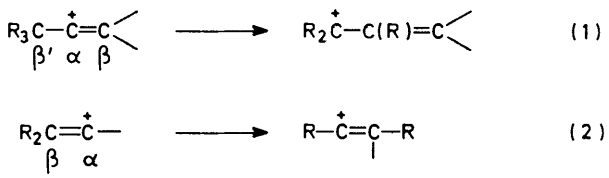
Vinylic Cations from Solvolysis. Part XV.[1,2] β-Phenyl and β-*p*-Methoxyphenyl Rearrangement during the Solvolysis of 2,2-Diaryl-1-phenylvinyl Bromides

By **Zvi Rappoport** * and **Yoram Houminer**, Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel

Triphenylvinyl bromide (1), *trans*- and *cis*-2-*p*-methoxyphenyl-1,2-diphenylvinyl bromides (2) and (3), and 2,2-bis-*p*-methoxyphenyl-1-phenylvinyl bromide (4) were solvolysed in 2,2,2-trifluoroethanol (TFE) and in 60% EtOH. In TFE, the products were the trifluoroethyl ether from (1), 15% of a 1 : 1 *cis–trans* mixture of the unrearranged and 85% of the β-phenyl rearranged trifluoroethyl ethers from (2) and (3), and a 1 : 1 *cis–trans* mixture of the β-*p*-methoxyphenyl rearranged trifluoroethyl ethers from (4). With toluene-*p*-thiolate ion, (4) gave only a rearranged sulphide, whilst the sulphides from (2) and (3) are 70% rearranged. The trifluoroethanolysis of (1)—(3) was accompanied by common ion rate depression. The relative initial k_1 (120°) values were 1 (1) : 3·4 (2) : 3·7 (3) : 9·5 (4). In 60% EtOH the products were mostly the unrearranged acetophenone derivative from (2) and (3) and only the rearranged ketone from (4), and the relative k_1 (140°) values were 1 (1) : 2·14 (2) : 2·44 (3) : 5·45 (4). It is concluded that (a) the initial ionisation does not involve β-aryl participation, (b) the products are derived from free, open, linear vinyl cations, which return to covalent bromide (k_{Br}), rearrange (k_r), and react with the solvent (k_{ROH}) or toluene-*p*-thiolate ion (k_{SR^-}), (c) β-*p*-methoxyphenyl (An) rearrangement is the dominant process for the ion $An_2C{=}\overset{+}{C}Ph$ in the two solvents, (d) β-phenyl rearrangement is dominant for the ion $AnC(Ph){=}\overset{+}{C}Ph$ (19) in TFE ($k_{Br} : k_{r(Ph)} : k_{ROH}$ = 214 : 5·7 : 1 at 120°) while in 60% EtOH $k_{ROH} : k_{r(Ph)}$ = 19 : 1 ; the apparent abnormal order of migratory aptitudes Ph > An is either due to a hidden β-*p*-methoxyphenyl rearrangement or to a higher energy loss in the deconjugation of the migrating aryl group with the double bond than the energy gain in the bridging by the migrating aryl, and (e) the effects of β-aryl substituents on the solvolysis rate are nearly additive.

REARRANGEMENTS involving vinyl cations can commence either from a saturated β′-position where only the migration terminus is unsaturated [equation (1)] or across the double bond from the β-vinyl carbon atom, where both reaction centres are unsaturated [equation (2)]. The first type was observed in the solvolyses of 1-t-butylvinyl,[3] 1-adamantylvinyl,[4] 2-methylcyclohexen-1-yl,[5] and 2,3-dimethylcyclohexen-1-yl [5] trifluoromethanesulphonates (triflates), and in the addition of HCl to 3,3-dimethylbut-1-yne [6] and of acetylene to 1-hydroxyadamantane in acidic solution.[7]



(1)

(2)

The second type was observed in several systems. Modena and his co-workers studied the migration of β-ArS and β-RS groups during the solvolysis of α,β-diaryl-β-arylthio (or α,β-dialkyl-β-alkylthio) 2,4,6-trinitrobenzenesulphonates.[8] A complete β-aryl rearrangement accompanied the acetolysis of 2,2-bis-*p*-methoxyphenyl-1-phenylvinyl bromide,[1] the solvolysis of 1-methyl-2,2-diphenylvinyl tosylate in 80% EtOH,[4] and the decomposition (*via* vinyl cations) of 2,2-diphenylvinyltriazenes in AcOH.[9] However, the 1-methyl-2,2-diphenylvinyl and the 1-phenyl-2,2-di-(*p*-tolyl)vinyl cations from the decomposition of the corresponding triazenes mainly gave the aryl rearranged product but also some of the skeletally unrearranged product.[9] β-Alkyl migration was not observed with trimethylvinyl triflate,[4] but alkyl migrations and Wagner–Meerwein rearrangement accompanied the solvolyses of several cyclic vinyl triflates.[5]

Several mechanistic questions arise in connection with the rearrangement across the double bond. (a) Does the rearranging group participate in the transition state of the heterolysis, or does the initial ionisation give an unrearranged vinyl cation? (b) What is the stereochemistry of the rearrangement? (c) Does the migratory aptitude of the migrating groups follow the order established [10] for saturated compounds? (d) What is

[1] Part XIV, Z. Rappoport, A. Gal, and Y. Houminer, *Tetrahedron Letters*, 1973, 641.

[2] For a preliminary communication see: Y. Houminer and Z. Rappoport, Abstracts, 42nd Meeting of the Israel Chemical Society, Rehovoth, Israel, 1972, p. 8. For general references dealing with vinyl cations see (*a*) M. Hanack, *Accounts Chem. Res.*, 1970, **3**, 209; (*b*) C. A. Grob, *Chimia*, 1971, **25**, 87; (*c*) G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, 1971, **9**, 185; (*d*) P. J. Stang, *Progr. Phys. Org. Chem.*, 1973, **10**, 276.

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[4] M. A. Imhoff, R. H. Summerville, P. v. R. Schleyer, A. G. Martinez, M. Hanack, T. E. Dueber, and P. J. Stang, *J. Amer. Chem. Soc.*, 1970, **92**, 3802.

[5] W. D. Pfiefer, C. A. Bahn, P. v. R. Schleyer, S. Bocher, C. E. Harding, K. Hummel, M. Hanack, and P. J. Stang, *J. Amer. Chem. Soc.*, 1971, **93**, 1513.

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[7] K. Bott, *Tetrahedron Letters*, 1969, 1747.

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[9] W. M. Jones and F. W. Miller, *J. Amer. Chem. Soc.*, 1967, **89**, 1960.

[10] W. E. Bachmann and J. W. Ferguson, *J. Amer. Chem. Soc.*, 1934, **56**, 2081; Y. Pocker in 'Molecular Rearrangements,' ed. P. de Mayo, Interscience, London, 1963, vol. 1, ch. 1; G. W. Wheland, 'Advanced Organic Chemistry,' Wiley, New York, 3rd edn., 1960.

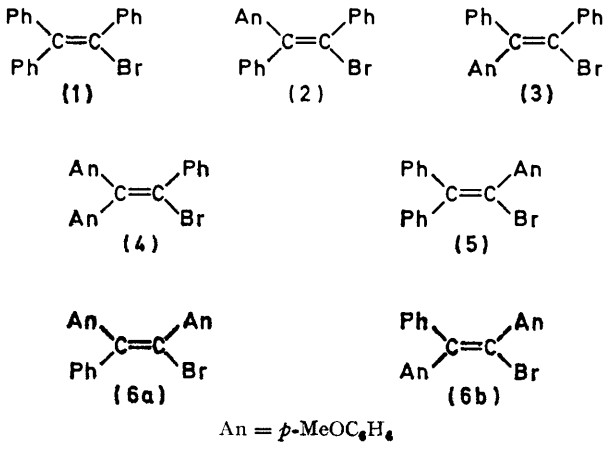
the relative reactivity order of an open vinyl cation towards rearrangement and capture by the solvent and by the leaving group? (e) What is the solvent effect on the rearrangement?

Questions (a) and (b) were partially answered in several systems. For example, there is ample evidence that the migrating ArS and RS groups anchimerically assist the heterolysis in most cases.[8] It was suggested that *trans*-α,β-dimethyl-β-phenylvinyl triflate is solvolysed in buffered 60% EtOH *via* β-phenyl participation, while the *cis*-isomer reacts *via* an open ion.[11] This was based on the higher stereospecificity in the phenyl migration and the higher reactivity of the *trans*-isomer, and was supported by deuterium isotope effects.[11,12] The only information regarding question (d) is that the rearrangement of the 1-phenyl-2,2-di-(*p*-tolyl)vinyl cation can be completely suppressed by excess of KOAc.[9] Question (c) seems to us the most interesting since Kost and Sprecher [13] * had found an order of migratory aptitudes *p*-ClC_6H_4 > *p*-$MeOC_6H_4$ in the Schmidt rearrangement of dialkyl aroylphosphonates. This is contrary to that found in saturated systems [10] or in the Schmidt reaction of substituted benzophenones,[15] and it suggests that the order of migratory aptitudes may differ in saturated and in unsaturated systems.

We therefore studied the solvolytic reactions of α-phenylvinyl bromides carrying two β-phenyl, one β-phenyl and one β-*p*-methoxyphenyl, and two β-*p*-methoxyphenyl groups. Rearrangements are expected in these systems, and questions (a)—(e) could be investigated. We employed two solvents which differ only slightly in their ionisation power on the Winstein–Grunwald scale,[16] but which differ considerably in their nucleophilicities, *i.e.*, 60% EtOH ($Y = 1{\cdot}124$) [16b] and 2,2,2-trifluoroethanol ($Y = 1{\cdot}045$).[17]

RESULTS

Triphenylvinyl bromide (1),[18] *trans*- and *cis*-2-*p*-methoxyphenyl-1,2-diphenylvinyl bromides (2) and (3),[19,20] 2,2-bis-*p*-methoxyphenyl-1-phenylvinyl bromide (4),[19] and 1-*p*-methoxyphenyl-2,2-diphenylvinyl bromide (5) [21] were prepared by the bromination of the corresponding ethylenes. A *trans*-configuration for (2) was earlier deduced on the basis of carbonation to the known cinnamic acid.[20] The assignment is substantiated by the u.v. spectra if we assume that the chromophore is a *trans*-stilbene entity, since (3) which is a *p*-methoxy-substituted derivative has higher $\lambda_{max.}$ [$\lambda_{max.}$ (EtOH) 241 (ε 20,400) and 302 nm (9100)] than (2) which is an unsubstituted system [$\lambda_{max.}$ (EtOH) 232 (ε 21,600) and 297 nm (8800)]. We note however, that the methoxy-singlet of (2) (δ 3·79) and its *p*-methoxyphenyl quartet (δ 6·82) are at lower field than those of (3) [δ 3·64 (OMe) and 6·56 and 6·83 (An)]. This is in contrast with what was observed with the *cis*–*trans* pairs of triarylvinyl



