# Rearrangement Studies with <sup>14</sup>C. XXXIX. 1,2-Phenyl Shifts in Solvolyses of Triphenylvinyl-2-<sup>14</sup>C Triflate

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Solvolysis of triphenylvinyl-2-<sup>14</sup>C triflate was carried out in HOAc, 97% HCOOH, or CF<sub>3</sub>COOH. The reaction products showed rearrangements of the <sup>14</sup>C-label from C-2 to C-1 averaging about 6.7, 7.7, and 27.0%, respectively, for the acetolysis, formolysis, and trifluoro-acetolysis. The presence of the conjugate base of the solvent, added as the sodium salt, did not affect the extent of rearrangement. It is suggested that the 1,2-phenyl shift across the double bond of the triphenylvinyl cation takes place during the ion-pair stage and that the extent of rearrangement is related to the lifetime of the ion-pair and the nucleophilicity of the solvent.

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On effectue la solvolyse du triflate du triphénylvinyl <sup>14</sup>C-2 dans AcOH, 97% HCOOH ou CF<sub>3</sub>COOH. Les produits de réaction présentent des réarrangements du <sup>14</sup>C marqué passant de C-2 à C-1 avec des moyennes respectives de 6.7, 7.7 et 27.0% pour l'acétolyse, la formolyse et la trifluoroacétolyse. La présence de la base conjuguée du solvant, ajoutée à l'état de sel de sodium, n'affecte pas le taux de réarrangement. On suppose que le réarrangement du groupe phényle de 1 vers 2 à travers la double liaison du cation triphénylvinyle se produit durant le stade ion-pairé et que le taux de réarrangement est relié à la durée de vie de l'ion-pairé et la nucléophilie du solvant. [Traduit par le journal]

The formation and reactions of vinyl cations, including rearrangements, have been the subject of recent extensive reviews (1,2). Much of the reported rearrangements that arose from 1,2-aryl shifts across the double bond of vinyl cations involved conversion of less stable to more stable cations. For example, the decomposition of 1-phenyl-2,2-di-p-tolylvinyldiazonium ion generated from the triazene in HOAc gave 20% of the rearranged product, 2-phenyl-1,2-di-p-tolylvinyl acetate (3). According to Stang (2), the first example of an aryl migration across the double bond of a vinyl cation generated by solvolysis was reported in 1970 in the reaction of 1-methyl-2,2-diphenylvinyl triflate in 80% EtOH to give almost exclusively the rearranged phenyl 1phenylethyl ketone (4). Another early example was the 1,2-anisyl migration observed in the acetolysis in the presence of silver acetate of 2,2-dianisyl-1-phenylvinyl bromide quoted by Hanack (5) as a personal communication from Z. Rappoport. Very recently, Rappoport and co-workers (6, 7) have carried out extensive studies on rearrangements arising from 1,2phenyl or *p*-methoxyphenyl shifts during the solvolyses of a number of 2,2-diaryl-1-phenylvinyl bromides in HOAc-AgOAc (6) or in 60%EtOH or 2,2,2-trifluoroethanol (7). On the basis of stereochemical and kinetic evidence, these workers (6,7) concluded that the initial ionization did not involve  $\beta$ -aryl participation. On the other hand, solvolytic studies on cis- and trans-1,2-dimethyl-2-phenylvinyl triflates by Stang and Dueber (8,9) have implicated the phenyl-bridged or vinylidene phenonium ion as a reaction intermediate. Since rearrangements involving degenerate cations can be observed only through the use of isotopic tracers, Stang and Dueber utilized D-labeling of one of the methyl groups in order to study the extent of phenyl shifts across the double bond in the 1,2-dimethyl-2-phenylvinyl system. In the present paper, observations are reported on degenerate rearrangements arising from 1,2-phenyl shifts in the triphenylvinyl cation generated from solvolyses of triphenylvinyl-2-14C triflate (1-OTf-2-14C).

