Phenyl Participation in the Generation of Carbocations from the Reactions of Some 1-Methyl-ω-phenylalkyl Toluene-*p*-sulphonates and ω-Phenylalk-1-enes in Trifluoroacetic Acid

By **Timothy J. Mason**, Department of Chemistry and Metallurgy, Lanchester Polytechnic, Priory Street, Coventry CV1 5FB

The rates of reaction of four 1-methyl-ω-phenylalkyl toluene-*p*-sulphonates and four ω-phenylalk-1-enes in buffered trifluoroacetic acid have been measured and the products determined. There is evidence for anchimeric assistance by the phenyl group in both solvolysis and addition reactions when the phenyl group is either β or δ to the incipient carbocation. The nature of such participation is discussed.

A STUDY of the reactions of a series of ω-phenylalk-1-enes in unbuffered trifluoroacetic acid at 25° has been reported in which 5-phenylpent-1-ene showed an enhanced rate of addition due to phenyl participation in the protonation step.[1] Addition of trifluoroacetic acid to alkenes is a two step process involving initial protonation [2] which for these substrates leads to 1-methyl-ω-phenylalkyl cations. We report here the trifluoroacetolysis of a series of 1-methyl-ω-phenylalkyl toluene-*p*-sulphonates which, on ionisation, should produce cations formally analogous to those generated directly by protonation. Since the solvolyses were studied in buffered trifluoroacetic acid at 29° the reactions of the corresponding alkenes were re-run under these conditions and allylbenzene was included for comparison with the trifluoroacetolysis of 1-methyl-2-phenylethyl toluene-*p*-sulphonate. A comparison of rate and product data then affords some insight into the nature of any anchimeric assistance involved in these reactions and also the effect of the toluene-*p*-sulphonate counter-ion on product distributions from the first-formed carbocations.

Trifluoroacetic acid is a highly ionising and weakly

[1] T. J. Mason and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 1972.

[2] H. C. Brown, J. H. Kawakami, and Kwang-Ting Liu, *J. Amer. Chem. Soc.*, 1970, **92**, 3816.

nucleophilic solvent [3,4] which has been used extensively as a solvolysis medium particularly where anchimeric assistance to ionisation is to be probed.[5]

RESULTS

The reported method for determining the rates of trifluoroacetolysis of toluene-*p*-sulphonate esters has involved the use of u.v. spectroscopy in following the loss of sulphonate absorption at 273 nm.[6] Unfortunately the major product from the trifluoroacetolysis of 1-methyl-4-phenylbutyl toluene-*p*-sulphonate is 1-methyltetralin which also shows a u.v. absorption at 273 nm thus rendering this technique unsuitable. In trifluoroacetic acid the proton α to the sulphonate group in each substrate shows a signal in the n.m.r. spectrum separate from that of protons in the trifluoroacetate ester products and from all other proton resonances in the spectrum. The kinetics were therefore determined in an n.m.r. tube in the probe of a ^{1}H n.m.r. spectrometer at 29° by direct observation of the loss of the α-proton signal from each toluene-*p*-sulphonate dissolved in buffered trifluoroacetic acid.

Under the relatively strong (0.25M) substrate concentrations involved, the reactions followed good first-order kinetics with a reproducibility of ±2%. The rates of addition of trifluoroacetic acid to the alkenes were obtained at the same temperature and concentrations as above by the reported g.l.c. technique.[1] The loss of alkene followed good first-order kinetics with the same reproducibility as above. The addition of trifluoroacetic acid to compounds (6)—(8) at 25° has been reported; [1] in the presence of added sodium trifluoroacetate the relative rates of addition at 29° are very similar although some differences in product distributions were found. The kinetic results appear in Table 1 together

TABLE 1

First-order rate constants for the reactions of 1-methyl-ω-phenylalkyl toluene-*p*-sulphonate and ω-phenylalk-1-enes in buffered trifluoroacetic acid.

