1,2-Hydride Shift in the 2-Phenylvinyl Cation[1]

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Recently, degenerate 1,2-aryl shifts across the double bond in triarylvinyl cations were investigated in this laboratory using the ^{14}C label as tracer or ^{13}C labeling coupled with ^{1}H NMR and ^{13}C NMR analyses. The reactions studied were the solvolyses of triphenylvinyl-2-^{14}C triflate,[2] the reaction of triphenylvinyl-2-^{14}C or triphenylvinyl-2-^{13}C bromide with HOAc–AgOAc,[3] and the acetolysis and trifluoroacetalysis of trianisylvinyl-2-^{13}C bromide.[4] As an extension of this work, it was thought that the possibility of a 1,2-phenyl shift in the 2-phenylvinyl cation might be similarly studied using labeling with isotopic carbon. However, when either *cis*- or *trans*-β-bromostyrene (*cis*-**1** or *trans*-**1**) was treated with HOAc–AgOAc, the product obtained was acetophenone (**2**). The reaction was very slow. For example, when the heterogeneous mixture of 3.8 mmol of *cis*-**1** or *trans*-**1** and a 10% excess of AgOAc in 100 ml of HOAc was refluxed with stirring for 3 weeks, the ratio of product **2** to unreacted *cis*-**1** or *trans*-**1**, as measured by VPC, was about 20:80. When the AgOAc was replaced by NaOAc, no reaction was detected after 3 weeks, indicating that the presence of Ag^+ ion was essential and suggesting that the reaction was a cationic process.

The formation of **2** from *cis*-**1** or *trans*-**1** likely is attributable to a 1,2-hydride shift in the 2-phenylvinyl cation.

$$\underset{\mathbf{3}}{\mathrm{PhCH{=}CH^+}} \longrightarrow \underset{\mathbf{4}}{\mathrm{Ph\overset{+}{C}{=}CH_2}}$$

The driving force for the reaction, as in many reported rearrangements of vinyl cations,[5] is the formation of the more stable 1-phenylvinyl cation (**4**) from the less stable 2-phenylvinyl cation (**3**). Recently, Jäckel and Hanack[6] have reported the first observation of a 1,2-hydride shift in a vinyl cation in the formation of cyclopropyl ethyl ketone from the solvolysis of *cis*- or *trans*-3-cyclopropyl-2-propen-2-yl triflate in aqueous trifluoroethanol. The present finding is another example of a 1,2-hydride shift in a vinyl cationic system.

Although the use of labeled *cis*-**1** and *trans*-**1** as a means of studying degenerate 1,2-phenyl shifts no longer applies, *cis*- and *trans*-β-bromostyrene-α-^{14}C are utilized in the present work so that data on yields may be obtained by isotope dilution. The results are summarized in Table I. Moreover, from the reactions with labeled substrates, oxidation of the active acetophenone product, as expected, gave a benzoic acid with essentially no loss of ^{14}C activity. This finding thus also eliminated the remote possibility that a 1,2-phenyl shift might have occurred prior to the 1,2-hydride shift.

$$\mathrm{Ph^{14}CH{=}CH^+ \not\rightleftarrows PhCH{=}^{14}CH^+ \longrightarrow Ph\overset{+}{C}{=}^{14}CH_2}$$

From Table I, it is seen that phenylacetylene was detected by isotope dilution as a minor product. The yields of **2** at different stages of the reactions, as summarized in Table I, showed no significant difference with either *cis*-**1**-α-^{14}C or *trans*-**1**-α-^{14}C as reactant. Thus the stereochemical difference in the initial substrate has been lost during the reaction, indicating that the 1,2-hydride shift took place via classical vinyl cations **3** and **4**, rather than via a hydrogen-bridged ion. A similar conclusion was drawn by Jäckel and Hanack[6] for the rearrangement of the 2-cyclopropyl-1-methylvinyl cation to the 1-cyclopropyl-2-methylvinyl cation.

Table I
Yields from Isotope Dilution Experiments in the Reaction of *cis*- or *trans*-β-Bromostyrene-α-^{14}C (*cis*- or *trans*-1-α-^{14}C) with HOAc–AgOAc at 120°

Reactant	Reaction time, days	Yield, % PhCOCH$_3$	Yield, % PhC≡CH
cis-**1**-α-^{14}C	4	5.7[a]	0.6
	8	9.1	0.5
	14	14.2	0.6
	21	19.4	0.5
	29	29.4	0.5
trans-**1**-α-^{14}C	4	5.3	0.5
	8	9.4	0.8
	14	15.4	0.3
	21	16.8	0.5
	29	33.8	0.5

[a] As an illustration, in this experiment, the specific activity of the 1.769 mmol of reactant was 2.32×10^6 dpm/mmol. The amount of PhCOCH$_3$ carrier added was 3.02 mmol and the specific activity of the diluted PhCOCH$_3$ product was 7.90×10^4 dpm/mmol. Calculation from these data gave the yield of 5.7%.