Phenylacetic acid-1-<sup>14</sup>C was converted to the ethyl ester and treated with PhMgBr to give 1,1,2-triphenylethanol-1-<sup>14</sup>C, which on reaction with  $Br_2$  in HOAc gave triphenylvinyl-2-<sup>14</sup>C

	Specific activity <sup><i>a</i></sup> (d.p.m./mmol) $\times 10^{-5}$				P	
	(Ph)2CHCH(Ph)OH		PhCOPh <sup>b</sup>		from C-2 to C-1, %	
Solvent	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
Dioxane-H <sub>2</sub> O-NaOH	18.1	8.52	18.1	8.59	0	0
HOAc-NaOAc	18.1	9.18	16.9	8.54	6. <b>6</b>	7.0
HOAc	4.56	3.06	4.25	2.86	6.8	6.5
HCOOH-HCOONa	18.1	10.5	16.7	9.70	7.7	7.6
НСООН	6.41	3.74	5.92	3.45	7.6	7.8
CF <sub>3</sub> COOH-CF <sub>3</sub> COONa	3.63	4.89	2.64	3.49	27.3	28.6
CF <sub>3</sub> COOH	6.41	24.8	4.73	18.4	26.2	25.8

TABLE 1.	Data from	solvolvses o	f triphenvlvinvl-2	- <sup>14</sup> C triflate	$(1-OTf-2-^{14}C)$
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<sup>a</sup>Measured by a liquid scintillation counter. <sup>b</sup>Assayed as the oxime.

bromide (1-Br-2-<sup>14</sup>C), presumably via bromination of triphenylethylene (10). The 1-Br-2-<sup>14</sup>C was converted to the Grignard reagent and reacted with I<sub>2</sub> to give 1-I-2-<sup>14</sup>C (11), which in turn was treated with AgOTf in a nonpolar solvent, pentane, to give 1-OTf-2-<sup>14</sup>C (12). That all the <sup>14</sup>C-label was located at the C-2 position was demonstrated by the conversion of 1-OTf-2-<sup>14</sup>C to isotopically unrearranged  $\alpha, \alpha$ -diphenylacetophenone- $\alpha$ -<sup>14</sup>C upon reaction with a 60:40 mixture of dioxane and 5% NaOH solution (see Table 1).

The solvolyses were carried out by treating about 5.0 mmol of 1-OTf-2-14C in 10 ml of HOAc, 97% HCOOH, or CF<sub>3</sub>COOH, with or without the presence of a 10% excess of NaOAc, HCOONa, or CF<sub>3</sub>COONa, respectively. The acetolysis and formolysis were effected at reflux temperature for 2 h and it was subsequently noted that refluxing the reaction mixture for 24 h did not materially affect the degree of isotopic scrambling in these reactions. The trifluoroacetolysis was carried out at room temperature for 2 h and changing the conditions to heating the reaction mixture at 40° for 24 h also did not significantly change the extent of scrambling. From n.m.r. analyses, the products from reactions in HOAc and CF<sub>3</sub>COOH were the expected esters, 1-OAc and 1-OAcF<sub>3</sub>, whereas formolysis in 97% HCOOH gave as product  $\alpha, \alpha$ -diphenylacetophenone (2) instead of the formate.

All of the products from the active runs were converted to 1,2,2-triphenylethanol ( $3^{-14}$ C) which, in most cases, was isolated with the aid of added carrier. When the product was  $2^{-14}$ C, LiA1H<sub>4</sub> reduction directly gave  $3^{-14}$ C, whereas in the case of 1-OAc<sup>-14</sup>C or 1-OAcF<sub>3</sub>-<sup>14</sup>C, re-

duction with LiA1H<sub>4</sub> first gave a mixture of  $2^{-14}$ C and  $3^{-14}$ C which was treated once more with LiA1H<sub>4</sub> to give pure  $3^{-14}$ C. Each sample of  $3^{-14}$ C was oxidized with alkaline KMnO<sub>4</sub> to benzophenone ( $4^{-14}$ C) and the difference in specific activity between  $3^{-14}$ C and  $4^{-14}$ C gave the extent of scrambling of the isotopic label from C-2 to C-1. The results are summarized in Table 1.

