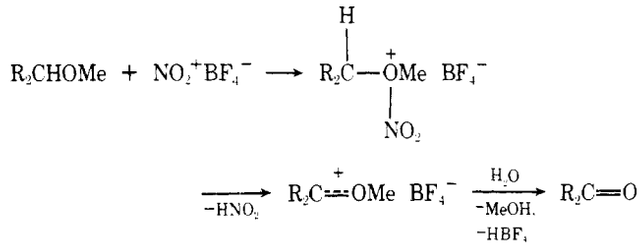
Table I. Oxidative Cleavage of Methyl Ethers ROMe with NO_2BF_4

R	Registry no.	Product	Registry no.	Yield, %
Benzyl	538-86-3	Benzaldehyde	100-52-7	89
p-Methylbenzyl	3395-88-8	*p*-Tolualdehyde	104-87-0	85
o-Methylbenzyl	15018-12-9	*o*-Tolualdehyde	529-20-4	82
p-Nitrobenzyl	1515-83-9	*p*-Nitrobenzaldehyde	555-16-8	93
2-Octyl	1541-09-9	2-Octanone	111-13-7	63
Cycloheptyl	42604-04-6	Cycloheptanone	502-42-1	57
Cyclohexyl	931-56-6	Methyl 5-oximinocaproate	62344-93-8	60
Cyclopentyl	5614-37-9	Methyl 4-oximinovalerate	62842-23-3	53

the nitration (nitrolysis) of alkanes,[6] respectively. Thus alkyl ethers are expected to react smoothly with nitronium salts to form oxonium ion intermediates which should decompose via nitrous acid elimination. The direction of proton loss is dictated by the stability of the incipient cation; therefore, in most methyl ethers the methoxycarbenium ions would ensue, and the net reaction (with hydrolytic workup) is then a formal demethanation.

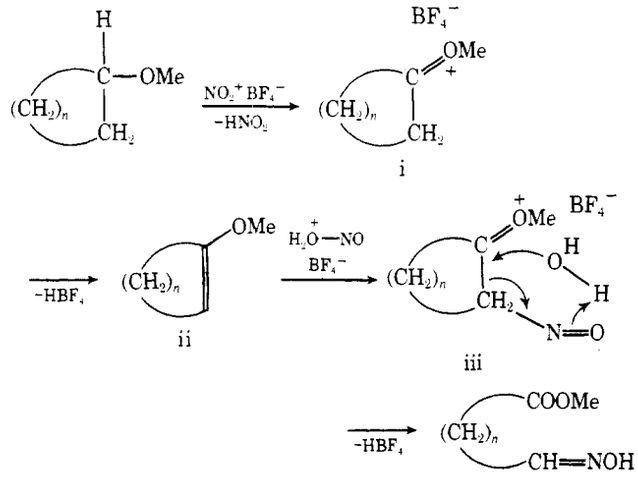


Results summarized in Table I clearly show the generality of methyl ether oxidation. Interestingly, under the experimental conditions methyl ethers of cyclohexanol and cyclopentanol suffer ring fission which is readily accommodated by Scheme I.

It should be noted that cyclohexanone undergoes ring cleavage[7] on reaction with nitrosyl chloride in alcoholic solvents. A similar mechanism involving enol ether formation and nitrosation steps has been formulated. In our cases the enol ethers and the nitrosating agent are only inferred as intermediates. The different behaviors of the cycloalkyl ethers (e.g., cyclohexyl vs. cycloheptyl) can be correlated with the enolizabilities of the corresponding ketones. Thus tautomerization of the methoxycarbenium ions (i) to enol ethers (ii) by elimination of HBF_4 is more favorable when the ring size is either five or six membered.

Methods for oxidative cleavage of *simple* primary alkyl ethers are scarce. One addition is our recently reported process utilizing uranium(VI) fluoride.[8] Most of the existing procedures are concerned with fission of tertiary ethers[9] using trityl salts and silyl and stannyl derivatives of alcohols with various reagents.[2,10] The present method is complementary to others and suggests the feasibility of cleaving enol ethers with nitrosonium salts.

