of DNBF and DNBZ is of the same order as that of H$^+$ or 2,4-dinitrobenzenediazonium cation.

Experimental Section

4,6-Dinitrobenzofuroxan was prepared by the procedure of Drost,[31] mp 172 °C (lit.[31] mp 172 °C). 4,6-Dinitrobenzofurazan was prepared through reduction of DNBF by triphenylphosphine in xylene,[32,33] mp 131 °C (lit.[32] mp 129–132 °C). 2,5-Dimethylpyrrole, -thiophene, and -furan were commercially available products (Aldrich) which were purified according to standard procedures.

As those formed from other nucleophiles,[1,2b,13,32] the DNBF and DNBZ adducts formed in this work are all very sensitive explosives and extremely difficult to handle under normal conditions. However, we succeeded in isolating the adducts as their potassium salts by adding potassium acetate and methylene chloride to the Me$_2$SO solutions. The red crystals thus obtained did not melt but decomposed at about 180–200 °C with gas evolution. Dissociation of these salts in Me$_2$SO-d_6 gave NMR spectra identical with those recorded in the "in situ" generation of the adducts in their "acid" form. Also, the visible spectra were typical of C-bonded DNBF and DNBF adducts: λ_{max} 500 nm, $\epsilon \simeq 30000$ M^{-1} cm^{-1} in Me$_2$SO.[1,13]

Definitive evidence that the adducts **O-7** and **O-7′** were isolated as the potassium salts comes from mass spectra experiments performed with the FAB (Fast Atomic Bombardment) technique. For instance, we obtain for the parent peaks of **O-7′**: M = 305 (negative ion) and M = 383 (negative ion, 2K$^+$).

^{1}H NMR spectra were recorded on a Varian XL-100-12 WG spectrometer, using the C.W. mode. The temperature of the probe was 31 ± 2 °C. Chemical shifts were measured with Me$_4$Si as an internal reference. The spectrum of **O-7** was also recorded at 400.13 MHz on a Bruker WM 400 spectrometer, using the F.T. mode.

Acknowledgment. We are indebted to Dr Daniel Davoust (Centre de Spectrochimie, Université Pierre et Marie Curie, Paris) for the spectra recorded at 400.13 MHz (Bruker WM 400) and Pr. Patrick G. Farrell (Mc Gill University, Montréal) for helpful comments and discussion. We also thank Mr. Drochon (Rhone Poulenc) for the mass determinations.

Registry No. **NH-5**, 625-84-3; **S-5**, 638-02-8; **O-5**, 625-86-5; **NH-6**, 91949-36-9; **NH-6′**, 91949-37-0; **S-6**, 91949-38-1; **S-6′**, 91949-39-2; **O-7**, 91949-40-5; **O-7′**, 91949-41-6; **8**, 4265-25-2; **9**, 91949-42-7; **9′**, 91949-43-8; DNBF, 5128-28-9; DNBZ, 5128-28-9.

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[31] Drost, P. *Liebigs Ann. Chem.* **1899**, *307*, 49.

[32] Read, R. W.; Spear, R. J.; Norris, W. P. *Aust. J. Chem.* **1983**, *36*, 1227.

[33] Terrier, F.; Soudais, P.; Hlaibi, M.; Chatrousse, A. P. *J. Org. Chem.*, in press.

Solvolytic Rearrangements of 2,2-Dianisyl-1-tolylvinyl Bromide and (*E*)- and (*Z*)-1,2-Dianisyl-2-tolylvinyl Bromide[1]

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The solvolysis of 2,2-dianisyl-1-tolylvinyl bromide (**3-Br**) in AcOH–AgOAc, AcOH–NaOAc, or 2,2,2-trifluoroethanol (TFE)–2,6-lutidine gave complete rearrangement to (*E*)- and (*Z*)-1,2-dianisyl-2-tolylvinyl acetates or 2,2,2-trifluoroethyl ethers, respectively, while a similar solvolysis of **3-Br** in 60% EtOH–2,6-lutidine gave 86% rearranged 1,2-dianisyl-2-tolylethanone and 14% unrearranged 2,2-dianisyl-1-tolylethanone. Solvolyses of 1,2-dianisyl-2-tolylvinyl bromide (**4-Br**) in AcOH–AgOAc, AcOH–NaOAc, TFE–2,6-lutidine, or 60% EtOH–2,6-lutidine all gave structurally unrearranged products derived from the 1,2-dianisyl-2-tolylvinyl cation (**4**). Degenerate rearrangements arising from 1,2-tolyl shifts in cation **4** were observed by using isotopically labeled (*E*,*Z*)-1,2-dianisyl-2-tolyl[2-^{14}C]vinyl bromide ((*E*,*Z*)-**4-Br-2-^{14}*C***) as reactant. Reaction of (*E*,*Z*)-**4-Br-2-^{14}*C*** in AcOH–AgOAc resulted in only about 0.5% scrambling of the label from C-2 to C-1 in the reaction product. For solvolyses of (*E*,*Z*)-**4-Br-2-^{14}*C*** in TFE–2,6-lutidine, without or with the presence of added Et$_4$NBr, extensive scramblings of the label from C-2 to C-1 were observed in both the reaction product and the recovered, unconsumed reactant, indicating the occurrence of repeated cycles of ionizations, 1,2-tolyl shifts, and returns to covalent reactant. At complete reaction, the trifluoroethanolysis of (*E*)- or (*Z*)- or a 1:1 mixture of (*E*)- and (*Z*)-**4-Br-2-^{14}*C*** gave essentially the same extent of scrambling in the reaction product, the mean value being 25.5% scrambling or 51% rearrangement.

Introduction

The solvolytic rearrangement of triarylvinyl bromides and triflates has been extensively studied in recent years.[2] In various investigations, all the degenerate and nondegenerate β-aryl rearrangements which accompany the solvolysis of the eight triarylvinyl substrates with various combinations of *p*-anisyl (An) and phenyl (Ph) groups (listed on p 397, ref 2a) have been studied.[2] Quantitative relationships between the rate of migration of the β-aryl group (k_r) and the capture rate by the solvent (k_{SOH}) or added nucleophiles have been established. An important factor which determines the k_{SOH}/k_r ratios in the triarylvinyl cations is the relative ability of various aryl groups in stabilizing the cations and the bridged transition states for their rearrangements. Consequently, the much higher positive charge stabilizing ability of anisyl compared with phenyl results in a large preference for one reaction route over others. For example, in the solvolysis of 2,2-

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[1] Part 41 of the series "Vinylic Cations from Solvolysis", from the Hebrew University. For Part 40, see: Rappoport, Z.; Fiakpui, C. Y.; Yu, X.-D.; Lee, C. C. *J. Org. Chem.* **1984**, *49*, 570–571. Part 48 of the series "Rearrangement Studies with ^{14}C", from the University of Saskatchewan. For Part 47, see: Lee, C. C.; Obafemi, C. A. *Can. J. Chem.* **1982**, *60*, 2410–2414.

[2] For reviews, see: (a) Stang, P. J.; Rappoport, Z.; Hanack, M., Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979; pp 395–432. (b) Lee, C. C. In "Isotopes in Organic Chemistry"; Buncel, E., Lee, C. C., Eds.; Elsevier: Amsterdam, 1980; Vol. 5, pp 1–44. (c) Shchegalev, A. A.; Kanishchev, M. J. *Russ. Chem Revs.* **1981**, *50*, 553–564.