When the formation of products was followed by n.m.r., it was found that at the n.m.r. probe temperature of about 34°, the time required for complete reaction was about 10 h, 5 h, and less than 3 min for acetolysis, formolysis, and trifluoroacetolysis, respectively. The kinetics of acetolysis of a number of triphenylvinyl sulfonates, including the triflate, have been studied by Jones and Maness (13) and it was concluded that the reaction followed an  $S_N$  mechanism. The reported specific rate constant for the acetolysis of 1-OTf in the presence of an excess of NaOAc at 25° was  $1.12 \times 10^{-5}$  s<sup>-1</sup> (13). This was an extrapolated value based on kinetic data determined at higher temperatures by u.v. Because the u.v. absorptions of 1-OTf and 1-OAc overlap extensively, we measured the acetolysis rate by titration with NaOAc in HOAc and found a somewhat lower value of  $0.78 \times 10^{-5}$  $s^{-1}$  for the unbuffered acetolysis of 1-OTf at 24°. The specific rate constant for the formolysis, also at 24°, was determined by u.v. at 310 nm and was found to be  $0.86 \times 10^{-5}$  s<sup>-1</sup>. These kinetic results, together with the qualitative n.m.r. observations, indicate that the rates of acetolysis, formolysis, and trifluoroacetolysis do parallel the extents of isotopic scrambling as recorded in Table 1.

The data in Table 1 definitely demonstrate the occurrence of degenerate rearrangements arising from 1,2-phenyl shifts across the double bond of the triphenylvinyl cation. The extent of isotopic scrambling from C-2 to C-1 averaged about 6.7, 7.7, and 27.0%, respectively, for the acetolysis, formolysis, and trifluoroacetolysis of 1-OTf-2-<sup>14</sup>C.<sup>1</sup> Before discussing any possible mechanistic explanations of these rearrangements, it may be of interest to compare the present data with the magnitudes of 1,2-phenyl shifts in similar solvolyses of isotopically labeled 2-phenylethyl tosylate (5-OTs). Rearrangements of the <sup>14</sup>C- or D-label from C-1 to C-2 amounted to about 6, 45, and 50%, respectively, in solvolyses of 5-OTs-1-<sup>14</sup>C or 5-OTs-1- $d_2$  in HOAc, HCOOH, and CF<sub>3</sub>COOH, buffered by the presence of the conjugate base of the solvent (14, 15). The relative rates for the acetolysis, formolysis, and trifluoroacetolysis, respectively, of 5-OTs at 75° were 1:137:1118 (15). Thus it appears that both in the extents of rearrangement and in relative rates, a change in solvent did not show parallel effects on the vinyl system, 1-OTf, and on the saturated system, 5-OTs. The similarity in the rates of acetolysis and formolysis of 1-OTf at 24°, with the formolysis being faster than the acetolysis only by a factor of about 1.1, is contrary to expectation on the basis of the higher ionizing power of HCOOH. A full explanation of this anomaly is not apparent from the present work, although a contributing factor may be that in the Grunwald-Winstein mYcorrelation (16), the m value is reported to be low for solvolyses of triarylvinyl systems (17).

The different extents of rearrangement observed in the different solvents as recorded in Table 1 conceivably could be attributed to different degrees of  $\beta$ -phenyl participation during the solvolysis of 1-OTf-2-<sup>14</sup>C in the various solvents. Although strong evidence for phenyl participation has been observed in the 1,2-dimethyl-2-phenylvinyl system (8, 9), kinetic and stereochemical results have indicated that  $\beta$ -aryl participation is not important in solvolyses of triarylvinyl systems (6, 7, 17). It is of interest to note from Table 1 that the presence of the conjugate base of the solvent, added as the sodium salt, did not materially affect the extent of isotopic scrambling. This finding is contrary to the observation that in the decomposition of 1-(triarylvinyl)-3-phenyl-1-triazene in HOAc, the extent of rearrangement was suppressed by the addition of an excess of KOAc (3). This difference may be due to the possibility of ion-pair formation under the conditions of the present experiments, while in the decomposition of triazenes, no counter ion was present to give rise to ion-pairs. It may be suggested that under solvolytic conditions where the presence of the conjugate base does not affect the amount of rearrangement, the rearrangement takes place in the ion-pair stage.<sup>2,3</sup> The longer the lifetime of the ion-pair, the greater will be the extent of rearrangement. It may also be pointed out that the presently observed rearrangements, averaging about 6.7, 7.7, and 27.0%, respectively, for acetolysis, formolysis, and trifluoroacetolysis, appear to be related to the nucleophilicity of the solvents, the nucleophilicity of HOAc and HCOOH being quite similar, and that of  $CF_3COOH$  being much lower (18, 19). Such a relationship suggests a competition between rearrangement via 1,2-phenyl shifts in the ionpair and reaction of the ion-pair with solvent to give the product. Consequently, the highest rearrangement was observed in the solvent of lowest nucleophilicity. When 1-OTf-2-14C was hydrolyzed in aqueous dioxane in the presence of NaOH, apparently 1,2-phenyl shift could not compete with product formation and no rearrangement was found in the hydrolysis product.

