Solvolyses of some ^{13}C- or ^{14}C-labeled triarylvinyl bromides in aqueous acetic acid[1]

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Received October 4, 1985

This paper is dedicated to Professor Arthur N. Bourns

CHOI CHUCK LEE, DAVE WANIGASEKERA, and CHARLES Y. FIAKPUI. Can. J. Chem. **64**, 1235 (1986).

The presence of different amounts of added $LiClO_4$ in the solvolysis of triphenyl[2-^{14}C]vinyl bromide (**1**-Br-2-^{14}C) or trianisyl[2-^{14}C]vinyl bromide (**2**-Br-2-^{14}C) in 70% HOAc did not materially affect the extent of scrambling of the label arising from 1,2-aryl shifts in the triarylvinyl cation or k_r, the rate constant for the 1,2-aryl shift. Solvolysis of a 2:3 mixture of (*E*)- and (*Z*)-1,2-diphenyl-2-tolylvinyl bromide ((*E*,*Z*)-**3**-Br) in 70% HOAc gave an 85:15 mixture of 1,2-diphenyl-2-tolylethanone (**5**) and 2,2-diphenyl-1-tolylethanone (**6**), the latter product, **6**, being derived from a 1,2-phenyl shift in the 1,2-diphenyl-2-tolylvinyl cation to the more stable 2,2-diphenyl-1-tolylvinyl cation. With (*E*,*Z*)-**3**-Br-2-^{13}C as substrate and analysis by gc–ms, about 26–27% scrambling of the ^{13}C label was found in both products, **5**-1,2-^{13}C and **6**-1,2-^{13}C. Solvolyses of (*E*,*Z*)-**3**-Br-2-^{13}C in 50% and 70% HOAc showed that the extent of scrambling in the major products, **5**-1,2-^{13}C, was lower in 50% HOAc than in 70% HOAc, similar to a trend previously observed for solvolyses of **1**-Br-2-^{14}C. In contrast, solvolyses of **2**-Br-2-^{14}C in 50, 70, or 90% HOAc gave essentially the same extent of scrambling. Mechanistic implications of these results are discussed.

CHOI CHUCK LEE, DAVE WANIGASEKERA et CHARLES Y. FIAKPUI. Can. J. Chem. **64**, 1235 (1986).

L'addition de diverses quantités de $LiClO_4$ lors de la solvolyse du bromure de triphénylvinyle [^{14}C-2] (**1**-Br-^{14}C-2) ou du bromure de trianysylvinyle [^{14}C-2] (**2**-Br-^{14}C-2) dans de l'acide acétique à 70% n'affecte pas matériellement le taux de répartition au hasard du marqueur provenant de glissements-1,2 des groupements aryles dans le cation triarylvinyle ou la constante de vitesse, k_r, des glissements-1,2 des groupements aryles. La solvolyse d'un mélange 2:3 des bromures (*E*) et (*Z*) de diphényl-1,2 tolyl-2 vinyle (**3**-Br-(*E*,*Z*)), dans de l'acide acétique à 70%, conduit à un mélange 85:15 de diphényl-1,2 tolyl-2 éthanone (**5**) et de diphényl-2,2 tolyl-1 éthanone (**6**). Ce dernier composé (**6**) provient d'un glissement-1,2 du groupement phényle dans le cation diphényl-1,2 vinyle pour donner le cation diphényl-2,2 tolyl-1 vinyle qui est plus stable. Dans le cas du **3**-Br-^{13}C-2-(*E*,*Z*), et sur la base d'une analyse par sm/cpg, on note la présence d'un mélange correspondant à environ 26–27% de répartition au hasard du marqueur ^{13}C dans les 2 produits **5**-^{13}C-1,2 et **6**-^{13}C-1,2. Le taux de répartition au hasard du marqueur dans les produits majoritaires, **5**-^{13}C-1,2, qui est obtenu lors de la solvolyse du composé **3**-Br-^{13}C-2-(*E*,*Z*) dans de l'acide acétique à 50% est inférieur à celui observé lors de la même réaction dans de l'acide acétique à 70%; cette tendance est analogue à celle observée antérieurement lors des solvolyses du **1**-Br-^{14}C-2. Par ailleurs, les solvolyses du **2**-Br-^{14}C-2 dans de l'acide acétique à 50, 70 ou 90% donnent essentiellement le même taux de répartition au hasard du marqueur. On discute des implications mécanistiques de ces résultats.