An = *p*-$MeOC_6H_4$

bromides (6a and b),[22] triarylimines,[23] and methoxystilbenes.[24]

Solvolysis in 2,2,2-Trifluoroethanol (TFE).—Solvolysis of (1) at 140° in dry TFE gave exclusively 2,2,2-trifluoroethyl triphenylvinyl ether (7). Solvolysis of either (2) or (3) gave identical products which consisted (by n.m.r.) of *ca.* 80% of the phenyl rearranged 1-*p*-methoxyphenyl-2,2-diphenylvinyl 2,2,2-trifluoroethyl ether (8) [δ 3·71 (OMe), and 3·82 (CH_2)] and *ca.* 20% of a 1 : 1 mixture of *cis*- and *trans*-2-*p*-methoxyphenyl-1,2-diphenylvinyl 2,2,2-trifluoroethyl ethers (9a and b). Compound (8) was isolated and found to be identical with the only ether produced in the trifluoroethanolysis of 1-*p*-methoxyphenyl-2,2-diphenylvinyl bromide (5). Attempts to isolate and purify the minor components (9a and b) by g.l.c. and t.l.c. failed, although oily fractions richer (*ca.* 30%) in (9a and b) were obtained after repeated fractional crystallisation. Analogy of the positions of the methoxy-singlets of (9a and b) with those of (2) and (3) served as a base for the assignment of configuration of the trifluoroethyl ethers. Our evidence that (9a and b) are formed in a 1 : 1 ratio is based on the appearance of two methoxy-singlets at δ 3·66 and 3·77 in a 1 : 1 ratio, and two methylene quartets centred at δ 3·89 and 3·92 in a 1 : 1 ratio in the crude solvolysis mixture. Corroboration for the formation of (9a and b) is obtained from the acid hydrolysis of the crude solvolysis mixture of either (2) or (3) in 0·7N-HCl in refluxing 70% EtOH. This hydrolysis proceeded to the extent of only 80% after 46 h, but was complete after 96 h. The n.m.r. spectrum of the hydrolysis mixture in C_6D_6 showed the presence of only two ketones (which were

* Further examples of an inverted order of migratory aptitudes are reported in ref. 14.

[11] P. J. Stang and T. E. Dueber, *J. Amer. Chem. Soc.*, 1973, **95**, 2683.
[12] P. J. Stang and T. E. Dueber, *J. Amer. Chem. Soc.*, 1973, **95**, 2686.
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[14] D. Kost, Ph.D. Thesis, Tel-Aviv University, 1970; M. Sprecher, personal communication, 1970.
[15] P. A. S. Smith and J. P. Horowitz, *J. Amer. Chem. Soc.*, 1950, **72**, 3718.
[16] (*a*) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846; (*b*) A. H. Fainberg and S. Winstein, *ibid.*, 1956, **78**, 2770.
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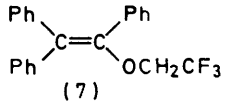
[20] D. Y. Curtin, E. E. Harris, and E. K. Meislich, *J. Amer. Chem. Soc.*, 1952, **74**, 2901.
[21] Z. Rappoport and A. Gal, *J. Amer. Chem. Soc.*, 1969, **91**, 5246.
[22] Z. Rappoport and Y. Apeloig, *J. Amer. Chem. Soc.*, 1969, **91**, 6734.
[23] D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Amer. Chem. Soc.*, 1966, **88**, 2775.
[24] H. Güsten and M. Salzwedel, *Tetrahedron*, 1967, **23**, 173, 187.

prepared independently), (10) [δ 3·15 (OMe) and 5·90 (CH)] and (11) (δ 3·25 (OMe) and 5·86 (CH)] [25] which were formed in a 85 : 15 ratio. While ketone (10) was isolated and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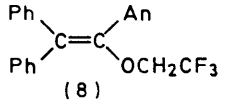
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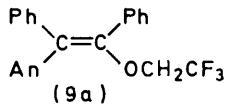
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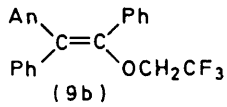
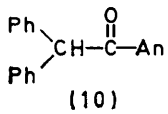

(9b)

identified from the hydrolysis of the reaction mixture of (2), (11) could not be isolated owing to the small quantity formed, although the presence of its methine signal established its formation unambiguously. A 1,2-phenyl rearrangement during the hydrolysis of the trifluoroethyl ethers is unlikely since the (8) : (9a and b) ratio is similar to the (10) : (11) ratio. Moreover, (10) and (11) are stable to mutual isomerisation under the reaction conditions. The 85 : 15 ratio is taken as the ratio of (8) to (9a and b) which are formed in the trifluoroethanolysis, since the error in the determination of (10) and (11) is lower than that for (8) and (9a and b).

The solvolysis of (2) in the presence of a two-fold excess of sodium toluene-*p*-thiolate gave only triarylvinyl sulphides. No methylene quartet of (8) or (9a and b) was detected. The rearranged sulphide (12) [δ 3·57 (MeO)] was isolated and was identical with authentic (12) which was obtained from the solvolysis of (5) in 80% EtOH containing sodium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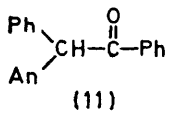
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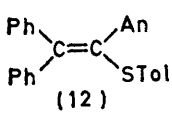
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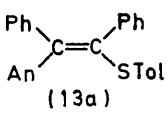
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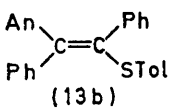
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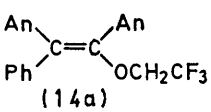
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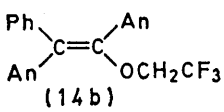
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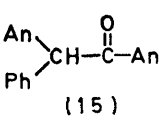
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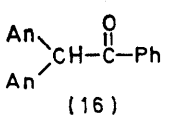
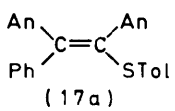

(16)

toluene-*p*-thiolate.[21] Two additional methoxy-signals at δ 3·61 and 3·72 in a 1 : 1 ratio appeared in the n.m.r. spectrum of the crude reaction mixture, and were ascribed to the *cis*- and the *trans*-sulphides (13a and b). The (12) : (13a and b) ratio was 7 : 3.

Solvolysis of (4) gave a 1 : 1 mixture of the trifluoroethyl ethers (14a and b), as judged from the appearance of four methoxy-singlets with equal intensities at δ 3·57, 3·60, 3·62, and 3·68, and of two methylene quartets at δ 3·88 and 3·91 in a 1 : 1 ratio. The mixture also contained *ca.* 3% of the known ketone (15),[23] recognised by the signals of the CH and the *o*-anisoyl protons. It is not known whether (15) is formed in the solvolysis or during the work-up. Repeated fractional crystallisation afforded two fractions, (14a) contaminated with 25% of (14b), and (14b) contaminated with 20% of (14a). The two isomers were identical (mixed m.p., n.m.r.) with authentic samples which were formed in a 1 : 1 ratio and isolated from the trifluoroethanolysis of a 73 : 27 mixture of (6a and b). The configurational assignments for (14a and b) are based on the analogy with those of (6a and b).[22] The isomer with the higher m.p., and the lower methoxy-signal absorptions was assigned the *trans*-configuration (14b).

Hydrolysis of the crude solvolysis mixture from (4) with 1N-HCl in refluxing 70% EtOH for 50 h gave an oil with an n.m.r. spectrum identical with that of (15). No signal corresponding to the known ketone (16) [26] which could originate from a presumably unrearranged 2,2-bis-*p*-methoxyphenyl-1-phenylvinyl 2,2,2-trifluoroethyl ether was observed. Compounds (15) and (16) were stable to mutual isomerisation under these conditions.

Solvolysis of (4) in the presence of a two-fold excess of sodium toluene-*p*-thiolate gave a mixture whose n.m.r. spectrum showed four methoxy-singlets of equal intensities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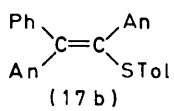
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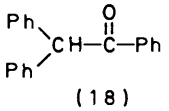

(18)

at δ 3·56, 3·58, 3·62, and 3·71 and no methylene signal for (14a and b). The n.m.r. spectrum of the mixture in the methyl, methoxy, and aromatic regions was identical with that of an authentic 1 : 1 mixture of the sulphides (17a and b) which was obtained previously in the solvolysis of either (6a and b) in 80% EtOH containing sodium toluene-*p*-thiolate.[22]

Reactions in 60% EtOH.—Solvolysis of (1) in 60% EtOH (v/v) gave α,α-diphenylacetophenone (18), which was identical with an authentic sample.[27] Solvolysis of either (2) or (3) gave identical product mixtures consisting (by n.m.r.) of 95% of the unrearranged ketone (11), which was isolated, and *ca.* 5% of the phenyl rearranged ketone (10). Solvolysis of (4) gave only the rearranged ketone (15). No unrearranged ketone was detected by n.m.r. spectroscopy. Ethyl vinyl ethers were not detected in any of the above reactions.

Kinetics.—The reaction in 60% EtOH buffered with excess of 2,6-lutidine was followed titrimetrically at 140°. The rate coefficient remained constant up to 4—5 half-lives. Table 1 summarises the data and the relative reactivities. One- and two-point experiments were also conducted at 120 and 160° and the derived approximate activation parameters are $\Delta H^{\ddagger} = 42{\cdot}5$ kcal mol^{-1}, $\Delta S^{\ddagger} = 18$ cal K^{-1} mol^{-1} for compound (1) and $\Delta H^{\ddagger} = 35 \pm 3$ kcal mol^{-1}, $\Delta S^{\ddagger} = 2 \pm 9$ cal K^{-1} mol^{-1} for the other compounds.

In TFE buffered with 2,6-lutidine, (4) showed first-order kinetics up to 3 half-lives. However, for compounds (1)—(3) the rate coefficient of the first-order equation $kt = 2{\cdot}3 \log [a/(a - x)]$ decreased during the kinetic run. A sample run is given in Table 2. This behaviour is ascribed to

[25] D. Y. Curtin and E. K. Meislich, *J. Amer. Chem. Soc.*, 1952, **74**, 5518.

[26] A. Orekoff and M. Tiffeneau, *Bull. Soc. chim. France*, 1921, **29**, 445.