Scheme I



Experimental Section

Oxidative Cleavage of Methyl Ethers with Nitronium Tetrafluoroborate. To a suspension of nitronium tetrafluoroborate[11] (0.565 g, 5 mmol) in dry dichloromethane (5 mL) was added dropwise a solution of a methyl ether (5 mmol) in the same solvent (5 mL) with ice cooling and magnetic stirring. After the vigorous reaction subsided, the ice bath was removed and stirring was continued for 1 h at room temperature. The reaction mixture was quenched with water and extracted with dichloromethane (3 × 20 mL), and the dried ($MgSO_4$) extracts were rotary evaporated to give the product which was microdistilled or recrystallized, and identified by comparison with an authentic sample.

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

Registry No.—Nitronium tetrafluoroborate, 13826-86-3.

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Analysis of Reactivity of Alkenylidenecyclopropanes with Electrophilic Reagents

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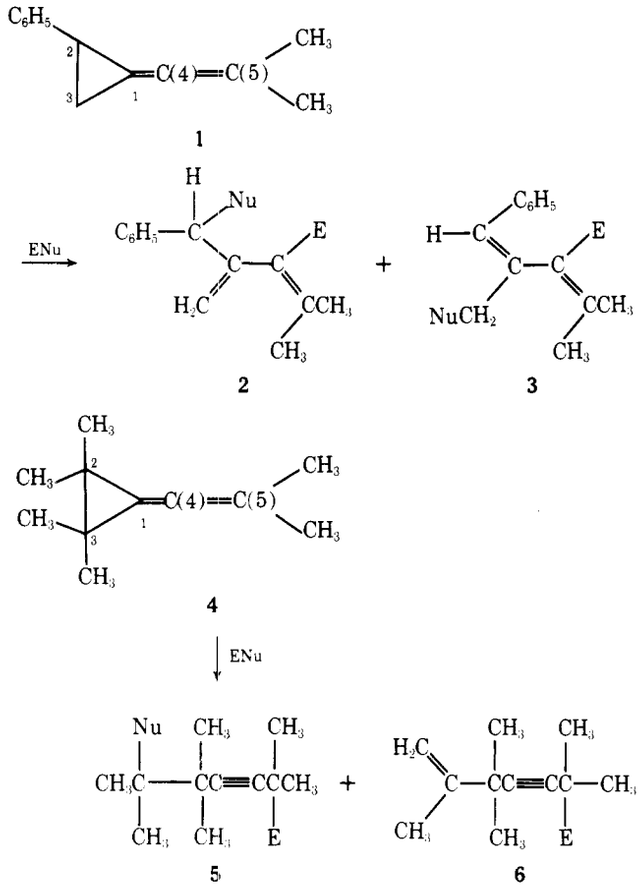
In previous studies on the reactions of differently ring-substituted alkenylidenecyclopropanes with electrophilic reagents, differences in both mode of reaction and reactivity were noted.[1,2] Notably, the phenyl-substituted compound 1 reacted with chlorosulfonyl isocyanide (CSI),[1] acetic acid in the presence of *p*-toluenesulfonic acid (*p*-TS),[2] mercuric acetate,[2] and benzenesulfenyl chloride[2] exclusively at the p orbital on central allene carbon C(4) of the C(1)–C(4) double

bond to produce ring-opened products of general structure 2 and 3. In contrast, the tetramethyl compound 4 reacted with the same reagents exclusively at the terminal allene carbon C(5) (of the C(4)–C(5) double bond) to produce products having the general structure 5 and 6 (or the cyclic lactam in



the case of CSI).[2] The present note describes the results of a qualitative kinetic study of the reaction of alkenylidenecyclopropanes with an electrophilic reagent, and a molecular orbital rationale for the dramatic differences in mode of reaction and reactivity.

Results

Preliminary kinetic studies of 1 and 4 with a variety of electrophilic reagents indicated that a single reagent could not be found which would allow a convenient and accurate measurement of the rates of reactions of the two extremes of the reactivity scale. Reaction with trichloroacetic acid (TCA) in carbon tetrachloride solution proved to be the most acceptable system for rate measurements.[3] The structures of the reaction products formed under the kinetic conditions were determined by comparison of chemical shifts with the products formed in the *p*-TS-catalyzed addition of acetic acid.[2] In several cases, however, isolation of all of the initially formed products was precluded by the presence of facile acid-catalyzed isomerizations (for example 7 → 8) and apparent further addition reactions of TCA to the initial products. The products characterized in this manner are illustrated in Scheme I.