No.	Substrate	10^5k/s^{-1} [a,b]
(1)	$PhCH_2CH(OTs)CH_3$	158.0
(2)	$Ph[CH_2]_2CH(OTs)CH_3$	10.9
(3)	$Ph[CH_2]_3CH(OTs)CH_3$	370.0
(4)	$Ph[CH_2]_4CH(OTs)CH_3$	55.8
(5)	$PhCH_2CH{=}CH_2$	2.1
(6)	$Ph[CH_2]_2CH{=}CH_2$	4.0
(7)	$Ph[CH_2]_3CH{=}CH_2$	43.8
(8)	$Ph[CH_2]_4CH{=}CH_2$	13.0
(9)	$CH_3CH(OTs)CH_3$	2.49 [c]
(10)	$CH_3CH_2CH(OTs)CH_3$	14.6 [c]
(11)	$CH_3[CH_2]_2CH(OTs)CH_3$	19.0 [c]
(12)	$CH_3[CH_2]_3CH(OTs)CH_3$	19.2 [c]

[a] 0.25M in substrate, 0.5M in sodium trifluoroacetate at 29°. [b] Rates quoted as mean of at least two runs, reproducibility ±2%. [c] At 25°, ref. 6.

with the reported trifluoroacetolysis rates of some 1-methylalkyl derivatives.[6]

Reaction products were determined after 10 half-lives. All products were found to be stable to the reaction and work-up conditions and appear in Table 2. No evidence

TABLE 2

Products from the reactions of 1-methyl-ω-phenylalkyl toluene-*p*-sulphonates and ω-phenylalk-1-enes in buffered trifluoroacetic acid at 29° (R = $COCF_3$)

Substrate	Products (yields in mol %)		
	$PhCH_2CH(OR)CH_3$ (13)		
(1)	100		
(5)	100		
	$Ph[CH_2]_2CH(OR)CH_3$ (14)	$PhCH_2CH(OR)CH_2CH_3$ (15)	
(2)	60	40	
(6)	82	18	
	1-Methyltetralin (16)	$Ph[CH_2]_3CH(OR)CH_3$ (17)	$Ph[CH_2]_2CH(OR)CH_2CH_3$ (18)
(3)	93	3	0.5
(7)	77	20	1.0
	1-Ethyltetralin (19)	$Ph[CH_2]_4CH(OR)CH_3$ (20)	$Ph[CH_2]_3CH(OR)CH_2CH_3$ (21)
(4)	63	26	11
(8)	22	69	9

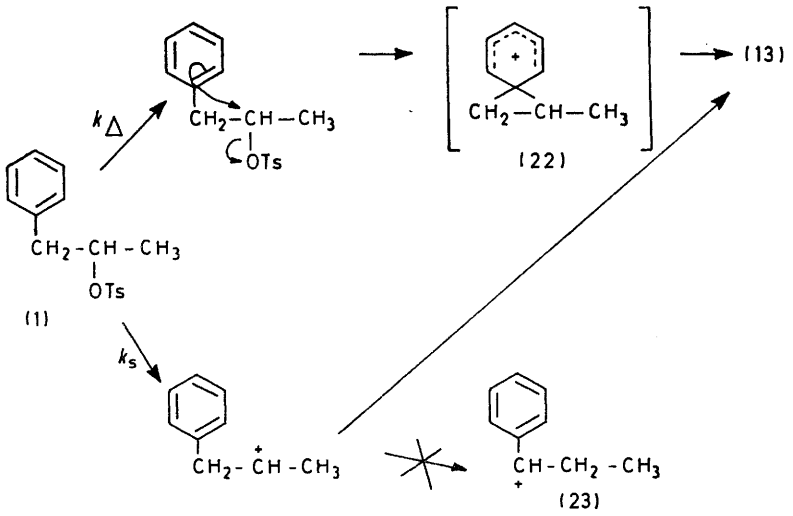
was found for alkene formation in the trifluoroacetolyses of the toluene-*p*-sulphonates (1)—(4) either during the reaction (by ^{1}H n.m.r. spectroscopy) or in the final products (by g.l.c.). Other studies have shown that elimination–addition is a minor pathway compared to hydride shifts in the formation of isomerised products from the trifluoroacetolyses of toluene-*p*-sulphonate esters.[7-9]