[27] H. Ley and W. Manecke, *Ber.*, 1923, **56***B*, 777.

common ion rate depression by the bromide ion formed (Scheme 1, the k_{-1} step). Integration of the rate equation $dx/dt = k_1(a - x)/(1 + (k_{-1}/\Sigma k_2)[X^-])$ which corresponds to Scheme 1 gave the relationship $t/\ln[a/(a - x)] = 1/k_1^0 + (k_{-1}/k_1^0\Sigma k_2)\{a - x/\ln[a/(a - x)]\}$ where k_1^0 is the initial rate coefficient. When Σk_2 corresponds to the capture of R^+ only by the solvent, we designate the selectivity factor $k_{-1} : \Sigma k_2$ by α, and when Σk_2 is a combination of rate coefficients for the capture of R^+ and for its internal rearrangement the $k_{-1} : \Sigma k_2$ ratio is designated α' (see Discussion section). We used a computer programme which searches for the best k_1^0 and α (or α') values, and these with the corresponding activation parameters are given in Table 3. Also given are $k_1^0 : k_1^{50}$ ratios, which are the ratios of the rate coefficients at the beginning of the reaction to those at 50% reaction as calculated by the first-order equation, and hence show the deviation from first-order behaviour. The relative reactivities of compounds (1)—(4) at 120 and at 140° (Table 3) show the order (4) > (3) ~ (2) > (1).

TABLE 1

Solvolysis of 0·035M-triarylvinyl bromides in 60% EtOH in the presence of 0·07M-2,6-lutidine [a]

Compound	T/°C	10^7k_1/s^{-1}	Relative rate (140°)
(1)	140	8·46 ± 0·07	1
	160	100 ± 11	
(2)	120	2·24 ± 0·13 [b]	
	140	18·0 ± 0·6	2·14
(3)	140	20·6 ± 0·2	2·44
	160	176 [c]	
(4)	140	46·0 ± 0·5	5·45
	160	370 ± 30 [b]	

[a] Concentrations are corrected for the reaction temperature. [b] Based on a two-point experiment. [c] A one-point experiment.

TABLE 2

Solvolysis of 0·035M-(1) in TFE containing 0·07M-2,6-lutidine at 120°

t/h	0	46	69	95	168	268	609
Reaction (%)	0	13·4	18·5	23·9	33·7	47·7	70·9
10^7k_1/s^{-1} [a]	9·4 [b]	8·5	8·2	8·0	6·8	6·7	5·6

[a] Based on the first order equation $kt = 2{\cdot}3 \log [a/(a - x)]$. [b] Extrapolated value.

The small to moderate decrease of the rate coefficient during a run gave a relatively high error in α and in α'. We tried to reduce the error by discarding kinetic points at <8% reaction.

The reactions of (1), (2), and (4) were also studied in the presence of added Et_4NBr or Bu_4NBr. In these two-point experiments the rate coefficients for compounds (1) and (2) begun at a lower value than k_1^0 and remained constant along the run. The reaction of (4) was unaffected by the added salt.

Preliminary trifluoroethanolysis experiments using NaOAc as the neutralising base gave a rate coefficient for (4) which was constant at 14—56% reaction and was 10% higher than k_1 in the presence of 2,6-lutidine. The rate coefficient for (1) was 67% higher than in the presence of an equivalent amount of 2,6-lutidine, and decreased during the run. The vinyl acetates consisted of *ca.* 10% of the products in these reactions. However, since precipitation of NaBr was already apparent at 25% reaction, these reactions were not investigated further.

DISCUSSION

Rearrangement in our systems can occur either *via* β-aryl participation in the transition state of the heterolysis, or *via* heterolysis to an open vinyl cation which rearranges *via* a bridged transition state. Capture of the various cationic intermediates by the solvent or other nucleophiles may compete with the rearrangement. The data will be discussed in relation to the questions of β-aryl participation, β-*p*-methoxyphenyl *versus* β-phenyl migration, common ion rate depression in α-phenylvinyl bromides, and the solvent and substituent effects on the various rate coefficients.

TABLE 3

Solvolysis of 0·035M-triarylvinyl bromides in TFE containing 0·07M-2,6-lutidine [a]

Compound	T/°C	$10^7k_1^0$/s^{-1}	α or α′/1 mol^{-1}	$k_1^0 : k_1^{50}$ [b]	Relative k_1 (120°)	Relative k_1 (140°)	$\Delta H^\ddagger$/kcal mol^{-1}	$\Delta S^\ddagger$/cal K^{-1} mol^{-1}
(1)	120	9·4 ± 0·4	46 ± 7	1·45	1	1	20·5	−35
	140	34·6 ± 4·1	42 ± 16	1·3				
	140	16·0 ± 1·0 [c-e]						
	140	16·0 [c,e,f]						
	140	57·8 ± 2·6 [h,i]	24 ± 6					
(2)	120	31·7 ± 1·7	31 ± 8	1·3	3·4	2·9	20·5	−32
	140	120·1 ± 1·6	11 ± 1	1·1				
	140	86·0 ± 1·0 [c,f,g]						
(3)	120	35·1 ± 1·3	33 ± 6	1·3	3·7	3·4	22·0	−28
	140	142·9 ± 3·3	18 ± 3	1·2				
(4)	120	89·0 ± 3·0	0	1·0	9·5	12·5	22·5	−25
	120	88 ± 1 [c,d]						
	120	97 ± 2 [c,h,j]						
	140	378·0 ± 4·0	0					

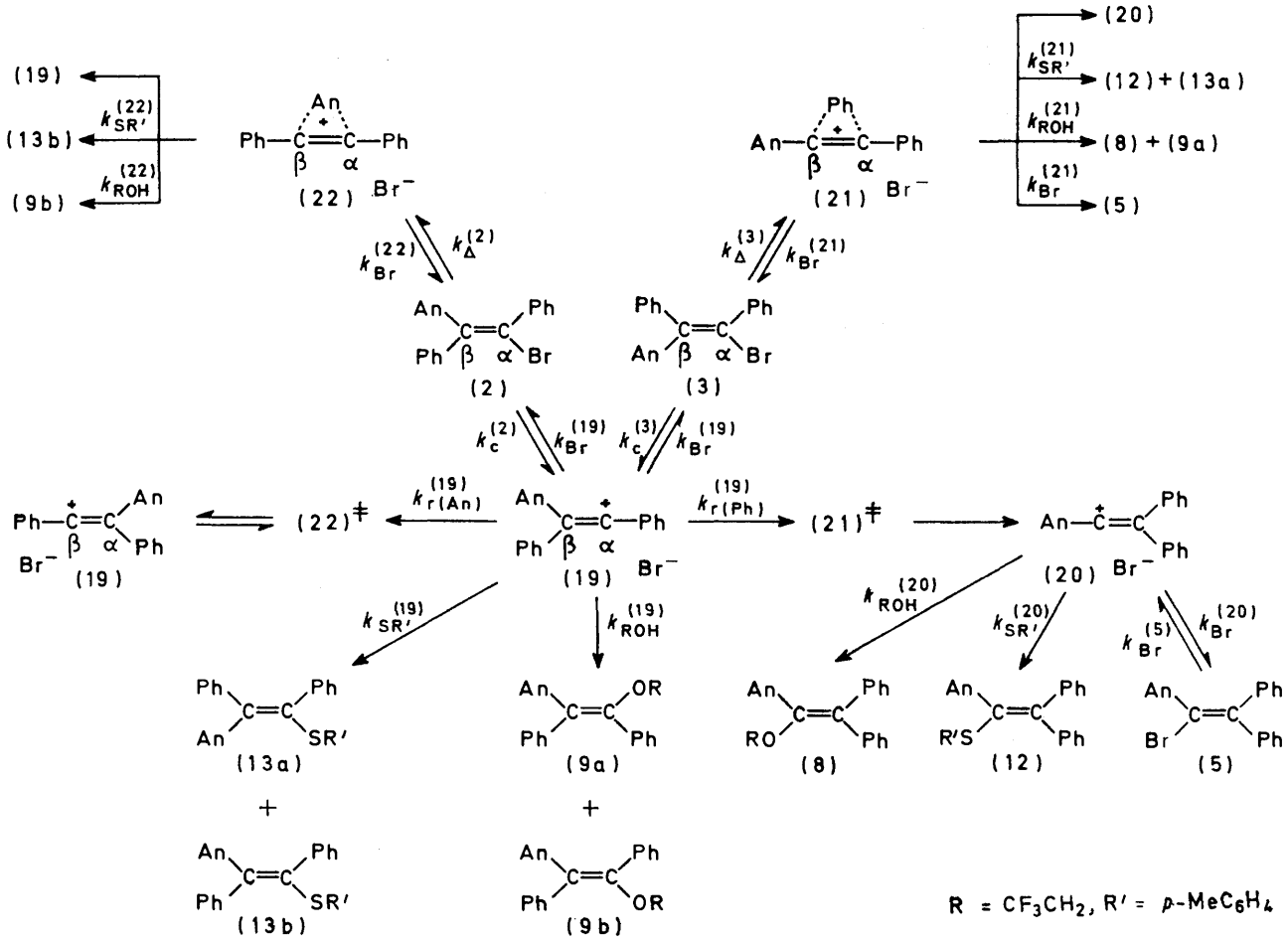
[a] The concentrations are at the reaction temperature. [b] Ratio of the initial rate coefficient to the integrated k (according to the first-order equation) at 50% reaction. [c] A two-point experiment. [d] In the presence of 0·031M-Bu_4NBr. [e] At 3—23% reaction. [f] In the presence of 0·033M-Et_4NBr. [g] At 40—50% reaction. [h] In the presence of 0·07M-NaOAc and no 2,6-lutidine. [i] Four-point experiment at 10—70% reaction. [j] At 14—56% reaction.

$$RBr \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+ + Br^- \xrightarrow{\Sigma k_2} \text{Products}$$

SCHEME 1

β-*Aryl Participation.*—If analogy with the behaviour of saturated systems prevails (however, see later), β-aryl participation should be more important for (2) where a *p*-methoxyphenyl group is *trans* to the leaving group,

than for (3) where phenyl and bromine are *trans*.[28] Likewise, β-aryl participation is much more likely with (4) as compared with (1). However, the greater capability of α-aryl groups in stabilising a positive charge compared with α-alkyl groups, and the involvement of only *open* cations in the solvolyses of 1,2,2-triphenylethyl derivatives[29] suggest that β-aryl participation has little importance in our systems. A similar conclusion was



SCHEME 2

deduced previously regarding the solvolysis of (6a and b).[30]

We will discuss separately the question of β-aryl participation for (a) compounds (2) and (3) where the β-groups are different and both stereochemical and kinetic probes for participation could be used, and (b) compounds (1) and (4) where in each the two β-groups are identical.