An attempt was made to determine the kinetic order of the reaction of TCA with 1. Although third-order kinetic plots (first-order in 1, second-order in TCA) were reasonably linear, the resulting specific rate constants were not constant with change in TCA concentration, the k_3's increasing with increasing TCA concentration. A plot of ln k_3 vs. TCA concentration gave a slope of approximately 1.8, indicating a kinetic order in TCA of approximately 4. Instead of trying to measure accurate specific rate constants, a standard set of reaction conditions was adopted and half-lives of the reactions were measured for comparison purposes. The half-lives thus measured are tabulated in Table I.

Table I. Relative Reactivities of Alkenylidenecyclopropane with Trichloroacetic Acid in Chloroform at 30 °C

Compd	Registry no.	$t_{1/2}$, min	% attack at C(5)
1	4544-23-4	30	0
13a	33530-27-7	22	0
13b	33530-26-6	19	0
10	40922-91-6	16	0
15a	37817-46-2	0.25	>95[a]
15b	37817-36-0	≤0.1	>95[a]
4	13303-30-5	<0.1	>90[a]

[a] Peaks corresponding to the products indicated in Scheme I were evident in the NMR spectra up to ~50% reaction, whereupon peaks arising from isomerization and apparent further addition of TCA became evident. The indicated minimum percentages are based on analysis of the spectra early in the course of the reactions.

Table II. Orbital Energies and Charges for 22, 23, and 4 from CNDO/2 Calculations

			Total charge	
Compd	E_{HOMO}, eV	$E_{2nd\ OMO}$	C(5)	C(4)
4	−10.0259	−12.1638	−0.0059	−0.0073
22[a]	−10.1592	−11.8211	+0.0133	−0.0037
23	−10.2653	−11.8320	+0.0171	−0.0060

[a] Registry no.: 22, 59055-15-1.