### Experimental

1, 1, 2-Triphenylethanol-1-14C

A solution of 1.64 g (0.01 mol) of ethyl phenylacetate-1-<sup>14</sup>C (from esterification of phenylacetic acid-1-<sup>14</sup>C) in 10 ml of ether was added slowly to a solution of PhMgBr (from 0.02 mol of PhBr) in 20 ml of ether. The mixture was gently refluxed for 1 h and then 30 ml of 3 M NH<sub>4</sub>Cl was added. The product was recovered by ether extraction and the extract was washed with water and dried over MgSO<sub>4</sub>. The ether was then removed and the colorless

<sup>&</sup>lt;sup>1</sup>Quoting from a private communication, Rappoport and Houminer (7) reported that B. M. Benjamin and C. J. Collins have noted a 3.6% degenerate  $\beta$ -phenyl rearrangement during the acetolysis of **1**-OTf.

<sup>&</sup>lt;sup>2</sup>The ion-pair mechanism was suggested to us by Prof. Z. Rappoport.

<sup>&</sup>lt;sup>3</sup>In the solvolysis of D-labeled *cis*-1,2-dimethyl-2phenylvinyl triflate in 60% ethanol, which did not involve phenyl participation, a 34.5% 1,2-phenyl shift was observed and it was suggested that this rearrangement arose from the initial formation of an ion-pair with a classical vinyl cation which subsequently rearranged to the phenylbridged vinyl cation (8).

residue recrystallized from hexane to give 1.8 g (66%) of 1,1,2-triphenylethanol-1- $^{14}$ C, m.p. 88° (lit. (20) m.p. 88–89°).

#### Triphenylvinyl-2- $^{14}C$ Bromide (1-Br-2- $^{14}C$ )

A solution of 0.80 g (0.01 mol) of  $Br_2$  in 5.0 ml of HOAc was added dropwise with stirring to a solution of 1.37 g (0.005 mol) of 1,1,2-triphenylethanol-1-<sup>14</sup>C in 10 ml of HOAc. Stirring was continued for 4 h and during this period a pale yellow solid precipitated. The product was recovered by filtration and washed with water. The filtrate was concentrated and upon cooling yielded more product. The combined product was recrystallized from methanol, giving 1.0 g (60%) of 1-Br-2-<sup>14</sup>C, m.p. 115° (lit. (21) m.p. 114–115.5°).

#### Triphenylvinyl-2- $^{14}C$ Triflate (1-OTf-2- $^{14}C$ )

1-Br-2-<sup>14</sup>C was converted to the Grignard reagent and treated with  $I_2$  to give 1-I-2-<sup>14</sup>C as described by Morrison (11). 1-I-2-<sup>14</sup>C was converted to 1-OTf-2-<sup>14</sup>C by reaction with AgOTf using the procedure of Gramstad and Haszeldine (12) for the preparation of ethyl triflate, except that pentane instead of ether was used as solvent. The 1-OTf-2-<sup>14</sup>C product, recrystallized from pentane, was obtained in 50% yield, m.p. 83°, dec. (lit. (13) m.p. 83.5-84°, dec.). Its mass spectrum gave the molecular ion with *m/e* at 404. Its n.m.r. spectrum in CDCl<sub>3</sub> showed aromatic multiplets at 7.1–7.5 p.p.m., with three main signals at 7.10, 7.36, and 7.46 p.p.m.

#### Solvolyses

Solvolyses of 1-OTf or 1-OTf-2-14C were carried out in a 60:40 mixture of dioxane and 5% NaOH solution, glacial acetic acid, reagent grade 97% HCOOH, and CF<sub>3</sub>COOH. Preliminary examination by n.m.r. indicated that the products were the expected  $\alpha, \alpha$ -diphenylacetophenone (2), 1-OAc, and 1-OAcF<sub>3</sub>, respectively, from basic hydrolysis, acetolysis, and trifluoroacetolysis. In the formolysis, however, the product was also ketone 2 and not the formate ester. A similar formation of an analogous ketone has also been reported by Rappoport and Apeloig (22) from the reaction of 1,2-dianisyl-2-phenylvinyl bromide with dry HCOOH. All of the products, 2, 1-OAc, and 1-OAcF3, gave the expected molecular ions in their respective mass spectra. The n.m.r. spectrum of 2, in CDCl<sub>3</sub>, was the same as that reported by Rappoport and Houminer (7). The n.m.r. spectrum of 1-OAc in CDCl<sub>3</sub> showed a singlet at 1.98 p.p.m. for the CH<sub>3</sub> protons and three main signals in the aromatic region at 7.15, 7.20, and 7.35 p.p.m. For 1-OAcF<sub>3</sub>, the aromatic protons gave peaks at 7.24, 7.32, and 7.40 p.p.m.