(a) cis- *and* trans-2-p-*Methoxyphenyl*-1,2-*diphenylvinyl bromides* (2) *and* (3) *in TFE*. Scheme 2 summarises the various mechanistic possibilities for the trifluoroethanolysis of (2) and (3). The rate coefficients for the unassisted heterolysis which leads to the open ion (19) are designated k_c. The rate coefficients for the heterolysis with anchimeric assistance by the *trans*-β-aryl group which give the bridged ions (21) and (22) are designated k_Δ. The rate coefficients for the rearrangement of β-*p*-methoxyphenyl and β-phenyl groups which give the open cations (19) and (20), respectively, are $k_{r(An)}$ and $k_{r(Ph)}$. k_{Br} Is the second-order coefficient and k_{ROH} and $k_{SR'}$ are the pseudo-first-order rate coefficients for the capture of the various cationic species by bromide ion, the solvent (TFE), and toluene-*p*-thiolate ion, respectively. The superscript designates the cationic or neutral species which take part in these reactions.

As exemplified in Scheme 2, capture of the symmetrical bridged intermediate (22) from its less hindered side by nucleophiles would give only products with retained *trans*-configuration, *i.e.* (2), (9b), and (13b). Similar

[28] D. J. Cram, *J. Amer. Chem. Soc.*, 1949, **71**, 3863; 1952, **74**, 2129; S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *ibid.*, 1953, **75**, 147; H. J. Schaeffer and C. J. Collins, *ibid.*, 1956, **78**, 124; E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, 1958, **41**, 807; S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Amer. Chem. Soc.*, 1961, **83**, 618; H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *ibid.*, 1967, **89**, 370.

[29] W. A. Bonner and C. J. Collins, *J. Amer. Chem. Soc.*, 1953, **75**, 5372; 1955, **77**, 99, 6725; 1956, **78**, 5587; C. J. Collins and W. A. Bonner, *ibid.*, 1953, **75**, 5379; 1955, **77**, 92; C. J. Collins, W. A. Bonner, and C. T. Lester, *ibid.*, 1959, **81**, 466.

[30] Z. Rappoport and Y. Apeloig, *Tetrahedron Letters*, 1970, 1817.

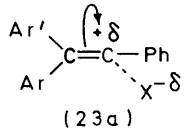
capture of (21) [which is *a priori* a less likely intermediate than (22)] at the α-position would give unrearranged (3), (9a), and (13a) with retained *cis*-configuration, and capture at the β-carbon atom would give (5), (8), and (12). On the other hand, all the open ions carry β-substituents of similar bulk on both sides of the empty *p* orbital, and the probability of capture by nucleophiles from either side is nearly equal, as observed in the solvolysis of (6a and b) in AcOH or with toluene-*p*-thiolate ion in 80% EtOH.[22] Consequently, a pair of *cis–trans* isomers [*i.e.* (9a)–(9b) and (13a)–(13b)] in *ca.* 1 : 1 ratio is expected from (19), while only one product will be formed from the more symmetrical ion (20). Indeed, the n.m.r. evidence shows that the ethers (9a and b) on the one hand, and the sulphides (13a and b) on the other are formed in *ca.* 1 : 1 ratios. There is little doubt, therefore, that they are formed from the open ion (19).

Not all the 1 : 1 isomer mixtures are formed directly *via* this route. Partial capture of the ion (19) by Br^- gives (in addition to the ethers and the sulphides) a 1 : 1 mixture of the vinyl bromides (2) and (3). These bromides solvolyse further *via* (19), also to give a 1 : 1 isomer mixture. This added route is an essential part of the mechanism since the kinetics indicate that capture of (19) [$k_{Br}^{(19)}$] does occur to a certain extent (see below), and bromide ion return to the structurally related tris-*p*-methoxyphenylvinyl cation takes place in TFE.[31] It also calls for a (2) ⇌ (3) isomerisation [*via* $k_c^{(2)} \longrightarrow k_{Br}^{(19)}$] during the trifluoroethanolysis, which was indeed observed.

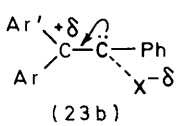
The stereochemical results do not exclude ionisation with anchimeric assistance, if the bridged ion rearranges to an open ion before capture. However, *if analogy with saturated systems prevails*, the slightly higher reactivity of (3) as compared with (2) (Table 3) excludes β-*p*-methoxyphenyl participation.[28] Instead, the effects of the β-aryl groups are nearly additive: If *cis*- and *trans*-β-*p*-methoxyphenyl groups increase the reactivity over the corresponding β-phenyl groups by 3·4- and by 2·9-fold, respectively, (4) is predicted to be 9·9-times more reactive than (1). The actual ratio is 12·5. Similar additivity was observed earlier in the solvolysis of (5), (6a and b), and tris-*p*-methoxyphenylvinyl bromide in 80% EtOH.[30]

As discussed later, the analogy with saturated systems is not straightforward, so that this route cannot be unequivocally excluded.

The relative reactivities could be explained by a combination of inductive effects, and gain and loss in the aryl–double bond conjugation (see later). Moreover,



(23a)



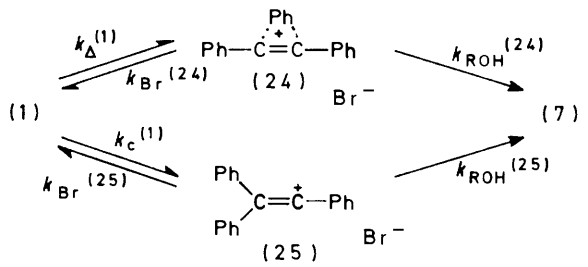
(23b)

partial delocalisation of the positive charge formed in the transition state on the α-carbon atom (23a) by the substituents on the β-carbon atom may also contribute as in (23b). Such delocalisation was previously suggested to be low on the basis of the similarity in solvolysis rates of the vinyl iodides analogous to (1) and to (2) and (3) in 70% DMF.[32]

In discussing the reactions of our intermediates we did not include explicitly ion pairs in the schemes. This was done in order not to introduce further complications, although ion pairs play a role in some vinylic solvolyses, and they are mentioned briefly below.

(b) *Triphenylvinyl bromide* (1) *and* 2,2-*bis*-p-*methoxyphenyl*-1-*phenylvinyl bromide in TFE.* The possible mechanisms for (1) are given in Scheme 3 where (24) and (25) are the possible bridged and open intermediates, which give the ether (7) on reaction with the solvent. No stereochemical probe for participation is available for an isotopically unlabelled (1), but such information could be obtained by comparing the solvolysis rates of (1) with those of (2)—(4) (see earlier).

A solvolysis–rearrangement scheme for (4) is given in Scheme 4. An unassisted solvolysis [$k_c^{(4)}$] gives the open ion (27) while a β-*p*-methoxyphenyl assisted solvolysis [$k_\Delta^{(4)}$] leads to the bridged ion (26). Both cationic species can return to the covalent bromide (4) [*via* $k_{Br}^{(26)}$ and $k_{Br}^{(27)}$], and both can rearrange to the rearranged open ion (28) with rate coefficients $k_{r(An)}^{(26)}$



Scheme 3

and $k_{r(An)}^{(27)}$. The ion (27) may be also captured before rearrangement, giving the unrearranged vinyl sulphide (29) [*via* $k_{SR}^{(27)}$] or the trifluoroethyl ether (30) [*via* $k_{ROH}^{(27)}$]. Analogous arguments to those brought above for the capture of the ions (19) and (21) suggest that capture of the bridged ion (26) at the β-carbon atom by the solvent, by thiolate ion, and by bromide ion would give exclusively the *cis*-isomers (14a), (17a), and (6a), respectively, and capture of (28) by the same nucleophiles would give *ca.* 1 : 1 *cis–trans* mixtures of the ethers (14a and b), the sulphides (17a and b), and the bromides (6a and b).

The strongest stereochemical evidence that products are derived from the open ion (28) is the formation and isolation of the 1 : 1 mixture of the ethers (14a and b) from (4). Moreover, the formation of 1 : 1 mixtures of the sulphides (17a and b) starting either from (4), (6a), or (6b) argues strongly that the sulphides are also derived from the open ion (28).

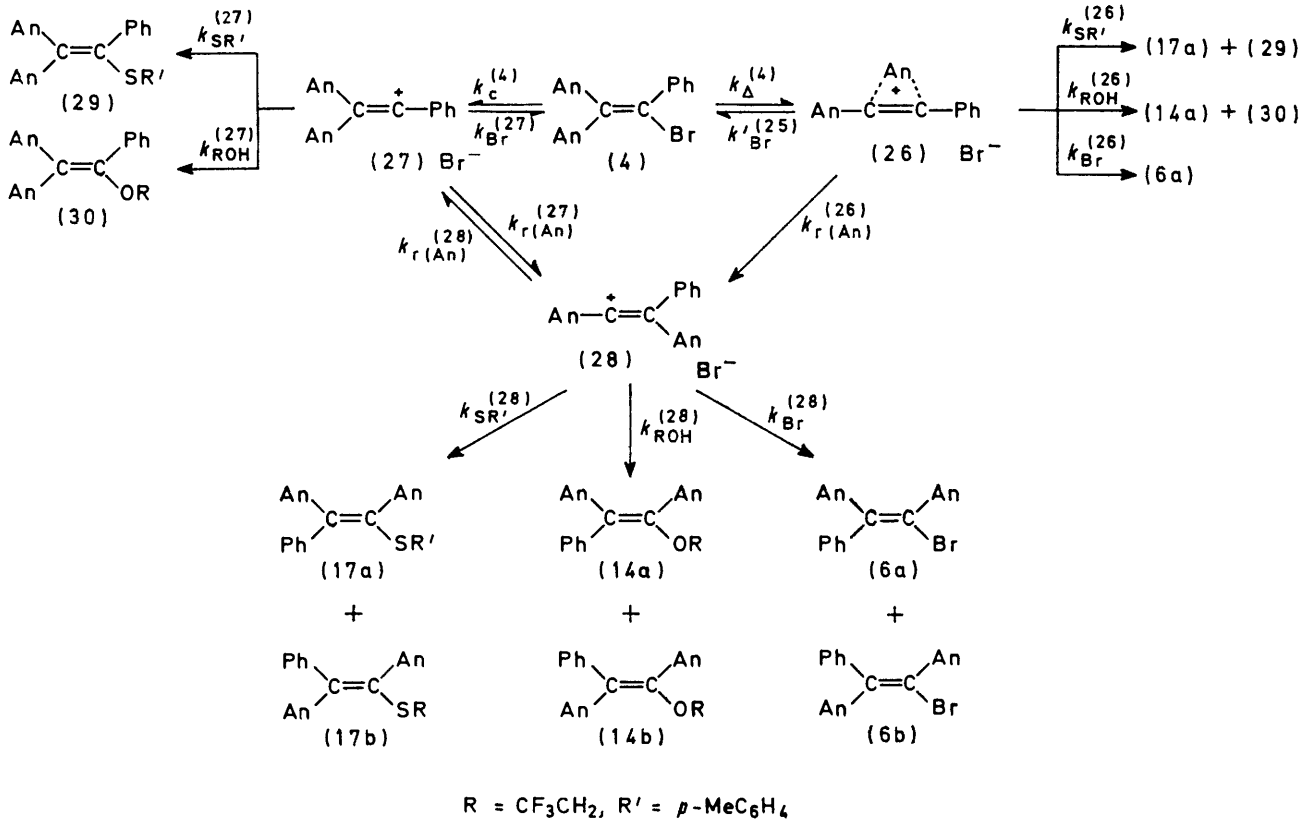
Since bromide ion return to the ion (28) is extensive in

[31] Z. Rappoport and Y. Apeloig, unpublished results.
[32] L. L. Miller and D. A. Kaufman, *J. Amer. Chem. Soc.*, 1968, **90**, 7282.

