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1-Ethynylcyclopropyl Tosylate Solvolysis. 2.[1] *p*-Aryl Substituent Effect upon Rate and Product Distribution

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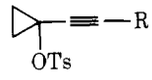
Received June 18, 1976

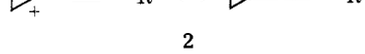
1-*p*-Tolylethynylcyclopropyl tosylate (**4**) and 1-*p*-anisylethynylcyclopropyl tosylate (**5**) have been prepared. Their rates of reaction and the resulting products of solvolysis in various solvents were compared with those of 1-phenylethynylcyclopropyl tosylate (**3**). The relative rates (k_{rel}) in 50% ethanol (70 °C) are **3**, k_{rel} = 1; **4**, k_{rel} = 7.5; and **5**, k_{rel} = 152. The rate enhancements over the parent system **3** due to *p*-methyl (**4**) and *p*-methoxy substitution (**5**), the solvent effects (m = 0.583–0.505), and the ρ value (−2.98) are clearly consistent with a SN'i ionization process involving anchimeric assistance of the triple bond (k_Δ), and leading to the mesomeric cation **11**, which is highly stabilized by further delocalization of the positive charge through the adjacent aryl ring. A cyclopropyl tosylate solvolysis, involving no ring opening at all, is reported.

In a previous solvolytic investigation, we reported the behavior of a variety of substituted 1-ethynylcyclopropyl tosylates **1**.[1]



1

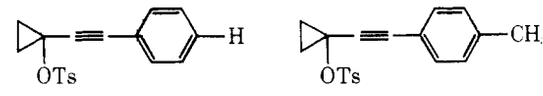
The solvolytic reactions of simple cyclopropyl derivatives usually afford, in the absence of steric[2] or direct conjugative interaction,[3] only allyl products[4] through concerted ionization and disrotatory ring opening.[5] On the other hand, it has been shown that the resonance-stabilized cation **2** does not undergo such a ring opening.



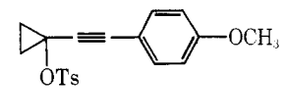
2

However, the formation of **2** as an intermediate in the solvolysis of 1-ethynylcyclopropyl tosylates **1** appeared to be strongly dependent upon the nature of the substituent R, as evidenced from product distribution and kinetic data. Thus, for instance, the products of aqueous ethanolysis of **1** (R = CH_3) were only allylic derivatives from opening of the cyclopropane ring while unrearranged cyclopropanols (or derivatives) were obtained from **1** (R = cyclopropyl) in high yield.[1] Therefore, the stabilization of the positive charge of **2**, by delocalization over the three carbons of the mesomeric propargyl allenyl system, entails a powerful electron-releasing substituent at the allenyl end.

We report here the solvolysis reactions of the 1-*p*-arylethynyl 1-tosyloxy cyclopropanes **3**, **4**, and **5** in order to determine the increase in the stabilization of the intermediate mesomeric



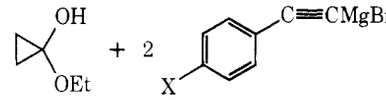
3 **4**



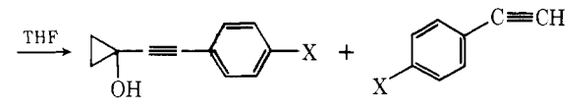
5

cations induced by the increased electron-releasing effect of the para substituents H, CH_3, OCH_3.

Syntheses. The reaction of the hemiketal of cyclopropanone **6**[6] with 2 equiv of the acetylenic magnesium bromides **7** provides the 1-*p*-arylethynylcyclopropanols **8** in high yield.