Solvolyses of 1-OTf- $2^{-14}$ C, with or without the presence of a 10% excess of the conjugate base of the solvent, were carried out in duplicate. A typical run is described below.

A solution of 2.02 g (0.005 mol) of 1-OTf-2-<sup>14</sup>C and 0.52 g (0.0055 mol) of NaOAc in 10 ml of HOAc was heated under reflux for 2 h. Most of the solvent was then distilled off and the residue taken up in 100 ml of ether. The ether solution was washed successively with saturated Na<sub>2</sub>CO<sub>3</sub> and with water, and then dried over MgSO<sub>4</sub>. To the resulting ether solution, 2.0 g of LiA1H<sub>4</sub> was added in small portions and the reaction mixture was stirred under reflux for 2 h. Water and dilute HCl were added dropwise to decompose the excess hydride. The ether layer was separated and the aqueous layer was ex-

tracted with more ether. The combined ether extracts were dried over MgSO<sub>4</sub> and the solvent was removed to give a product consisting chiefly of ketone 2-<sup>14</sup>C contaminated with a small amount of 1,2,2-triphenylethanol (3-<sup>14</sup>C). This product mixture, together with about 2.0 g of ordinary 2 as carrier, was dissolved in 125 ml of ether and added dropwise to a stirred solution of 3.0 g of LiA1H<sub>4</sub> in 250 ml of ether. The reaction mixture was gently refluxed for 4 h and then worked up as before to give 3-<sup>14</sup>C which was repeatedly recrystallized from ethanol-water until its specific activity was constant, m.p. 88° (lit. (23*b*) m.p. 88–89°).

## Oxidation of 1,2,2-Triphenylethanol- ${}^{14}C$ (3- ${}^{14}C$ )

One gram of the alcohol (3-14C) was suspended in 80 ml of water and 5 ml of 10% NaOH. Powdered KMnO<sub>4</sub> (4.0 g) was added in small portions and then the mixture was refluxed for 4 h. Shorter reaction times would result in incomplete oxidation and longer reaction times would cause excessive loss of the desired benzophenone through further oxidation to benzoic acid. CH<sub>3</sub>OH was added to the reaction mixture to destroy the excess permanganate and the resulting reaction mixture was acidified with dilute H<sub>2</sub>SO<sub>4</sub>. The MnO<sub>2</sub> was filtered off and washed with acetone. Much of the acetone was distilled off and then the filtrate was repeatedly extracted with ether. The combined ether extract was washed with a saturated NaHCO<sub>3</sub> solution to remove the benzoic acid. After drying and removal of the ether, the residual benzophenone was converted to the oxime which was repeatedly crystallized from methanol-water until its specific activity was constant, m.p. 144° (lit. (23a) m.p. 144°).

#### Kinetic Measurements

A 2.5 mM solution of 1-OTf in glacial acetic acid was maintained at 24° and the rate of acetolysis was followed by titration of the liberated sulfonic acid in 5.0-ml aliquots of the reaction mixture with standardized (about 0.001 N) NaOAc in HOAc using bromophenol blue as indicator. The mean value of the specific rate constant from triplicate runs was  $(0.78 \pm 0.01) \times 10^{-5} \text{ s}^{-1}$ .

The solubility of 1-OTf in 97% HCOOH at 24° was low. A saturated solution was prepared by stirring 1-OTf in 97% HCOOH at 24° for about 10 min and the undissolved 1-OTf was removed by filtration. The solution was diluted with 97% HCOOH to give an appropriate u.v absorbance reading of about 0.8 at 310 nm and the rate of formolysis was followed by u.v. at 310 nm. The mean value of the specific rate constant from triplicate runs was  $(0.86 \pm 0.01) \times 10^{-5} s^{-1}$ .

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2682

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