

retention times of 155, 270, and 195 s for compounds 1-3, respectively. The trans (2) to cis (3) ratio is about 11:1.

In a typical reaction, a 50-cm³ round-bottomed flask with a side arm for sampling was charged with 243 mg (0.755 mmol) tetrabutylammonium bromide and with a 15.1 mmol allylbenzene in 8.00 cm³ of toluene solution (1.42 M at 75 °C). The mixture was heated to 75 °C and 5.00 mL of aqueous 50% NaOH preheated to 75 °C was added, stirring was commenced, and the time was taken. At regular intervals, 5.0-μL samples of the upper organic layer were taken and immediately injected into the gas chromatograph. Phase separation was almost immediate after stopping

the stirring. No less than nine samples were taken per run. The temperature was maintained ±0.4 °C by a Fried thermoregulator, electric relay, and thermostated bath. Stirring was provided by a Heidolph mechanical stirrer with appropriate gears attached to a flat-bladed Teflon paddle. The stirring speed was determined by a Jaquet tachometer to ±10 rpm.

Registry No. 1, 300-57-2; TBA-HSO₄, 32503-27-8; TBA-Cl, 1112-67-0; Bu₄NBr, 1643-19-2; Pnt₄NBr, 866-97-7; Hex₄NBr, 4328-13-6; Hep₄NBr, 4368-51-8; Oct₄NBr, 14866-33-2; Dec₄NBr, 14937-42-9; Dodec₄NBr, 14866-34-3.

Mass Spectrometric Analysis of the Isotopomeric Species in the Solvolysis of 1,2-Diphenyl-2-[²H₅]phenyl[2-¹³C]vinyl Bromide in 70% HOAc-30% H₂O

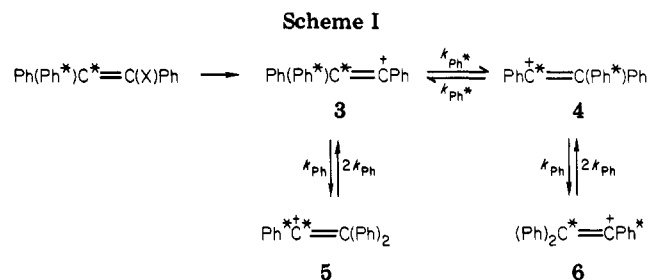
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The distributions of products from four possible isotopomeric triphenylvinyl cations derived from solvolyses in 70% HOAc-30% H₂O of the doubly labeled 1,2-diphenyl-2-[²H₅]phenyl[2-¹³C]vinyl bromide (1-Br-2-¹³C-2-Ph-*d*₅) were determined by mass spectrometry. The electron-impact spectra of the reaction products, the various labeled 1,2,2-triphenylethanones derived from the four isotopomeric cations, did not give consistent or reproducible results probably because of complications by multiple fragmentation. After degradation of the reaction products to give (C₆H₅)₂CO, (C₆H₅)₂¹³CO, C₆H₅(C₆D₅)CO, and C₆H₅(C₆D₅)¹³CO, the chemical ionization spectra of these isotopomeric benzophenones gave, for each solvolysis reaction, the relative amounts of the four isotopomers and hence the distribution of products derived from the four isotopomeric triphenylvinyl cations. The results obtained showed agreements between the mass spectrometric data and previous ¹⁴C scrambling data or the ¹³C scrambling data obtained in the present work by ¹³C NMR, with the ¹⁴C or ¹³C scrambling data showing greater precision. For example, the scrambling of the ¹³C label from C-2 to C-1 as determined by ¹³C NMR for the solvolysis of 1-Br-2-¹³C-2-Ph-*d*₅ in 70% HOAc in the presence of various amounts of added NaOAc was found to be 15.2 ± 0.5%, while the analogous value derived from the CI spectral analysis was 13.9 ± 2.2%. The observed formation of the various possible isotopomeric products also demonstrated definitely the occurrence of successive 1,2-phenyl shifts in the triphenylvinyl cation, and this would not have been detected with the use of only a singly labeled substrate.