Experimental Section

Reaction of *cis*- or *trans*-β-Bromostyrene (*cis*-1 or *trans*-1) with HOAc–AgOAc. In a typical run, 7.0 g (38 mmol) of *cis*-**1** or *trans*-**1** and 7.0 g (42 mmol) of AgOAc in 100 ml of HOAc were placed in a 200-ml flask equipped with a magnetic stirrer and fitted with a reflux condenser and CaCl$_2$ tube. All the AgOAc did not dissolve and the heterogeneous mixture was gently refluxed with stirring for 21 days. The resulting material was poured into a saturated NaCl solution and then extracted several times with petroleum ether (bp 40–60°). The extract was washed with 10% NaHCO$_3$ solution and with H$_2$O and then dried over MgSO$_4$. After removal of the solvent, the only product recovered from the residue by preparative VPC (12 ft × 0.375 in. copper column packed with 20% FFAP on Chromosorb W at 150°), besides the unreacted bromide, was acetophenone (**2**), which showed identical NMR and ir spectra with those of an authentic sample. From a number of experiments, the ratio of **2** to unreacted *cis*-**1** or *trans*-**1** was found to average about 20:80, with individual values ranging from 17:83 to 22:78.

Acetophenone also was the only isolable product when the reaction with HOAc–AgOAc was carried out in the presence of Ac$_2$O or when the reaction mixture was worked up by distilling off most of the HOAc and extracting with petroleum ether without being poured into saturated NaCl solution. If the initial product was 1-phenylvinyl acetate, during the reaction, this product must have been cleaved to the vinyl alcohol which ketonized to **2**. A similar cleavage of the expected product ester to the corresponding ketone was observed in the formolysis of triphenylvinyl triflate[2] and in the formolysis of *cis*- or *trans*-1,2-dianisyl-1-phenylvinyl bromide.[7]

***cis*- and *trans*-β-Bromostyrene-α-^{14}C (*cis*-1-α-^{14}C and *trans*-1-α-^{14}C).** Ph^{14}COOH was converted by standard procedures to the acid chloride and then reduced to Ph^{14}CHO,[8a] in yields of 95 and 84%, respectively. The aldehyde, through the Perkin reaction, was converted in 50% yield to the labeled *trans*-cinnamic acid, $\mathrm{Ph^{14}CH{=}CHCOOH}$.[8b] Conversion of the *trans*-cinnamic acid to the dibromide followed by dehydrobromination in H$_2$O–NaOH as described by Grovenstein and Lee[9] gave predominantly *trans*-**1**-α-^{14}C. After recrystallization from pentane at −20°, pure *trans*-**1**-α-^{14}C, as indicated by VPC, was obtained. When the dehydrobromination of the labeled *trans*-cinnamic acid dibromide was carried out with NaHCO$_3$ in dry acetone,[10] the product was *cis*-**1**-α-^{14}C.

Determination of Yields by Isotope Dilution. The reactions were carried out in sealed tubes. Each tube, equipped with a small magnetic stirring bar, contained 1.769 mmol of *cis*-**1**-α-^{14}C or 1.795 mmol of *trans*-**1**-α-^{14}C, 2.0 mmol of AgOAc, and 5.0 ml of a 9:1 (v/v) mixture of HOAc–Ac$_2$O. The tubes were heated with stirring in an oil bath at 120 ± 2°. At different intervals ranging from 4 to 29 days, samples were quenched by cooling in an ice bath, appropriate amounts of ordinary acetophenone and phenylacetylene were added as carriers, and the reaction mixtures poured into saturated NaCl and worked up as described earlier. Samples of the diluted acetophenone and phenylacetylene were recovered by preparative VPC and their specific activities determined. From the known weights of carriers added and the known specific activities before and after dilution, the yields of acetophenone and phenylacetylene were calculated. The results are summarized in Table I.

Registry No.—*cis*-**1**, 588-73-8; *trans*-**1**, 588-72-7; **3**, 24343-35-9.