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dianisyl-1-phenylvinyl bromide (**1**-Br) under various conditions, a complete β-anisyl rearrangement in the 2,2-dianisyl-1-phenylvinyl cation (**1**) to the 1,2-dianisyl-2-phenylvinyl cation (**2**) occurs before capture by the solvent, and only products derived from **2** were formed.[3] This is due to stabilization of both the anisyl-bridged transition state for the rearrangement and the rearranged ion **2** by the anisyl group. In contrast, when the transition state is bridged by phenyl as in the degenerate β-phenyl rearrangement in the 1,2-dianisyl-2-phenylvinyl cation (**2**), the extent of degenerate rearrangement is small or negligible in aqueous EtOH or AcOH.[4]

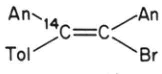
A *p*-tolyl group (Tol) ($\sigma^+(p\text{-CH}_3) = -0.31$)[5] is intermediate between Ph ($\sigma^+(\text{H}) = 0$) and An ($\sigma^+(p\text{-CH}_3\text{O}) = -0.78$)[5] in its delocalizing ability on a positive charge. Consequently, reactions of *p*-tolyl-substituted triarylvinyl cations which are further substituted with phenyl or anisyl groups are of interest for comparison with those of the phenyl/anisyl substituted ions. Some reactions of tolyl-substituted systems have already been studied. The degenerate rearrangements in the tritolylvinyl cations[6a] and the 2-phenyl-1,2-ditolylvinyl cation[6b] were investigated by Lee and co-workers, but reactions of triarylvinyl cations substituted by both tolyl and anisyl groups have not yet been reported. In the present work, we have investigated the solvolysis and rearrangement of three such systems: 2,2-dianisyl-1-tolylvinyl bromide (**3**-Br) and (*E*)- and (*Z*)-1,2-dianisyl-2-tolylvinyl bromides ((*E*)- and (*Z*)-**4**-Br). In order to obtain data on the possibility of degenerate rearrangements in the 1,2-dianisyl-2-tolylvinyl cation (**4**) arising from 1,2-tolyl shifts, studies are also carried out on ^{14}C-labeled (*E*)- and (*Z*)-**4**-Br.

Results

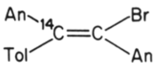
Syntheses and Geometrical Assignments. **3**-Br was prepared by the additions of Br_2 to 1,1-dianisyl-2-tolylethene which was accompanied by a spontaneous dehydrobromination, the triarylethene being obtained from dehydration of the carbinol, $An_2C(OH)CH_2Tol$, formed from a Grignard reaction between dianisyl ketone and (*p*-tolylmethyl)magnesium bromide. Analogous to previous preparations of labeled triarylvinyl bromides,[4b,6] (*E*)- and (*Z*)-1,2-dianisyl-2-tolyl[2-^{14}C]vinyl bromides ((*E*)- and (*Z*)-**4**-Br-*2*-^{14}*C*) were prepared from reaction of carbonyl-labeled desoxyanisoin[4b] with TolMgBr to give An(Tol)^{14}C(OH)CH$_2$An, which was treated with Br_2 in AcOH directly, without the isolation of any triarylethene, to give an approximately 1:2 mixture of (*E*:*Z*)-**4**-Br-*2*-^{14}*C*. Upon crystallization from acetone–methanol, a 1:1 mixture of (*E*)- and (*Z*)-**4**-Br-*2*-^{14}*C* (to be referred to as (*E*,*Z*)-**4**-Br-*2*-^{14}*C*) was recovered as the major fraction and this was utilized in most of the subsequent solvolysis experiments. The pure *E* and *Z* isomers were also obtained by fractional crystallization from 95% ethanol.

$An_2C{=}C(Br)Tol$

3-Br



(*E*)-**4**-Br-*2*-^{14}*C*



(*Z*)-**4**-Br-*2*-^{14}*C*

Table I. Crystallographic Parameters for Compound (*E*)-4-Br[a]

bond	length,[b] Å	bond	length,[b] Å	bond	length,[b] Å
Br–Cl	1.92	C3–C8	1.39	C13–C14	1.37
O1–C6	1.37	C4–C5	1.38	C14–C15	1.35
O1–C9	1.43	C5–C6	1.38	C17–C18	1.40
O2–C13	1.41	C6–C7	1.38	C17–C22	1.41
O2–C16	1.43	C7–C8	1.39	C18–C19	1.41
C1–C2	1.33	C10–C11	1.39	C19–C20	1.38
C1–C3	1.49	C10–C15	1.40	C20–C21	1.37
C2–C10	1.49	C11–C12	1.39	C20–C23	1.54
C2–C17	1.49	C12–C13	1.39	C21–C22	1.35
C3–C4	1.37				

angle	deg[c]	angle	deg[c]
Br–C1–C2	119.5	C2–C10–C15	120.7
Br–C1–C3	112.9	C11–C10–C15	117.9
C2–C1–C3	127.6	C10–C11–C12	121.2
C6–O1–C9	117.0	C11–C12–C13	118.4
C13–O2–C16	115.7	O2–C13–C12	125.6
C1–C2–C10	120.9	O2–C13–C14	113.4
C1–C2–C17	123.1	C12–C13–C14	120.9
C10–C2–C17	115.9	C13–C14–C15	120.0
C1–C3–C4	124.2	C10–C15–C14	121.5
C1–C3–C8	117.6	C2–C17–C18	121.3
C4–C3–C8	118.1	C2–C17–C22	120.9
C3–C4–C5	121.5	C18–C17–C22	117.8
C4–C5–C6	119.7	C17–C18–C19	119.5
O1–C6–C5	115.8	C18–C19–C20	121.3
O1–C6–C7	123.8	C19–C20–C21	117.5
C5–C6–C7	120.4	C19–C20–C23	124.0
C6–C7–C8	118.7	C21–C20–C23	118.5
C3–C8–C7	121.7	C20–C21–C22	123.2
C2–C10–C11	121.4	C17–C22–C21	120.6

[a] Compound (*E*)-**4**-Br crystallized in space group *C*2/*c*. Its unit cell constants are $a = 18.967$ Å, $b = 9.652$ Å, $c = 22.585$ Å and $\beta = 109.55°$. [b] Error, ±0.01 Å. [c] Error, ±0.9°.

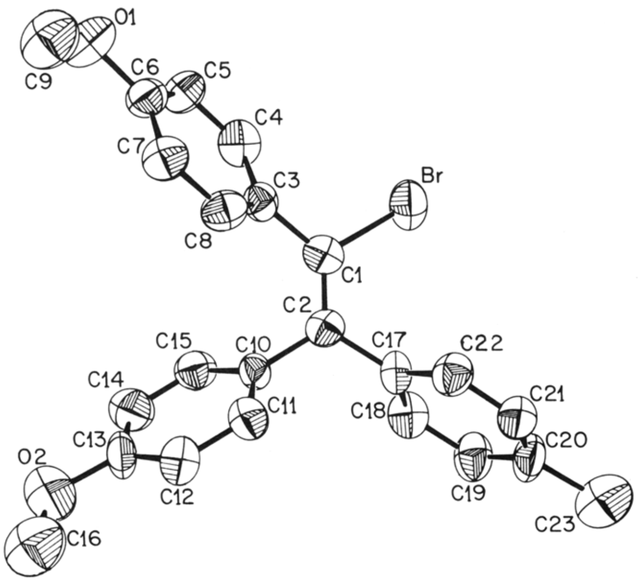


Figure 1. Stereoview of (*E*)-1,2-dianisyl-2-tolylvinyl bromide ((*E*)-**4**-Br).