Degenerate rearrangements arising from 1,2 phenyl shifts in the triphenylvinyl cation were first observed in 1974 in the solvolysis of triphenyl[2-¹⁴C]vinyl triflate (1-OTf-2-¹⁴C) in HOAc, HCOOH, or CF₃COOH.² Subsequently, extensive isotopic scrambling studies on a variety of singly labeled triarylvinyl cationic systems have been carried out, and the results have been summarized in a recent book on vinyl cations³ as well as in a recent review.⁴ It is anticipated that in a triarylvinyl cation, repeated cycles of 1,2 aryl shifts may be possible. In the acetolysis of trianisyl[2-¹⁴C]vinyl bromide (2-Br-2-¹⁴C), for example, scrambling of the label from C-2 to C-1 was observed in both reaction product and recovered, unconsumed reactant.⁵ In the later stages of reaction, the scrambling in the recovered reactant was found to be even higher than that in the corresponding product, thus indicating the occurrence of many cycles of ionization, 1,2 shift, and return to covalent bonding, leading to the accumulation of large amounts of scrambled reactant.⁵ In the case of triphenyl[2-¹⁴C]vinyl bromide (1-Br-2-¹⁴C), however, solvo-



lysis in HOAc was too slow, and in reactions in 70% HOAc-30% H₂O (70% HOAc), no significant extent of scrambling was observed in the recovered, unconsumed reactant.⁶

A more definitive measure of successive 1,2 shifts could be obtained from studies with doubly labeled substrates. With a single isotopic label such as 1-Br-2-¹⁴C or 2-Br-2-¹⁴C, 1,2 aryl shifts could only give rise to two different isotopomers with the label at C-2 or C-1. With a doubly labeled substrate, as illustrated in Scheme I for a triphenylvinyl system labeled at C-2 and at one of the C-2 phenyl groups, four isotopomeric cations (3-6) would be detectable.

It should be pointed out, however, that labeling with a radioisotope would involve only a tracer amount of the

(1) College of Pharmacy, University of Saskatchewan.
 (2) Lee, C. C.; Cessna, A. J.; Davis, B. A.; Oka, M. *Can. J. Chem.* 1974, 52, 2679-2683.
 (3) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1978; pp 359-432.
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 (5) Lee, C. C.; Weber, U.; Obafemi, C. A. *Can. J. Chem.* 1979, 57, 1384-1387.

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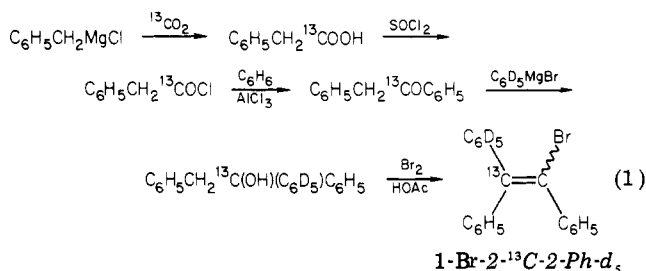
Table I. Peaks in the Molecular Ion Region for the 10 eV EI and CI Spectra of Unlabeled Benzophenone

EI spectrum		CI spectrum			
<i>m/z</i>	rel abundance	<i>m/z</i>	rel abundance	<i>m/z</i>	rel abundance
180	1.22	181		198	
181	4.97	182	1.48	199	
182 (M ⁺)	100.00	183 ([M + H] ⁺)	54.43	200 ([M + NH ₄] ⁺)	100.00
183	14.18	184	8.87	201	14.55
184	0.90	185	1.82	202	1.70

isotope. If two radioisotopes were used, the number of molecules that would actually contain both labels would be extremely small, and any isotopic scrambling results observed would be derived essentially from an intermolecular mixture of the singly labeled substrates. Even with the use of ¹³C and ¹⁴C as labels, as in the acetolysis of 1,2-dianisyl-2-*p*-[¹⁴C]methoxyphenyl[2-¹³C]vinyl bromide (2-Br-2-¹³C-2-methoxy-¹⁴C), since the ¹³C and ¹⁴C contents were measured by two independent methods, the scrambling results were the same as those obtained from a 1:1 mixture of singly labeled 2-Br-2-¹³C and 2-Br-2-methoxy-¹⁴C.⁷ In the present work, triphenylvinyl bromide doubly labeled with ¹³C and D, namely, 1,2-diphenyl-2-[²H₅]phenyl[2-¹³C]vinyl bromide (1-Br-2-¹³C-2-*Ph-d*₅), was solvolyzed in 70% HOAc, and the results were analyzed by mass spectrometry in order to determine the relative extents of involvement of isotopomeric cations 3–6.