DISCUSSION

Trifluoroacetolyses of the Toluene-p-*sulphonates.*—In the absence of any phenyl participation in ionisation the rates of trifluoroacetolysis of (1)—(4) would be expected to parallel those observed in the trifluoroacetolyses of the corresponding 1-methylalkyl toluene-*p*-sulphonates (9)—(12) (Table 1) with rates attenuated due to the inductive affects of the ω-phenyl substituents. This would lead to a predicted order of reactivity of (1) < (2) < (3) < (4) and, clearly, the rates of trifluoroacetolysis of (1) and (3) are much faster than expected on this rationale. A rate enhancement of 17.1 at 25° has been reported for the trifluoroacetolysis of 1-methyl-2-phenylethyl toluene-*p*-sulphonate (1) compared with that of 1-methylethyl toluene-*p*-sulphonate (9), a factor of 33 was included as the inductive decelerating factor for the phenyl group which led to a calculated rate enhancement of 564 in the

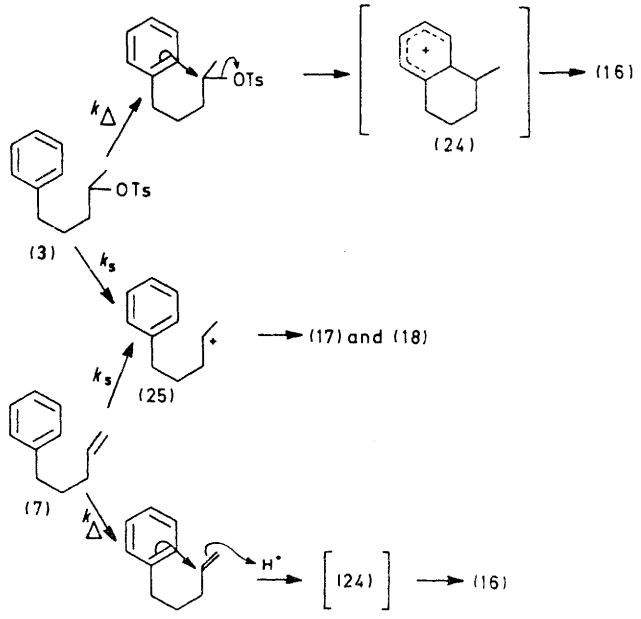
[3] A. Pross and R. Koren, *Tetrahedron Letters*, 1974, 1949.
[4] P. E. Peterson and F. J. Waller, *J. Amer. Chem. Soc.*, 1972, **94**, 991 and previous papers in this series.
[5] See for example, F. L. Schadt and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1973, **95**, 7860; Y. Yukawa, S.-G. Kim, and H. Yamataka, *Tetrahedron Letters*, 1973, 373; T. Ando, N. Shimizu, S.-G. Kim, Y. Tsuno, and Y. Yukawa, *ibid.*, p. 117; Y. Yukawa, T. Ando, M. Kawada, K. Token, and S.-G. Kim, *ibid.*, 1972, 847.
[6] P. E. Peterson, R. E. Kelly, R. Belloli, and K. A. Sipp, *J Amer. Chem. Soc.*, 1965, **87**, 5169.
[7] I. L. Reich, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, 1969, **91**, 5634.
[8] J. B. Lambert and G. J. Putz, *J. Amer. Chem. Soc.*, 1973, **95**, 6313.
[9] J. J. Dannenburg, D. H. Weinwurzel, K. Dill, and B. J. Goldberg, *Tetrahedron Letters*, 1972, 1241.

reaction of (1).[10] The absence of any phenyl participation in the ionisation of (2) may be inferred from the work of Heck and Winstein [11] so that the factor of 14.5 by which (1) reacts faster than (2) (Table 1) also provides an estimate of the degree of anchimeric assistance to ionisation in the trifluoroacetolysis of (1) neglecting the greater inductive decelerating effect of the phenyl group in this substrate. Schleyer has suggested that for this reaction ionisation proceeds almost exclusively through the anchimerically assisted (k_Δ) pathway *via* the phenonium ion (22); [12] this ion precludes hydride shift to the relatively stable benzyl cation (23) (Scheme 1) and thus leads to the single product 1-methyl-2-phenylethyl trifluoroacetate (13) (Table 2).