The same reactions starting with unlabeled desoxyanisoin, of course, gave the unlabelled (*E*)- and (*Z*)-**4**-Br. Neither UV nor IR or mass spectra are useful for the configurational assignment of (*E*)-**4**-Br and (*Z*)-**4**-Br. Similar to the assignment in previously studied (*E*)- and (*Z*)-triarylvinyl bromide pairs,[3b,7] the isomer with a lower melting point was assigned the *E* (cis) configuration. To verify such an assignment, we have determined the structure of the lower melting isomer by X-ray diffraction

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(3) (a) Rappoport, Z.; Gal, A.; Houminer, Y. *Tetrahedron Lett.* **1973**, 641–644. (b) Rappoport, Z.; Houminer, Y. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1506–1518. (c) Rappoport, Z.; Schnabel, I.; Greenzaid, P. *J. Am. Chem. Soc.* **1976**, *98*, 7726–7733. (d) Ikeda, T.; Kobayashi, S.; Taniguchi, H.; Rappoport, Z. *J. Org. Chem.* **1982**, *47*, 1916–1922.

(4) (a) Houminer, Y.; Noy, E.; Rappoport, Z. *J. Am. Chem. Soc.* **1976**, *98*, 5632–5642. (b) Lee, C. C.; Oka, M. *Can. J. Chem.* **1976**, *54*, 604–609.

(5) Exner, O. In "Correlation Analysis in Chemistry"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; pp 439–540.

(6) (a) Lee, C. C.; Paine, A. J.; Ko, E. C. F. *Can. J. Chem.* **1977**, *55*, 2310–2315. (b) Lee, C. C.; Paine, A. J.; Ko, E. C. F. *J. Am. Chem. Soc.* **1977**, *99*, 7267–7277.

(7) Rappoport, Z.; Apeloig, Y. *J. Am. Chem. Soc.* **1969**, *91*, 6734–6742.

Table II. Products from Solvolyses of 2,2-Dianisyl-1-tolylvinyl Bromide (3-Br) and of (*E*)- or (*Z*)-1,2-Dianisyl-2-tolylvinyl Bromide ((*E*)- or (*Z*)-4-Br)

reactant	reactn medium	products
3-Br[a]	AcOH–AgOAc	55 ± 2:45 ± 2 (*E*:*Z*)-**4**-OAc
3-Br[a]	AcOH–NaOAc	55 ± 2:45 ± 2 (*E*:*Z*)-**4**-OAc
(*E*)- or (*Z*)-**4**-Br[b]	AcOH–AgOAc	1:1 (*E*:*Z*)-**4**-OAc
(*E*)- or (*Z*)-**4**-Br[b]	AcOH–NaOAc	1:1 (*E*:*Z*)-**4**-OAc
3-Br[c]	60% EtOH–2,6-lutidine	86 ± 2:14 ± 2 **5**:**6**
(*E*)- or (*Z*)-**4**-Br[d]	60% EtOH–2,6-lutidine	**5**
3-Br[e]	TFE–2,6-lutidine	1:1 (*E*:*Z*)-**4**-OTFE
(*E*)- or (*Z*)-**4**-Br[e]	TFE–2,6-lutidine	1:1 (*E*:*Z*)-**4**-OTFE

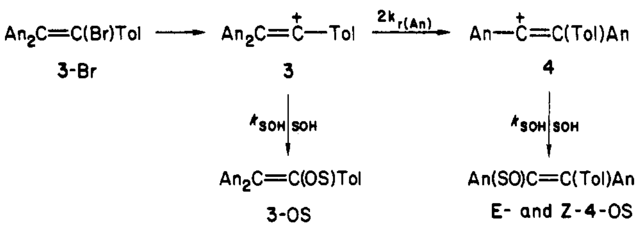
[a] Solvolysis of 20 mM **3**-Br in AcOH containing 1.2 equiv of AgOAc or 2.5 equiv of NaOAc at 140 °C for 24 or 90 h, respectively. Solvolysis of **3**-Br in AcOH alone failed and the solution turned black; solvolysis of **3**-Br in AcOH containing 0.25, 0.50, or 2.5 equiv of NaOAc gave 40%, 50%, or 75% yields of the rearranged products, (*E*)- and (*Z*)-**4**-OAc. [b] Solvolysis of 15 mM (*E*)- or (*Z*)-**4**-Br in AcOH containing 1.1 equiv of AgOAc or NaOAc at 120 °C for 2 or 48 h, respectively. [c] Solvolysis of 34 mM **3**-Br in 60% EtOH containing 2.0 equiv of 2,6-lutidine at 140 °C for 96–161 h gave an average value of 86% ± 2% of the rearranged An(Tol)CHCOAn (**5**) and 14% ± 2% of the unrearranged $An_2CHCOTol$ (**6**). [d] Solvolysis of 34 mM (*E*)- or (*Z*)-**4**-Br in 60% EtOH containing 2.0 equiv of 2,6-lutidine at 140 °C for 24 h. [e] Solvolysis of **3**-Br or (*E*)- or (*Z*)-**4**-Br in TFE containing 2.0 equiv of 2,6-lutidine at 120–140 °C for 8–70 h gave an essentially 1:1 mixture of (*E*)- and (*Z*)-1,2-dianisyl-2-tolylvinyl 2,2,2-trifluoroethyl ethers (*E*)- and (*Z*)-**4**-OTFE); in some experiments, a small amount (<5%) of ketone **5** was detected.

crystallography and found it indeed to be the *E* isomer. The bond lengths and angles are given in Table I together with the atomic notations. A stereoview of (*E*)-**4**-Br is given in Figure 1.

Solvolyses of 3-Br and (*E*)- or (*Z*)-4-Br. Solvolyses of **3**-Br or the unlabeled (*E*)- or (*Z*)-**4**-Br were carried out in AcOH containing AgOAc or NaOAc, in 60% ethanol containing 2,6-lutidine, and in 2,2,2-trifluoroethanol (TFE)–2,6-lutidine. The products were estimated by NMR and the results are summarized in Table II. For example, in the acetolyses, the products obtained were a mixture of (*E*)- and (*Z*)-1,2-dianisyl-2-tolylvinyl acetates ((*E*)- and (*Z*)-**4**-OAc), the lower melting isomer being assigned the *E* configuration by analogy with the findings for (*E*)- and (*Z*)-**4**-Br. The *E*:*Z* ratios were estimated by the relative NMR peak intensities for the acetoxy protons at δ 1.88 and 1.85 and for the tolyl methyl protons at δ 2.25 and 2.32. As another example, in the solvolysis of **3**-Br in 60% EtOH, NMR analysis showed that the major product (86% ± 2%) was the rearranged An(Tol)CHCOAn (**5**) with about 14% unrearranged $An_2CHCOTol$ (**6**). The mass spectrum of the product mixture also confirmed the extensive rearrangement to **5** as indicated by major signals at *m/z* 135 ($AnCO^+$) and 211 ($An(Tol)CH^+$) with peaks of lower intensities at *m/z* 119 ($TolCO^+$) and 227 (An_2CH^+).

Degenerate Rearrangements in Solvolyses of (*E*)- and (*Z*)-4-Br-*2*-^{14}*C*. When (*E*,*Z*)-**4**-Br-2-^{14}C was solvolyzed in AcOH containing either 1.1 or 10 mol equiv of NaOAc at 120 °C for 48 h, the product obtained was a 1:1 mixture of (*E*)- and (*Z*)-**4**-OAc-*2*-^{14}C with no scrambling of the ^{14}C label. For the solvolysis in AcOH containing 1.1 equiv of AgOAc at 120 °C for 2 h, a mean value of 0.5% scrambling of the ^{14}C label from C-2 to C-1 was obtained from triplicate runs. The extents of scrambling were determined by the degradation of the product, (*E*)- and (*Z*)-**4**-OAc-^{14}C, by ozonolysis to give anisyl tolyl ketone (**7**) which was converted to its oxime. Upon repeated recrystallizations until a constant specific activity was obtained, the difference between the specific activities of the oxime and the (*E*)- and (*Z*)-**4**-OAc-^{14}C gave the amount of ^{14}C that has rearranged from C-2 to C-1.