6 **7**



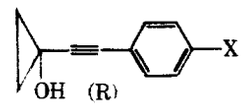
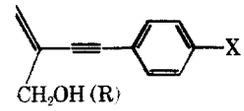
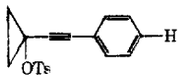
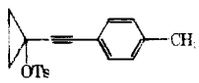
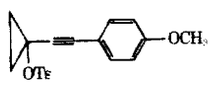
8 **9**

75-86%

X = H, CH_3, OCH_3

The hemiketal **6** is now readily available from ethyl 3-chloropropanoic ester;[1] the para arylacetylenic compounds which give the Grignard reagents **7** by exchange with ethylmagnesium bromide[7] were prepared from the suitable para-

Table I. Solvolysis Products (%) of 1-Arylethynylcyclopropyl Tosylates[a]

	Solvent	Reaction time, h	 8	 10
 3	EtOH–H_2O (50:50)	40	85[b]	15[b]
	Acetone–H_2O (60:40)	48	73.5	26.5
	Trifluoroethanol	8	52[c]	48[c]
 4	EtOH–H_2O (50:50)	40	95[b]	5[b]
	Acetone–H_2O (60:40)	48	82.5	17.5
	Trifluoroethanol	8	65[c]	35[c]
 5	EtOH–H_2O (50:50)	40	100[b]	0
	Acetone–H_2O (60:40)	48	92.5	7.5
	Trifluoroethanol	8	94[c]	6[c]

[a] Temperature 70 °C, buffered with 1.1 equiv of triethylamine. [b] As a mixture of the alcohol and its ethyl ether. [c] As tri fluoroethyl ether.

Table II. Solvolysis Rates of the 1-Arylethynylcyclopropyl Tosylates

	Solvent[a]	Temp, °C	$k \times 10^4$, s^{-1}[b]	Rel rate, 50E, 70 °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	m
3, X = H	50E	70	0.838 ± 0.017	1	19.67 ± 0.01	−20.10 ± 0.01	0.583
	50E	75	1.320 ± 0.006				
	80E	70	0.090 ± 0.003				
4, X = CH_3	50E	50	0.481 ± 0.019				
	50E	70	6.266 ± 0.025	7.47	23.27 ± 0.01	−6.45 ± 0.01	0.540
	50E	75	16.79 ± 0.17				
	80E	70	0.80 ± 0.01				
	80E	75	1.02 ± 0.02				
5, X = OCH_3	50E	50	19.84 ± 0.52				
	50E	60	39.23 ± 0.06				
	50E	70	127.30 ± 0.01	151.55	19.89 ± 0.01	−9.51 ± 0.01	0.505
	80E	70	18.58 ± 0.01				

[a] 50E refers to 50% aqueous ethanol, v/v before mixing. [b] The errors reported were determined by means of a least-squares computer program.

substituted benzaldehyde following a reported procedure.[8] The tosylates **3**, **4**, and **5** were then readily obtained from the cyclopropanols **8** by usual procedures.

Results and Discussion

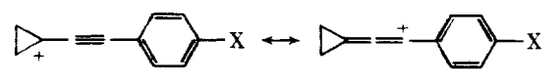
The 1-*p*-arylethynyl-1-tosyloxycyclopropanes **3**, **4**, and **5** were solvolyzed in solvents of different ionizing power and nucleophilicity, buffered with 1.1 equiv of triethylamine in order to avoid any acid-catalyzed rearrangement of the products.[9]

The temperature of the reaction was chosen low enough, i.e., 70 °C, to avoid the subsequent homoketonization of the cyclopropanols.[1,10] For each run, the products were separated by gas chromatography and their structures unequivocally proven by ir, NMR, and mass spectroscopy.

The cyclopropyl tosylates **3**, **4**, and **5**, as shown by the product distribution, listed in Table I, solvolyze with the formation of a mixture of the unrearranged cyclopropanols (or ethyl ethers) **8** and of the open ring allylic derivatives **10**, solely. As expected, the amount of unrearranged products **8** is clearly dependent upon the electron-donating power of the para substituent X of the phenyl ring. Moreover, the higher the ionizing power and the lower the nucleophilicity of the solvent, the more marked is the *p*-phenyl substituent effect; thus, for instance, the aqueous ethanolysis of the tosylates **3** (X = H) and **5** (X = OCH_3) afforded 85 and 100% of unrearranged cyclopropanols **8**, while in trifluoroethanol the corresponding values were 52 and 94%, respectively.

The solvolysis rates of the tosylates **3–5** in aqueous ethanol, measured by automatic continuous titration at pH 7.0, are presented in Table II. They increase too with X: the tosylates **4** (X = CH_3) and **5** (X = OCH_3) reacted 7.5 and 151.5 times faster than the parent tosylate **3** (X = H), respectively.