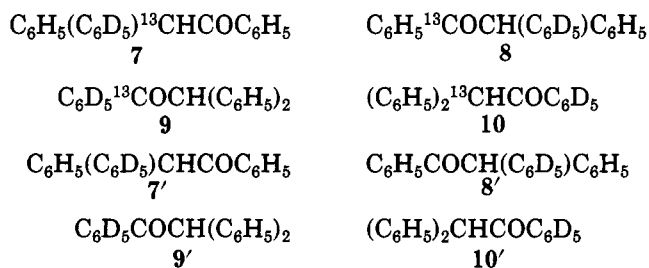
Results and Discussion

By use of procedures similar to those employed in the synthesis of (*Z*)- and (*E*)-1,2-dianisyl-2-phenyl[2-¹³C]vinyl and (*Z*)- and (*E*)-2-phenyl-1,2-ditolyl[2-¹³C]vinyl bromides,⁸ 1-Br-2-¹³C-2-*Ph-d*₅ was prepared via the series of reactions in eq 1. The isotopic enrichments, as indicated by the



supplier, were 90% and 99%, respectively, for ¹³C and D (as Ba¹³CO₃ and C₆D₅Br), and mass spectrometry confirmed the 90% ¹³C enrichment and the essentially complete deuteration (see Experimental Section). No attempt was made in separating the possible *Z* and *E* isomers of 1-Br-2-¹³C-2-*Ph-d*₅.

Solvolyzes of 1-Br-2-¹³C-2-*Ph-d*₅ were carried out in 70% HOAc with or without the presence of added NaOAc. The products obtained were the various labeled 1,2,2-triphenylethanones 7–10, derived from the isotopomeric



(7) Lee, C. C.; Obafemi, C. A.; Quail, J. W.; Rappoport, Z. *Can. J. Chem.* 1981, 59, 2342–2349.

(8) (a) Lee, C. C.; Oka, M. *Can. J. Chem.* 1976, 54, 604–609. (b) Lee, C. C.; Paine, A. J.; Ko, E. C. F. *J. Am. Chem. Soc.* 1977, 99, 7267–7272.

cations 3–6, respectively. Since the ¹³C enrichment was 90%, 10% of the products did not contain ¹³C. Thus in conjunction with the formation of 7–10, 7'–10' were also formed from 3–6, respectively, the ratio of 7/7', 8/8', 9/9', and 10/10' being 90:10.

It might be anticipated that the mass spectrum of 1,2,2-triphenylethanone should give two major fragment ions, (C₆H₅)₂CH⁺ (*m/z* 167) and C₆H₅CO⁺ (*m/z* 105). The relative abundance of the various isotopomeric species for these fragments should then provide two sets of internally consistent results on the relative amounts of products derived from the isotopomeric cations 3–6. These expectations, however, were not realized. Inconsistent and nonreproducible results were obtained from electron-impact (EI) mass spectrometry even when a low energy of 10 eV was used in order to reduce the extent of fragmentation. Similar inconsistent and nonreproducible results, ascribed to the possibility of multiple fragmentation patterns, have also been observed by Houminer et al.⁹ when the EI method was employed in the determination of degenerate rearrangements in various solvolyses of (*Z*)- and (*E*)-1,2-dianisyl-2-phenylvinyl and trianisylvinyl bromides labeled with a *p*-CD₃O group at a C-2 anisyl substituent.

As an illustration of the EI results, the 10-eV mass spectrum for the mixture of isotopomeric 1,2,2-triphenylethanones obtained in a solvolysis of 60 mM 1-Br-2-¹³C-2-*Ph-d*₅ in 70% HOAc at 150 ± 2 °C for 2 days (run 1, expt 1) showed relative abundance values of 100.00, 25.69, 1.59, 0.06, 2.36, 11.79, 0.73, 1.60, 0.35, 0.10, 4.20, 19.08, 2.62 and 0.17, respectively, for *m/z* 105 (C₆H₅CO⁺), 106, 107, 109, 110, 111, 112, 167 ((C₆H₅)₂CH⁺), 168, 171, 172, 173, 174, and 175. On the basis of the relative abundance of the isotopomeric C₆H₅CO⁺ ions, the product distributions were calculated to be 73.3%, 16.2%, 9.7%, and 0.8%, respectively, from precursor ions 3–6, a detailed illustration of the calculations being given in the Experimental Section. On the other hand, with the relative abundance of the isotopomeric (C₆H₅)₂CH⁺ ions obtained in the same experiment, the analogous product distributions were found to be 83.4%, 8.6%, 6.3%, and 1.6%, clearly showing poor agreements between the two sets of results.