Scheme I



Trifluoroethanolyses of (*E*,*Z*)-**4**-Br-2-^{14}C were carried out in sealed tubes at 120 °C in the presence of 2.0 equiv of 2,6-lutidine and without or with the presence of various amounts of added Et_4NBr. The reactions were stopped at different stages of completion and the extents of scrambling of the ^{14}C label from C-2 to C-1 in the reaction products, a 1:1 mixture of vinyl ethers (*E*)- and (*Z*)-**4**-OTFE-^{14}C, and in the unconsumed reactants, (*E*,*Z*)-**4**-Br-^{14}C, were determined. While a direct separation of the product ethers and the unreacted bromides was not possible, it was found that (*E*,*Z*)-**4**-OTFE-^{14}C could be separated from (*E*,*Z*)-**4**-OAc-^{14}C through an alumina column with CH_2Cl_2/petroleum ether as eluant. Since it has already been shown that (*E*,*Z*)-**4**-Br-*2*-^{14}C could be converted to the acetate without scrambling when treated with AcOH–NaOAc, the reaction mixture from a trifluoroethanolysis was treated with AcOH containing an excess of NaOAc and the resulting (*E*,*Z*)-**4**-OAc-^{14}C derived from the unconsumed (*E*,*Z*)-**4**-Br-^{14}C was separated from the original reaction product, (*E*,*Z*)-**4**-OTFE-^{14}C, by column chromatography. Ozonolysis of the separated ether product or the acetate from the unconsumed reactant gave samples of anisyl tolyl ketone (**7**) and hence the extents of scrambling upon comparison of the specific activities of the oxime of **7** and the ether or acetate from which **7** was obtained. The results are summarized in Table III.

Discussion

Rearrangements in the Solvolysis of 3-Br. The rearrangement processes arising from the solvolysis of **3**-Br are given in Scheme I. Assuming that **3** → **4** is practically irreversible, which is reasonable since no **3**-OS has been observed in the solvolysis of (*E*)- and (*Z*)-**4**-Br. Consequently, eq 1 can be derived for cation **3**.

$$k_{\mathrm{SOH}}/k_{r(\mathrm{An})} = 2[\mathbf{3}\text{-OS}]/[[(E)\text{-}\mathbf{4}\text{-OS}] + [(Z)\text{-}\mathbf{4}\text{-OS}]] \qquad (1)$$

The observed extent of β-anisyl rearrangement in the solvolysis of **3**-Br, and hence in ion **3**, was found to be solvent dependent. In AcOH containing AgOAc or NaOAc or in TFE–2,6-lutidine, only the two rearranged (*E*)- and (*Z*)-**4**-OAc or (*E*)- and (*Z*)-**4**-OTFE, respectively, were obtained. No detectable amount of unrearranged **3**-OAc or **3**-OTFE was found. Since ^1H NMR could detect 2% of the unrearranged product, **3**-OS, in the presence of a large excess of (*E*)- and (*Z*)-**4**-OS, for ion **3** from the acetolysis of trifluoroethanolysis of **3**-Br, according to eq 1, $k_{\mathrm{SOH}}/k_{r(\mathrm{An})}$ would be <0.04. In the solvolysis of **3**-Br in 60% EtOH, the major product was the rearranged ketone **5**, formed together with 14% ± 2% of the unrearranged ketone **6**. Applying eq 1, $k_{\mathrm{SOH}}/k_{r(\mathrm{An})}$ for ion **3** from solvolysis of **3**-Br in 60% EtOH would be 0.32 ± 0.05. The

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(8) Lee, C. C.; Ko, E. C. F.; Rappoport, Z. *Can. J. Chem.* **1980**, *58*, 884–888.

Table III. Isotopic Scrambling Data from Trifluoroethanolyses of 15 mM (*E*,*Z*)-4-Br-2-^{14}C at 120 ± 2 °C in the Presence of 2.0 Equiv of 2,6-Lutidine and with or without Added Et_4NBr

					scrambling from C-2 to C-1, %	
expt	[RX],[a] mM	[Et_4NBr], mM	reactn time, min	% reactn[b]	product	recovered reactant
1	15.3		14	28	8.9	9.7
2	15.3		14	28	9.0	9.0
3	15.1		17	51	14.0	20.9
4	15.1		17	51	14.2	20.8
5	15.0		20	62	19.8	31.5
6	15.0		20	63	19.4	30.8
7	15.1		35	81	21.4	39.8
8	15.1		35	80	22.0	39.1
9	15.2		1440	88	23.3	
10	15.2		1440	88	23.5	
11	15.4		2880	99	25.8	
12	15.4		2880	98	24.8	
13	15.2[c]		2880	98	25.7	
14	15.2[d]		2880	97	25.6	
15	15.1	15.4	28	53	14.9	28.3
16	15.1	15.3	28	53	15.4	28.6
17	15.2	30.7	1440	99	26.1	
18	15.2	30.5	1440	95	26.2	
19	15.2	76.2	52	56	14.2	29.9
20	15.2	76.2	52	56	13.2	29.5
21	15.3	76.9	180	91	22.4	
22	15.2	76.9	180	91	21.4	
23	15.2	76.2	2880	98	22.9	
24	15.2	76.2	2880	99	24.2	
25	15.2	152.0	60	57	14.9	24.0
26	15.2	152.1	60	57	11.4	23.9
27	15.2	152.1	1440	92	24.5	
28	15.2	152.1	1440	92	20.1	

[a] RX is a 1:1 mixture of (*E*)- and (*Z*)-1,2-dianisyl-2-tolyl[2-^{14}C]vinyl bromides ((*E*,*Z*)-4-Br-2-^{14}C). [b] Measured by titration of the liberated bromide ion. [c] Pure (*E*)-4-Br-2-^{14}C. [d] Pure (*Z*)-4-Br-2-^{14}C.

k_{SOH} term should increase on increasing the solvent nucleophilicity, and 60% EtOH is the most nucleophilic of the three solvents studied.[9] The rearrangement process leads to a charge dispersal in the transition state and k_r should, therefore, be decreased on increasing solvent polarity. Hence the k_r value should be lowest in 60% EtOH and $k_{SOH}/k_{r(An)}$ is thus higher for reaction in 60% EtOH than for acetolysis or trifluoroethanolysis.

Comparisons of the extents of rearrangement for the three 2,2-dianisyl-1-arylvinyl cations (eq 2) are of interest.

$$\mathrm{An_2C{=}\overset{+}{C}\text{-}Ar} \xrightarrow{2k_{r(\mathrm{An})}} \mathrm{An(Ar)C{=}\overset{+}{C}\text{-}An} \qquad (2)$$

1, Ar = Ph **2**, Ar = Ph
3, Ar = Tol **4**, Ar = Tol
8, Ar = An **8**, Ar = An

When Ar(aryl) = Ph, the **1** → **2** rearrangement is complete before solvent capture in all the solvents studied (i.e., $k_{SOH}/k_{r(An)} < 0.02$).[3] In contrast, when Ar = An, the $\mathbf{8} \rightleftarrows \mathbf{8}$ rearrangement is degenerate and is complete only in TFE–2,6-lutidine, incomplete but extensive (35% ± 2%) in AcOH–NaOAc, and appreciable (11% ± 2%) in buffered 60% EtOH,[4a] with corresponding $k_{SOH}/k_{r(An)}$ values of <0.08, 5.5, and 23, respectively.[4a,8] As expected, ion **3** (Ar = Tol) occupies an intermediate position. The **3** → **4** rearrangement is complete in TFE and AcOH, but incomplete, although extensive, in 60% EtOH. Since the migrating group in **1**, **3**, and **8** is identical, the relative order for $k_{SOH}/k_{r(An)}$ of **1** < **3** < **8** may reflect either a decreased k_r or an increased k_{SOH} as the stability of the cation is increased. Since it is expected that a more stable cation (e.g., **8**) will be less electrophilic than a less stable one (e.g., **3** or **1**), the k_{SOH} value should be lower for the more stable ion. Hence, the k_r term is likely to be responsible for the observed trend and the results are best explained by a lower $k_{r(An)}$ for the more stable ion.