SCHEME 1

Though many studies of β-phenyl participation in solvolysis reactions appear in the literature, the investigation of δ-phenyl participation has been somewhat neglected. Winstein and his co-workers characterised two types of δ-phenyl participation in ionisation which they labelled Ar_1-5 and Ar_2-6.[11,13] A small rate enhancement (*ca.* 1%) was observed in the formolysis rate of 4-phenylbutyl *p*-bromobenzenesulphonate over that of the 5-phenylpentyl derivative at 75° and this was attributed to anchimeric assistance by the phenyl group in the ionisation of the former. Any anchimeric assistance in the formolysis of (3) would be expected to be less than that in the formolysis of the 4-phenylbutyl derivative since the ionisation of (3) leads to the more stable secondary cation (25). The formolysis of (3) has been studied but no direct evidence for an enhanced rate of reaction was found though anchimeric assistance to ionisation by the δ-phenyl group was suggested and 1-methyltetralin was formed in 35% yield.[13] In the more ionising, less nucleophilic solvent trifluoroacetic acid however the rate of solvolysis of (3) is enhanced by a factor of at least 6.6 by comparison with that of (4) (Table 1). This enhanced reactivity, together with the formation of 93% 1-methyltetralin (Table 2) provides strong evidence for anchimeric assistance in the ionisation of (3) in this medium. The solvolysis data for (3) could thus be interpreted in terms of a greater degree of discrete k_Δ component in trifluoroacetolysis as compared with formolysis. Recent studies have shown that in the formolysis of 4-phenylbutyl *p*-bromobenzenesulphonate

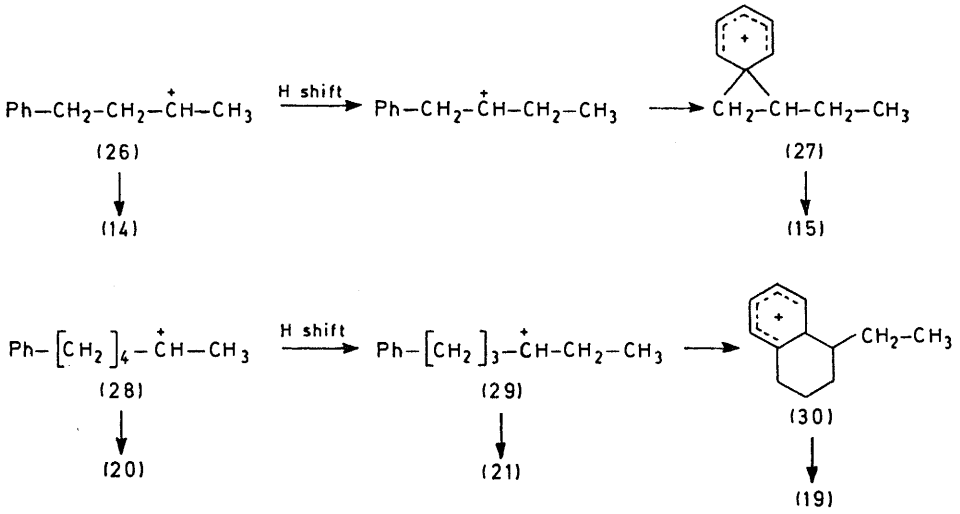


SCHEME 2

[10] J. E. Nordlander and W. J. Kelly, *J. Amer. Chem. Soc.*, 1969, **91**, 996.
[11] R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, 3105.
[12] P. von R. Schleyer and C. J. Lancelot, *J. Amer. Chem. Soc.*, 1969, **91**, 4297.
[13] R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, 3115.

participation in ionisation occurs predominantly *via* an Ar_2-6 pathway,[14] and there is no reason to suppose that the Ar_2-6 mode should not be predominant in the trifluoroacetolysis of (3). If k_Δ and k_s processes are assumed to be discrete then 93% of the reaction proceeds *via* the former pathway and bridged ion (24) while 3.5% proceeds *via* solvent assisted ionisation through open ion (25) leading to trifluoroacetate (17) (3%) and the hydride-shifted trifluoroacetate (18) (0.5%) (Scheme 2).