When the product mixture of isotopomeric 1,2,2-triphenylethanones was reduced to 1,2,2-triphenylethanol (11) and then subsequently oxidized to benzophenone (12), the EI spectra of 11 or 12 also failed to give consistent, reproducible results. In order to minimize complications arising from multiple fragmentations and variations between runs in the EI method, we adopted a chemical ionization (CI) procedure¹⁰ in order to evaluate the distribution of products from cations 3–6. The CI spectra, with NH₃ as the reagent gas, were obtained from the degradation product, the mixture of isotopomeric benzophenones (12). Both [M + H]⁺ and [M + NH₄]⁺ ions were

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Table II. CI Spectra in the [M + NH₄]⁺ Region for the Isotopomeric Benzophenones Derived from the Products of Solvolyses of 60 mM 1-Br-2-¹³C-2-Ph-d₅ in 70% HOAc

m/z	rel abundance									
	expt 1 ^a		expt 2 ^a		expt 3 ^a		expt 4 ^b	expt 5 ^b	expt 6 ^b	
	run 1	run 2	run 1	run 2	run 1	run 2				
200	10.55	9.30	7.45	10.41	7.89	10.76	7.65	5.49	7.82	
201	2.29	2.37	1.61	2.11	1.46	2.25	2.59	1.28	1.71	
202			0.08	0.13		0.31				
204	0.92	1.00	0.85	0.53	0.73	0.82	1.51		0.57	
205	22.94	22.28	20.64	19.76	19.44	21.62	27.48	18.76	19.20	
206	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	
207	13.46	13.79	13.54	13.44	13.30	13.63	15.30	15.06	13.23	
208	1.07	1.74	1.10	0.79	1.02	0.82	1.08	1.21	1.00	

^a Experiments 1-3, respectively, were carried out in the presence of 0, 5, and 10 molar equiv of NaOAc at 150 ± 2 °C for 2 days. ^b Experiments 4-6, respectively, were carried out in the presence of 0, 5, and 10 molar equiv of NaOAc at 150 ± 2 °C for 10 days.

Table III. Distribution of Products from Isotopomeric Cations 3-6 Calculated from the Data in Table II and Scrambling of the ¹³C Label from C-2 to C-1 from ¹³C NMR

expt	distribution of products from precursor ions, %										scrambling of ¹³ C from C-2 to C-1, %	
	3		4		5		6		4 + 5		run 1	run 2
	run 1	run 2	run 1	run 2	run 1	run 2	run 1	run 2	run 1	run 2		
1	81.2	82.4	9.1	8.7	7.8	6.9	1.9	2.0	16.9	15.6	15.8	15.6
2	85.4	83.9	7.7	6.9	5.8	8.0	1.1	1.3	13.5	14.9	15.7	15.1
3	85.9	82.9	6.7	8.2	6.1	8.2	1.3	0.7	12.8	16.4	14.5	14.9
4	86.3		5.4		6.0		2.3		11.4		15.3	
5	88.0		6.5		4.4		1.2		10.9		15.2	
6	85.9		6.6		6.1		1.5		12.7		14.4	
mean ^a	84.7 ± 2.2		7.3 ± 1.2		6.6 ± 1.2		1.5 ± 0.5		13.9 ± 2.2		15.2 ± 0.5	

^a Mean of the nine values ± standard deviation.

observed in these CI spectra. Given in Table I are comparisons of the peaks in the molecular ion regions for the spectra of the unlabeled 12 obtained by the CI process and by the 10-eV EI process. Since the least number of peaks appeared in the [M + NH₄]⁺ region, this region would probably be the least affected by multiple fragmentations. The relative abundance of the [M + NH₄]⁺ ions derived from the isotopomeric compounds (C₆H₅)₂CO, (C₆H₅)₂¹³CO, C₆H₅(C₆D₅)CO, and C₆H₅(C₆D₅)¹³CO at m/z 200, 201, 205, and 206, respectively, were, therefore, utilized to calculate the product distribution from cations 3-6. A detailed illustration of the calculations is given in the Experimental Section.

Six solvolysis experiments were carried out by using 60 mM 1-Br-2-¹³C-2-Ph-d₅. Experiments 1-3, respectively, were carried out in the presence of 0, 5, and 10 molar equiv of added NaOAc at 150 ± 2 °C for 2 days, while expt. 4-6, respectively, were done in the presence of 0, 5, and 10 molar equiv of added NaOAc at 150 ± 2 °C for 10 days. Experiments 1-3 were carried out in duplicate, and the conditions of these experiments were similar to some of the reaction conditions used in previous studies with 1-Br-2-¹⁴C.^{6b} Each solvolysis product, a mixture of isotopomeric 1,2,2-triphenylethanones, was reduced to the isotopomeric 1,2,2-triphenylethanol (11) which were analyzed for ¹³C scrambling from C-2 to C-1 by using ¹³C NMR.¹¹ The isotopomeric alcohols 11 were then oxidized to the corresponding benzophenones (12) for CI mass spectrometric analysis with NH₃ as a reagent gas. The CI mass spectra in the [M + NH₄]⁺ region for the benzophenones from these experiments are summarized in Table II. From these data, the distribution of products from

cations 3-6 were calculated, and the results, together with the ¹³C scrambling data, are given in Table III.