AcOH,[33] it is likely that part of the ethers and the sulphides are formed by solvolysis of (6a and b) which are formed, in turn, by capture of (28) by Br^- in TFE.

The stereochemistry of the products from (4) is also accounted for if the bridged ion (26) is captured mainly or exclusively at its β-carbon atom to give (6a). The further solvolysis of (6a) to a 1 : 1 mixture of (14a and b) above interpretation of the rate data suggest that the solvolysis of (1) proceeds *via* the open ion (25).

Compounds (1)—(4) *in* 60% EtOH.—Reaction Schemes 2—4 could be applied also for the reactions in 60% EtOH, when k_{ROH} values with the appropriate superscripts are related to the rate coefficients of the various cationic species with both components of the solvent. In



SCHEME 4

would be kinetically undetected, since it would be *ca.* 10^3 times faster than that of (4), judging by the $k_{\alpha\text{-An}}/k_{\alpha\text{-Ph}}$ ratios in other vinylic solvolyses.[34] This (4) $\xrightarrow{k_{\Delta}^{(4)}}$ (26) $\xrightarrow{k_{Br}^{(26)}}$ (6a) $\xrightarrow{k_{c}^{(6a)}}$ (28) $\xrightarrow{k_{ROH}^{(28)}}$ (14a + b) (1 : 1) [or $\xrightarrow{k_{SR'}^{(28)}}$ (17a + b) (1 : 1)] route is excluded by the following reasoning. Since toluene-*p*-thiolate ion is more nucleophilic than bromide ion toward saturated[35] and unsaturated carbon,[36] or carbocations,[37] $k_{SR'}^{(26)}$ is greater than $k_{ROH}^{(26)}$. Consequently, the vinyl sulphides should be (17a) and (29) which are derived from the capture of (26), and not (17b), contrary to what was found.

The evidence against bridging in the solvolysis of (4), the presumably higher stability of (26) over (24), and the our cases, where ethyl ethers were not formed, the k_{ROH} values relate to capture by water.

A priori, β-aryl participation is less important in 60% EtOH since the participation is reduced with the increase in the nucleophilicity of the medium[38] and 60% EtOH is much more nucleophilic than TFE.[39] This is substantiated by (a) the lower degree of phenyl migration as compared with that in TFE, (b) the near additivity of the effects of β-substituents, and (c) the reactivity scale (4) > (3) ~ (2) > (1), which is compressed two-fold compared with TFE. The stereochemical probe for participation in 60% EtOH is lost since the products are only the ketones.

We want to emphasise that since the rates of reactions

[33] Z. Rappoport and Y. Apeloig, *Tetrahedron Letters*, 1970, 1845.

[34] (*a*) C. A. Grob and G. Cseh, *Helv. Chim. Acta*, 1964, **47**, 194; (*b*) Z. Rappoport and J. Kaspi, *J.C.S. Perkin II*, 1972, 1102; (*c*) Z. Rappoport and A. Gal, *J. Org. Chem.*, 1972, **37**, 1174.

[35] A. J. Parker, *Adv. Phys. Org. Chem.*, 1967, **5**, 173; R. F. Hudson and G. Klopman, *J. Chem. Soc.*, 1962, 1062.

[36] Z. Rappoport, *Adv. Phys. Org. Chem.*, 1969, **7**, 1.

[37] C. D. Ritchie, *Accounts Chem. Res.*, 1972, **5**, 348.

[38] *E.g.* A. Diaz, I. Lazdins and S. Winstein, *J. Amer. Chem. Soc.*, 1968, **90**, 6546; A. F. Diaz and S. Winstein, *ibid.*, 1969, **91**, 4300.

[39] W. S. Trahanovsky and M. P. Doyle, *Tetrahedron Letters*, 1968, 2155; G. A. Dafforn and A. Streitwieser, jun., *ibid.*, 1970, 3159; S. H. Liggero, J. J. Harper, P. v. R. Schleyer, A. P. Krapcho, and D. E. Horn, *J. Amer. Chem. Soc.*, 1970, **92**, 3789; M. D. Bentley and J. A. Lacadie, *Tetrahedron Letters*, 1971, 741.

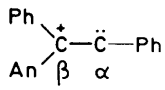
and the products from (2) and (3) are similar, our arguments both for the reactions in TFE and in 60% EtOH are independent of the validity of the configurational assignments of the two isomers.

β-p-*Methoxyphenyl* versus β-*Phenyl Migration*.—The main solvolysis product of (2) and (3) in TFE and the minor product in 60% EtOH are derived from phenyl migration. This is in contradiction to the order of migratory aptitudes An > Ph in saturated systems.[10] The stereochemistry of the unrearranged products and the absence of β-*p*-methoxyphenyl participation exclude geometrically biased rearrangement of an aryl group *trans* to the leaving group. The apparent 'abnormal' order of migratory aptitudes can then be explained in two ways.

(a) It may be an artefact, since it is deduced from product analysis alone. Collins and his co-workers[40] have shown that an apparently 'abnormal' order of migratory aptitudes in saturated cations which is deduced from product studies results from an inherently 'normal' order, which is masked by the involvement of non-migration steps in the rate for the overall process. Thus, the degenerate β-*p*-methoxyphenyl rearrangement in (19) (Scheme 2) may be faster (although unobserved) than the phenyl rearrangement. Our product distribution results from a faster phenyl migration in (19) as compared with its capture by the nucleophile. The steady-state treatment gives the ratio of the rearranged to the unrearranged product as $k^{(19)}_{r(Ph)} : k^{(19)}_{ROH}$, provided that the rearrangement of (19) to (20) is irreversible, as is evident from the absence of rearrangement during the solvolysis of (5). This is consistent with the higher ratio of unrearranged to rearranged product in more nucleophilic media *e.g.* (i) in 60% EtOH compared with TFE and (ii) with toluene-*p*-thiolate in TFE where the (12) : (13a and b) ratio is 2·33 as compared with the ratio (8) : (9a and b) of 5·7 in TFE where the solvent itself is the nucleophile.

Some degenerate *p*-methoxyphenyl rearrangement (which is being investigated by us with labelled compounds) is expected, since 3·6% of degenerate β-phenyl rearrangement occurs during the acetolysis of triphenylvinyl triflate.[41]

(b) The migratory aptitudes in vinylic rearrangements may be the same or different from those in saturated systems, depending on the importance of the loss and the gain in the aryl–double bond conjugation in the vinylic systems. If the bridged ions (21) and (22) are taken as models for the transition states for β-phenyl and β-*p*-methoxyphenyl rearrangement, their relative stabilities compared with the ion (19) are determined by the combination of five factors. (i) Stabilisation is achieved by charge delocalisation on the bridging group. In our α-phenyl activated systems, this will favour (22) over (21) by at most 2 kcal mol^{-1}, which is the value calculated from the reactivity ratio *k*[*threo*-*p*-$MeOC_6H_4CH$(Me)CH(OTs)Me] : *k*[*threo*-PhCH(Me)CH(OTs)Me] = 37 in formolysis.[42] (ii) A partial positive charge is formed on the β-carbon atom. This favours (21) over (22). (iii) Deconjugation of the migrating group and the double bond occurs. We found no thermochemical data for comparing An–C=C and Ph–C=C conjugation, but by using heats of formation[43] we found that a *p*-methoxy-substituent contributes *ca.* 2·5 kcal mol^{-1} to the delocalisation energy of AnCHO compared with PhCHO. If we use a somewhat lower value as an approximation in our system, the deconjugation loss in (22) over that in (21) nearly balances the gain by bridging. (iv) Enhanced conjugation of the non-migrating group with the double bond takes place. The two β-groups in (19) are probably twisted by *ca.* 30° from the plane of the double bond, as found with 1,1-diarylethylenes.[44] Bending of the migrating aryl group reduces its steric interaction with the non-migrating group, increases the planarity of the Ar–C=C system, and thus stabilises the transition state. This favours (21) over (22). (v) There is partial loss of the extra stabilisation in the ground state [the ion (19)] due to structure (31). This would again favour (21) over (22), although the contribution of this extra-stabilisation is probably low.[32]



(31)

Only (i) and (ii) are considered for saturated systems, where (i) is always more important. In vinylic systems (i)—(v) should be considered, regardless of the order of migratory aptitudes observed. While (i), (iii), and (v) could be used in explaining the 'abnormal' order for (19), (ii) and (iv) should be also invoked to explain the exclusive rearrangement of (27).

Several apparent 'abnormal' reactivity differences were previously explained in terms of aryl–double bond conjugation. These include the higher migratory aptitudes of electron-attracting aryl groups compared with electron-donating ones in the Schmidt reaction,[13,14] the formation of α-azido-β-iodo-β-methylstyrene in the addition of IN_3 to phenylmethylacetylene,[45] and the relatively low α-Ph : α-Me reactivity ratios in the addition of acids to the α-substituted olefins.[46]

[40] For summaries see C. J. Collins, *Adv. Phys. Org. Chem.*, 1964, **2**, 1; A. Fry in 'Mechanisms of Molecular Migrations,' ed. B. S. Thyagarajan, Wiley, New York, 1971, vol. 4, p. 113.

[41] B. M. Benjamin and C. J. Collins, personal communication.

[42] S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlesinger, *J. Amer. Chem. Soc.*, 1952, **74**, 1140.

[43] Data taken from J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, London, 1970, ch. 5.

[44] G. E. Coates and L. E. Sutton, *J. Chem. Soc.*, 1942, 567; H. Suzuki, *Bull. Chem. Soc. Japan*, 1960, **33**, 619; M. Simonetta and S. Carra, *Tetrahedron Suppl.*, 1963, **2**, **19**, 467; R. van der Linde, O. Korver, P. K. Korver, P. J. van der Haak, J. U. Veenland, and T. J. de Boer, *Spectrochim. Acta*, 1965, **21**, 1893; M. Rabinovitz, I. Agranat, and E. Bergmann, *Israel J. Chem.*, 1969, **7**, 795; G. Casalone and M. Simonetta, *J. Chem. Soc.* (*B*), 1971, 1180.