The formation of a 1:1 mixture of (*E*)- and (*Z*)-**4**-OAc or **4**-OTFE from the acetolysis or trifluoroethanolysis, respectively, or **3**-Br and of (*E*)- or (*Z*)-**4**-Br suggests that free, linear vinyl cations are involved as reaction intermediates. In a previous extensive analysis,[10] it was shown that capture of a *free* β,β-disubstituted vinyl cation will lead to ca. 1:1 *E*/*Z* products if the steric bulk of the β-substituents is nearly identical. Since this is the case with anisyl and tolyl groups, the stereochemistry of these reactions, therefore, indicates no neighboring group participation in the transition state nor any product formation from an ion pair whose anionic part is preferentially located on one side of the vacant cationic orbital.

Degenerate Rearrangements in the Solvolysis of (*E*)- and (*Z*)-4-Br-*2*-^{14}C. About 0.5% scrambling of the ^{14}C label from C-2 to C-1 was found for the reaction of (*E*,*Z*)-4-Br-2-^{14}C in AcOH–AgOAc. Since this reaction was carried to completion, eq 3 holds.[8] If eq 3 is applied to

$$[\text{unrearranged product}]/[\text{rearranged product}] = 1 + (k_{SOH}/k_r) \qquad (3)$$

the reaction of (*E*,*Z*)-4-Br-2-^{14}C in AcOH–AgOAc with 0.5% scrambling, $k_{SOH}/k_{r(Tol)} = 198$. A comparison can be made with the reaction of trianisyl[2-^{13}C]vinyl bromide (**8**-Br-2-^{13}C) with AcOH–AgOAc. In these two systems, the migration origin and migration terminus are the same while the migrating groups are different, thus allowing for an estimate of the relative migratory aptitudes for the two migrating groups.[6b,8] For **8**-Br-2-^{13}C, reaction with AcOH–AgOAc gave 20% scrambling of the label from C-2 to

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(9) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667–7674.

(10) Reference 2a, pp 355–391.

Table IV. Percentage Distribution among Rearranged and Unrearranged Product and Rearranged and Unrearranged Reactant

		scrambling, %[a]		distribution, %			
				product		reactant	
expt[a]	% reactn[a]	product	recovered reactant	rearranged	unrearranged	rearranged	unrearranged
1	28	8.9	9.7	2.5	25.5	7.0	65.0
2	28	9.0	9.0	2.5	25.5	6.5	65.5
3	51	14.0	20.9	7.1	43.9	10.2	38.8
4	51	14.2	20.8	7.2	43.8	10.2	38.8
5	62	19.8	31.5	12.3	49.7	12.0	26.0
6	63	19.4	30.8	12.2	50.8	11.4	25.6
7	81	21.4	39.8	17.3	63.7	7.6	11.4
8	80	22.0	39.1	17.6	62.4	7.8	12.2
15	53	14.9	28.3	8.0	45.0	13.3	33.7
16	53	15.4	28.6	8.2	44.8	13.4	33.6
19	56	14.2	29.9	8.0	48.0	13.2	30.8
20	56	13.2	29.5	7.4	48.6	13.0	31.0
25	57	14.9	24.0	8.5	48.5	10.3	32.7
26	57	11.4	23.9	6.5	50.5	10.3	32.7

[a] From Table III.

C-1,[11] with $k_{SOH}/k_{r(An)} = 6.0$.[8] Since $k_{SOH}/k_{r(Tol)}$ from the reaction of (*E,Z*)-4-Br-2-^{14}C with AcOH–AgOAc is 198, if one assumes that k_{SOH} for the two reactions, i.e., the solvent capture of ion **4** and of ion **9**, were the same, the migratory ratio for An:Tol may then be calculated:

$$(k_{SOH}/k_{r(Tol)})/(k_{SOH}/k_{r(An)}) = k_{r(An)}/k_{r(Tol)} = 198/6.0 = 33$$

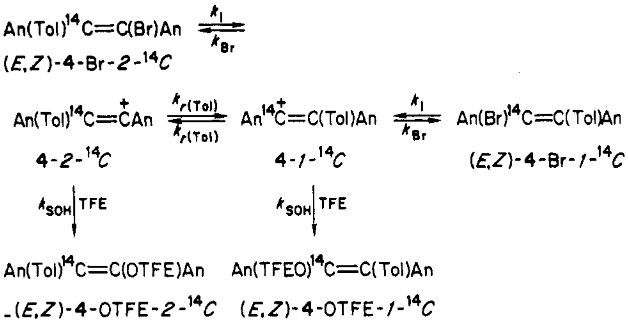
In a previous estimate with data from reactions in AcOH–AgOAc, the relative migratory ratios for Ph:Tol:An in triarylvinyl cationic systems were found to be 1:5:162,[8] i.e., the An:Tol ratio was 162/5 = 32, in remarkable agreement with the present finding.

In the solvolysis of (*E,Z*)-4-Br-2-^{14}C in TFE–2,6-lutidine, as recorded in Table III, extensive scramblings of the label from C-2 to C-1 in both the reaction product and recovered reactant are observed. The β-tolyl rearrangement ($k_{r(Tol)}$), therefore, competes effectively with capture of the vinyl cation by the solvent (k_{SOH}). The scramblings in the recovered reactant also indicate that return processes must have occurred during the reaction as depicted in Scheme II.

The extents of reaction at different reaction times shown in Table III also indicate qualitatively that the presence of added Et_4NBr decreases the reaction rate, in spite of the expected rate increase due to a normal salt effect, thus suggesting the occurrence of a common ion rate depression.[12] While extensive kinetic studies have not been carried out in the present work, it was found that the solvolysis of 15 mM of (*E,Z*)-4-Br in TFE–2,6-lutidine at 120 ± 0.2 °C gave an initial rate constant of $(1.40 \pm 0.02) \times 10^{-3}$ s^{-1}, with the rate falling off significantly after only about 25% reaction, in agreement with the occurrence of extensive returns. In the same solvolysis carried out in the presence of 5.5 mol equiv of added Et_4NBr, the initial rate constant was decreased to $(0.43 \pm 0.02) \times 10^{-3}$ s^{-1}, in confirmation of a common ion rate depression, showing that the solvolytically generated ion **4** is a free cation which is captured both by the solvent to give product and by Br^- ion to return to covalent reactant.

It is of interest to note that in almost all the experiments in which the scramblings in both the product and recovered reactant are determined, the extent of scrambling in the recovered reactant is higher than in the corresponding reaction product (Table III). These results are consistant with a high selectivity for cation **4** in which the rate constant for capture by Br^- ion (k_{Br}) is higher than k_{SOH} for capture by TFE. From the extent of reaction and the percent of scramblings in the product and in the recovered reactant, a percent distribution for the rearranged and unrearranged product and the rearranged and unrearranged reactant can be calculated. For example, in experiment 1 (Table III), after 28% reaction, the scramblings in the product and recovered reactant are 8.9% and 9.7%, respectively. Thus of the 28% product, there are 28 × (8.9/100) = 2.5% rearranged product and 28 − 2.5 = 25.5% unrearranged product. Similarly, of the 72% unconsumed reactant, there are 72 × (9.7/100) = 7.0% rearranged reactant and 72 − 7.0 = 65.0% unrearranged reactant. Similar calculations can be made on all the experiments for which the scramblings in the product and in the recovered reactant have been measured and the results are given in Table IV.