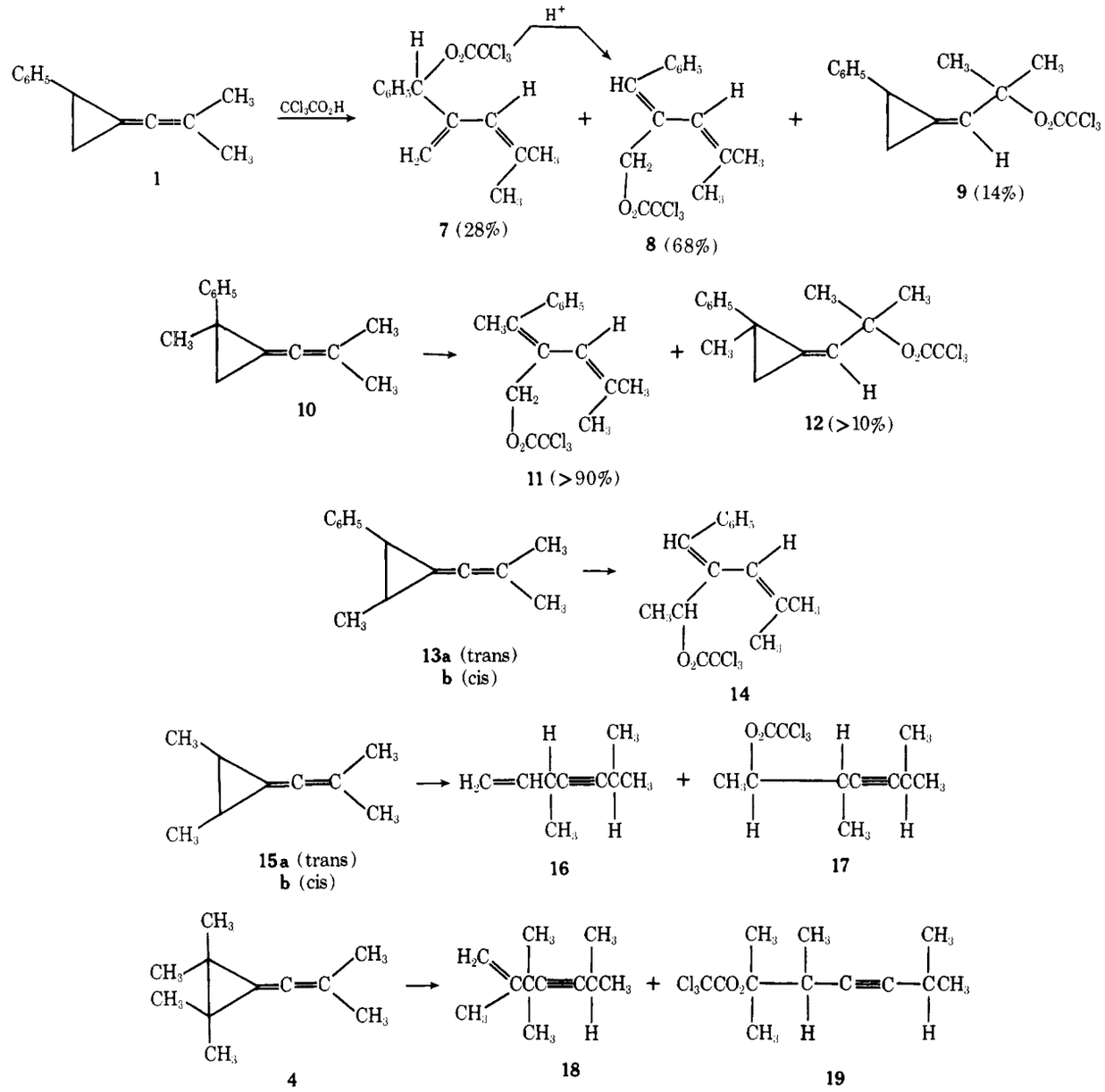
Discussion

Inspection of the structural data presented in Scheme I shows that the phenyl-substituted substrates 1 and 10 undergo attack by proton predominantly on the p orbital on C(4) of the C(1)–C(4) double bond, while 13a and 13b react exclusively in this manner. Adducts 9 and 12 are formed by addition across the C(4)–C(5) double bond, a process not previously observed in electrophilic additions to these systems. The formation of 9 and 12 is attributed to a possible concerted electrophilic addition component due to the less polar solvent used in these reactions, as indicated by the more complex reaction kinetics. Integration of the product distribution data with the relative reactivity data shows a difference in reactivity toward electrophilic attack at C(4) vs. C(5) in the phenyl- and tetramethylalkenylidenecyclopropanes of *>10 000!*

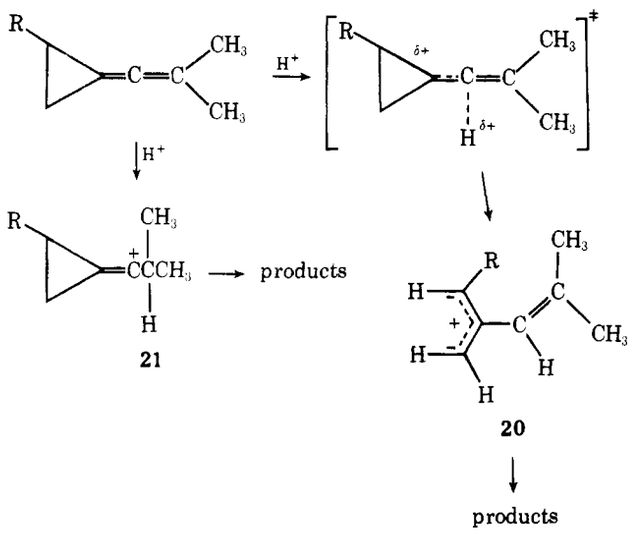
This large difference in reactivity cannot be attributed solely to the stability of intermediates (or transition states) formed in the two different modes of reaction. Electrophilic attack at C(4) of the C(1)–C(4) double bond results in the formation of a cyclopropyl cation which opens to the allyl cation intermediate 20.[5] The greater stabilization afforded the allyl cation portion of 20 by the phenyl relative to a methyl group cannot be a factor until very late in the ring-opening process. Thus, on this basis one would not expect functions attached to the ring to have a great effect on the reactivity of electrophilic attack at C(4) of the C(1)–C(4) π bond.

Electrophilic attack at C(5) results in the formation of cation 21, which derives extensive stabilization by interaction of the vacant p orbital on C(4) with the Walsh orbitals[6] of the ring.[1,2,7] Alkyl groups attached to the three-membered ring interact moderately strongly with Walsh orbitals of the ring,[8] whereas an aryl group does not.[9] On this basis alkyl-substi-

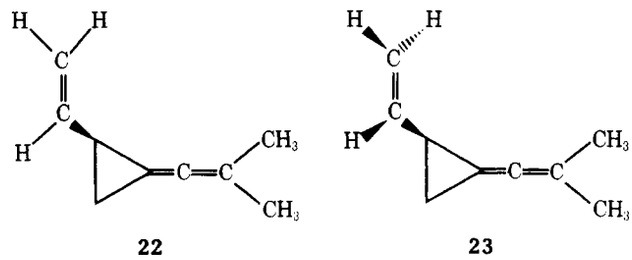
Scheme I



tuted alkenylidenecyclopropanes should be more reactive toward electrophilic attack at C(5) than aryl derivatives. This does not, however, explain the difference in position of electrophilic attack between the alkyl- and aryl-substituted systems.