[Traduit par la revue]

α-Arylvinyl cations derived from solvolytic reactions have been extensively discussed (2). Because the solvolysis of triphenylvinyl bromide (**1**-Br) in glacial HOAc without the presence of AgOAc was found to be too slow, isotopic scrambling studies with triphenyl[2-^{14}C]vinyl bromide (**1**-Br-2-^{14}C) have been carried out in aqueous acetic acid containing different proportions of HOAc and H_2O as solvent (3). Subsequently, a mixture of 70% HOAc – 30% H_2O (by volume) (to be designated as 70% HOAc) was arbitrarily chosen as solvent in other solvolytic studies on systems such as **1**-Br or **1**-Br-2-^{14}C and trianisylvinyl bromide (**2**-Br) or trianisyl[2-^{14}C]vinyl bromide (**2**-Br-2-^{14}C) (4, 5). In the present paper, further observations on isotopic scramblings are reported for solvolyses in aqueous HOAc of ^{14}C- or ^{13}C-labeled triphenylvinyl, trianisylvinyl, and (*E*,*Z*)-1,2-diphenyl-2-tolylvinyl bromides.

In a previous study (5), the solvolysis of **1**-Br or **2**-Br in 70% HOAc in the presence of $LiClO_4$ was found to give a normal salt effect (6), with the specific rate constant increasing linearly with increasing concentrations of the added salt. In the initial part of the present work, the effect of added $LiClO_4$ on the extent of isotopic scrambling arising from 1,2-aryl shifts in a triarylvinyl cation was investigated. When **1**-Br-2-^{14}C or **2**-Br-2-^{14}C was solvolyzed in 70% HOAc in the presence of different concentrations of added $LiClO_4$, the product, 1,2,2-triphenyl[1,2-^{14}C]ethanone or 1,2,2-trianisyl[1,2-^{14}C]ethanone, degraded to give the extent of isotopic scrambling (3, 4), showed that the added $LiClO_4$ did not significantly affect the extent of scrambling of the ^{14}C-label from C-2 to C-1 (Table 1).

For the scrambling processes as depicted in Scheme 1, it has been shown that eq. [1] holds (7). When Ar and Ar′ are the same, e.g., with **1**-Br-2-^{14}C or **2**-Br-2-^{14}C, a statistical factor of 2 applies and eq. [1] is modified to eq. [2] (8). While $LiClO_4$ could affect the rate-determining ionization step and gave rise to a normal salt effect, the finding that it did not influence the extent of scrambling indicated that k_{SOH}/k_r did not change significantly in the presence of added $LiClO_4$. Since the medium in all of these experiments is 70% HOAc, k_{SOH} is not expected to vary. A model of the transition state for the 1,2-aryl shift process is an aryl-bridged vinyl cation with dispersal of the positive charge, and hence k_r might be expected to show a decrease with increasing polarity of the medium (9). However, this effect is apparently very small since k_{SOH}/k_r remained essentially constant in the presence of different concentrations of $LiClO_4$.

$$[1] \quad [RY]/[R'Y] = 1 + (k_{SOH}/k_r)$$

$$[2] \quad [RY]/[R'Y] = 1 + (k_{SOH}/2k_r)$$

In the preceding paper of this series (1), we studied the solvolysis of a 2:3 mixture of C-2 labeled (*E*)- and (*Z*)-1,2-diphenyl-2-tolylvinyl bromides (to be designated as (*E*,*Z*)-**3**-Br) in HOAc–AgOAc and in 2,2,2-trifluoroethanol (TFE)–

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[1] Rearrangement studies with ^{14}C, LI; for part L, see ref. 1.

TABLE 1. Isotopic scrambling data from solvolyses of triphenyl[2-^{14}C]vinyl bromide (**1**-Br-1-^{14}C) or trianisyl[2-^{14}C]vinyl bromide (**2**-Br-1-^{14}C) in 70% HOAc in the presence of added LiClO$_4$

RX	[RX] (mmolar)	[LiClO$_4$] (mmolar)	Scrambling from C-2 to C-1 (%)		
			Run 1	Run 2	k_{SOH}/k_r[a]
1-Br-1-^{14}C[b]	15	0	15.8[c]	15.3[c]	8.8
	15	15	15.2	15.8	8.9
	15	75	15.7	15.7	8.7
	15	150	15.8	15.1	8.9
2-Br-1-^{14}C[d]	6	0	29.5[e]	30.5[e]	2.7
	6	30	29.5	30.8	2.6
	6	60	30.0	30.9	2.6
	6	100	30.7	30.9	2.5

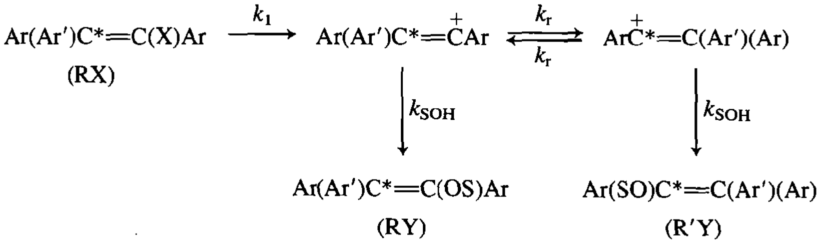
[a] Calculated from eq. [2] using the average scrambling values for the duplicate runs.

