sil G/UV pre-coated plastic sheets; with the starting ketone and product triflate having R_f values in ether of approx. 0·8–0·2, respectively. After 2 days the mixture still showed only ketone by TLC, therefore it was warmed to 16° for an additional 10 days, after more triflic anhydride (0·600 g, 0·0021 mole) had been added. After an additional 4 days at room temp., 20 ml CCl_4 was added to the mixture; the black fluid mixture was filtered, dried with $MgSO_4$ and the solvent was removed by Rotovap. This residue was chromatographed on a column containing 30 g Silica Gel G, 100–120 mesh (Fisher Scientific Co) using benzene as eluant. The first fraction contained the desired product. After removal of solvent, the product was distilled under reduced pressure to yield 0·9 g (30·0%) colorless oil (b.p. 54·5–55·5° (0·03 mm)).

As in the case of cyclononenyl triflate, deuteriobenzene was added in order to separate *cis*- and *trans*-isomers in the NMR. NMR (50% C_6D_6) δ4·86 (t, 1H, J = 8·2 Hz, *cis* vinylic), 4·49 (t, 1H, J = 8·0 Hz, *trans* vinylic), 1·70 (m, 4H, allylic), 0·88 (bd.s., 14H, $-CH_2-$); IR (thin film), 2945 (CH), 1692 (C=C), 1412 (S=O), 1212, 1145, 905 cm^{-1}. By NMR integration the product mixture was 33·9% *cis*- and 66·1% *trans*-cycloundecenyl triflate, and was used without separation for the kinetic and product studies.

Preparation of cyclododecenyl triflate (7). Cyclododecanone (Aldrich Chemical Co) (5·42 g, 0·03 mole) was placed into a 50 ml Erlenmeyer flask containing 25 ml CCl_4 and wired with a serum cap. To this soln was added pyridine (2·61 g, 0·03 mole) and then the soln was cooled to −40°. Triflic anhydride (10·05 g, 0·036 mole) previously cooled to −40° was added with a cold syringe in 2 ml portions over a period of 15 min. The reaction was allowed to warm to −20° for 6 days. The mixture showed only ketone by TLC (previously described for cycloundecenyl triflate). The mixture was warmed to room temp for 13 days. 20 ml CCl_4 was added to the mixture, and the entire mixture was filtered by suction. The resultant solid was dissolved in a mixture of 20 ml CCl_4 and 10 ml H_2O. The combined organic extracts were dried with $MgSO_4$ and the solvent was removed by Rotovap. The residue was placed on a column containing 100 g silica Gel G, 60–100 Mesh (Fisher Scientific Co) with benzene as eluant. The triflate eluted before the ketone. The combined triflate fractions were vacuum distilled giving 3 fractions. Fraction No. 1 (b.p. 61–66° (0·035 mm)), No. 2 (b.p. 68–70° (0·035 mm)) and No. 3 (b.p. 70° (0·035 mm)) were 85%, 81·5% and 91·8% triflate by NMR analysis for a combined yield of 2·73 g (29·0%). NMR (CCl_4), δ5·63 (b.d. triplet, 1H, vinylic) 2·57 (b.d. multiplet, 4H, allylic) 1·45 (b.d.s., 16H, $-CH_2-$); IR (thin film), 2932 (CH), 1686 (C=CH), 1412 (S=O), 1210, 1145, 910 cm^{-1}.

Since both *cis*- and *trans*-isomers are possible as products, deuteriobenzene was added in increasing amounts to separate the *cis*- and *trans*-vinylic protons in the NMR. The pure triflate was diluted to approximately a 50% soln in deuteriobenzene at which point the NMR spectrum showed two distinct triplets. NMR (50% C_6D_6), δ5·66 (t, 1H, J = 8·3 Hz, *cis*-vinylic), 5·23 (t, 1H, J = 7·5 Hz, *trans*-vinylic). By NMR integration the product mixture was 32·9% *cis*- and 67·1% *trans*-cyclododecenyl triflate and used without separation in the kinetic and product studies.