In our previous work, the solvolyses of 1-Br-2-¹⁴C in 70% HOAc in the presence of different amounts of added salts, including NaOAc, gave 14.7 ± 0.7% scrambling of the ¹⁴C label from C-2 to C-1.⁶ The presently observed 15.2 ± 0.5% scrambling of the ¹³C label obtained from ¹³C NMR (Table III) is in good agreement with the earlier ¹⁴C data. It may also be noted from Scheme I that if only the ¹³C label were considered, the sum of the products from cations 4 and 5 should be equal to the scrambling of the ¹³C from C-2 to C-1. From Table III it is seen that the mean values of 13.9 ± 2.2% for the products from 4 and 5 and 15.2 ± 0.5% for the ¹³C scrambling are in agreement within the standard deviations for these mean values, the greater deviations for the data obtained from mass spectrometry indicating that the scrambling data obtained from ¹³C NMR or ¹⁴C activity are capable of greater precision.

In the previous work,⁶ it was found that the presence of added NaOAc did not materially affect the extent of scrambling in the solvolysis of 1-Br-2-¹⁴C in 70% HOAc. The results in Table III also show no significant or consistent changes in the distribution of products from 3-6 when the reaction was carried out with 0, 5, or 10 molar equiv of added NaOAc. It has been suggested previously that in the triphenylvinyl cationic system, the 1,2-phenyl shifts may have taken place in the ion-pair stage, and thus the extent of scrambling would be insensitive to the presence of the nucleophilic acetate ion.⁶ Recently, however, Obafemi in this laboratory has found that both common-ion rate depression and exchange with added ⁸²Br⁻ ions took place in the solvolysis of 1-Br in 70% HOAc.¹² Since both of these observations are diagnostic of the involvement of dissociated ions rather than ion

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(12) Results of C. A. Obafemi, to be submitted for publication.

pairs,¹³ the previously suggested role for ion pairs has to be reconsidered. Probably, the insensitivity of the extent of scrambling to the presence of added acetate ions may be due to the relatively low stability of the triphenylvinyl cation which would show a low selectivity or low ability to discriminate between different nucleophiles.¹⁴

If complete equilibration among cations 3–6 were to take place according to Scheme I, assuming, for example, that 60 molecules of 1-Br-2-¹³C-2-Ph-d₅ were involved, initially there would be 60 cations 3. If half were equilibrated between 3 and 5, at complete equilibration there would be 20 of 3 and 10 of 5. Similarly, the other half would equilibrate between 3, 4, and 6, and at complete equilibration there would be 15 of 3, 10 of 4, and 5 of 6. The net result would be a distribution of 35, 10, 10, and 5, corresponding to 58.3%, 16.7%, 16.7%, and 8.3% distribution of products from 3–6, respectively. The results in Table III certainly show that complete equilibration has not been achieved in the solvolysis of 1-Br-2-¹³C-2-Ph-d₅ in 70% HOAc. In accord with Scheme I, the mean values for the products from 4 and 5 do show the expected equality when deviations from the mean are taken into account. Finally, the results in Table III show the presence of some product from cation 6, definitely demonstrating the occurrence of successive 1,2 shifts, and this would not have been detectable if only a singly labeled substrate was utilized.

Experimental Section

1,2-Diphenyl-2-[²H₅]phenyl[2-¹³C]vinyl Bromide (1-Br-2-¹³C-2-Ph-d₅). 1,2-Diphenyl[1-¹³C]ethanone (carbonyl-labeled deoxybenzoin; 13) was prepared from the Friedel-Crafts acylation of benzene with phenyl[1-¹³C]acetyl chloride in the same way as in the previous preparation of carbonyl-labeled deoxybenzoin.^{8a} Treatment of 13 with C₆D₅MgBr (from C₆D₅Br supplied by Merck, Sharp and Dohme Canada Ltd.) again, as previously reported for the similar treatment of deoxybenzoin,^{8a} gave a 91% yield of 1,2-diphenyl-1-[²H₅]phenyl[1-¹³C]ethanol (14), mp 88–89 °C (lit.² mp 88 °C). Reaction of 14 with Br₂ in HOAc as described in the preparation of 1-Br-2-¹⁴C₂ gave a 62% yield of the doubly labeled 1-Br-2-¹³C-2-Ph-d₅, mp 115–116 °C (lit.² mp 115 °C).