The effect of an electron-releasing group X on the solvolysis reaction is therefore noticeable. If the rate data for the cyclopropyl tosylates **3**, **4**, and **5** are plotted vs. Brown σ_p^+ substituent constants a ρ value of −2.98 is obtained, for the solvolysis in 80% aqueous ethanol. This result is highly consistent with an intermediate mesomeric carbenium ion **11**, in which

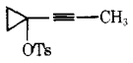
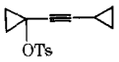
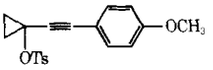


11

substantial delocalization of the positive charge through the 3 carbon unit exists.

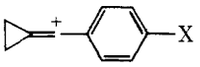
It must be noted that the substituent effect on the solvolysis rates of triarylchloroallenes[11] (80% aqueous acetone) and of 1-arylcyclopropyl tosylates[12] (acetic acid) corresponds to ρ values of −2.0 and −4.31, respectively.

Table III. Comparison of the Solvolysis Rate and Product Distribution of Some *tert*-1-Tosyloxycyclopropane Derivatives[a]

	$k \times 10^4$, s^{-1}	Rate ratios	Unrearranged product,[c] %	Ref
 13	0.18	1	0	9
 14	2915	16.10^3	68.5	9
 15	0.53[b]		0	12
 16	0.14	1	0	1
 17	18.81	133	90	1
 5	127.3	909	100	This work

[a] In 50% aqueous ethanol at 70.0 °C. [b] In acetic acid at 70.5 °C. [c] The counterpart is the product from ring opening, i.e., the allylic derivatives.

We have recently reported the generation of the vinyl cations **12** from the solvolytic reaction of the corresponding (1-bromo-1-*p*-arylmethylene)cyclopropanes.[13]



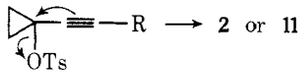
12

The enhancement of the rate of solvolysis by varying X under the same conditions correspond to a ρ value of -2.8.

These highly comparable data represent further convincing evidence that the solvolysis of *p*-aryl substituted ethynyl cyclopropyl tosylates **3–5** does indeed proceed through a resonance-stabilized vinyl cation **11**. Such a similarity of substituents effects in the generation of the vinyl cations **12** and in the generation of the mesomeric cations **11** confirms our previous findings.[1]

The activation parameters calculated from the temperature dependence of the solvolysis rates listed in Table II are consistent with the data reported on such vinyl cations; thus, for example, solvolysis of triphenylchloroallene (80% aqueous acetone) gives $\Delta H^{\ddagger} = 20.1$ kcal/mol and $\Delta S^{\ddagger} = -10.9$ eu,[11] solvolysis of 2,2-diphenyl-1-anisyliodoethylene (70% aqueous DMF) gives $\Delta H^{\ddagger} = 23.5$ kcal/mol and $\Delta S^{\ddagger} = -16.3$ eu,[14] solvolysis of 3,4-dimethyl 2-bromo-1,3-butadiene (80% aqueous ethanol) involving a mesomeric vinyl cation as intermediate gives $\Delta H^{\ddagger} = 25.6$ kcal/mol and $\Delta S^{\ddagger} = -17.2$ eu.[15]

The *m* values listed in Table II, which are a measure of the sensitivity of the substrate to changes in solvent ionizing power *Y*,[16] are lower than would be expected for anchimerically and nucleophilically unassisted solvolysis (k_c, $m \sim 1$),[17] but they fall in the range normally found for k_s and k_Δ processes.[18] From the low propensity of the parent cyclopropyl substrate to changes in solvent nucleophilicity, Schleyer et al. have reported that the solvolyses of cyclopropyl derivatives are not k_s processes; i.e., there is no specific back-side nucleophilic involvement of solvent in the transition state, but mainly k_Δ processes ($m = 0.508$) where the electrons from the breaking cyclopropane bond take the place of the attacking nucleophile.[19] In the absence of ring opening here, the anchimeric assistance is likely provided by the electrons of the adjacent triple bond moving toward the back side of the C–tosylate bond; thus, the solvolysis of the 1-ethynylcyclopropyl tosylates **1** can be regarded more likely as a SN'i ionization process.