Scheme II



As shown in Scheme II, as the reaction proceeds, there should be repeated cycles of ionization, β-tolyl rearrangement, and return to rearranged and unrearranged reactant by capture of the rearranged and unrearranged cations by Br^- ions. Part of the rearranted and unrearranged cations are, of course, also captured by solvent to give rearranged and unrearranged product. From Table IV, it is seen that after 28% reaction (experiments 1 and 2), there are present in the reaction mixture 6.5–7.0% rearranged reactant and only 2.5% rearranged product. Even after 51% reaction (experiments 3 and 4), there are more rearranged reactant than rearranged product. These results are clearly consistent with a higher value for k_{Br} than k_{SOH}. At the later stages of reaction, the amount of unconsumed reactant falls below 50% and the number of

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[11] Lee, C. C.; Oka, M. *Can. J. Chem.* **1975**, *53*, 320–325.

[12] Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. In "Ions and Ion Pairs in Organic Reactions"; Szwarc, M., Ed.; Wiley: New York, 1974; Vol. 2, pp 247–373.

rearranged reactant molecules will eventually become less than the number of rearranged product molecules. For example, after 80–81% reaction (experiments 7 and 8), there are only 7.6–7.8% rearranged reactant and 17.3–17.6% rearranged product in the reaction mixture. However, the proportion of rearranged reactant to the total amount of unconsumed reactant (i.e., percent of scrambling in the recovered reactant) is much higher than the proportion of rearranged product to the total amount of product (i.e., percent of scrambling in the product), again indicating the relatively greater accumulation of rearranged reactant due to the higher value for k_{Br}.

After complete reaction, the β-tolyl rearrangement in the trifluoroethanolysis of (*E,Z*)-4-Br-2-^{14}C is about 51 ± 1% (100% rearrangement gives 50% scrambling) ($k_{SOH}/k_{r(Tol)} = 1.9$, experiments 11–14, Table III). Using *p*-[$^2H_3$]-methoxyphenyl at C-2 as label and with analysis by NMR, Houminer, Noy, and Rappoport[4a] have shown that the solvolysis in TFE-2,6-lutidine of 1,2-dianisyl-2-phenylvinyl bromide (**2-Br**) or trianisylvinyl bromide (**8-Br**) gave 53% ± 6% β-phenyl rearrangement ($k_{SOH}/k_{r(Ph)} = 1.8$) or 100% ± 3% β-anisyl rearrangement ($k_{SOH}/k_{r(An)} < 0.06$), respectively. These results indicate that in trifluoroethanolysis, cations **2**, **4**, and **8**, in which the migration origin and migration terminus are the same, show migratory aptitudes for the migrating groups with the order of An > Ph ≃ Tol. The near equality for the migratory aptitudes of Ph and Tol is quite surprising. A somewhat similar order of relative migratory ratios has been reported by Burr and Ciereszko[13] for the internal competition of migrating Ar and Ph in the acid-catalyzed rearrangement of $Ph(Ar)^{14}CHCH_2OH$, for which the migratory ratios for Ph:Tol:An were about 1:2:21. In this case, the Ph:Tol ratio is still 1:2. In view of the probability that the errors involved in determining the extent of rearrangement with D label and NMR may be fairly large,[4a] we feel that for a better understanding of the migratory aptitudes for ions **2**, **4**, and **8** in TFE, a more accurate evaluation of the $k_{SOH}/k_{r(Ph)}$ ratio for ion **2** in TFE is needed before further discussion.

Besides comparing systems such as cations **2**, **4**, and **8** with the same migration origin and migration terminus, the degenerate β-tolyl rearrangement in **4** may also be compared with the degenerate β-tolyl rearrangement in the tritolylvinyl cation (**9**). The only data available for such a comparison are from reactions with AcOH–AgOAc. In the reaction of tritolyl[2-^{13}C]vinyl bromide (**9**-Br-2-^{13}C) with AcOH–AgOAc, 13–14% scrambling of the label from C-2 to C-1 was observed (27% ± 1% rearrangement, $k_{SOH}/k_{r(Tol)} = 11$),[6a] and this result may be compared with the present finding for the reaction of (*E,Z*)-4-Br-2-^{14}C in AcOH–AgOAc which gave only 0.5% scrambling (about 1% rearrangement, $k_{SOH}/k_{r(Tol)} = 198$). Thus β-tolyl migration between anisyl-substituted migration origin and migration terminus is much less favorable than between tolyl-substituted migration origin and migration terminus. A similar trend for β-phenyl migration has also been discussed for reactions of C-2-labeled triphenylvinyl, 2-phenyl-1,2-ditolylvinyl, and 1,2-dianisyl-2-phenylvinyl bromides with AcOH–AgOAc.[6b] In all of these cases, the more stable the cation the less is the extent of scrambling and the greater is the value for k_{SOH}/k_r. Since a more stable cation is expected to have a lower k_{SOH}, to account for the observed trend, the predominant effect must again be attributed to a lower k_r for the more stable cation. With **9** and **4**, for example, k_{SOH} is lower for **4** than for **9**, but the difference between the k_{SOH} values, the rates of capture of **4** and **9** in AcOH–AgOAc, may not be very large, while $k_{r(Tol)}$ may be much lower for **4** than for **9**, thus giving the observed result of a higher $k_{SOH}/k_{r(Tol)}$, or lesser amount of rearrangement, for ion **4** than ion **9**.

Experimental Section

The melting points are uncorrected. The NMR spectra were obtained with a T-60 or HA-100 spectrometer, and the mass spectra with a MAT-311 instrument. The ^{14}C activities were measured with a liquid scintillation counter.

1,1-Dianisyl-2-tolylethanol (10). A Grignard reagent was prepared from 70 g (0.38 mol) of *p*-methylbenzyl bromide and 41 g (1.7 mol) of Mg in 380 mL of dry tetrahydrofuran (THF). The filtered solution was added slowly to a solution of 9.0 g (0.037 mol) of dianisyl ketone in 90 mL of dry THF. The mixture was refluxed for 2 h, poured into ice-cooled 0.2 M aqueous NH_4Cl (1.0 L), extracted with $CHCl_3$ (3 × 100 mL), and then dried over $MgSO_4$. After removal of the solvent by evaporation, the NMR spectrum of the oil obtained showed the presence of **10** and 1,2-ditolylethane. Upon addition of petroleum ether to the residual oil, 12.0 g (93%) of **10** crystallized: ^{1}H NMR $\delta(CDCl_3)$ 2.27 (1 H, s, OH, disappears in D_2O), 2.29 (3 H, s, CH_3), 3.56 (2 H, s, CH_2), 3.75 (6 H, s, CH_3O), 6.83, 7.37 (8 H, centers of A and B protons of q, An), 6.90 (4 H, center of m, Tol).

After the removal of **10**, evaporation of the petroleum ether and crystallization of the residue from methanol gave 4.0 g of 1,2-ditolylethane (presumably from dimerization during the Grignard preparation): ^{1}H NMR δ ($CDCl_3$) 2.28 (6 H, s, CH_3), 2.83 (4 H, s, CH_2), 7.07 (8 H, s, Tol). When 0.037 mol of dianisyl ketone was treated with the Grignard reagent prepared from 0.037 mol of *p*-methylbenzyl bromide, only a 35% yield of **10** was obtained.

1,1-Dianisyl-2-tolylethene (11). The alcohol **10** (12.0 g, 34.5 mmol) was refluxed for 1 h in 10% H_2SO_4 (150 mL) to give, after workup, 11.0 g (96%) of **11** as an oil. It had a similar NMR spectrum as that for **11** obtained by an alternative method as described below.