The EI spectrum of 1-Br-2-¹³C-2-Ph-d₅ showed relative intensities at *m/z* 339, 340, 341, 342, and 343, respectively, of 4.85%, 46.24%, 13.71%, 45.64%, and 8.49% of the base peak, the base peak being at *m/z* 261 for the M – Br ion. The *m/z* 339 and 341 peaks, respectively, would correspond to the ⁷⁹Br and ⁸¹Br molecular ions with only the Ph-d₅ label, while the *m/z* 340 and 342 peaks, respectively, would correspond to the ⁷⁹Br and ⁸¹Br molecular ions with both Ph-d₅ and ¹³C labels. For the doubly labeled molecular ions at *m/z* 340 and 342, the intensity ratio of 46.24:45.64 would correspond to 50.3% ⁷⁹Br and 49.7% ⁸¹Br, in good agreement with the natural abundance of 50.5% and 49.5% for these isotopes. For the molecular ions labeled only with Ph-d₅ at *m/z* 339 and 341, a correction for M + 1 was made on the *m/z* 341 peak. Since M + 1 at *m/z* 343 amounted to 18.6% of the intensity of the *m/z* 342 peak, 18.6% of the intensity of the peak at *m/z* 340 was subtracted from that of the *m/z* 341 peak, giving a corrected intensity for *m/z* 341 of 5.11%. For the ⁷⁹Br molecular ions with only the Ph-d₅ label and with both Ph-d₅ and ¹³C labels at *m/z* 339 and 340, respectively, the relative intensities of 4.85% and 46.24% would correspond to the presence of 9.5% 1-Br-2-Ph-d₅ and 90.5% 1-Br-2-¹³C-2-Ph-d₅. Similarly, for the ⁸¹Br molecular ions at *m/z* 341 and 342, the relative intensities of 5.11 and 45.64 would correspond to the presence of 10.1% 1-Br-2-Ph-d₅ and 89.9% 1-Br-2-¹³C-2-Ph-d₅. These results thus constituted a confirmation of the 90% enrichment of the ¹³C label as indicated

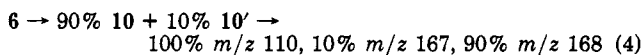
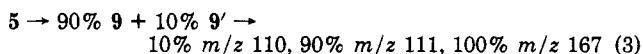
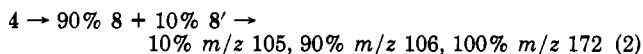
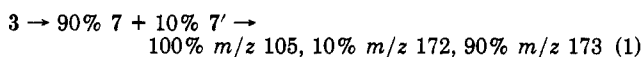
by the commercial supplier. In the EI spectrum of this doubly labeled substrate, no molecular ions were found at *m/z* 334, 335, 336, and 337, indicating no detectable amount of either unlabeled 1-Br or 1-Br labeled with only ¹³C, thus showing that the degree of deuteration in 1-Br-2-¹³C-2-Ph-d₅ was essentially complete.

Solvolysis Reactions. The reactions were carried out by heating in sealed tubes 60 mM solutions of 1-Br-2-¹³C-2-Ph-d₅ in 70% HOAc–30% H₂O (by volume) containing 0, 5, or 10 molar equiv of NaOAc at 150 ± 2 °C for 2 or 10 days. Under these conditions, the reactions proceeded to 60–66% or 96–98% completion after 2 or 10 days, respectively. The yields of product, the isotopomeric 1,2,2-triphenylethanones, were in the range of 70–80% based on the consumed reactant. A typical experiment is described below.

A mixture of 400 mg (1.2 mmol) of 1-Br-2-¹³C-2-Ph-d₅ and 490 mg (6.0 mmol) of NaOAc in 20 mL of 70% HOAc in a sealed tube was heated in an oil bath at 150 ± 2 °C for 2 days (expt 2, run 1). After cooling, the tube was opened and its content poured into H₂O and then extracted with CHCl₃ (3 × 25 mL). The extract was washed with a dilute NaHCO₃ solution and then with H₂O. The liberated Br[–] ion in the combined aqueous phase was titrated potentiometrically with AgNO₃ which showed that the extent of reaction in this experiment was 62%. The CHCl₃ extract was dried over MgSO₄, the solvent was removed in a rotatory evaporator, and the residual oil was purified by passage through an alumina column.^{8a} The unconsumed reactant was removed first by elution with a 9:1 mixture of petroleum ether–ether. The desired product was then eluted with CHCl₃, and after crystallization from ethanol containing a small amount of acetone, 172 mg (78% based on 62% reaction) of the mixture of isotopomeric 1,2,2-triphenylethanones [mp 136–137 °C (lit.¹⁵ mp 136–137 °C)] was obtained.