[45] A. Hassner, R. J. Isbister, and A. Friederang, *Tetrahedron Letters*, 1969, 2939.

[46] D. S. Noyce and R. M. Pollack, *J. Amer. Chem. Soc.*, 1969, **91**, 7158.

Application of considerations similar to (i)—(v) above for the transition state of the initial C–Br bond heterolysis have also important consequences regarding the utility of the rate probe for participation in vinylic solvolyses. For example, comparison of the rate of compounds with a different migrating group but with the same non-migrating group is more justified than the comparison of the rates of a pair of *cis–trans*-isomers, where the non-migrating groups are different, but both comparisons still suffer from the neglect of the effects (iii)—(v) above.

Common Ion Rate Depression in α-Phenylvinyl Bromides.—The small decrease of the integrated first-order coefficients for compounds (1)—(3) during a kinetic run in TFE was ascribed to common ion rate depression by the formed bromide ion, *i.e.* to $k_{Br}^{(19)}$ and $k_{Br}^{(25)}$. This was verified by the rate depression in the presence of added external bromide ion and by the (2) ⇌ (3) isomerisation which accompanies the solvolysis. Ion return to the linear ion (19) unequivocally requires such a *cis*-⇌*trans*-isomerisation.[33]

The competition ratios for return by bromide ions *versus* capture by the solvent $\alpha = k_{Br}^{(25)} : k_{ROH}^{(25)}$, or for return by bromide ions *versus* capture by the solvent and rearrangement $\alpha' = k_{Br}^{(19)}[k_{ROH}^{(19)} + k_{r(Ph)}^{(19)}]$ were calculated from Scheme 1 by equations (3) and (4), where k_d is the depressed rate coefficient in the presence of added bromide ion.[47] The values, $\alpha = 36$ for (1) and $\alpha' = 12$

$$k_d = k_c^{(1)}/(1 + \alpha[Br^-]) \quad (3)$$

$$k_d = k_c^{(2)}/(1 + \alpha'[Br^-]) \quad (4)$$

for (2) at 140° are within 20% of the values calculated from the decrease of k_1 during a run. Likewise, the negligible effect of Br^- in the solvolysis of (4) gives $\alpha' = 0$. A correction for the salt effect of the added $R_4N^+Br^-$ on k_d was not introduced since the effect was not observed in the solvolysis of (4).

We did not attempt to depress completely these slow reactions by using higher $[Br^-]$ concentrations. From our k_d/k_c values, *at least* 54% of 2,2,2-trifluoroethyl triphenylvinyl ether and 30% of the unrearranged ether from (2) arise from the *dissociated* (free) vinyl cations (19) and (25).

These are the first cases where α-phenylvinyl compounds show a common ion rate depression during a kinetic run. Moreover, the data of Table 4 show also that the ratio of the α values of triphenylvinyl bromide and tris-*p*-methoxyphenylvinyl bromide in TFE is the lowest known for α-Ph and α-An substituents in vinylic as well as in saturated systems. Both these factors point to a special stabilisation of the vinyl cations (19) and (25) in TFE. The low nucleophilicity of TFE [39] contributes to this phenomenon, but the detailed nature of this effect is not yet clear.

Solvent and Substituent Effects on the Various Rate Coefficients.—The k_1^0 values for compounds (1)—(4) in TFE are 4·5—8·2 times higher than the k_1 values in 60% EtOH which has a slightly higher ionisation power. This difference is of little diagnostic value since the Winstein–Grunwald *m* values for the same substrate are much lower in aqueous TFE compared with aqueous EtOH.[48] The reaction in aqueous TFE could be even slower than in aqueous EtOH of the same ionisation power, since the rate coefficients for the closely related 1-*p*-methoxyphenyl-2-methylprop-1-enyl tosylate decrease with the addition of water to the TFE.[49]

Our data enable us to compare the rate coefficients for the rearrangement, return, and capture of the same ion as a function of a change in the solvent and the β-substituents. The absence of common ion rate depression and of the unrearranged vinyl sulphide in the presence of sodium toluene-*p*-thiolate show that among our compounds, (4) is unique in that the rearrangement is faster than the capture processes [*i.e.* $k_{r(An)}^{(27)} \gg k_{Br}^{(27)}$, $k_{ROH}^{(27)}$, $k_{SR}^{(27)}$] in TFE, in 60% EtOH, and in AcOH.[1] This is due to the combination of the effects which were discussed in detail above. The rearranged ion (28) is selective since it gives the sulphides (17a and b) and none of the ethers (14a and b) with toluene-*p*-thiolate ion in TFE [*i.e.* $k_{SR}^{(28)} \gg k_{ROH}^{(28)}$]. Any capture of (28) by bromide ion would be hidden, since it gives the bromides (6a and b) which solvolyse much faster than (4).[30]

TABLE 4

Competition factors α for α-phenyl and α-*p*-methoxyphenyl substrates $R^1R^2R^3CX$

Solvent	R^1	R^2 R^3	X	α	R^1	R^2 R^3	X	α	Reference
70% Me_2CO	An	$=CPh_2$	OTs	9	Ph	$=CPh_2$	OTs	0(0·6) [a]	*b*
70% DMF	An	$=CPh_2$	I	30—50	Ph	$=CPh_2$	I	0	*c*
85% Me_2CO	An	An H	Cl	2300	Ph	An H	Cl	700	*d*
TFE	An	$=CAn_2$	Br	78	Ph	$=CPh_2$	Br	46	*e*

[a] Calculated by using an estimated correction for the salt effect. [b] Ref. 34*b*. [c] Ref. 32. [d] T. H. Bailey, J. R. Fox, J. Jackson, G. Kohnstam, and A. Queen, *Chem. Comm.*, 1966, 122. [e] Y. Apeloig, unpublished results, and this work.

On the other hand, the ion (19) from the trifluoroethanolysis of (2) and (3) returns to (2) and (3) $[k_{Br}^{(19)}]$, rearranges to (20) $[k_{r(Ph)}^{(19)}]$, and is being captured by the solvent $[k_{ROH}^{(19)}]$ and by toluene-*p*-thiolate ion $[k_{RS}^{(19)}]$. Combination of the product ratio (8) : (9a and b) of 5·7 which is equal to $k_{r(Ph)}^{(19)} : k_{ROH}^{(19)}$ [where $k_{ROH}^{(19)}$ is a pseudo-first-order coefficient] with the average α′ values of 32 ± 1 at 120 and 14·5 ± 3·5 at 140° (Table 3) gives the order of rate coefficients $k_{Br}^{(19)} : k_{r(Ph)}^{(19)} : k_{ROH}^{(19)}$ as 214 : 5·7 : 1 at 120 and 97 : 5·7 : 1 at 140°.

[47] S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Amer. Chem. Soc.*, 1956, **78**, 328.

[48] D. E. Sunko, I. Szele, and M. Tomić, *Tetrahedron Letters*, 1972, 1827.

[49] J. Kaspi and Z. Rappoport, Abstracts, 42nd Meeting of the Israel Chemical Society, Rehovoth, Isreal, 1972, p. 7.

A corollary of the low sensitivity of α to the nature of the α-aryl group is that the α values are little affected by the change in the β-aryl group, and $\alpha = k_{Br}^{(25)} : k_{ROH}^{(25)} = 44 \pm 2$ is a good approximation for $k_{Br}^{(19)}/k_{ROH}^{(19)}$. Hence, $\alpha : \alpha' = 1 + [k_{r(Ph)}^{(19)}/k_{ROH}^{(19)}]$ since return to (20) is also hidden. However, although the $\alpha : \alpha'$ ratios indeed increase from (2) to (4) with the increased importance of the rearrangement, the actual $\alpha : \alpha'$ ratios are much higher than the value of 6·7 which is predicted by the above relationship, even if the error in the α and α′ values is taken into account. A possible source for this discrepancy is that α values are based on capture of dissociated ions, while part of the products may be derived from ion pairs, making the above treatment inadequate.

In 60% EtOH the k_{ROH} processes are more important than in TFE. While for (4) $k_{r(An)}^{(27)} \gg k_{Br}^{(27)}, k_{ROH}^{(27)}$, capture by the solvent of the ion (19) is dominant, and from the product ratio, $k_{ROH}^{(19)} : k_{r(Ph)}^{(19)}$ is *ca.* 19. The absence of common ion rate depression for all the compounds, combined with our [Br^-] concentrations gives a maximum value of 40 for the $k_{Br}^{(19)} : k_{ROH}^{(19)}$ ratio, although the actual value may be much lower. The solvent effect on the rearrangement and capture processes can be expressed by the following product of ratios: $[k_{r(Ph)}^{(19)}(TFE)/k_{r(Ph)}^{(19)}(60\%\ EtOH)] \times [k_{ROH}^{(19)}(60\%\ EtOH)/k_{ROH}^{(19)}(TFE)] = 108$. To a first approximation $k_{r(Ph)}^{(19)}$ is mainly determined by the ionisation power, which is close for both solvents. The 108-fold increase in capture over rearrangement in 60% EtOH compared with TFE, is then mainly due to the second term which reflects the much higher nucleophilicity of the aqueous EtOH.

Information regarding the competitive capture of the cationic intermediates by water and ethanol is absent since the ethyl ethers probably hydrolyse to the ketones at our high temperature and long reaction times. This is in contrast with the high stability of the trifluoroethyl ethers under similar conditions.

In AcOH, (4) undergoes complete β-*p*-methoxyphenyl rearrangement,[1] the α-phenyl-β,β-di-(*p*-tolyl)vinyl cation (from the decomposition of the triazene) undergoes partial β-*p*-tolyl migration [9] whereas preliminary experiments with (2) show no β-phenyl migration.[1] Hence, compounds (1)—(4) and the α-phenyl-β,β-di-(*p*-tolyl)-vinyl compound constitute a series where the increased tendency for rearrangement follows the order of migratory aptitudes of the β-aryl groups, and the decreased nucleophilicity of the solvent. TFE is a superior solvent for promoting rearrangement, but the data for comparison between 60% EtOH and AcOH are too limited.

The stabilisation of the positive charge of all members of the series by the α-phenyl group is sufficient to make the participation by the β-substituent unimportant. Our compounds are then at the extreme end of the series $R^3R^2C{=}CR^1X$ (R^1, R^2, R^3 = Me or Ar), where no rearrangement was observed when R^1, R^2, and R^3 are low-activating methyl groups,[4] and the rearrangement with β-phenyl participation [10,11] or partial rearrangement [9-11] occurs when R^1 = Me, R^2 = Me or Ph, but R^3 is a phenyl group.

Conclusions.—Our conclusions regarding the five mechanistic questions which were raised in the Introduction section could be summarised for compounds (1)—(4) as follows.

(a) The initial ionisation does not involve β-aryl participation.