1

In the study of neighboring group effects, it has been postulated that the more stable the carbenium ion center, the less demand that center will make upon a neighboring group for additional stabilization through π or σ participation.[20] This postulate seems to be valid too for the mesomeric cation **11**. Indeed, increasing the electron supply at the cationic center by varying the substituent X on the aryl group increases the anchimeric assistance of the triple bond (see the decreasing values of *m*, Table II) and reduces the ring opening of the cyclopropyl moiety into allyl derivatives, while, for instance, the tosylate **1** (R = CH_3) solvolysis entailed high carbon–carbon bond participation from the cyclopropane ring and afforded only the ring open derivatives.[1]

In Table III are gathered the kinetic data and product distribution for the solvolysis of various tertiary substituted 1-tosyloxycyclopropanes. An increase in the solvolysis rates, implying an increase in the stabilization of the intermediate cation, is therefore clearly observed when a more powerful electron-releasing group is successively substituted at the electron deficiency. Thus changing from an isopropyl **13** to a cyclopropyl **14** provides a rate enhancement of 16.10^3 and affords, at most, 68.5% of unrearranged cyclopropyl derivatives;[9] while changing from a methyl **16** to a cyclopropyl **17** or to a *p*-anisyl **5** provides rate increases of 133 and 909 only, but a higher proportion of unrearranged products, 90 and 100%, respectively. The present result, which is the first example of a cyclopropyl tosylate solvolysis via cationic intermediate involving no ring opening *at all*, provides a particularly straightforward demonstration of the stabilizing effect of a suitably substituted triple bond.

The lack of carbonyl or (and) allenic absorptions in the ir and of vinylic or (and) dimethylenallenic absorptions in the NMR spectra of the crude solvolytic products confirms our

previous findings that the mesomeric cations such as **11** react exclusively at the propargyl position.[1] This result is not at all a point of controversy; as a matter of fact, several alkynyl carbenium ions for which spectroscopic data indicate a strong contribution from the allenyl cation form have the same behavior,[11,21-24] unless the propargyl position is sterically hindered.[24]

A more detailed description of the charge distribution in the mesomeric cation **2** on the basis of ^{13}C NMR chemical shifts is under investigation.

Experimental Section

The preparation and description of 1-(phenylethynyl)cyclopropanol **8** (X = H) and of 1-(phenylethynyl)-1-tosyloxycyclopropane **3** have been previously reported.[1]

***p*-Tolylacetylene 9 (X = CH_3)** was prepared using the procedure of Corey and Fuchs[8] by adding 16.8 g (140 mmol) of freshly distillated *p*-tolualdehyde to a reagent prepared from interaction of 18.35 g (281 mmol) of zinc dust, 73.7 g (281 mmol) of triphenylphosphine, and 93.2 g (281 mmol) of carbon tetrabromide in 500 ml of methylene chloride at room temperature for 30 h.

After a reaction time of 2 h at room temperature, 2000 ml of pentane was added to the reaction mixture, and the insoluble material removed by filtration. The insoluble fraction was reworked by several cycles of methylene chloride extraction and pentane precipitation to remove all of the olefinic product.

The solvents were removed by rotary evaporation and distillation of the residue at reduced pressure gave 32.7 g (85%) of 1,1-dibromo-2-*p*-tolylethylene: bp 85 °C (0.05 mm); NMR (CCl_4) δ 2.30 (s, 3 H), 7.35 (s, 1 H) and 7.0–7.45 (q, 4 H).

A solution of 32.7 g (118 mmol) of the dibromo olefin in 250 ml of tetrahydrofuran at −78 °C was treated with 237 mmol (103 ml of a 2.3 N hexane solution) of *n*-butyllithium. The reacting mixture was allowed to stir overnight at −78 °C and then for 1 h at 25 °C. The mixture was poured on crushed ice containing 118 mmol of hydrochloric acid. The organic layer was washed with water and dried over $MgSO_4$ and the solvent removed by distillation. Fractional distillation of the crude material yielded 9.6 g (68%) of *p*-tolylacetylene: bp 54 °C (10 mm) [lit.[25] bp 65–67 °C (18 mm)]; ir (neat) 3280 (ν ≡C–H) and 2100 cm^{-1} (ν C≡C); NMR (CCl_4) δ 2.30 (s, 3 H), 2.85 (s, 1 H), and 6.95–7.35 ppm (q, 4 H).