As an illustration of the treatment of the EI spectrometric data for the isotopomeric mixture of 1,2,2-triphenylethanones, first let us consider the isotopomeric ions C₆H₅CO⁺, C₆H₅¹³CO⁺, C₆D₅CO⁺, and C₆D₅¹³CO⁺ at *m/z* 105, 106, 110, and 111, respectively. For run 1 of expt 1, the abundance of the *m/z* 107 peak is 6.19% of the abundance of the *m/z* 106 peak, and 6.19% is a reasonable M + 1 abundance for C₆H₅¹³CO⁺ (*m/z* 106). The abundance of the *m/z* 105 peak is 100.00%, and the M + 1 correction for the *m/z* 106 peak should be 6.19% of 100.00%. Hence the corrected abundance for the *m/z* 106 peak should be 25.69 – 6.19 = 19.50%. Similarly, for the peak at *m/z* 111 (C₆D₅¹³CO⁺), the M + 1 ion at *m/z* 112 is also 6.19%. Subtracting 6.19% of the peak abundance at *m/z* 110 from that at *m/z* 111 would give a corrected abundance for *m/z* 111 of 11.64%. In summary, the corrected relative abundance for run 1 of expt 1 should be 100.00%, 19.50%, 2.36%, and 11.64% for *m/z* 105, 106, 110, and 111, respectively.

Since cation 3 would give rise to a 90:10 mixture of 7 and 7', fragmentations of 7 and 7' would both give C₆H₅CO⁺ (*m/z* 105), while 7 and 7' would also give C₆H₅(C₆D₅)¹³CH⁺ (*m/z* 173) and C₆H₅(C₆D₅)CH⁺ (*m/z* 172), respectively. In a similar way, the fragmentation ions from 4–6 can be deduced, and these are summarized in eq 1–4.



From eq 1 and 2 it is seen that the *m/z* 105 peak is derived from all of the product from 3 and from 10% of the product from 4. Similar considerations on eq 2–4 gave the sources of the *m/z* 106, 110, and 111 peaks, and these are summarized in eq 5–8. For abundance of *m/z* 105 =

$$\text{product from 3} + 0.10(\text{product from 4}) \quad (5)$$

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(15) Pollock, J. R. A.; Stevens, R., Eds. "Dictionary of Organic Compounds"; 4th ed.; Eyre and Spottiswoode: London, 1965; Vol. 3, p 1270.

$$\text{abundance of } m/z 106 = 0.90(\text{product from 4}) \quad (6)$$

$$\text{abundance of } m/z 110 = \text{product from 6} + 0.10(\text{product from 5}) \quad (7)$$

$$\text{abundance of } m/z 111 = 0.90(\text{product from 5}) \quad (8)$$

run 1 of expt 1, using eq 5-8 and the corrected relative abundances of 100.00, 19.50, 2.36, and 11.64, respectively, for the m/z 105, 106, 110, and 111 peaks, the relative amounts of products from 3-6 are calculated to be 97.83, 21.67, 12.93, and 1.07, respectively. On normalization of these results on a percentage basis, the distribution of products from 3-6 would become 73.3%, 16.2%, 9.7%, and 0.8%, respectively. In an analogous way, another set of distribution of products from 3-6 was calculated to be 83.4%, 8.6%, 6.3%, and 1.6% for the same run from the isotopomeric $(C_6H_5)_2CH^+$ ions at m/z 167, 168, 172, and 173.

Degradation Products. The 1,2,2-triphenylethanone was reduced with $LiAlH_4$ to give 1,2,2-triphenylethanol (11) which in turn was oxidized with $KMnO_4$ to give benzophenone (12). The procedures used have been described previously.²

Alcohol 11 showed ^{13}C NMR absorptions at δ (acetone- d_6) 60.8 (C-2), 76.9 (C-1), 126.8, 127.6, 127.9, 128.4, 128.8, 129.6, 130.0 (arom), 143.5, 143.9, and 145.2 (quat arom). The ^{13}C enrichments at C-1 and C-2, and hence the extents of scrambling from C-2 to C-1, were measured by using a relative intensity ratio method with a suitable absorption containing ^{13}C in its natural abundance as an internal reference standard.¹¹ The method utilized in calculating the extents of scrambling was the same as that described in the determination of the extents of scrambling during solvolyses of trianisyl[2- ^{13}C]vinyl bromide (2-Br-2- ^{13}C).^{11b} In the work with 2-Br-2- ^{13}C ,^{11b} the internal reference standard was the CH_3O absorption, while in the present work, the most intense aromatic absorption at 128.8 ppm was used as the internal standard. The results obtained on the extents of scrambling of the ^{13}C label from C-2 to C-1 are given in Table III.