[b] Solvolyses of **1**-Br-1-^{14}C were carried out at 150 ± 2°C for 10 days, giving essentially complete reaction.

[c] Previously reported (3) mean scrambling value for similar reactions was 15.3%.

[d] Solvolyses of **2**-Br-2-^{14}C were carried out at 120 ± 2°C for 3 days, giving essentially complete reaction.

[e] A previously reported (4) mean scrambling value for similar reactions was somewhat lower at 27.7%.



SCHEME 1

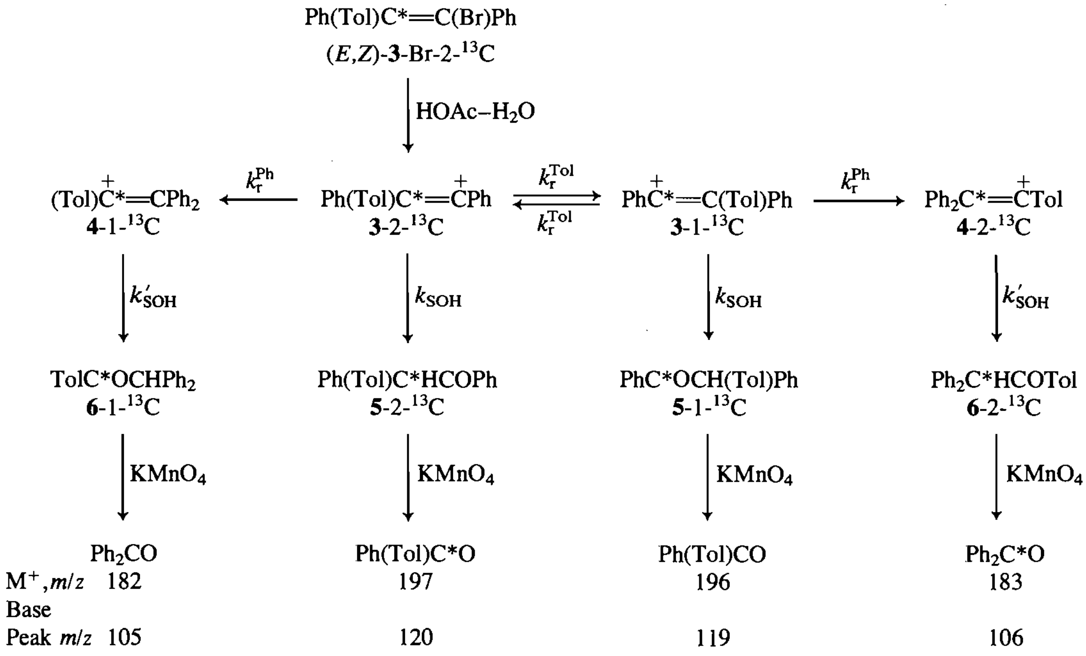
2,6-lutidine. In the present work, the solvolysis of (*E*,*Z*)-**3**-Br-2-^{13}C in aqueous HOAc was investigated. In preliminary work with nonlabeled (*E*,*Z*)-**3**-Br, solvolysis in 70% HOAc was found to give, according to ^{1}H nmr, a mixture of 85% 1,2-diphenyl-1-tolylethanone (**5**) and 15% 2,2-diphenyl-1-tolylethanone (**6**), the latter product, **6**, being derived from a 1,2-phenyl shift in the 1,2-diphenyl-2-tolylvinyl cation (**3**) to the more stable 2,2-diphenyl-1-tolylvinyl cation (**4**). An analogous reaction of (*E*,*Z*)-**3**-Br-2-^{13}C in 70% HOAc gave a mixture of isotopically scrambled products, **5**-1,2-^{13}C and **6**-1,2-^{13}C. Oxidation of this product mixture to give nonlabeled and labeled diphenyl and phenyl tolyl ketones, followed by gc–ms analyses as described previously for the solvolysis of (*E*,*Z*)-**3**-Br-2-^{13}C in TFE–2,6-lutidine (1), gave the extents of scrambling of the ^{13}C-label between C-1 and C-2 in **5**-1,2-^{13}C arising from degenerate 1,2-tolyl shifts in the 1,2-diphenyl-2-tolylvinyl cation (**3**), and in **6**-1,2-^{13}C arising from nondegenerate 1,2-phenyl shifts in cation **3** before and after the degenerate 1,2-tolyl shifts. The processes involved are depicted in Scheme 2.