(b) The products are derived from free, open, linear vinyl cations which are selective enough to be involved in capture processes by the solvent, the leaving group, and added nucleophiles, as well as in internal β-aryl migration.

(c) An apparent 'abnormal' order of migratory aptitudes Ph > An may be deduced from the behaviour of the ion (19). This may be an artefact due to the presence of a hidden β-*p*-methoxyphenyl rearrangement, or may be a special feature of the vinylic solvolysis, where the loss in the migrating aryl–double bond conjugation energy exceeds the gain achieved by bridging by the migrating aryl group.

(d) The effects of β-aryl groups on the solvolysis rate are nearly additive.

(e) In TFE, the rearrangement processes in the vinyl cations are dominant, while the ions show an appreciable selectivity between bromide ion and the solvent. In 60% EtOH, the capture processes are dominant for the ion (19), while the rearrangement is the dominant process for the ion (27).

EXPERIMENTAL

M.p.s are uncorrected. I.r. spectra were recorded with a Perkin-Elmer IR 257 instrument, u.v. spectra with a Perkin-Elmer 450 instrument, and mass spectra with a MAT 311 instrument. N.m.r. spectra were recorded with a Varian HA 100 instrument and the chemical shifts are given in δ units downfield from internal tetramethylsilane.

Solvents and Materials.—Commercial 2,2,2-trifluoroethanol was refluxed for 2 h over a mixture of anhydrous $CaSO_4$ and anhydrous K_2CO_3, distilled, and the fraction boiling at 73—74° was used. Ethanol was purified according to Lund and Bjerrum.[50] 60% EtOH (v/v) was prepared by using conductivity water. 2,6-Lutidine was distilled from solid KOH. Triphenylvinyl bromide (1), m.p. 116—118°,[18] and 2,2-bis-*p*-methoxyphenyl-1-phenylvinyl bromide (4), m.p. 111°,[19] were prepared according to Koelsch.[18,19] 1-(*p*-Methoxyphenyl)-2,2-diphenylvinyl bromide (5), m.p. 137—139°, and *cis*- and *trans*-1,2-bis-*p*-methoxyphenyl-2-phenylvinyl bromides, (6a and b), m.p.s 117 and 131°, respectively, were prepared by known procedures.[21,22] *cis*- and *trans*-2-*p*-Methoxyphenyl-1,2-diphenylvinyl bromides (3) and (2) were prepared according to Curtin *et al.*[20] The *cis*-isomer, m.p. 96—98° (lit.,[20] 97—98°), had δ ($CDCl_3$) 3·64 (3H, s, MeO), 6·56 and 6·83 (4H, AA′BB′ q, *J* 9 Hz, An), 7·31 (5H, s, Ph), and 7·24 (5H, m, Ph), *m/e* 367, 365 (84, 86%, *M*), 285 (100, *M* − Br), 270 (14, *M* − Br − Me), 253 (22, *M* − Br − MeO − H), 252 (20), 241 (18), 239 (16), and 165 (12), $\nu_{max.}$ (CCl_4) 1295, 1180, 1155, 1100, 1040, 960, and 590 cm^{-1}. The *trans* isomer, m.p. 118—119° (lit.,[20] 118—119·5°), had δ 3·79 (3H, s, MeO), 6·82—7·34 (14H, m, Ar), and a mass spectrum identical with that of the *cis*-isomer.

[50] H. Lund and J. Bjerrum, *Ber.*, 1931, **64**, 210.

The i.r. spectrum was also identical with that of the *cis*-isomer except for an absorption at 610 cm^{-1} instead of that for (3) at 590 cm^{-1}. *p*-Methoxy-α,α-diphenylacetophenone (10), m.p. 127—128° (lit.,[21] 127—128°), α-*p*-methoxyphenyl-α-phenylacetophenone (11), m.p. 85—86° (lit.,[25] 85—89°), *p*-methoxy-α-*p*-methoxyphenyl-α-phenylacetophenone (15), m.p. 73—75° (lit.,[22] 75°) and α,α-bis-*p*-methoxyphenylacetophenone (16), m.p. 56—58° (lit.,[26] 57—58°) were prepared by known methods.[21,22,25,26] Identification and quantitative evaluation of these ketones were by mass and by n.m.r. spectra and these data are given in Table 5.

2,2,2-*Trifluoroethyl triphenylvinyl ether* (7). Triphenylvinyl bromide (1 g, 3 mmol) in TFE (20 ml) containing 2,6-lutidine (0·74 g, 7·1 mmol) was kept in a sealed ampoule at 140° for 500 h (>96% reaction). The mixture was poured into water (100 ml), the product extracted with ether (50 ml), the extract washed with dilute HCl, then with water, and dried (Na_2SO_4). The solution was filtered through silica gel and the solvent was removed *in vacuo*, giving the ether (7) (0·95 g, 90%), whose n.m.r. and i.r. spectra showed the absence of any ketone. Recrystallisation (aqueous EtOH) afforded *needles*, m.p. 80—82° (Found: 74·45; H, 4·7; F, 15·7. $C_{22}H_{17}F_3O$ requires C, 74·55; H, 4·85; F, 16·1%), $\lambda_{max.}$ (EtOH) 228 (ε 16,700) and 291 nm (11,900), $\nu_{max.}$ (CCl_4) 1290s, 1180br,s, 1100s, 970s, and 615s cm^{-1}, δ ($CDCl_3$): 3·91 (2H, centre of q, *J* 8·5 Hz, CH_2), 7·03 (5H, m, Ph), 7·22 (5H, s, Ph), and 7·29 (5H, s, Ph), *m/e* 354 (54%, *M*), 271 (21, *M* − CH_2CF_3), 243 (54, Ph_3C^+), 228 (11), 165 (100, fluorenyl cation), 105 (14, $PhCO^+$), and 77 (26, Ph^+).

1-p-*Methoxyphenyl*-2,2-*diphenylvinyl* 2,2,2-*trifluoroethyl ether* (8). 1-*p*-Methoxyphenyl-2,2-diphenylvinyl bromide (2 g, 5·4 mmol) in TFE (35 ml) containing 2,6-lutidine (1·86 g, 17·8 mmol) was kept at 110° in a sealed ampoule for 10 h. Water (20 ml) was added and the solution which was kept for 16 h at 0° gave the ether (8) (1·2 g, 57%), m.p. 78—83°, which was pure by n.m.r. spectroscopy. Recrystallisation (aqueous EtOH) gave *needles*, m.p. 86—87° (Found: C, 71·65; H, 4·75; F, 15·1. $C_{23}H_{19}F_3O_2$ requires C, 71·85; H, 5·0; F, 14·85%), $\lambda_{max.}$ (EtOH), 234 (ε 17,700) and 296 nm (15,200) $\nu_{max.}$ (CCl_4) 1280, 1160, 1100, 1035, and 695 (all s) cm^{-1}, δ ($CDCl_3$) 3·71 (3H, s, MeO), 3·89 (2H, centre of q, *J* 8·5 Hz, CH_2), 6·68—7·32 (9H, m, An + Ph), and 7·26 (5H, s, Ph), *m/e* 384 (76%, *M*), 301 (18, *M* − CH_2CF_3), 273 [100, An(Ph)$_2C^+$], 195 (24), 165 (48), 135 (15, $AnCO^+$), and 77 (24, Ph^+).

cis- *and* trans-1,2-*Bis*-p-*methoxyphenyl*-2-*phenylvinyl* 2,2,2-*trifluoroethyl ethers* (14a *and* b). A 73 : 27 mixture of *cis*- and *trans*-1,2-bis-*p*-methoxyphenyl-2-phenylvinyl bromides (2 g, 5·1 mmol) and 2,6-lutidine (1·86 g, 17·8 mmol) in TFE (35 ml) was kept in a sealed ampoule at 130° for 16 h The solution was poured into water, extracted with ether, the extract washed with HCl, then with water, dried ($MgSO_4$), and evaporated, giving an oil (1·8 g, 81%). The n.m.r. spectrum of the oil (200 mg) in $CDCl_3$ (0·5 ml) showed four singlets of equal intensity at δ 3·57, 3·60, 3·62, and 3·68, but their positions were strongly concentration dependent. A shift of all the signals by 0·10—0·15 Hz was found for a sample containing 50 mg of the oil in 0·5 ml of $CDCl_3$. Also observed were two quartets for the CH_2CF_3 groups, centred at δ 3·91 and 3·88 (*J* 8·5 Hz) the positions of which were concentration dependent. The integration of the two quartets was 1 : 1. Very weak signals (<3%) at δ 5·92 and 7·90—8·00 corresponding to (15) were also observed. Repeated crystallisation of the oil from dilute ethanol gave the *isomer* (14b) (400 mg), m.p. 115—117° (Found: C, 69·55; H, 5·05; F, 13·5. $C_{24}H_{21}F_3O_3$ requires C, 69·55; H, 5·1; F, 13·75%), $\nu_{max.}$ (Nujol): 1650(m), 1250, 1170, and 1030 (all s) cm^{-1}, $\lambda_{max.}$ (EtOH) 237 (ε 18,200) and 298 nm (17,500), δ (1M in $CDCl_3$) 3·60 (3H, s, MeO), 3·68 (3H, s, MeO), 3·91 (2H, centre of q, *J* 8·5 Hz, OCH_2CF_3), and 6·58—7·27 (13H, m, Ar), *m/e* 414 (85%, *M*), 331 (77, *M* − CH_2CF_3), 303 (100, An_2CPh^+), 195 (46), 165 (27, fluorenyl cation), 152 (50), and 135 (61, $AnCO^+$). The n.m.r. spectrum showed that this fraction contained *ca.* 20% of the second isomer (14a). Repeated recrystallisation (aqueous EtOH) afforded a second fraction (100 mg) of the *isomer* (14a), m.p. 89—92° (Found: C, 69·2; H, 5·25; F, 14·05%), $\lambda_{max.}$ (EtOH) 238 (ε 17,400) and 299 nm (15,600), $\nu_{max.}$ (Nujol) identical with that of (14b), δ (1M in $CDCl_3$) 3·57 (3H, s, MeO), 3·62 (3H, s, MeO) (both δ values are concentration dependent), 3·88 (2H, centre of q, *J* 8·5 Hz, CH_2), and 6·50—7·40 (13H, m, Ar), *m/e* 414 (95, *M*), 331 (79, *M* − CH_2CF_3), 303 (100, An_2CPh^+), 195 (22), 152 (13), and 137 (17, $AnCO^+$). The n.m.r. spectrum showed the presence of *ca.* 25% of the isomer (14b), but due to the low amount of the material, further purification was not attempted.