In an alternative method, to a Grignard solution prepared from 37.5 g (200 mmol) of *p*-methoxybromobenzene and 4.8 g (200 mmol) of Mg in 200 mL of dry ether a solution of 11.0 g (62 mmol) of ethyl *p*-methylphenylacetate in 50 mL of dry ether was added under reflux and over a period of 30 min. The resulting mixture was refluxed for an additional 2 h, cooled, and then poured into 500 mL of ice–H_2O containing HCl. The organic layer was separated, washed with H_2O, and dried ($MgSO_4$), and then the solvent was removed by distillation. The residual oil was crystallized from 2-propyl alcohol to give 13.0 g (64%) of **11**, mp 86 °C: ^{1}H NMR $\delta(CCl_4)$ 2.17 (3 H, s, CH_3), 3.73, 3.77 (6 H, 2 s, CH_3O), 6.63–7.27 (13 H, m, Ar + olefinic H). Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.64; H, 6.67. Calcd for $C_{23}H_{22}O_2H_2O$: C, 79.31; H, 6.89. Found: C, 79.37; H, 6.79.

2,2-Dianisyl-1-tolylvinyl Bromide (3-Br). To a stirred solution of 9.0 g (27 mmol) of olefin **11** in 50 mL of glacial acetic acid was added a solution of 4.3 g (27 mmol) of Br_2 in 30 mL of glacial acetic acid and the mixture was stirred at room temperature for 2 h. About one-half of the solvent was distilled off and H_2O was added until turbidity was observed. The oil obtained was crystallized from methanol, giving 10.0 g (90%) of yellow crystals of **3-Br**, mp 108–109 °C: ^{1}H NMR $\delta(CCl_4)$ 2.30 (3 H, s, CH_3), 3.66 3.78 (6 H, 2 s, CH_3O), 6.46–7.33 (12 H, m, Ar). Anal. Calcd for $C_{23}H_{21}O_2Br$: C, 67.48; H, 5.17; Br, 19.53. Found: C, 67.54; H, 4.97; Br, 19.42.

1,2-Dianisyl-1-tolyl[1-^{14}C]ethanol (12-*1*-^{14}C). To a Grignard solution prepared from 13.5 g (78.9 mmol) of *p*-bromotoluene and 4.5 g (185 mmol) of Mg in 300 mL of dry THF, and cooled in an ice bath, was added dropwise and with stirring over a period of 1.5 h a solution of 10.0 g (39.0 mmol) of 1,2-dianisyl[1-^{14}C]ethanone (carbonyl-labeled desoxyanisoin[4b]) in 150 mL of dry THF. The resulting material was stirred at room temperature for 1 h, refluxed for 2 h, and then poured into 200 mL of H_2O containing 25 g of NH_4Cl and 5 mL of NH_4OH. The organic layer was separated and washed with H_2O (3 × 25 mL). After drying over $MgSO_4$, the solvent was evaporated off to give 10.0 g (74%) of **12**-*1*-^{14}C which was crystallized from acetone–methanol, mp 103–104 °C.

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[13] Burr, J. G., Jr.; Ciereszko, L. S. *J. Am. Chem. Soc.* **1952**, *74*, 5426–5430.

The unlabeled **12** was prepared in the same way by using ordinary desoxyanisoin: ^{1}H NMR δ ($CDCl_3$) 2.26 (should, OH), 2.30 (4 H, s, CH_3 + OH), 3.50 (2 H, s, CH_2), 3.66, 3.72 (6 H, 2 s, CH_3O), 6.60–7.40 (12 H, m, Ar). Anal. Calcd for $C_{23}H_{24}O_3$: C, 79.28; H, 6.94. Found: C, 79.14; H, 6.66.

(*E*)- and (*Z*)-1,2-Dianisyl-2-tolyl[2-^{14}C]vinyl Bromide ((*E*)- and (*Z*)-4-Br-*2*-^{14}*C*). To a solution of 10.0 g (28.7 mmol) of **12**-*1*-^{14}C in 150 mL of AcOH was added dropwise and with stirring 4.60 g (28.8 mmole) of Br_2 over a period of 0.5 h. During this period, the reaction mixture was maintained at below 50 °C by cooling in an ice bath when necessary. The resulting mixture was stirred at room temperature for about 5 h when crystals of the product were formed. After standing overnight, the crystals were collected by filtration and washed with a 10% solution of $Na_2S_2O_3$ and with water. The yield of product was 9.0 g (76%), consisting of an approximately 1:2 mixture of (*E*)- and (*Z*)-**4**-Br-*2*-^{14}C. After recrystallization from acetone–methanol, the major fraction obtained was a 1:1 mixture of (*E*)- and (*Z*)-**4**-Br-*2*-^{14}C.

The unlabeled (*E*)- and (*Z*)-**4**-Br was prepared in the same way by using the unlabeled **12**. The two isomers were then separated by fractional crystallization from 95% ethanol, with the *Z* isomer crystallizing first when a dilute solution of the *E* and *Z* mixture was allowed to evaporate slowly at room temperature. The *E* isomer was obtained from the mother liquor after the removal of the *Z* isomer. The pure (*Z*)-**4**-Br melted at 120–121 °C: ^{1}H NMR δ ($CDCl_3$) 2.17 (3 H, s, CH_3), 3.70, 3.79 (6 H, 2 s, CH_3O), 6.60–740 (12 H, m, Ar). The *E* isomer melted at 101–102 °C: ^{1}H NMR δ ($CDCl_3$) 2.33 (3 H, s, CH_3), 3.67, 3.77 (6 H, 2 s, CH_3O), 6.47–7.30 (12 H, m, Ar). Anal. Calcd for $C_{23}H_{21}O_2Br$: C, 67.49, H, 5.17; Br, 19.53. Found: *Z* isomer, C, 67.50; H, 4.89; Br, 19.28; *E* isomer, C, 67.99; H, 5.05.

The X-ray crystallographic data for (*E*)-**4**-Br were determined by using a PW1100/20 Philips four-circle computer-controlled diffractometer, with all computing done on a Cyber 74 computer at the Hebrew University.

Solvolysis Reactions. Typical reactions illustrating the experimental procedures are given below.

Reaction of (*E*)- or (*Z*)-4-Br with AcOH–AgOAc. A mixture of 870 mg (2.1 mmol) of (*E*)- or (*Z*)-**4**-Br and 400 mg (2.4 mmol) of AgOAc in 13 mL of glacial AcOH and 1.0 mL of Ac_2O was heated under reflux for 2 h. The resulting material was filtered to remove the AgBr and the solvent was then removed from the filtrate by distillation. The residue was redissolved in 100 mL of CH_2Cl_2 and washed successively with H_2O, dilute $NaHCO_3$ solution, and H_2O. After drying over $MgSO_4$, removal of the solvent gave 0.75 g (91%) of product the NMR spectrum of which showed that it was a 1:1 mixture of (*E*)- and (*Z*)-**4**-OAc.

The mixture of (*E*)- and (*Z*)-**4**-OAc was separated by fractional crystallization from 95% ethanol. The pure *Z* isomer, which crystallized first, melted at 121–122 °C: ^{1}H NMR δ (CCl_4) 1.85 (3 H, s, AcO), 2.32 (3 H, s, CH_3), 3.70 (6 H, s, two CH_3O), 6.58–7.20 (12 H, m, Ar). Anal. Calcd for $C_{25}H_{24}O_4$: C, 77.29; H, 6.22. Found: C, 77.38; H, 6.08. The *E* isomer melted at 86–87 °C: ^{1}H NMR δ (CCl_4) 1.88 (3 H, s, AcO), 2.25 (3 H, s, CH_3), 3.69, 3.75 (6 H, 2 s, two CH_3O), 6.58–7.22 (12 H, m, Ar). Anal. Calcd for $C_{25}H_{24}O_4$: C, 77.29; H, 6.22. Found: C, 77.45; H, 6.03.