The extents of scrambling were calculated from the intensities of the ms absorptions in the molecular ion region and in the base peak region. The observed data are summarized in Tables 2 and 3, and the method of calculation has been described previously (1). A steady-state treatment of the scrambling processes in Scheme 2 gives eq. [3], an equation analogous to that used previously for the reaction of (*E*,*Z*)-**3**-Br-2-^{13}C with TFE–2,6-lutidine (1).

$$[3]\quad [\mathbf{5}\text{-}2\text{-}^{13}\text{C}]/[\mathbf{5}\text{-}1\text{-}^{13}\text{C}] = [\mathbf{6}\text{-}1\text{-}^{13}\text{C}]/[\mathbf{6}\text{-}2\text{-}^{13}\text{C}]$$

From Tables 2 and 3, it is seen that the mean scramblings in **5**-1,2-^{13}C and **6**-1,2-^{13}C are 26.3 ± 0.9% and 27.5 ± 0.5%, respectively, and these values are identical within experimental errors, in agreement with eq. [3]. Again, analogous to the treatment of data from trifluoroethanolysis (1), the distribution of unrearranged and rearranged products **5**-2-^{13}C, **5**-1-^{13}C, **6**-1-^{13}C, and **6**-2-^{13}C (Scheme 2) can be calculated. Since the ratio of **5** to **6** was 85:15, and since the mean scrambling values were 26.3% from **5**-2-^{13}C to **5**-1-^{13}C and 27.5% from **6**-1-^{13}C to **6**-2-^{13}C, in the product mixture, there would be 85 × 0.263 = 22% **5**-1-^{13}C, 85 × 0.737 = 63% **5**-2-^{13}C, 15 × 0.275 = 4% **6**-2-^{13}C, and 15 × 0.725 = 11% **6**-1-^{13}C. As depicted in Scheme 2, nondegenerate 1,2-phenyl shifts gave **4**-1-^{13}C from **3**-2-^{13}C and **4**-2-^{13}C from **3**-1-^{13}C, respectively, before and after the degenerate 1,2-tolyl shifts in cation **3**. since the ratios of [**6**-1-^{13}C]/[**5**-2-^{13}C] = 11/63 = 0.17 and [**6**-2-^{13}C]/[**5**-1-^{13}C] = 4/22 = 0.18 are essentially the same, the product distribution observed thus indicated that in cation **3**, the same extent of nondegenerate 1,2-phenyl shifts occurred before or after the degenerate 1,2-tolyl shifts, a conclusion that was also reached in the previous study on the trifluoroethanolyis of (*E*,*Z*)-**3**-Br-2-^{13}C (1).

It is of interest to note that from the present work, reaction of (*E*,*Z*)-**3**-Br in 70% HOAc gave, as major product, ketone **5** derived from the less stable cation **3**, while the minor product, ketone **6**, was derived from the more stable cation **4**. In contrast, for the trifluoroethanolysis of (*E*,*Z*)-**3**-Br (1), the major product was derived from the more stable cation **4** while the minor product was derived from the less stable cation **3**. Moreover, in the reaction of (*E*,*Z*)-**3**-Br with HOAc–AgOAc, the only



SCHEME 2

product was derived from cation **3**, with no detectable amount of product derived from the more stable cation **4**. As was suggested (1), the nucleophilic character of the reaction medium and the lifetime of the vinyl cations may play a role in determining these variations. In TFE with its low nucleophilic character and long cationic lifetime, the nondegenerate 1,2-phenyl shifts from **3** to **4** could be extensive, while in HOAc–AgOAc, the cationic lifetime was short and there was no detectable amount of rearrangement from **3** to **4**. In 70% HOAc, the cationic lifetime would be intermediate between HOAc–AgOAc and TFE and only a small extent of rearrangement from **3** to **4** could take place, resulting in the formation of a minor amount of product derived from **4**.