Product study of cyclododecenyl triflate (7) *in 70% aqueous 2,2,2-trifluoroethanol*. Two samples were prepared, one containing 7 (0·1042 g, $3{\cdot}32 \times 10^{-4}$ mole) in 1 ml 70% TFE, and the other containing 7 (0·1055 g, $3{\cdot}36 \times 10^{-4}$ mole) in 1 ml 70% TFE containing hexadecane, as an internal standard. Each was placed in an ampoule, sealed, and allowed to react for 8 min at 75°. Each mixture was extracted 3 times with 1 ml CCl_4. The organic layer was dried with $CaCl_2$, and the volume was reduced to about 1 ml by Rotovap. Gas chromatographic analysis at 161° yielded 3 products, cyclododecyne, 1,2-cyclododecadiene and cyclododecanone. For the buffered mixture they were 17·1, 80·0 and 2·9%, respectively; whereas the unbuffered mixture was 7·6, 87·6 and 4·8%, respectively. The ketone was identified by coinjection of authentic sample. The structures of the acetylene and allene were assigned on the basis of the IR spectra: cyclododecyne: IR (thin film), 2933, 1447, 1260, 1075, 697 cm^{-1}; 1,2-cyclododecadiene IR (thin film), 2933, 1957, 1449, 1261, 1976, 810 cm^{-1}.

Product study of cyclononeyl triflate (5) *in 70% aqueous 2,2,2-trifluoroethanol*. Cyclononenyl triflate 5 (0·1655 g, $6{\cdot}08 \times 10^{-4}$ mole) and pyridine (0·0644 g, $8{\cdot}41 \times 10^{-4}$ mole) was placed in 1 ml 70% TFE containing nonane, as an internal standard. The mixture was placed in an ampoule, sealed, and allowed to react at 75° for 6 min. To the solvolysis mixture was added 3 ml ether, and the aqueous layer was saturated with NaCl. The organic layer was analyzed by gas chromatography at 100°. Eight components were observed as products of which five have been identified. They are as follows: (a) Cyclononyne, 47·1%; mass spectrum (70 eV) m/e (rel. intensity), 122 (M^-, 61), 94 (58), 93 (68), 92 (18), 91 (33), 81 (41), 80 (86), 79 (100), 77 (26), 67 (21); NMR (CCl_4), δ2·23–1·62 (bd.m., 14H); IR (CCl_4), 2915, 2283, 1546, 1445, 1300, 1261, 1206, 1136 cm^{-1}. (b) 1,2-Cyclononadiene, 21·6% coinjection of authentic sample; mass spectrum (70 eV) m/e (rel. intensity), 122 (M^+, 3), 121 (5), 107 (10), 95 (32), 94 (51), 91 (15), 81 (40), 80 (56), 79 (100), 77 (24), 67 (25), 66 (10), 54 (14), 53 (14), 53 (12), 41 (23), 39 (29). (c) Cyclononenol (an unknown isomer), 31·1%; white needles, m.p. 52·5–53·0; IR (CCl_4), 3355, 2915, 1738, 1449, 1263, 962 cm^{-1}. (d) Cyclononenyl 2,2,2-trifluoroethyl ether, 4·1%; IR (thin film), 2958, 1700, 1263, 1081, 806 cm^{-1}; mass spectrum (70 eV) m/e (rel. intensity), 222 (M^+, 44), 192 (29), 181 (17), 180 (100), 123 (19), 122 (71), 112 (19), 98 (36), 97 (95), 94 (25), 93 (33), 81 (37), 80 (46), 79 (68), 69 (52), 64 (44). (e) Cyclononanone, 3·5%; coinjection with authentic sample; mass spectrum was duplicate of that of authentic sample; IR was superimposable with that of the literature.[11] Preparative gas chromatography of the remaining three products, 11·1%, 6·2% and 3·3% did not yield enough material to be identified.

Kinetic measurements. 2,2,2-Trifluoroethanol (Columbia Organic Chemical Co) was dried by double distillation from P_2O_5 and then diluted by weight with H_2O to be desired mixture. Pyridine was dried by distillation from barium oxide. Rate studies were done conductiometrically with approximately 0·2 μl compound per 4·0 ml solvent in controlled constant temp baths. First order rates were observed in all instances for over 5 half-lives. The rates were calculated by a non-linear, least squares program.[12]

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