1-(*p*-Tolylethynyl)cyclopropanol 8 (X = CH_3) was prepared using the reported procedure.[1] To 70 mmol of ethylmagnesium bromide prepared from 1.7 g of magnesium and 8.65 g of ethyl bromide in 50 ml of anhydrous tetrahydrofuran was added a solution of 8.4 g (70 mmol) of *p*-tolylacetylene in 20 ml of tetrahydrofuran. The mixture was refluxed for 2 h. To the cold *p*-tolylacetylenemagnesium bromide was added with stirring 3.57 g (35 mmol) of 1-ethoxycyclopropanol[1] and the reacting mixture was refluxed for 4 h. The cold mixture was poured on a mixture of crushed ice and 70 ml of H_2SO_4 (1 N) and extracted with ether. The organic layer was dried over $MgSO_4$ and concentrated to yield a light yellow oil. Thin layer chromatography, ir, and NMR spectra showed two compounds in equal amount. The first was readily removed by distillation [bp 54 °C (10 mm)] and identified as the starting *p*-tolylacetylene. The residue was 4.5 g (75%) of practically pure 1-(*p*-tolylethynyl)cyclopropanol 8 (X = CH_3): ir (neat) 3080 (ν C–H) and 2210 cm^{-1} (ν C≡C); NMR (CCl_4) δ 1.08 (m, 4 H), 2.32 (s, 3 H), 3.50 (m, 1 H), and 6.95–7.35 ppm (m, 4 H); MS M^+ *m/e* (rel intensity) 172 (62.5), 157 (12.5), 143 (100), 129 (29), 128 (17.5), 115 (41), 92 (35), 58 (72.5).

***p*-Anisylacetylene 9 (X = OCH_3)** was prepared by the procedure of Corey and Fuchs[8] using 20.9 g (320 mmol) of zinc dust, 84 g (320 mmol) of triphenylphosphine, 106.2 g (320 mmol) of carbon tetrabromide, and 21.7 g (159 mmol) of freshly distillated *p*-anisaldehyde yielding 36 g (80%) of 1,1-dibromo-2-*p*-anisylethylene: bp 114 °C (0.025 mm); NMR (CCl_4) δ 3.75 (s, 3 H), 7.45 (s, 1 H), and 6.70–7.50 ppm (q, 4 H). Treatment with 2 equiv of *n*-BuLi as described above for *p*-tolylacetylene yielded 12.16 g (75%) of *p*-anisylacetylene: bp 85–86 °C (10 mm) [lit.[26] 86–87 °C (17 mm)]; ir (neat) 3280 (ν ≡C–H) and 2100 cm^{-1} (ν C≡C); NMR (CCl_4) δ 2.85 (s, 1 H), 3.78 (s, 3 H), and 6.80–7.45 ppm (q, 4 H).

1-(*p*-Anisylethynyl)cyclopropanol 8 (X = OCH_3) was prepared analogously to 8 (X = CH_3) by the reaction of the *p*-anisylacetylenemagnesium bromide [obtained from 18.22 g (138 mmol) of *p*-anisylacetylene and 138 mmol of ethylmagnesium bromide] with 7.04 g (69 mmol) of 1-ethoxycyclopropanol.[1] After the usual workup a mixture of two compounds in equal amount was obtained. The first, liquid, was simply removed by filtration under vacuum through a glass-sintered funnel and identified as the starting *p*-anisylacetylene. The solid residue was 11.15 g (86%) of practically pure 1-(*p*-anisylethynyl)cyclopropanol 8 (X = OCH_3), recrystallizable from ethyl acetate, mp (ethyl acetate) 91.8 °C.

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.42; O, 16.99. Found: C, 76.47; H, 6.36.

Ir (CCl_4) 3590 (ν O–H), 3090 (ν C–H), and 2290 cm^{-1} (ν C≡C); NMR (CCl_4) δ 1.04 (m, 4 H), 3.75 (s, 3 H) and 6.65–7.30 ppm (q, 4 H); MS M^+ *m/e* (rel intensity) 188 (71.5), 173 (15.5), 159 (100), 145 (17), 144 (17), 127 (12), 117 (17), 115 (17), 108 (65), 55 (64).