Another method, involving analysis by ^{13}C nmr, may also be utilized to determine the extent of scrambling arising from degenerate 1,2-tolyl shifts in the solvolysis of (*E*,*Z*)-**3**-Br-2-^{13}C. Experiments were carried out in 70% and in 50% aqueous HOAc. The major product, **5**-1,2-^{13}C, was recovered after separation by thin-layer chromatography and then reduced with $LiAlH_4$ to give a mixture of *erythro*- and *threo*-1,2-diphenyl-2-tolyl[1,2-^{13}C]ethanol (**7**-1,2-^{13}C). The ^{13}C enrichments at C-2 and C-1, and hence the extent of scrambling, were determined from the ^{13}C nmr spectrum of **7**-1,2-^{13}C by the intensity ratio method as previously described (10, 11). From duplicate solvolyses of (*E*,*Z*)-**3**-Br-2-^{13}C in 70% HOAc, the scramblings from C-2 to C-1 in **5**-1,2-^{13}C, as measured by ^{13}C nmr, were 26.1 and 27.0%, in good agreement with the data obtained from gc–ms analyses given in Tables 2 and 3. In similar solvolyses in 50% HOAc, 22.3 and 23.2% scramblings from C-2 to C-1 were observed for duplicate runs. It is seen that a higher proportion of H_2O in the HOAc–H_2O solvent mixture gave rise to a lower extent of scrambling (mean scrambling values of 26.6% and 22.8%, respectively, in 70% and 50% HOAc). This trend was also observed in the earlier study on the solvolysis of triphenyl[2-^{14}C]vinyl bromide (**1**-Br-2-^{14}C) in different mixtures of HOAc and H_2O (3). For comparison, some of the data from the earlier work with **1**-Br-2-^{14}C (3) and the present results from reactions of (*E*,*Z*)-**3**-Br-2-^{13}C in 50% and 70% HOAc are summarized in Table 4.

In Table 1, it is shown that solvolysis of trianisyl[2-^{14}C]vinyl bromide (**2**-Br-2-^{14}C) in 70% HOAc gave a product with 29.5 and 30.5% scrambling in duplicate runs. It is of interest to note that similar reactions of **2**-Br-2-^{14}C in 50% or 90% HOAc also gave essentially the same extent of about 30% scrambling, the results being included in Table 4. These results for **2**-Br-2-^{14}C, therefore, do not follow the same trend of decreasing amounts of scrambling with increasing proportions of H_2O in the HOAc–H_2O solvent mixture that was observed with **1**-Br-2-^{14}C or (*E*,*Z*)-**3**-Br-2-^{13}C. Recently, isotopic scramblings from reactions of C-2 labeled (*E*,*Z*)-1,2-dianisyl-2-tolylvinyl bromides ((*E*,*Z*)-**8**-Br) with HOAc–AgOAc or with TFE–2,6-lutidine have been reported (12). It may also be of interest to note that preliminary work on the solvolysis of (*E*,*Z*)-**8**-Br-2-^{13}C in aqueous HOAc also indicates no significant changes in the extent of scrambling for different proportions of HOAc and H_2O.

To account for the difference in behavior for the solvolysis of **1**-Br-2-^{14}C, (*E*,*Z*)-**3**-Br-2-^{13}C, and **2**-Br-2-^{14}C in aqueous HOAc containing different amounts of H_2O, the nature of the triarylvinyl cations involved may be considered. As given in Table 4, a lower extent of scrambling corresponds to a higher value for k_{SOH}/k_r. For the α-phenyl substituted triarylvinyl cations generated from **1**-Br-2-^{14}C or (*E*,*Z*)-**3**-Br-2-^{13}C, a higher H_2O content in the solvent would increase the nucleophilic character of the reaction medium and would give a higher value for k_{SOH}. As well, a higher H_2O content would also increase the polar character of the solvent and may give rise to a lower k_r, although this effect may be small since it was shown earlier that the presence of $LiClO_4$ in 70% HOAc did not materially influence k_{SOH}/k_r. Thus for solvolyses of **1**-Br-2-^{14}C or (*E*,*Z*)-**3**-Br-2-^{13}C in HOAc–H_2O, a higher proportion of H_2O in the solvent would increase k_{SOH}/k_r and hence decrease the extent of scrambling as observed. For the reaction of **2**-Br-2-^{14}C, however, the α-anisyl substituted triarylvinyl cation that is generated is more stable than an α-phenyl substituted triarylvinyl cation and would have a longer lifetime and a lower value for k_{SOH}. Apparently, changes in H_2O content in the HOAc–H_2O solvent did not greatly affect the relatively low value of k_{SOH} and since the effect of k_r would also be small,

TABLE 2. Data from the mass spectra of PhCOTol and $Ph^{13}COTol$

	Observed intensity		Corrected for $(M + 1)^+$		Corrected for 90% ^{13}C enrichment		% Distribution[b]	
m/z[a]	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
195	0.86	0.85						
196	24.88	27.54	24.76	27.42	17.54	19.19	27.0	25.9
197	51.03	58.85	47.47	54.91	47.47	54.91	73.0	74.1
198	7.28	8.42						
118	0.12	0.03						
119	49.95	46.59	49.94	46.59	35.38	32.33	27.0	25.2
120	100.00	100.00	95.65	95.96	95.65	95.96	73.0	74.8
121	8.70	8.68						

[a] Molecular ions for $[TolCOPh]^+$ and $[Tol^{13}COPh]^+$ at *m/z* 196 and 197, respectively; the base peak is $[Tol^{13}CO]^+$ at *m/z* 120.