The trifluoroacetolyses of (2) and (4) almost certainly proceed without anchimeric assistance from the remote phenyl groups.[11,13] In these reactions the trifluoroacetates (14) (60%) and (20) (26%) respectively (Table 2) may be derived either from direct displacement of the leaving group by solvent or attack by solvent on the first-formed carbocation (or ion-pair). The greater proportion of unrearranged product from the reaction of (2) is probably due to the closer proximity of the inductive-withdrawing phenyl group in this substrate giving the solvolysis more S_N2 character. The other products from the trifluoroacetolyses of (2) and (4) are derived from only one hydride shift in each case. Such a shift in the reaction of (2) leads to the 1-ethyl-2-phenylethyl cation which can be stabilised by phenyl bridging to a phenonium ion (27) and hence to the isomerised product (15). A hydride shift in the solvolysis of (4) leads to the 1-ethyl-4-phenylbutyl cation (29) which can ring-close *via* phenonium ion (30) to 1-ethyltetralin (19) or suffer solvent attack to form isomerised trifluoroacetate (21). The ratio of cyclised: open products from carbocation (29) (5.7) is substantially lower than that from the trifluoroacetolysis of (3) (26). This difference is to be expected since, in the former case, the δ-phenyl group and solvent compete for stabilisation of a preformed cation whereas in the latter the δ-phenyl group and solvent compete to displace the covalently bound leaving group.



Comparison of the Reactions of Toluene-p-*sulphonates and Alkenes in Trifluoroacetic Acid.*—Ionisation of the 1-methyl-ω-phenylalkyl derivatives and protonation of the corresponding ω-phenylalk-1-enes lead to formally analogous 1-methyl-ω-phenylalkyl cations modified by the presence of toluene-*p*-sulphonate counter-ion in the former series.

Despite the markedly enhanced rate of trifluoroacetolysis of (1) compared with (2), the rate of addition of trifluoroacetic acid to (5) is a factor of 2 slower than that to (6). Similarly a comparison of the rates of trifluoroacetolysis of (3) and (4) shows some anchimeric assistance in the former reaction resulting in an enhanced rate of at least 6.6, somewhat larger than the corresponding rate enhancement for the addition of trifluoroacetic acid to (7) compared with (8) of at least 3.3. The results indicate that both β- and δ-phenyl participation in the trifluoroacetolyses of these toluene-*p*-sulphonates provide greater rate enhancement than such participation in the addition of trifluoroacetic acid to the corresponding alkenes. The proportion of k_Δ component in the ionisation of a toluene-*p*-sulphonate will be the result of competition between the phenyl group and solvent for displacement of the leaving group from an initially sp^3 hybridised carbon. Such participation in protonation however will involve phenyl group attack on an initially sp^2 hybridised, electron rich centre. Further, the trifluoroacetate product from the addition reaction would probably be formed from attack by the trifluoroacetate counter-ion generated in the solvent cage around the carbocation from the acid during protonation. These factors indicate that phenyl participation should indeed be more significant in solvolysis (in competition with solvent–ion reactions) than in addition (in competition with ion–ion reactions). For anchimerically assisted solvolysis reactions Schleyer has argued that the two routes to ionisation k_Δ and k_s are discrete and that there is no crossover of products from each pathway.[12] The

[14] V. R. Hadden and L. M. Jackman, *J. Amer. Chem. Soc.*, 1971, **93**, 3832; 1974, **96**, 5130.

greater k_Δ component in the reaction of (1) as compared with (5) may only be argued in terms of the greater rate enhancement in the former case since both reactions lead to the same product 1-methyl-2-phenylethyl trifluoroacetate (13). The 1-methyltetralin product (16) from the reaction of both (3) and (7) in trifluoroacetic acid (Table 2) would however be the exclusive product from the k_Δ component if the two routes were discrete for these systems (Scheme 2). Thus it could be argued that a greater k_Δ component exists in the solvolysis of (3) leading to 93% (16) as compared with that in the addition reaction of (7) which yields 77% (16), a result in accord with the kinetics.

