and the methanol was removed in vacuo to give 2.62 g of crude 2-[(thymyloxy)methyl]-4-acetylimidazole hydrochloride: mp 163–166 °C; ^{1}H NMR (Me_2SO) δ 7.87 (s, 1), 7.1–6.5 (m, 3), 5.03 (s, 2), 3.17 (m, 1), 2.43 (s, 3), 2.27 (s, 3), 2.77 (d, 6). This material was dissolved in hot water and the pH was brought to 9 with solid sodium bicarbonate. A solid formed and was collected by filtration and dried to give 0.58 g (9%) of 2-[(thymyloxy)methyl]-4-acetylimidazole; mp 175–176 °C. Anal. ($C_{16}H_{20}N_2O_2$) C, H, N.

Registry No. 1, 87005-15-0; 3, 88158-39-8; 4, 87005-17-2; 5, 78210-66-9; 6, 82982-60-3; 7, 88158-40-1; 8, 88158-41-2; 3-bromo-4-ethoxy-3-buten-2-one, 82982-59-0; 2,2-dibromoacetoacetaldehyde, 82176-32-7; sodium methoxide, 124-41-4; acetone, 67-64-1; ethyl formate, 109-94-4; sodium 4-hydroxy-3-buten-2-one, 14975-15-6; acetamidine acetate, 36896-17-0; hydroxyacetamidine hydrochloride, 54198-71-9; isonicotinamidine hydrochloride, 1452-60-4; (thymyloxy)acetamidine hydrochloride, 20287-83-6; 2-[(thymyloxy)methyl]-4-acetylimidazole, 88158-42-3.

On the Distribution of Products in the Degenerate Rearrangement of Doubly Labeled Triarylvinyl Cations[1]

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Lee and co-workers have described recently some double labeling experiments on the solvolysis–rearrangement of 1,2-diphenyl-2-[$^2H_5$]phenyl[2-^{13}C]vinyl bromide (1) in 70% HOAc–30% H_2O.[2] From mass spectrometric analyses of the four isotopomeric benzophenones obtained from reduction and cleavage of the solvolysis products, the distribution of the product-forming isotopomeric triphenylvinyl cations **2**–**5** (Scheme I) was deduced to be **2** (84.7 ± 2.2%)/**3** (7.3 ± 1.2%)/**4** (6.6 ± 1.2%)/**5** (1.5 ± 0.5%). Analysis of the ^{13}C NMR spectra showed a 15.2 ± 0.5% scrambling of ^{13}C from C-2 to C-1.

In a qualitative interpretation of the above results, it was suggested[2] that if half of the initially formed cation **2** were equilibrated between **2** and **4** and the other half equilibrated between **2**, **3**, and **5**, then "complete equilibration" for such a mechanism would give rise to a distribution of products of 58.3%, 16.7%, 16.7%, and 8.3%, respectively, from cations **2**–**5**. Since the observed results did not agree with this distribution, it was concluded that equilibration among the various isotopomeric triphenylvinyl cations was not complete in the solvolysis of **1**, but the observed presence of some product from **5** was regarded as a definite demonstration of the occurrence of successive 1,2 shifts in the triphenylvinyl cation.[2]

One of us (Z.R.) has pointed out to the Canadian group (Lee et al.) that the assumption that **2** should equilibrate half with **4** and half with **3** and **5** may be incorrect. In analyzing the formation of products from the precursor isotopomeric cations **2**–**5**, one is dealing not only with equilibration but also with capture of these cations vs. their equilibration. A more quantitative interpretation of the double-labeling results may be obtained by using a steady-state treatment of Scheme I, with both the scrambling processes and product-forming capture reactions taken into account. Such a steady-state treatment, neglecting isotope effects and assuming that $k_{Ph} = k_{Ph}{}^*$ and that the rate constants (k_{SOH}) for the capture of **2**–**5** are identical, gives eq 1 for the relative ratios of **2**–**5** in terms

$$2/3/4/5 = 1.0:(2+\alpha)/[(2+\alpha)^2-2]:1/(2+\alpha):1/[(2+\alpha)^2-2] \qquad (1)$$

of the capture vs. rearrangement ratio α ($\alpha = k_{SOH}/k_{Ph}$). Consequently, when $k_{SOH} \gg k_{Ph}$, i.e., α is large so that $(2+\alpha)^2 \gg 2$, the [**3**]/[**4**] ratio will be very close to unity. For example, when $\alpha = 8$, the [**3**]/[**4**] ratio will be 1.02, and even when $\alpha = 3$, the [**3**]/[**4**] ratio is 1.09. In the solvolysis of **1**,[2] the results showed approximately equal amounts of products derived from **3** (7.3 ± 1.2%) and from **4** (6.6 ± 1.2%). This near equality of products from **3** and **4** thus reflects a high value for α and is not the result of half of **2** equilibrated with **4** and the other half equilibrated with **3** and **5**.