[b] Percentages for *m/z* 196 $[TolCOPh]^+$ and for *m/z* 119 ($[TolCO]^+$ correspond to % scrambling from C-2 to C-1 in **4**-1,2-^{13}C (see Scheme 2); mean value = (27.0 + 25.9 + 27.0 + 25.2)/4 = 26.3 ± 0.9%.

TABLE 3. Data from the mass spectra of PhCOPh and $Ph^{13}COPh$

	Observed intensity		Corrected for $(M + 1)^+$		Corrected for 90% ^{13}C enrichment		% Distribution	
m/z[a]	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
181	8.70	7.40						
182	64.26	44.05	63.28	54.39	54.71	47.17	72.8	72.6
183	27.69	24.05	20.43	17.81	20.43	7.81	27.2	27.4
184	3.12	2.27						
104	—	0.25						
105	100.00	100.00	100.00	100.00	86.76	86.60	72.8	71.8
106	38.51	40.30	32.38	34.03	32.38	34.03	27.2	28.2
107	2.36	2.59						

[a] Molecular ions from $[PhCOPh]^+$ and $[Ph^{13}COPh]^+$ at *m/z* 182 and 183, respectively; the base peak is $[PhCO]^+$ at *m/z* 105.

[b] Percentages for *m/z* 183 ($[Ph^{13}COPh]^+$) and ($[Ph^{13}CO]^+$) correspond to % of the isotopically rearranged product, **6**-2-^{13}C (see Scheme 2); mean value = (27.2 + 27.4 + 27.2 + 28.2)/4 = 27.5 ± 0.5%.

TABLE 4. Isotopic scrambling data from solvolyses in HOAc–H_2O

	Reaction with **1**-Br-2-^{14}C[b]		Reaction with (*E*,*Z*)-**3**-Br-2-^{13}C[c]		Reaction with **2**-Br-2-^{14}C[d]	
Solvent (% HOAc)[a]	Scrambling from C-2 to C-1 (%)[e]	k_{SOH}/k_r[f]	Scrambling from C-2 to C-1 (%)[g]	k_{SOH}/k_r[f]	Scrambling from C-2 to C-1 (%)[h]	k_{SOH}/k_r[f]
50	9.6	17.0	22.2; 23.2	2.4	31.2; 30.2	2.5
70	15.3	8.8	26.1; 27.0	1.8	29.5; 30.5	2.7
90	18.4	6.8			29.8; 31.0	2.6

[a] Proportion of HOAc by volume in mixtures of HOAc and H_2O.

[b] Reaction of triphenyl[2-^{14}C]vinyl bromide (**1**-Br-2-^{14}C) in HOAc–H_2O at 150 ± 2°C.

[c] Reaction of (*E*,*Z*)-1,2-diphenyl-2-tolyl[2-^{13}C]vinyl bromides ((*E*,*Z*)-**3**-Br-2-^{13}C) in HOAc–H_2O at 150 ± 2°C.

[d] Reaction of trianisyl[2-^{14}C]vinyl bromide (**2**-Br-1-^{14}C) in HOAc–H_2O at 120 ± 2°C.

[e] Mean scrambling values from ref. 3.

[f] Calculated from eq. [1] or eq. [2] using the mean scrambling values. For (*E*,*Z*)-**3**-Br-2-^{13}C, steady-state treatment of Scheme 2 gave $k_{SOH}/k_r = [RY]/[R'Y] - 1 - k_{Ph}/k_{Tol}$, but eq. [1] is used since k_{Ph}/k_{Tol} may be quite small.

[g] Scramblings for duplicate runs in the major product, 1,2-diphenyl-2-tolyl[1,2-^{13}C]ethanone (**5**-1,2-^{13}C).

[h] Scramblings for duplicate runs in the product, trianisyl[1,2-^{14}C]ethanone.

the net result is a relatively constant k_{SOH}/k_r, giving rise to about the same extent of scrambling for solvolyses in HOAc–H_2O of α-anisyl substituted triarylvinyl systems such as the trianisylvinyl and (*E*,*Z*)-1,2-dianisyl-2-tolylvinyl bromides.