Reaction of 3-Br with AcOH–AgOAc. A mixture of 80 mg (0.20 mmol) of **3**-Br and 40 mg (0.24 mmol) of AgOAc in 10 mL of AcOH in a sealed ampule was heated at 140 ± 1 °C for 24 h. The resulting material was poured into 50 mL of H_2O and then extracted with $CHCl_3$ (2 × 25 mL). The extract was washed successively with H_2O, dilute $NaHCO_3$ solution, and H_2O. The washed extract was dried over $MgSO_4$, the solvent was removed, and the residual material was purified by thin-layer chromatography (TLC) on silica gel G plates, with elution by light petroleum (bp 60–80 °C) containing 10% acetone. The product obtained was a mixture of (*E*)- and (*Z*)-**4**-OAc. According to the acetoxy or the tolyl methyl NMR absorptions, the product was an approximately 55:45 mixture of (*E*)- and (*Z*)-**4**-OAc.

Solvolysis of (*E*,*Z*)-4-Br in TFE–2,6-Lutidine. In a typical large scale experiment, 10.0 g (24.4 mmol) of (*E*,*Z*)-**4**-Br in 100 mL of reagent grade TFE containing 5.22 g (48.8 mmol) of 2,6-lutidine was heated in a round-bottom flank under reflux for 48 h. The solvent was then evaporated off under reduced pressure. The bright yellow residual oil was redissolved in 200 mL of ether and washed successively with H_2O, 1 M HCl, and H_2O. After drying over $MgSO_4$, the ether was removed and the residual oil purified by passage through an alumina column with elution by light petroleum (bp 40–60 °C) containing 30% CH_2Cl_2. The eluate was evaporated to dryness and the residual material was crystallized from 95% ethanol to give 6.3 g (60%) of a 1:1 mixture of (*E*)- and (*Z*)-**4**-OTFE. This 1:1 mixture melted at 79–80 °C and was subsequently used as inactive carriers in the tracer experiments. Fractional crystallization from 95% ethanol gave the pure (*Z*)-**4**-OTFE, which crystallized first, mp 107–108 °C: ^{1}H NMR δ ($CDCl_3$) 2.21 (3 H, s, CH_3), 3.67, 3.72 (6 H, 2 s, two CH_3O), 3.88 (2 H, q, partly overlapping with CH_3O, CH_2), 6.50–7.20 (12 H, m, Ar). Anal. Calcd for $C_{25}H_{23}O_3F_3$: C, 70.08; H, 5.41. Found: C, 70.34; H, 5.54. The pure *E* isomer was not obtained. A fraction containing about 90% (*E*)- and 10% (*Z*)-**4**-OTFE melted at 85–87 °C. The ^{1}H NMR absorptions due to the *E* isomer show δ ($CDCl_3$) 2.30 (3 H, s, CH_3), 3.62, 3.67 (6 H, 2 s, two CH_3O), 3.88 (2 H, q, partly overlapping with CH_3O, CH_2), 6.43–7.12 (12 H, m, Ar). Anal. Calcd for $C_{25}H_{23}O_3F_3$ C, 70.08; H, 5.41. Found: (9:1 *E*:*Z* isomers) C, 70.26; H, 5.48.

Solvolysis of (*E*,*Z*)-4-Br-*2*-^{14}*C* in TFE–2,6-Lutidine. In a typical experiment, 123.5 mg (0.302 mmol) of (*E*,*Z*)-**4**-Br-*2*-^{14}C in 20 mL of TFE containing 64.6 mg (0.604 mmol) of 2,6-lutidine in a sealed ampule was heated at 120 ± 2 °C for a desired length of time. After cooling the tube was opened, the contents poured into a rotary evaporator, and most of the solvent was removed under reduced pressure. The residue was redissolved in 100 mL of ether and 500 mg of nonlabeled (*E*,*Z*)-**4**-Br as well as 500 mg of nonlabeled (*E*,*Z*)-**4**-OTFE were added as carriers. The ether solution was washed with H_2O (3 × 20 mL) and the liberated bromide ions in the washing were determined by potentiometric titration to give the extent of reaction. The washed ether solution was dried over $MgSO_4$ and the ether was distilled off. The residual material containing both the reaction product, (*E*,*Z*)-**4**-OTFE-^{14}C, and unconsumed reactant, (*E*,*Z*)-**4**-Br-^{14}C, was heated under reflux with 50 mL of AcOH containing 1.0 g of NaOAc for 48 h, whereby the (*E*,*Z*)-**4**-Br-^{14}C was converted to (*E*,*Z*)-**4**-OAc-^{14}C. The AcOH was removed in a rotary evaporator, the residue redissolved in CH_2Cl_2, and the solution washed successively with H_2O, $NaHCO_3$ solution, and H_2O. After drying over $MgSO_4$, the CH_2Cl_2 was evaporated off giving a residual oil which was separated by passage through an alumina column, with elution by light petroleum (bp 40–60 °C) containing 15% CH_2Cl_2. The vinyl ethers, (*E*,*Z*)-**4**-OTFE-^{14}C, were eluted first, with the acetates, (*E*,*Z*)-**4**-OAc-^{14}C, derived from the original unconsumed reactant, appearing in the later fractions. The separated (*E*,*Z*)-**4**-OTFE-^{14}C and (*E*,*Z*)-**4**-OAc-^{14}C were degraded by ozonolysis[14] to give anisyl tolyl ketone (**7**), mp 88–89 °C (lit.[15] mp 89 °C) which was converted to its oxime, mp 120–121 °C, for ^{14}C activity measurement.

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Registry No. **3**-Br, 77385-77-4; (*E*)-**4**-Br, 92241-58-2; (*Z*)-**4**-Br, 77385-76-3; (*E*)-**4**-Br-*2*-^{14}C, 92241-62-8; (*Z*)-**4**-Br-*2*-^{14}C, 92241-63-9; (*E*)-**4**-OAc, 92241-64-0; (*Z*)-**4**-OAc, 92241-65-1; (*Z*)-**4**-OTFE, 92241-66-2; (*E*)-**4**-OTFE, 92241-67-3; (*E*)-**4**-OTFE-*1*-^{14}C, 92241-68-4; (*Z*)-**4**-OTFE-*1*-^{14}C, 92241-69-5; (*Z*)-**4**-OTFE-*2*-^{14}C, 92241-70-8; (*E*)-**4**-OTFE-*2*-^{14}C, 92241-71-9; **10**, 92241-59-3; **11**, 92241-60-6; **12**-*1*-^{14}C, 92241-61-7; $(MeO\text{-}p\text{-}C_6H_4)_2CO$, 90-96-0; $Me\text{-}p\text{-}C_6H_4(CH_2)_2C_6H_4\text{-}p\text{-}Me$, 538-39-6; $MeO\text{-}p\text{-}C_6H_4Br$, 104-92-7; $Me\text{-}p\text{-}C_6H_4CH_2Br$, 104-81-4; $Me\text{-}p\text{-}C_6H_4CH_2C(O)OEt$, 14062-19-2; $Me\text{-}p\text{-}C_6H_4Br$, 106-38-7; $MeO\text{-}p\text{-}C_6H_4CH_2{}^{14}C(O)C_6H_4\text{-}p\text{-}OMe$, 58367-73-0.

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(14) (a) Lee, C. C.; Weber, U.; Obafemi, C. A. *Can. J. Chem.* **1979**, *57*, 1384–1387. (b) Pappas, J. J.; Keaveney, W. P.; Gancher, E.; Berger, M. *Tetrahedron Lett.* **1966**, 4273–4278.

(15) Fahim, H. A.; Baddar, F. G.; Galaby, M. A. *J. Chem. Soc.* **1955**, 317–319.