Only two products, (14) and (15), are formed in the reaction of either (2) or (6) with trifluoroacetic acid. The absence of any 1-phenylbutyl trifluoroacetate in the products suggests that a phenonium ion intermediate (27) is involved in these reactions which, produced after hydride shift to the first-formed 1-methyl-3-phenyl propyl cation (26), precludes further isomerisation. The greater proportion of hydride shifted product (15) from the solvolysis of (2) (40%) compared with that from the addition to (6) (18%) is in agreement with previous work which has shown that 1-methylalkyl toluene-*p*-sulphonates yield more isomerised products than the corresponding alk-1-enes on reaction with trifluoroacetic acid.[15]

The reactions of (4) and (8) in trifluoroacetic acid lead to somewhat different product distributions again showing the greater propensity for isomerisation in the solvolysis reaction (Table 2). The 1-ethyl-4-phenyl butyl cation (29) formed after hydride shift to the initially produced 1-methyl-5-phenylpentyl cation (28) is open to either phenyl bridging to the phenonium ion species (30) leading to 1-ethyltetralin (19) or solvent attack to yield trifluoroacetate (21). There is however a clear difference in ratio of (19) : (21) between the two systems, 5.7 from the reaction of (4) and 2.3 from that of (8). This difference may be attributed to the presence of the toluene-*p*-sulphonate counter-ion produced in the ionisation of (4) which would be expected to be still associated with the hydride shifted cation (29). This counter-ion would somewhat disturb the solvation sheath around (29) thus allowing more effective competition for stabilisation by the phenyl group compared with solvent attack resulting in a higher proportion of ring-closed product from cation (29) generated in the trifluoroacetolysis of (4).

EXPERIMENTAL

^{1}H N.m.r. spectra were measured with a JEOL MH 100 instrument, chemical shifts are reported relative to tetramethylsilane as internal standard in deuteriochloroform or trifluoroacetic acid. Analytical and preparative g.l.c. were run on a Pye series 104 chromatograph with glass columns, nitrogen as carrier gas, and a flame ionisation detector. The analytical columns (5 ft × ¼ in) used with a carrier gas flow of 40 ml min^{-1} were (a) 10% SE 30 on Universal Support (60—80) and (b) 10% Carbowax 20M on Chromosorb W (60—80). The preparative column used in conjunction with a 100 : 1 splitter at the outlet port and with a carrier gas flow of 100 ml min^{-1} was (c) a 6 ft × ⅜ in 15% Apiezon L on Celite (60—100). The chromatograph was coupled to an A.E.I. MS 902 spectrometer for the determination of mass spectra.

1-*Methyl-ω-phenylalkyl Alcohols*.—The alcohols were prepared as described and all were at least 95% pure by g.l.c.; their n.m.r. spectra are reported in deuteriochloroform. 1-Methyl-2-phenylethyl alcohol, b.p. 60—61° at 6 mmHg, was prepared by the sodium borohydride reduction of commercially available benzyl methyl ketone, δ 7.30 (5 H, m), 4.00 (1 H, m), 2.80 (1 H, s), 2.65 (2 H, m), and 1.20 (3 H, d, *J* 3 Hz). 1-Methyl-3-phenylpropyl alcohol was prepared by the Grignard reagent from phenethyl bromide with acetaldehyde, b.p. 92—95° at 6 mmHg, δ 7.30 (5 H, m), 3.80 (1 H, m), 2.70 (2 H, m), 1.80 (2 H, m), 1.80 (1 H, s), and 1.20 (3 H, d, *J* 3 Hz). 1-Methyl-4-phenylbutyl alcohol was prepared by the reaction of the Grignard reagent from 3-phenylpropyl bromide with acetaldehyde, b.p. 96—100° at 5 mmHg, δ 7.30 (5 H, m), 3.78 (1 H, m), 2.60 (2 H, t), 1.75 (1 H, s), 1.80—1.20 (4 H), and 1.15 (3 H, d, *J* 3 Hz). 6-Phenylhexan-2-one, b.p. 110—111° at 1.5 mmHg, was prepared by hydrolysis of the condensation product between the anion of ethyl acetoacetate and 3-phenylpropyl bromide adapted from the method described.[16] Reduction of this ketone with sodium borohydride gave 1-methyl-5-phenylpentyl alcohol, b.p. 120—124° at 2 mmHg, δ 7.30 (5 H, m), 3.78 (1 H, m), 2.60 (2 H, t), 1.80 (1 H, s), 1.80—1.20 (6 H), and 1.15 (3 H, d, *J* 3 Hz).