Since the degenerate rearrangement processes in the triphenylvinyl and 1,2-diphenyl-2-tolylvinyl cations differ only in the migrating phenyl and tolyl groups, a comparison of the data from **1**-Br-2-^{14}C and (*E*,*Z*)-**3**-Br-2-^{13}C in Table 4 would give a measure of the Tol:Ph migratory aptitude. The k_{SOH}/k_r values in Table 4 may be more specifically designated as k_{SOH}/k_r^{Ph} and k'_{SOH}/k_r^{Tol}, respectively, for the triphenylvinyl and 1,2-diphenyl-2-tolylvinyl systems. If k_{SOH} and k'_{SOH} for the capture of the two ions in a given solvent system were assumed to be about the same, then $(k_{SOH}/k_r^{Ph})/(k'_{SOH}/k_r^{Tol}) =$

k_T^{Tol}/k_T^{Ph} would be 17.0/2.4 or about 7 and 8.8/1.8 or about 5, respectively, for solvolyses in 50% and 70% HOAc. These values of about 5–7 are of the same magnitude as previously reported Tol:Ph migratory ratios of 4–5 from comparisons of scrambling data for the tritolyvinyl and 2-phenyl-1,2-ditolylvinyl cations (8), and a k_T^{Tol}/k_T^{Ph} ratio of about 7 from comparisons of the scramblings observed in reactions of **1**-Br-1-^{14}C and (*E,Z*)-**3**-Br-2-^{14}C with HOAc–AgOAc (1).

Experimental

*Solvolyses with triphenyl[2-^{14}C]vinyl bromide (**1**-Br-2-^{14}C)*

Solutions of **1**-Br-2-^{14}C (15 mmolar) in 70% HOAc containing different amounts of $LiClO_4$ (Table 1) were heated in sealed tubes at 150 ± 2°C for 10 days. Each reaction mixture was worked up to give 1,2,2-triphenyl[1,2-^{14}C]ethanone (α,α-diphenylacetophenone), which was in turn degraded to diphenyl [^{14}C]ketone, using procedures previously described (3). The difference in specific activities between each sample of 1,2,2-triphenyl[1,2-^{14}C]ethanone and the corresponding diphenyl [^{14}C]ketone gave the extents of scrambling of the ^{14}C label from C-2 to C-1.

*Solvolyses with trianisyl[2-^{14}C]vinyl bromide (**2**-Br-2-^{14}C)*

Solutions of **2**-Br-2-^{14}C (6.0 mmolar) in 50, 70, or 90% HOAc or in 70% HOAc containing different amounts of $LiClO_4$ (Table 1) were heated in sealed tubes at 120 ± 2°C for 3 days. Each reaction mixture was worked up to give 1,2,2-trianisyl[1,2-^{14}C]ethanone, which was subsequently degraded to give dianisyl [^{14}C]ketone using procedures reported previously (4). The difference in specific activities between each sample of 1,2,2-trianisyl[1,2-^{14}C]ethanone and its degradation product, dianisyl [^{14}C]ketone, gave the extents of scrambling of the ^{14}C label from C-2 to C-1.

Solvolyses with (E,Z)*-1,2-diphenyl-2-tolyl[2-^{13}C]vinyl bromide ((*E,Z*)-**3**-Br-2-^{13}C)*

The substrate, (*E,Z*)-**3**-Br or (*E,Z*)-**3**-Br-2-^{13}C, consisting of an approximately 2:3 mixture of the (*E*) and (*Z*) isomers, was prepared as described in the preceding paper (1).

A solution of 1.00 g (2.86 mmol) of (*E,Z*)-**3**-Br in 100 mL of 70% HOAc in a sealed tube was heated in an oil bath at 150 ± 2°C for 10 days. After cooling, the tube was opened and the contents extracted 3 times with ether. The extract was washed with H_2O and dried over $MgSO_4$. Removal of the ether under reduced pressure gave about 700 mg of a mixture of 1,2-diphenyl-2-tolylethanone (**5**) and 2,2-diphenyl-1-tolylethanone (**6**) as an oil. Its ^{1}H nmr spectrum indicated that the ratio of **5**:**6** was about 85:15 based on the relative area of the tolyl-CH_3 peaks at δ 2.24 and 2.33 ppm and the CH peaks at δ 6.06 and 6.40 ppm, respectively, for **5** and **6**. The major product, **5**, was purified by preparative thin-layer chromatography using silica gel G/UV$_{254}$ (Brinkmann Instruments (Canada) Ltd.) as the stationary phase and 80% $CHCl_3$ – 20% petroleum ether (bp 40–60°C) as the moving phase. The major band was scraped off, thoroughly washed with 300 mL of $CHCl_3$, and filtered. After removal of the $CHCl_3$ from the filtrate, the colorless residue was recrystallized from methanol to give 320 mg (overall yield of 46% based on a product ratio of 85:15 for **5**:**6**) of **5**, mp 94–95°C; ^{1}H nmr ($CDCl_3$) δ: 2.24 (s, 3H, CH_3), 6.06 (s, 1H, CH), 7.2–8.1 (m, 14H, Ar). *Anal.* calcd. for $C_{21}H_{18}O$: C 88.07, H 6.34; found: C 88.58, H 6.58. Oxidation of a sample of this product gave phenyl tolyl ketone, confirming its structure as **5**. If the product were **6**, its oxidation would give rise to diphenyl ketone.