1-(*p*-Tolylethynyl)-1-tosyloxycyclopropane 4. The tosylate **4** was obtained by conventional means through the reaction of the cyclopropanol 8 (X = CH_3) with 1.1 equiv of tosyl chloride in pyridine (dried over molecular sieves) at 0 °C for 48 h. Two recrystallizations from pentane gave the pure 1-(*p*-tolylethynyl)-1-tosyloxycyclopropane **4**: mp 83.2 °C; NMR (CCl_4) δ 1.20–1.65 (m, 4 H), 2.32 (s, 6 H), 6.98 (s, 4 H), and 7.10–7.90 ppm (q, 4 H).

Anal. Calcd for $C_{19}H_{18}O_3S$: C, 69.91; H, 5.55; O, 14.70; S, 9.82. Found: C, 70.08; H, 5.57; S, 9.52.

1-(*p*-Anisylethynyl)-1-tosyloxycyclopropane 5. The tosylate **5** was obtained from cyclopropanol 8 (X = OCH_3) and 1.1 equiv of tosyl chloride in pyridine. Two recrystallizations from pentane gave the pure 1-(*p*-anisylethynyl)-1-tosyloxycyclopropane **5**: mp 65.0 °C; NMR (CCl_4) δ 1.20–1.60 (m, 4 H), 2.32 (s, 3 H), 3.78 (s, 3 H), 6.60–7.10 (q, 4 H), and 7.10–7.90 ppm (q, 4 H).

Anal. Calcd for $C_{19}H_{18}O_4S$: C, 66.65; H, 5.30; O, 18.69; S, 9.36. Found: C, 66.54; H, 5.36; S, 9.28.

Description of a Typical Comparative Product Analysis. The tosylates **3, 4, and 5** (150 mg, ~0.5 mmol) were dissolved in 2.5 ml of EtOH–H_2O (50:50) mixture containing 1.1 equiv of triethylamine as buffer, respectively. The three solvolysis mixtures were heated in sealed tubes at 70 °C for 40 h. After cooling the tubes were opened and the solvents removed on a rotary evaporator. The residues mixed with concentrated aqueous NaCl solutions were extracted with pentane three times each. The pentane extracts were dried over $MgSO_4$ and concentrated on a rotary evaporator.

The three crude solvolysis mixtures were worked up by gas chromatography and the products of each solvolysis were identified comparatively by combined GC and MS analysis and from their ir and NMR spectra.

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

1-Ethoxy-1-(phenylethynyl)cyclopropane 8 (X = H; R = CH_2CH_3) has been described.[1]

1-(2′,2′,2′-Trifluoroethoxy)-1-(phenylethynyl)cyclopropane 8 (X = H; R = CH_2CF_3): NMR (CCl_4) δ 1.15 (m, 4 H), 3.60–4.05 (q, 2 H, J = 8.7 Hz) and 7.30 ppm (m, 5 H); ir (neat) ν C≡C 2220 cm^{-1}; MS M^+ *m/e* (rel intensity) 240 (45), 171 (45), 157 (39), 141 (68), 129 (100), 128 (58), 127 (27), 115 (54).

2-Methylene-4-phenyl-2-butyn-1-ol 10 (X = H) has been described.[1]

1-Ethoxy-3-methylene-4-phenyl-3-butyne 10 (X = H; R = CH_2CH_3) has been described.[1]

1-(2′,2′,2′-Trifluoroethyl)-2-methylene-4-phenyl-3-butyne 10 (X = H; R = CH_2CF_3): NMR (CCl_4) δ 3.60–4.05 (q, 2 H, J = 8.7 Hz), 4.15 (m, 2 H), 5.55 (m, 2 H) and 7.30 ppm (m, 5 H); ir (neat) ν C≡C 2220 cm^{-1}; MS M^+ *m/e* (rel intensity) 240 (56), 171 (9), 157 (7.5), 142 (27), 141 (32), 127 (100), 115 (12), 77 (30).

1-Ethoxy-1-(*p*-tolylethynyl)cyclopropane 8 (X = CH_3; R = CH_2CH_3): NMR (CCl_4) δ 1.08 (m, 4 H), 1.10–1.32 (t, 3 H, J = 7 Hz), 2.32 (s, 3 H), 3.50–3.85 (q, 2 H, J = 7 Hz), and 6.95–7.35 ppm (q, 4 H); ir (neat) ν C≡C 2190 cm^{-1}; MS M^+ *m/e* (rel intensity) 200 (5), 185 (6), 172 (31.5), 157 (46), 143 (100), 129 (58), 115 (37), 89 (21).