1-*Methyl-ω-phenylalkyl Toluene*-p-*sulphonates*.—The derivatives were obtained from the corresponding secondary alcohols by standard procedures. Only (1) was obtained as a crystalline solid, m.p. 91—92° (lit., [6]92—93°). The remainder were colourless oils which were purified by preparative t.l.c. on methanol-washed silica gel plates using 3 : 1 light petroleum–ether as eluant. Using both t.l.c. and ^{1}H n.m.r. spectroscopy the purity of these derivatives was estimated to be at least 98% and each sample was found to undergo trifluoroacetolysis with good first order kinetics.

ω-*Phenylalk*-1-*enes*.—Allylbenzene and 4-phenylbut-1-ene were available commercially, 5-phenylpent-1-ene and 6-phenylhex-1-ene were prepared as described in the literature.[1]

Kinetic Measurements.—For each toluene-*p*-sulphonate the n.m.r. signal for the proton α to the sulphonate group in trifluoroacetic acid appeared at δ *ca.* 4.9, separate from all other signals in the spectrum including protons α to the trifluoroacetate ester products at δ *ca.* 5.5. In a typical run 1-methyl-2-phenylethyl toluene-*p*-sulphonate (27.6 mg, 0.1 mmol) together with anhydrous sodium carbonate (10.6 mg, 0.1 mmol) was dissolved in trifluoroacetic acid (0.4 ml; B.D.H.; 99.5%) in an n.m.r. tube. Tetramethylsilane was added as internal reference and the absorption of the α-proton was integrated periodically at the steady probe temperature, 29°. Up to 10 determinations were made in this way and the first-order rate constant was computed using a least squares program.

The g.l.c. technique employed in the determination of the first order rate constants for the addition of trifluoroacetic acid to alkenes (5)—(8) has been described.[1] The reaction

[15] P. E. Peterson and G. Allen, *J. Org. Chem.*, 1962, **27**, 1505.
[16] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, Green and Co., London, 1959, p. 481.

conditions were those used in the solvolysis reactions above using a constant temperature bath at 29°. Column (a) was used throughout and the internal g.l.c. standards used were phenetole [for (5)], mesitylene [for (6) and (7)], and *p*-dimethoxybenzene [for (8)].

Product Studies.—Substrate (0.25M) was allowed to react with trifluoroacetic acid (2.5 ml; 0.5M in sodium trifluoroacetate) at 29° for at least 10 half-lives and then quenched in 9 : 1 methanol–water (15 ml) containing potassium hydroxide (1.5 g) overnight at room temperature. The resulting solution was poured into saturated sodium chloride (50 ml) and extracted into ether (4 × 50 ml). The ethereal extract was washed with saturated sodium chloride (2 × 50 ml), dried ($MgSO_4$), filtered, and evaporated under reduced pressure at room temperature. It was shown that cyclised products were unaffected by this treatment whereas trifluoroacetates were hydrolysed quantitatively to the corresponding alcohols. The yields quoted (Table 2) are corrected for molar detector response and are calibrated with the same internal g.l.c. standards that were used in the kinetic study of the addition of trifluoroacetic acid to the alkenes.

Analytical g.l.c. on column (b) was combined with mass spectrometry and pure samples of the hydrolysed constituents were obtained by preparative g.l.c. on column (c). The products were identified by comparison of their physical data with that from the products characterised in a previous study.[1] The reactions of (3) and (7) gave small quantities (3.5 and 2.0% respectively) of different unidentified materials.

I am indebted to the Chemistry Department at Bradford University where these studies were pursued.

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