Insight into the reasons for the difference is gained from the results of CNDO/2 MO calculations for the planar and perpendicular conformations of 2-vinylisobutenylidenecyclopropane (**22** and **23**) (as abbreviated models of the corresponding phenyl derivatives[10]) and the 2,2,3,3-tetramethyl compound **4**. In all three molecules the HOMO is that derived by mixing of the C(4)–C(5) π bond with the Walsh orbitals of the three-membered ring,[8] while the second highest occupied MO is that of the C(1)–C(4) π bond. According to the principles of second-order perturbation MO theory,[11] electrophilic



attack on the tetramethyl compound **4** is favored both by orbital energy (i.e., the energy of the HOMO) and electrostatic interactions. In contrast, electrophilic attack on the phenyl-substituted derivatives involves attack on the lower energy second OMO[12] resulting in a slower reaction, the position of attack being governed by electrostatic interactions. In these cases the electrostatic interaction energy term dominates the attractive bonding interaction energy terms, whose magnitude is inversely proportional to the orbital energy.

Experimental Section

General Conditions for Reactions of Alkenylidenecyclopropanes with Trichloroacetic Acid. To a solution of 0.25 mequiv of the alkenylidenecyclopropane in 0.50 mL of carbon tetrachloride in an NMR tube was added 0.25 mequiv of trichloroacetic acid (TCA) in 0.10 mL of carbon tetrachloride. The solution was rapidly mixed and immediately placed in the NMR probe. The NMR spectrum was periodically integrated over a region containing only characteristic peaks of the starting alkenylidenecyclopropane (~5 s elapsed time from mixing to recording of first integral scan). The percent unreacted alkenylidenecyclopropane was plotted vs. time and $t_{1/2}$ taken as the time corresponding to 50% reaction. In all cases, the reactions proceeded to >95%.

Reaction of 1 with TCA. The final NMR spectrum at >95% reaction showed the presence of adducts **8** and **9**, which were separated by high-pressure liquid chromatographic techniques on a 2 ft × 3/8 in. Corasil column using hexane as eluent.

8: NMR ($CDCl_3$, ^1H FT spectrum on pure fraction isolated by HPLC, integral from CW spectrum of mixture of **8** and **9**) δ 1.77 (overlapping d's, J's = 2.2 and 1.6 Hz, 6 H), 4.95 (s, 2 H), 5.79 (br s, 1 H), 6.62 (br s, 1 H), 7.30 (m, 5 H); MS calcd for $C_{15}H_{15}{}^{35}Cl_3O_2$ 332.0137, obsd 332.0137.

9: NMR ($CDCl_3$) δ 1.38 (dd, J's = 10.6, 6.1 Hz, 1 H), 1.44 (s, 6 H), 1.75 (dd, J's = 8.1, 6.1 Hz), 2.56 (dd, J's = 10.6, 8.1 Hz, 1 H), 5.32 (br s, 1 H), 7.25 (br s, 5 H); MS calcd for $C_{15}H_{15}{}^{35}Cl_3O_2$ 332.0137, obsd 332.0144.

NMR spectra recorded early during the reaction indicated the presence of **7** (br s; at δ 5.11 and 5.46) which on longer reaction times is converted to **8**.[2] Integration of NMR spectra taken after low conversions indicate that **7**, **8**, and **9** are initially formed in a 2:4:1 ratio.

Reaction of 10 with TCA. NMR spectra recorded after short reaction times clearly showed the presence of **11** and **12** (>9:1 ratio), and possibly very small quantities of the isomer of **11** (corresponding to **7** formed from **1**). NMR spectra recorded later in the reaction showed the presence of other components (unidentified) and decreasing quantities of **11** and **12**. Attempts to isolate pure samples of **11** and **12** were not successful. **11**: NMR ($CDCl_3$, from a mixture of **11** and **12**) δ 1.70 (br s, 3 H), 1.83 (overlapping d's, $J \approx 1.2$ and 2.1 Hz, 6 H), 4.74 (s, 2 H), 5.75 (br s, 1 H), 7.30 (m, 5 H). **12**: NMR δ 1.52 (s, 3 H), 1.63 (s, 6 H), 5.11 (br s, 1 H), 7.3 (m, 5 H). The ring methylene hydrogens of **11** and **12** appear as poorly resolved multiplets partially obscured by the methyl resonances of **11** and **12**.