The CI spectra of the various samples of benzophenone (12) from the solvolysis experiments were obtained with 0.3 torr of NH_3 as the reagent gas. A GC/MS instrument was employed, each sample being passed through the gas chromatograph before the CI spectrum was obtained using a VG-16F mass spectrometer supplied by VG Micromass Ltd. Given in Table II are the CI spectral data in the $[M + NH_4]^+$ region for the isotopomeric benzophenones derived from the various solvolyses of 1-Br-2- ^{13}C -2-*Ph-d*₅, the $[M + NH_4]^+$ ions for $(C_6H_5)_2CO$, $(C_6H_5)_2^{13}CO$,

$C_6H_5(C_6D_5)CO$, and $C_6H_5(C_6D_5)^{13}CO$ appearing at m/z 200, 201, 205, and 206, respectively.

As an illustration of the calculations, consider the data for run 1 of expt 1 in Table II. Since $M + 1$ at m/z 207 is 13.46% of the abundance of the m/z 206 peak, after the 13.46% $M + 1$ corrections are made, the corrected relative abundance for the peaks at m/z 200, 201, 205, and 206, respectively, are 10.55%, 2.29%, 22.82%, and 96.91%.

Analogous to the formulation of eq 1-4, eq 9-12 can be written

$$3 \rightarrow 90\% 7 + 10\% 7' \rightarrow 90\% m/z 206, 10\% m/z 205 \quad (9)$$

$$4 \rightarrow 90\% 8 + 10\% 8' \rightarrow 100\% m/z 205 \quad (10)$$

$$5 \rightarrow 90\% 9 + 10\% 9' \rightarrow 100\% m/z 200 \quad (11)$$

$$6 \rightarrow 90\% 10 + 10\% 10' \rightarrow 90\% m/z 201, 10\% m/z 200 \quad (12)$$

as shown. From eq 9-12, the sources of the m/z 200, 201, 205, and 206 peaks are given by eq 13-16.

abundance of m/z 200 =

$$\text{Product from 5} + 0.10(\text{product from 6}) \quad (13)$$

$$\text{abundance of } m/z 201 = 0.90(\text{product from 6}) \quad (14)$$

abundance of m/z 205 =

$$\text{Product from 4} + 0.10(\text{product from 3}) \quad (15)$$

$$\text{abundance of } m/z 206 = 0.90(\text{product from 3}) \quad (16)$$

For run 1 of expt 1 in Table II, using eq 13-16 and the corrected relative abundance of 10.55%, 2.29%, 22.82%, and 96.91%, respectively, for the m/z 200, 201, 205, and 206 peaks, the relative amounts of products from 3-6 are calculated to be 107.68, 12.05, 10.30, and 2.54, respectively. After normalizing these results on a percentage basis, the distribution of products from 3-6, respectively, would become 81.2%, 9.1%, 7.8%, and 1.9%, as given in Table III.

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Mechanisms of Polymer-Supported Catalysis. 4. Alkylation of Phenylacetonitrile with 1-Bromobutane Catalyzed by Aqueous Sodium Hydroxide and Polystyrene-Bound Benzyltrimethylammonium Ions

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The rates of reaction of phenylacetonitrile with excess 1-bromobutane catalyzed by excess 50% aqueous sodium hydroxide and insoluble polystyrene-bound benzyltrimethylammonium ions at 80 °C depend upon several experimental variables. The rates (1) were up to 8 times faster when the phenylacetonitrile was added before the 1-bromobutane to the catalyst than when the opposite order of addition was employed, (2) increased as the stirring speed was increased up to a constant rate at ≥ 500 rpm with a conventional mechanical stirrer in a round-bottomed flask, (3) increased as the catalyst particle size was decreased from 250 to 50 μm in diameter at a 500-rpm stirring rate, (4) decreased markedly when polymer cross-linking was increased from 2% to 10%, and (5) were 3 times faster with the 50% ring-substituted, 2% cross-linked benzyltrimethylammonium ion catalyst than with the corresponding 17% ring-substituted catalyst. Commercial macroporous anion-exchange resins had activities comparable with the 2% cross-linked catalysts prepared in this investigation. The kinetic results are discussed in terms of mass transfer and intraparticle diffusional limitation of the rates. The 2% cross-linked polymer-bound catalysts were as selective for monobutylation of phenylacetonitrile as the best commercial anion-exchange resins or soluble phase-transfer catalysts reported earlier.

Insoluble, polymer-supported, phase-transfer catalysts can be separated easily from reaction mixtures by filtration

and can be reused.² The activities often are lower than the activities of soluble phase-transfer catalysts, because