Solvolysis of Compounds (2)—(4) *in* 2,2,2-*Trifluoroethanol* —A mixture of (2) (1 g, 2·7 mmol) and 2,6-lutidine (0·74 g 7·1 mmol) in TFE (35 ml) was kept in a sealed ampoule at 140° for 240 h (*ca.* 6 half-lives). The cooled solution was

TABLE 5

N.m.r. and mass spectra of the ketones (10), (11), (15), and (16)

Compound	δ ($CDCl_3$) [a] MeO	CH	An	Ph	*m/e* (relative abundance)
(10)	3·76	5·97	6·84; 7·97	7·25(s)	302(1, *M*), 167(38, Ph_2CH^+), 166(23), 165(44), 152(25),
	3·15 [b]	5·90 [b]	6·54 [b]; 7·96 [b]	7·18(s) [b]	135 (100, $AnCO^+$), 107 (31)
(11)	3·73	5·97	6·84; 7·20	7·25(s), 7·40(3H), 7·99(2H)	302(6, *M*), 197 [100, An(Ph)CH^+], 182(27), 165(45), 153(54), 105 (42, $PhCO^+$)
	3·25 [b]	5·86 [b]	6·66; *ca.* 7·02 [b,c]	7·12(8H), 7·95 (2H)	
(15)	3·67; 3·70	5·92	6·82; 7·18 6·82; 7·97	7·23(s)	332(8, *M*), 197[77, An(Ph)CH^+], 182 (23), 165(37), 153(40), 135(100, $AnCO^+$), 107 (26)
(16)	3·69; 3·69	5·92	6·81; 7·13 6·81; 7·13	7·36(3H); 7·97(2H)	332(2, *M*), 227 (100, An_2CH^+), 212, (27, An_2CH^+ − Me), 184(14), 169(21), 135(22, $AnCO^+$), 105 (21, $PhCO^+$)

Integrations are consistent with the assignments. The MeO and the CH signals are singlets. The An signals are quartets (*J* 8·5 Hz) and the centres of the protons are given. The *o*-protons of the ArCO groups are at the lower field. [b] In C_6D_6. [c] Hidden under the Ph multiplet.

poured into water (100 ml), extracted with ether (100 ml), the extract washed with dilute HCl and water, dried (Na_2SO_4), and evaporated *in vacuo*. The remaining oil (0·9 g, 84%) was (by n.m.r.) a mixture of ethers (8) and (9a and b) in a ratio of 8 : 1 : 1. Isomer (9a) absorbs at δ ($CDCl_3$) 3·66 (3H, s, MeO) and 3·89 (2H, centre of q, *J* 8 Hz, CH_2), and isomer (9b) at δ 3·77 (3H, s, MeO) and 3·92 (2H, centre of q, *J* 8 Hz, CH_2). The aromatic protons of (9a and b) merge.

Repeated crystallisation (aqueous EtOH) gave needles, m.p. 87—88° of pure 1-*p*-methoxyphenyl-2,2-diphenylvinyl 2,2,2-trifluoroethyl ether (8), identical with authentic (8) by mixed m.p., i.r., and n.m.r. spectroscopy. Attempted isolation of (9a and b) by g.l.c. or fractional crystallisation failed, and their structures were deduced by hydrolysis (see below).

A similar solvolysis and work-up of (3) gave a crude reaction mixture with identical i.r. and n.m.r. spectra to those obtained from the *trans*-isomer (2), indicating an identical product distribution.

A mixture of (4) (2 g, 5·1 mmol) and 2,6-lutidine (1·86 g, 17·8 mmol) in TFE (35 ml) was kept in a sealed ampoule at 140° for 93 h (>5 half-lives). Work-up as above gave an oil (1·6 g, 72%) with n.m.r. spectrum identical with that obtained in the solvolysis of (6a and b) which is described later. The two isomers (14a and b) were formed in a 1 : 1 ratio. Crystallisation (aqueous EtOH) afforded crystals (300 mg), m.p. 110—115°, and repeated crystallisation of the residue from the mother liquor gave a second fraction (70 mg) m.p. 89—92°. The two fractions were identical (n.m.r. mixed m.p.) with (14a and b) which were obtained from (6a and b) (see later).

Acid Hydrolysis of the Crude Trifluoroethanolysis Mixtures of Compounds (2)—(4).—A crude solvolysis mixture of (2) in TFE (218 mg) was refluxed in 70% EtOH (v/v) containing 0·7N-HCl (40 ml). The reaction was not complete after 46 h (t.l.c.), but only after 96 h. The mixture was poured into water (200 ml), extracted with ether (2 × 100 ml), the extract washed with dilute aqueous $NaHCO_3$, then with water, dried (Na_2SO_4), and evaporated *in vacuo*. N.m.r. analysis of the remaining oil in C_6D_6 and the data of Table 5 showed that the (10) : (11) ratio is 84 : 16. Crystallisation afforded the major component (10), m.p. 126—128°, mixed m.p. with authentic (10), 126—128°. The minor component (11) could not be isolated in a pure form either by t.l.c. or by fractional crystallisation.

A crude trifluoroethanolysis mixture of (3) (73 mg) was treated similarly as above. The n.m.r. spectrum of the hydrolysis mixture was identical with that obtained from (2), *i.e.* the (10) : (11) ratio is 85 : 15. Crystallisation (EtOH) afforded crystals, m.p. 125—127°, identical (n.m.r., mixed m.p.) with authentic (10).

The oily trifluoroethanolysis mixture of (4) (400 mg) was refluxed for 50 h in 65% EtOH (v/v) containing 1M-HCl (40 ml). After work-up as above the n.m.r. spectrum of the remaining oil (280 mg, 88%) was identical with that of the ketone (15). Repeated crystallisation (MeOH) gave crystals, m.p. and mixed m.p. with authentic (15), 73—75°.

Treatment of the Ketones (10), (11), (15), *and* (16) *with Acid*.—When (10), (11), (15), or (16) (100—200 mg, 0·3—0·6 mmol) was refluxed for 50—96 h in 60% EtOH containing 0·7—1·0M HCl, the n.m.r. spectrum of the crude reaction mixture was identical with that of the starting material, with no evidence for the isomeric ketone. Ketone (15) was also recovered from the reaction of (15).

Solvolysis of Triphenylvinyl Bromide in 60% EtOH.—Triphenylvinyl bromide (134 mg) in 60% EtOH (10 ml) containing 2,6-lutidine (0·1 ml) was kept for 850 h (*ca.* 90% reaction) in a sealed ampoule at 140°. Work-up as above gave an oil whose n.m.r. spectrum [δ ($CDCl_3$) 6·01 (1H, s, CHO), 7·22 (10H, s, 2Ph), 7·24 (3H, m, *m*- and *p*-H in PhCO), and 7·97 (2H, 2 d, *o*-H in PhCO)] was identical with that of authentic α,α-diphenylacetophenone (18).[27] No signal for the vinyl ethyl ether was observed.

Solvolysis of Compounds (2)—(4) *in* 60% EtOH.—A mixture of (2) (146 mg, 0·19 mmol) and 2,6-lutidine (0·1 g, 1 mmol) in 60% EtOH (10 ml) was kept at 140° for 600 h (*ca.* 5 half-lives). The solution was poured into water (50 ml), extracted with ether (50 ml), washed with dilute HCl, then with water, dried (Na_2SO_4), and evaporated. The n.m.r. spectrum of the remaining oil (100 mg) indicated that it consisted of *ca.* 95% of (11) and *ca.* 5% of (10), with no signal for the vinyl ethyl ethers. Crystallisation (EtOH) gave (11) (50 mg), m.p. and mixed m.p. 84—87°.

Solvolysis of the *cis*-isomer (3) and work-up under identical conditions to those described above for (2) gave an oil with an n.m.r. spectrum identical with that from (2). Crystallisation (EtOH) gave (11) (50 mg).

2,6-Lutidine (46 mg, 0·4 mmol) and compound (4) (79 mg, 0·2 mmol) in 60% EtOH (5 ml) were kept in a sealed ampoule at 140° for 350 h. Work-up as described above gave an oil with an n.m.r. identical with that of authentic (15). Crystallisation (MeOH) gave (15) (20 mg), m.p. and mixed m.p. 72—74°.

Solvolysis of Compounds (2) *and* (4) *in TFE containing Sodium Toluene*-p-*thiolate*.—A sealed ampoule containing (2) (73 mg) in TFE (20 ml) containing 0·08M-sodium toluene-*p*-thiolate was kept at 140° for 192 h. The mixture was poured into water, extracted with chloroform (50 ml), washed with dilute NaOH and with water, dried ($MgSO_4$), and evaporated. N.m.r. analysis of the remaining oil showed a 1 : 1 ratio of a methyl singlet at δ 2·09 to a methoxy-singlet at δ 3·57, a two proton doublet (half q of An, *J* 9 Hz) at δ 6·50, and an aromatic multiplet at δ 6·7—7·4 Two singlets at δ 3·61 and 3·72 were also formed and their intensity ratio to the δ 3·57 signal was *ca.* 3 : 7. Crystallisation (EtOH) gave needles, m.p. 148—151°, which solidified and remelted at 163—165°. The compound was identified as the sulphide (12) (lit.,[21] 147—148°) by n.m.r., i.r. [$\nu_{max.}$ (Nujol) 1255, 1175, 1030, 830, and 800 (all s) cm^{-1}], and mass spectra [*m/e* 408 (48%, *M*), 285 (100, *M* − SC_6H_4Me), and 253 (16)], and mixed m.p.

A solution of (4) (79 mg, 0·2 mmol) in TFE (5 ml) containing 0·08M-sodium toluene-*p*-thiolate was kept in a sealed ampoule at 140° for 42 h. Work-up as above afforded an oil with δ 2·13 (3H, s, Me), 3·56, 3·58, 3·62, 3·71 (6H, 4s, of equal intensities, MeO), and 6·40—7·40 (17H, m, Ar), *m/e* 438 (96%, *M*), 439 (89, *M* + H), 316 (90, *M* + H − SC_6H_4Me), 315 (100, *M* − SC_6H_4Me), 300 (24, *M* − Me − SC_6H_4Me), 284 (25, *M* − MeO − SC_6H_4Me), and 269 (25, *M* − MeO − Me − SC_6H_4Me). The n.m.r. spectrum is identical with that of a 1 : 1 mixture of (17a and b) which was obtained previously from the solvolysis of (6a or b) in aqueous EtOH containing sodium toluene-*p*-thiolate.

Kinetic Experiments.—Triarylvinyl bromide was weighed individually into each of six or seven Pyrex ampoules which were prepared according to Grob and Cseh.[34a] A solution of 2,6-lutidine in TFE or in 60% EtOH (5 ml) was added, the cooled (liquid air) ampoule was sealed, introduced into

an oil-bath, shaked to complete dissolution, and withdrawn at a predetermined time. The reaction was followed by potentiometric titration of the bromide ion, using a Radiometer TTTlc automatic titrator. The reactions in the presence of NaOAc or tetra-alkylammonium bromides were followed similarly.

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