Reaction of 13a and 13b with TCA. The NMR spectrum of the product derived from both **13a** and **13b** showed the presence of a single adduct, **14**: NMR ($CDCl_3$) δ 1.34 (d, J = 1.8 Hz, 3 H), 1.53 (d, J = 6.7 Hz, 3 H), 1.77 (d, J = 1.3 Hz, 3 H), 5.57 (q, J = 6.7 Hz, 1 H), 5.83 (m, 1 H), 6.65 (m, 1 H), 7.3 (br s, 5 H); MS calcd for $C_{16}H_{17}{}^{35}Cl_3O_2$ 346.0294, obsd 346.0288.

Reaction of 15a and 15b with TCA. The reaction of **15a** and **15b** with TCA produced a mixture whose NMR spectrum was very complex and could not be interpreted. No resonance in the δ 5.8 region (–CH=$C(CH_3)_2$) could be detected. Although the initial reaction was complete in ~1 min, the NMR spectrum of the product mixture continued to change. After 5 min a substantial portion of the initially formed product had disappeared.

Reaction of 4 with TCA. The reaction of **4** with TCA immediately produced a mixture of **18** and **19** in an approximate 1:1 ratio. Product **18** was identified by comparison of ^1H chemical shifts previously observed.[2] Product **19** was identified by comparison of the ^1H chemical shifts with the corresponding acetate previously characterized,[2] all chemical shifts corresponding to ±0.01 ppm. In addition to **18** and **19** a minor product appears to have been formed, as evidenced by the appearance of two methyl singlets in the NMR. This adduct could not be isolated and it is not known whether this adduct is a primary or secondary product.

Registry No.—**7**, 62861-82-9; **8**, 62861-83-0; **9**, 62861-84-1; **11**, 62861-85-2; **12**, 62861-86-3; **14**, 62861-87-4; trichloroacetic acid, 76-03-9.

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(4) Calculated on the basis of 95% situselectivity (assumed limits of NMR detectability of product formation) in the aryl- and alkyl-substituted cases. An assumed 99% situselectivity would yield a reactivity difference of >300 000.
(5) The formation of ring-retained products from **1** and **10** differs from earlier observations in which only ring-opened products were formed.[1,2] The formation of ring-retained products probably occurs via concerted addition pathways which are competitive with cation intermediate pathways in the less polar solvent carbon tetrachloride.
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(11) See A. Devaquet and L. Salem, *J. Am. Chem. Soc.*, **91**, 3793 (1969).
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High Pressure Assisted Synthesis. Evidence for Nucleophilic Displacement on 2,2,2-Trifluoro-1-phenylethyl Tosylate

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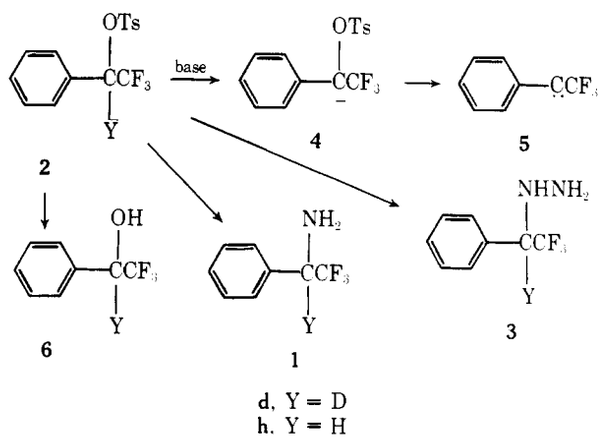
While searching for a practical synthesis of 2,2,2-trifluoro-1-phenylethylamine[1] (**1h**), we contemplated the report[2] that 2,2,2-trifluoro-1-phenylethyl tosylate (**2h**) reacts with hydrazine to afford the alkylated hydrazine **3h**. Trifluoromethyl groups severely impede S_N1 or S_N2 reactions when α to the reaction site.[3a-b] However, the hydrazinolysis reaction might conceivably proceed via attack upon hydrazine by the electrophilic carbene **5**, formed from α elimination of tosylate ion from carbanion **4**.



d, Y = D
h, Y = H