References and Notes

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Stereochemistry of Electrophilic Additions to Linear Enol Ethers

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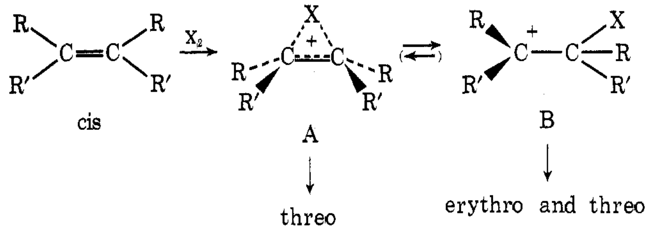
The stereospecific electrophilic anti addition of halogen to alkenes results from the existence of the bridged halonium ion A, generally more stable than the classical carbonium ion B.



Syn-addition products appear whenever the ion B is stabilized. A well-known illustration of this case is when an oxygen nonbonding electron pair stabilizes the carbocation by conjugation through the benzene ring, as in the case of anethole.[1]

The effect of an oxygen atom directly bound to the cationic carbon has been the subject of stereochemical studies in cyclic unsaturated ethers; in these cases, by adding chlorine to dihydropyrans[2] or dihydrofurans,[3] 70 and 78% of syn addition was obtained. Surprisingly, very few studies have been made on the stereochemistry of electrophilic addition to linear ethers as simple as $ROCH{=}CHCH_3$ (**1**, isomers *Z* and *E*).

In the present study, the results found when $R = C_2H_5$ (**1a**) or $R = CH_2C_6H_5$ (**1b**) are reported. In order to examine if it was possible to control the stereochemistry of the addition on this type of olefin by modifying the availability of the oxygen nonbonding electrons to the carbocation, the study of para-substituted phenol ethers (**2**) was simultaneously undertaken. In this case, the stabilization of the carbocation by oxygen electrons depends upon the nature of Y.

$$p\text{-}YC_6H_4OCH{=}CHCH_3$$

2

c, Y = OMe; **d**, Y = Me; **e**, Y = H; **f**, Y = Cl

Experimental Section

The halogenation of ethers was carried out by adding chlorine, bromine, or iodine monochloride to a 10% solution of olefin in CCl_4 at −20° in the dark. The halogens reacted rapidly and gave the expected products, as revealed by NMR spectroscopy and chemical results. There were no by-products except in the case of ether **1a**,

$$\text{R (or Ar)}OCH{=}CHCH_3 \xrightarrow{X_2} \underset{(A)}{\text{R (or Ar)}OCH}\underset{(M)}{XCH}\underset{(X)}{X'CH_3}$$

for which, even under these experimental conditions, some products due to radical reactions appeared. The reaction of iodine addition did not proceed at low temperature and polymerization occurred at higher temperature.

The mixtures obtained were periodically analyzed by NMR spectroscopy while being maintained at −20°, thus avoiding an excess of halogen, which catalyzes the isomerization between erythro and threo dihalogenated ethers.[3]

The ratio of erythro to threo isomers depended on the configuration (*Z* or *E*) of the starting olefin (Table I). Because the product mixtures were not in the equilibrium ratio and were stable in all cases under the experimental conditions, it appeared that the reaction proceeded by kinetic control.

Table I
Stereospecificity of the Addition of Halogens to *Z* or *E* Olefins[a]
R (or Ar) $OCH{=}CHCH_3$

	Cl_2 addition, % T		Br_2 addition, % T		ICl addition, % T	
Olefin, R or Ar	*Z*	*E*	*Z*	*E*	*Z*	*E*
1a, C_2H_5	50	37	71[b]	68[b]	74	
1b, $C_6H_5CH_2$	55	40	74	65	75	
2c, *p*-$MeOC_6H_4$	58	46	83	78	90	87
2d, *p*-MeC_6H_4	60	48	92	84	98	
2e, C_6H_5	61	50	95	86	100	
2f, *p*-ClC_6H_4	62	51	100	100	100	100

[a] Percent anti addition, reproducible within 2% (threo ether from the *Z* olefin, and erythro from the *E* olefin). [b] Approximate values owing to the presence of by-products.

In the NMR spectra of the addition products, the proton H_A signal appeared as two doublets, one having a coupling constant of 2 Hz and the other one having a coupling constant of 6–8 Hz (Table II). It was noticed, as in other well-known cases,[4] that the isomer having the smallest J_{AM} value appeared at a lower field.

These data allowed us to classify the isomers in two well-characterized families: in the present study, the isomer having the smallest coupling constant (lower field signal) is the threo isomer (vide infra).

Discussion

The assignment of the erythro or threo configuration to each of the two spectroscopic families is based on the two following criteria.

(a) The anti addition becomes more or less stereospecific depending on the nature of the electrophilic reagent: $I^+ > Br^+ > Cl^+$ (Table I).