1-(2′,2′,2′-Trifluoroethoxy)-1-(*p*-tolylethynyl)cyclopropane 8 (X = CH_3; R = CH_2CF_3): NMR (CCl_4) δ 1.20 (m, 4 H), 2.35 (s, 3 H), 3.60–4.05 (q, 2 H, J = 8.7 Hz), and 7.0–7.35 ppm (q, 4 H); ir (neat) ν C≡C 2190 cm^{-1}; MS M^+ *m/e* (rel intensity) 254 (31.5), 185 (70), 171 (42.5), 157 (31.5), 155 (30), 143 (100), 128 (65), 115 (37).

2-Methylene-4-*p*-tolyl-3-butyn-1-ol 10 (X = CH_3): NMR (CCl_4) δ 2.35 (s, 3 H), 3.50 (m, 1 H), 4.20 (m, 2 H), 5.50–5.60 (m, 2 H), and 6.95–7.35 (q, 4 H); ir (neat) ν C≡C 2190 cm^{-1}; MS M^+ *m/e* (rel intensity) 172 (20), (157) (5), 143 (100), 129 (11), 115 (15), 89 (10).

1-Ethoxy-2-methylene-4-*p*-tolyl-3-butyne 10 (X = CH_3; R = CH_2CH_3): NMR (CCl_4) δ 1.10–1.32 (t, 3 H, J = 7 Hz), 2.30 (s, 3 H), 3.50–3.85 (q, 2 H, J = 7 Hz), 4.15 (m, 2 H), 5.50 (m, 2 H) and 6.95–7.35 ppm (q, 4 H); ir (neat) ν C≡C 2190 cm^{-1}; MS M^+ *m/e* (rel intensity) 200 (4), 185 (9), 172 (37), 171 (100), 141 (56).

1-(2′,2′,2′-Trifluoroethyl)-2-methylene-4-*p*-tolyl-3-butyne 10 (X = CH_3; R = CH_2CF_3): NMR (CCl_4) δ 2.35 (s, 3 H), 3.60–4.05 (q, 2 H, J = 8.7 Hz), 4.20 (m, 2 H), 5.55 (m, 2 H), and 6.95–7.30 ppm

(q, 4 H); ir (neat) ν C≡C 2190 cm^{-1}; MS M$^+$ *m/e* (rel intensity) 254 (72), 185 (16), 156 (28), 141 (100), 128 (15), 115 (36).

1-Ethoxy-1-(*p*-anisylethynyl)cyclopropane 8 (X = OCH$_3$; R = CH$_2$CH$_3$): NMR (CCl_4) δ 1.02 (m, 4 H), 1.05–1.30 (t, 3 H, J = 7 Hz), 3.50–3.85 (q, 2 H, J = 7 Hz), 3.75 (s, 3 H), and 6.65–7.35 ppm (q, 4 H); ir (neat) ν C≡C 2185 cm^{-1} (very strong); MS M$^+$ *m/e* (rel intensity) 216 (3), 201 (6.5), 188 (41), 172 (20), 159 (100), 144 (35), 116 (20), 115 (15), 88 (20).

1-(2′,2′,2′-Trifluoroethoxy)-1-(*p*-anisylethynyl)cyclopropane 8 (X = OCH$_3$; R = CH$_2$CF$_3$): NMR (CCl_4) δ 1.10–1.20 (m, 4 H), 3.75 (s, 3 H), 3.80–4.20 (q, 2 H, J = 8.7 Hz), and 6.70–7.30 ppm (q, 4 H); ir (neat) ν C≡C 2190 cm^{-1}; MS M$^+$ *m/e* (rel intensity) 270 (24.5), 201 (100), 187 (47), 173 (30), 171 (27), 159 (89), 145 (36), 144 (32), 128 (38), 116 (28), 115 (24.5), 57 (32), 55 (45).