In analogous solvolyses in 70% HOAc of (*E,Z*)-**3**-Br-2-^{13}C, prepared from 90% enriched [^{13}C]$BaCO_3$, the mixture of products, **5**-1,2-^{13}C and **6**-1,2-^{13}C, was oxidized without prior separation to give a mixture of phenyl tolyl ketone, phenyl tolyl [^{13}C]ketone, diphenyl ketone, and diphenyl [^{13}C]ketone for analysis using a Model 4000 Finnigan gc–ms system. In contrast to the degradation of 1,2,2-triphenyl[1,2-^{14}C]ethanone and 1,2,2-trianisyl[1,2-^{14}C]ethanone, which involved reduction with $LiAlH_4$ to the corresponding ethanol followed by oxidation with alkaline $KMnO_4$ (3, 4), the mixtures of **5**-1,2-^{13}C and **6**-1,2-^{13}C were oxidized directly by $KMnO_4$ in the presence of H_2SO_4 to give the unlabeled and labeled phenyl tolyl and diphenyl ketones for gc–ms analyses.

In another set of experiments, (*E,Z*)-**3**-Br-2-^{13}C, with 45% ^{13}C enrichment, was solvolyzed in 50, 70, or 90% HOAc at 150 ± 2°C for 10 days. From each run, the major product, **5**-1,2-^{13}C, was recovered after separation by thin-layer chromatography and then reduced with $LiAlH_4$ (3, 4) to give a mixture of *erythro*- and *threo*-1,2-diphenyl-2-tolyl[1,2-^{13}C]ethanol (**7**-1,2-^{13}C), which, after crystallization from 95% ethanol, melted at 87–88°C; ^{1}H nmr ($CDCl_3$) δ: 2.17, 2.28 (4H, two s, CH_3 + OH), 2.21 (shr, OH), 4.10, 4.25 (1H, two d, C-2 CH), 5.23, 5.38 (1H, two d, C-1 CH), 6.97–7.35 (14H, m, Ar). *Anal.* calcd. for $C_{21}H_{20}O$: C 87.46, H 6.99; found: C 87.17, H 7.04. Determinations of the ^{13}C enrichments at C-2 and C-1 of **7**-1,2-^{13}C, and hence the extents of scrambling from C-2 to C-1 as recorded in Table 4, were carried out using the ^{13}C nmr spectrum of **7**-1,2-^{13}C by the intensity ratio method as previously described (10, 11). Although the ^{1}H nmr of **7**-1,2-^{13}C gave separate peaks for the *erythro* and *threo* diastereomers, the peaks of interest in the ^{1}H-decoupled ^{13}C nmr spectrum of **7**-1,2-^{13}C, in a 60-MHz instrument, appear as nearly overlapping doublets at 21.0, 60.6, and 76.9 ppm, respectively, for tolyl-CH_3, C-2, and C-1. Ratios of the integrated intensities for C-2 or C-1 relative to the integrated intensity of tolyl-CH_3 containing ^{13}C in its natural abundance as internal reference standard are utilized in the calculations (10, 11).

Acknowledgement

The financial support given by the Natural Sciences and Engineering Research Council of Canada is sincerely acknowledged.

1. C. C. Lee and D. Wanigasekera. Can. J. Chem. **64**, 1228 (1986).
2. P. J. Stang, Z. Rappoport, M. Hanack, and L. R. Subramanian. Vinyl cations. Academic Press, New York. 1979. Chapt. 6.
3. C. C. Lee and E. C. F. Ko. Can. J. Chem. **56**, 2459 (1978).
4. C. C. Lee, E. C. F. Ko, and Z. Rappoport. Can. J. Chem. **58**, 2369 (1980).
5. C. C. Lee, C. A. Obafemi, and Z. Rappoport. Can. J. Chem. **60**, 3019 (1982).
6. A. H. Fainberg and S. Winstein. J. Am. Chem. Soc. **78**, 2763 (1956).
7. Y. Houminer, E. Noy, and Z. Rappoport. J. Am. Chem. Soc. **98**, 5632 (1976).
8. C. C. Lee, E. C. F. Ko, and Z. Rappoport. Can. J. Chem. **58**, 884 (1980).
9. C. K. Ingold. Structure and mechanism in organic chemistry. 2nd ed. Cornell University Press, Ithaca, NY. 1969. pp. 457–463.
10. M. Oka and C. C. Lee. Can. J. Chem. **53**, 320 (1975).
11. C. C. Lee, A. J. Paine, and E. C. F. Ko. J. Am. Chem. Soc. **99**, 7267 (1977).
12. D. Wanigasekera, C. C. Lee, Y. Houminer, M. Aviv, and Z. Rappoport. J. Org. Chem. **49**, 4367 (1984).