The assumptions that $k_{Ph} = k_{Ph}{}^*$ and that k_{SOH} is identical for the capture of **2**–**5** are equivalent to assuming that the cationic species **2**–**5** are similar, or at least behave similarly. A possible alternative is the presence of a "memory effect", which will be reflected in different behaviors of the different cations according to their method of formation. For example, the initially formed **2** may differ in the position of the counterion from **5** which is formed only after two consecutive 1,2 shifts, and this may result in different k_{SOH} or k_{Ph} values for the two ions. In order to decide between the alternatives, we compared the observed and the calculated product distributions. By using an α value of 9.2,[3] which is based on 15.2% scrambling for the solvolysis in 70% HOAc–30% H_2O of triphenylvinyl bromide singly labeled at C-2 with ^{13}C or ^{14}C[2,4] and the relative ratios derived from the steady-state treatment as given by eq 1, the calculated distribution of products from the various isotopomeric cations is **2** (84.2%)/**3** (7.6%)/**4** (7.5%)/**5** (0.7%). These values are in excellent agreement with the observed results, except that the value for **5** is lower. Since the percentage of **5** is very low and the associated error is large, we believe that the deviation is mechanistically insignificant. We, therefore, conclude that the assumption that consecutive 1,2 shifts take place in structurally identical isotopomeric cations is quantitatively validated. A similar labeling analysis which requires the formation of a tetracyclic carbocation by consecutive rearrangements starting from an isotopomeric cation was described by Goldstein and Warren.[5] However, in their system the cationic species involved in the rearrangement are isotopic diastereomers, whereas in our system they are simple isotopomers.

Lee and co-workers[6] have extended the double labeling work to include a study on a doubly labeled trianisylvinyl cationic system. 1,2-Dianisyl-2-(*p*-[$^2H_3$]methoxyphenyl)[2-^{13}C]vinyl bromide (**6**) was solvolyzed in 70% HOAc–30% H_2O without or with the presence of 1, 5, 10, or 400 equiv of added NaOAc. The products were degraded to dianisyl ketone and analyzed by mass spec-

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[1] Part 40 in the series "Vinylic Cations from Solvolysis" from the Hebrew University. For part 39 see: Rappoport, Z.; Kaspi, J.; Tsidoni, D. *J. Org. Chem.* **1984**, *49*, 80–84.

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[3] For a review summarizing α values for many systems see: Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York 1979; Chapter 6.

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Table I. Distribution of Products from Isotopomeric Cations 2′, 3′, 4′, and 5′ in the Solvolysis of 1,2-Dianisyl-2-(p-[$^2H_3$]methoxyphenyl)[2-^{13}C]vinyl Bromide (6) in 70% HOAc-30% H_2O

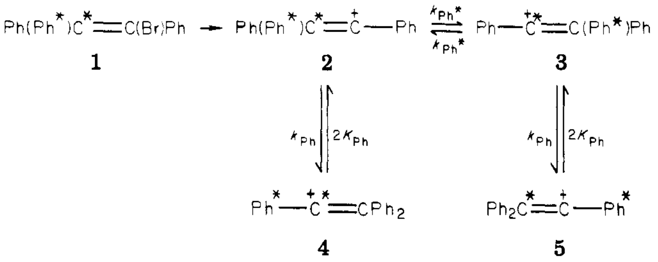
	distribution of products from precursor ions, %							
	2′		3′		4′		5′	
expt[a]	obsd[b]	calcd[c]	obsd[b]	calcd[c]	obsd[b]	calcd[c]	obsd[b]	calcd[c]
1	66.6, 67.5	69.4	14.5, 15.6	14.4	14.0, 14.0	13.3	4.9, 2.9	2.8
2	67.4, 66.1	69.4	15.3, 13.0	14.4	12.7, 15.9	13.3	4.6, 5.0	2.8
3	68.3, 69.7	71.7	12.9, 11.8	13.4	13.0, 13.1	12.5	5.8, 5.4	2.4
4	71.9, 71.0	72.5	11.9, 10.9	13.1	11.3, 13.2	12.3	4.9, 4.9	2.2
5	76.3, 78.3	80.8	9.6, 8.9	9.2	10.5, 9.7	9.0	3.6, 3.1	1.1

[a] Experiments 1-5, respectively, were carried out in the presence of 0, 1, 5, 10, and 400 equiv of added NaOAc. [b] From duplicate runs reports in ref 6. [c] Calculated from the relative ratios in terms of α given in eq 1, α for expts 1-5, respectively, being 3.2, 3.2, 3.7, 3.9, and 7.0, calculated[4b] from scrambling data in similar solvolysis experiments with trianisyl[2-^{14}C]vinyl bromide.[7]