2-Methylene-4-*p*-anisyl-3-butyn-1-ol 10 (X = OCH$_3$): NMR (CCl_4) δ 3.75 (s, 3 H), 4.20 (m, 2 H), 5.50 (m, 2 H), and 6.70–7.40 ppm (q, 4 H); ir (neat) ν C≡C 2185 cm^{-1}; MS M$^+$ *m/e* (rel intensity) 188 (7.5), 159 (100), 144 (4), 116 (3), 57 (4), 55 (2.8).

1-(2′,2′,2′-Trifluoroethoxy)-2-methylene-4-*p*-anisyl-3-butyne 10 (X = OCH$_3$; R = CH$_2$CF$_3$): NMR (CCl_4) δ 3.75 (s, 3 H), 3.80–4.20 (q, 2 H, J = 8.7 Hz), 4.15 (m, 2 H), 5.55 (m, 2 H), and 6.70–7.40 ppm (q, 4 H); ir (neat) ν C≡C 2180 cm^{-1}; MS M$^+$ *m/e* (rel intensity) 270 (70), 172 (25.5), 157 (100), 135 (25.5), 57 (60), 55 (29.5).

Kinetic procedures have been described in the preceding report.[1]

Acknowledgment. The author is grateful to Professor J. M. Conia for his interest and constant encouragement throughout this work.

Registry No.—**3**, 57951-60-7; **4**, 60512-41-6; **5**, 60512-42-7; **6**, 13837-45-1; **8** (X = CH$_3$), 60512-43-8; **8** (X = OCH$_3$), 60512-44-9; **8** (X = H; R = CH$_2$CF$_3$), 60512-45-0; **8** (X = CH$_3$; R = CH$_2$CH$_3$), 60512-46-1; **8** (X = CH$_3$; R = CH$_2$CF$_3$), 60512-47-2; **8** (X = OCH$_3$; R = CH$_2$CH$_3$), 60512-48-3; **8** (X = OCH$_3$; R = CH$_2$CF$_3$), 60512-49-4; **9** (X = CH$_3$), 766-97-2; **9** (X = OCH$_3$), 768-60-5; **10** (X = H; R = CH$_2$CF$_3$), 60512-50-7; **10** (X = CH$_3$), 60512-51-8; **10** (X = CH$_3$; R = CH$_2$CH$_3$), 60512-52-9; **10** (X = CH$_3$; R = CH$_2$CF$_3$), 60512-53-0; **10** (X = OCH$_3$), 60512-54-1; **10** (X = OCH$_3$; R = CH$_2$CF$_3$), 60512-55-2; 1,1-dibromo-2-*p*-tolylethylene, 60512-56-3; 1,1-dibromo-2-*p*-anisylethylene, 60512-57-4; tosyl chloride, 98-59-9.

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Oxyfunctionalization of Hydrocarbons.[1a] 5. Protolytic Cleavage–Rearrangement Reactions of Tertiary Alkyl (Arylalkyl) Peroxy Esters in Superacids

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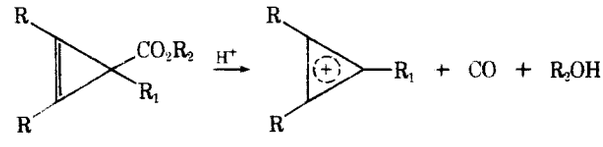
Received August 23, 1976

In continuation of our work on superacid induced cleavage–rearrangement reactions of hydroperoxides,[2a] we have undertaken a study of the superacid induced cleavage–rearrangement reactions of peroxy esters. Studies included those of *tert*-alkyl peroxyacetates, as well as various other *tert*-butyl peroxy esters. Particularly, *tert*-butyl peracetate was found to be unique in that both O–O and C–O cleavage products were observed, depending upon conditions. The yield of O–O and C–O cleavage products from various peroxy esters is discussed in terms of the inactivation (via protonation) of peroxy acid and the relative migratory aptitude of alkyl groups. The direct observation of the reaction intermediates, including the dimethylphenoxycarbenium ion **24** in the reactions of cumyl peroxy esters, is discussed.

Unlike the related acid-catalyzed cleavage–rearrangement reaction of hydroperoxides (**1**)[2] those of peroxy esters are considerably less studied.

Protolysis of peroxy esters has been employed as a means of preparation of stable carbenium ions. Thus Farnum et al., upon decarboxylation of the peroxy ester, obtained the corresponding cyclopropenium ion **2**.[3]



1 **2**