Table II. Distribution of Products from Isotopomeric Cations 2′, 3′, 4′, and 5′ in the Solvolysis of 6 in CF_3COOH-CF_3COOAg and in CF_3CH_2OH-2,6-Lutidine

	distribution of products from precursor ions, %							
	2′		3′		4′		5′	
medium	run 1	run 2	run 1	run 2	run 1	run 2	run 1	run 2
CF_3COOH-CF_3COOAg	33.2	36.0	31.9	33.0	18.6	16.4	16.3	14.5
CF_3CH_2OH-Lutidine	35.6	33.0	31.4	31.8	18.0	18.3	15.1	16.6

Scheme I[a]



[a] Ph* = C_6D_5, C* = ^{13}C.

trometry by using the chemical-ionization technique as was done with the doubly labeled triphenylvinyl system.[2] Products were derived from the four isotopomeric trianisylvinyl cations 2′-5′, analogous to 2-5 given in Scheme I, except that the aryl groups for 2′-5′ are An instead of Ph, and An* = p-$CD_3OC_6H_4$ instead of Ph* = C_6D_5. Summarized in Table I are the observed product distributions and the distributions calculated by using the relative ratios in terms of α ($\alpha = k_{SOH}/k_{An}$) as in eq 1. It is seen that fairly good agreements were obtained between the observed and calculated values, again giving support to the occurrence of consecutive 1,2 shifts in structurally identical isotopomeric trianisylvinyl cations.

In the work with the doubly labeled triphenylvinyl bromide 1,[2] it was concluded that complete equilibration among the various isotopomeric triphenylvinyl cations was not achieved, and a "complete equilibration" based on the assumption that 2 was half equilibrated with 4 and the other half equilibrated with 3 and 5 was discussed. Actually, for a truly complete equilibration, k_{Ph} would be much greater than k_{SOH}, and α would be negligible compared to 2. Then from eq 1, 2/3/4/5 would be 1:1:0.5:0.5; i.e., the distribution of products from 2-5 would be 33.3%, 33.3%, 16.7%, and 16.7%, respectively. If a triarylvinyl substrate were singly labeled at C-2, for complete equilibration the extent of scrambling from C-2 to C-1 would be 50%. It is known that the extent of scrambling is much less than 50% in the solvolysis of triphenyl[2-^{14}C]vinyl bromide in aqueous HOAc.[4a,7] On the other hand, 50% scrambling was observed in the reaction of trianisyl[2-^{13}C]vinyl bromide with CF_3COOH-CF_3COOAg,[8] and 100 ± 3% rearrangement (50 ± 1.5% scrambling) was reported for the solvolysis of 1,2-dianisyl-2-(p-[$^2H_3$]methoxyphenyl)vinyl bromide for 8 h in CF_3CH_2OH-2,6-lutidine.[9] To test the prediction for product distribution after complete equilibration according to eq 1, we solvolyzed the doubly labeled trianisylvinyl bromide 6 in CF_3COOH-CF_3COOAg and in CF_3CH_2OH-2,6-lutidine. The results are given in Table II. It is seen from Table II that the ratio of products from 2′/3′/4′/5′ is very close to the 1:1:0.5:0.5 ratio predicted for complete equilibration, thus giving strong support to the validity of the steady-state treatment.

Experimental Section

Reaction of 1,2-Dianisyl-2-(p-[$^2H_3$]methoxyphenyl)[2-^{13}C]vinyl Bromide (6) with CF_3COOH-CF_3COOAg. A solution of 900 mg (2.1 mmol) of 6[6] and 500 mg (2.3 mmol) of CF_3COOAg in 13 mL of CF_3COOH was stirred at room temperature for 30 min. The resulting products, the isotopomeric trianisylvinyl trifluoroacetates, were recovered and converted by $LiAlH_4$ reduction to the isotopomeric 1,2,2-trianisylethanols[8] and then oxidized with $KMnO_4$ to give the isotopomeric dianisyl ketones[7] for CI mass spectrometric analysis as previously described.[2,6]

Solvolysis of 6 in CF_3CH_2OH-2,6-Lutidine. A solution of 255 mg (0.60 mmol) of 6 and 200 mg (1.8 mmol) of 2,6-lutidine in 20 mL of CF_3CH_2OH in a sealed tube was heated in an oil bath at 120 ± 2 °C for 24 h. After cooling, the resulting material was poured into 80 mL of ether. The ether solution was washed three times with H_2O and dried over $MgSO_4$. After removal of the solvent, the residual products, the isotopomeric trianisylvinyl trifluoroethyl ethers, were purified by passage through an alumina column and then degraded by ozonolysis[10] to give the isotopomeric dianisyl ketones for mass spectrometric analysis.

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Registry No. 6, 85846-22-6.

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