Mechanisms of elimination reactions. 40. Attempted study of stereochemistry of elimination from 2-(*p*-nitrophenyl)ethyltrimethylammonium ion. Base-promoted *cis–trans* isomerization of *p*-nitrostyrene-β-*d*[1]

BRENT R. DOHNER AND WILLIAM H. SAUNDERS, JR.[2]

Department of Chemistry, University of Rochester, Rochester, NY 14620, U.S.A.

Received September 20, 1985

This paper is dedicated to Professor Arthur N. Bourns

BRENT R. DOHNER and WILLIAM H. SAUNDERS, JR. Can. J. Chem. **64**, 1026 (1986).

Stereospecifically deuterated $ArCHDCHDNMe_3^+I^-$ and $ArCHDCHDNMe_2O$ have been prepared, where Ar=C_6H_5 and *p*-$NO_2C_6H_4$. When Ar=C_6H_5, the elimination reaction of the quaternary salt with ethoxide in ethanol goes with >98% *anti* stereochemistry, and the Cope elimination of the amine oxide with >98% *syn* stereochemistry. When Ar=*p*-$NO_2C_6H_4$, however, both reactions lead to apparent 50:50 *anti*/*syn* product. Subjection of (*E*)-*p*-nitrostyrene-β-*d* to the conditions of both the ethoxide-promoted and Cope eliminations results in complete *cis–trans* equilibration. No loss of deuterium from *p*-nitrostyrene-α-*d* occurs under either set of conditions, excluding isomerization via an α-arylvinyl carbanion. The most likely mechanism for isomerization is reversible addition of ethoxide under E2 conditions and $ArCHDCHDNMe_2O$ under Cope conditions to the β-carbon of *p*-nitrostyrene. The *cis–trans* isomerization of the *p*-nitrostyrene is sufficiently rapid to preclude determination of the stereochemistry of base-promoted eliminations leading to it.

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On a préparé des $ArCHDCHDNMe_3^+I^-$ et des $ArCHDCHDNMe_2O$ spécifiquement deutérés, dans lesquels Ar=C_6H_5 et *p*-$NO_2C_6H_4$. Lorsque Ar=C_6H_5, la réaction d'élimination du sel quaternaire, sous l'influence de l'éthylate dans l'éthanol, se produit à >98% par une stéréochimie *anti* alors que l'élimination de Cope de l'oxyde d'amine se fait à >98% par une stéréochimie *syn*. Toutefois, lorsque Ar=*p*-$NO_2C_6H_4$, les deux réactions conduisent à un produit qui est apparemment 50:50 *anti*/*syn*. Lorsqu'on soumet le *p*-nitrostyrène-β-*d*-(*E*) à des réactions d'élimination tant de Cope que sous l'influence de l'éthylate, on obtient toujours un équilibre complet entre les isomères *cis–trans*. Ni l'une ni l'autre des conditions d'élimination ne provoque la perte de deutérium du *p*-nitrostyrène-α-*d*; ce résultat exclut la possibilité d'une élimination par le biais d'un carbanion α-arylvinyle. Le mécanisme le plus probable pour l'isomérisation est l'addition réversible d'éthylate, sous les conditions E2, et de $ArCHDCHDNMe_2O$, sous les conditions de Cope, au carbone β du *p*-nitrostyrène. L'isomérisation *cis–trans* du *p*-nitrostyrène est suffisamment rapide pour éliminer la possibilité de déterminer la stéréochimie des réactions d'élimination, effectuées sous l'influence de bases, qui lui donnent naissance.

[Traduit par la revue]

The mechanisms of base-promoted elimination from 2-arylethyl derivatives have been subjected to intensive scrutiny. Most of these reactions have been found to proceed via the E2 mechanism (2, 3). In the one reported stereochemical study in this series, 2-phenylethyl-1,2-d_2-trimethylammonium ion was found to give entirely (>95%) *anti* elimination when treated with ethoxide ion in ethanol or *tert*-butoxide ion in *tert*-butyl alcohol (4). Only when there is a second group, alkyl or aryl, in the 2-position is there appreciable *syn* elimination (1, 5).

Recently, evidence has been presented that 2-(*p*-nitrophenyl)ethyl quaternary ammonium salts eliminate by the E1cB mechanism (6, 7). The evidence included exchange of the β-hydrogens with solvent protons, an inverse solvent isotope effect on initial rates, and markedly curved plots of rate vs. buffer concentration. Even under conditions where there was no evidence for exchange, the lack of coupling between proton removal and leaving-group departure suggested an $(E1cB)_I$ mechanism.

In the light of these findings, the 2-arylethyl system seemed to offer an excellent opportunity to compare the stereochemical courses of E2 and E1cB reactions of closely similar substrates. What is to be expected in an E1cB reaction is by no means clear. A long-lived carbanion, free to rotate and invert prior to loss of the leaving group, should result in 50:50 *syn*/*anti* elimination. It is possible, however, that stereochemical randomization of the carbanion would be slowed by a hyperconjugative interaction of the lone pair with the bond between the α-carbon and the leaving group (8), by ion pairing (9), or simply by a very short lifetime. In such cases, considerable stereoselectivity, or even stereospecificity, could result.

In order to study the stereochemistry of elimination, we prepared 2-phenylethyl-1,1-d_2-trimethylammonium (**6**) and 2-(*p*-nitrophenyl)ethyl-1,2-d_2-trimethylammonium (**7**) iodides by stereospecific reactions. The synthetic sequence is shown in Scheme 1. The corresponding amine oxides, **8**, and **9***a*, were also prepared to provide checks on the stereochemical integrity of **6** and **7**. The commercial β-bromostyrene (**1**) was not stereochemically pure. It was shown by nmr to be 78.6% *E* and 21.4% *Z*. We thus needed to know whether this composition was preserved through the transformations leading to **6** and **7**. In order to do this, **5** was converted to **8**, which in turn was subjected to a Cope elimination, a reaction known to proceed via a stereospecifically *syn* pathway (10, 11). The products expected from *anti* and *syn* elimination are shown in Scheme 2.

By this procedure, **5** was shown to be 79.5% *RS,SR*. As a double check, **2** was deuteroborated as in Scheme 1, but then treated with NH_2OSO_3H (12). The resulting primary amine was converted to **5** by treatment with formaldehyde and formic acid (13). This sample of **5** was treated with hydrogen peroxide and the product subjected to Cope elimination, which showed it to be 79.0% *RR,SS*. It is clear that the synthesis of **5** is stereospecific, and there is no reason to believe that conversion of **5** to **6** or **8** affects its stereochemistry. Neither should the nitration to give **9**, but Cope elimination of **9***a* gave unexpected results, which will be discussed below.

[1]For previous paper in this series, see ref. 1.

[2]Author to whom correspondence may be addressed.

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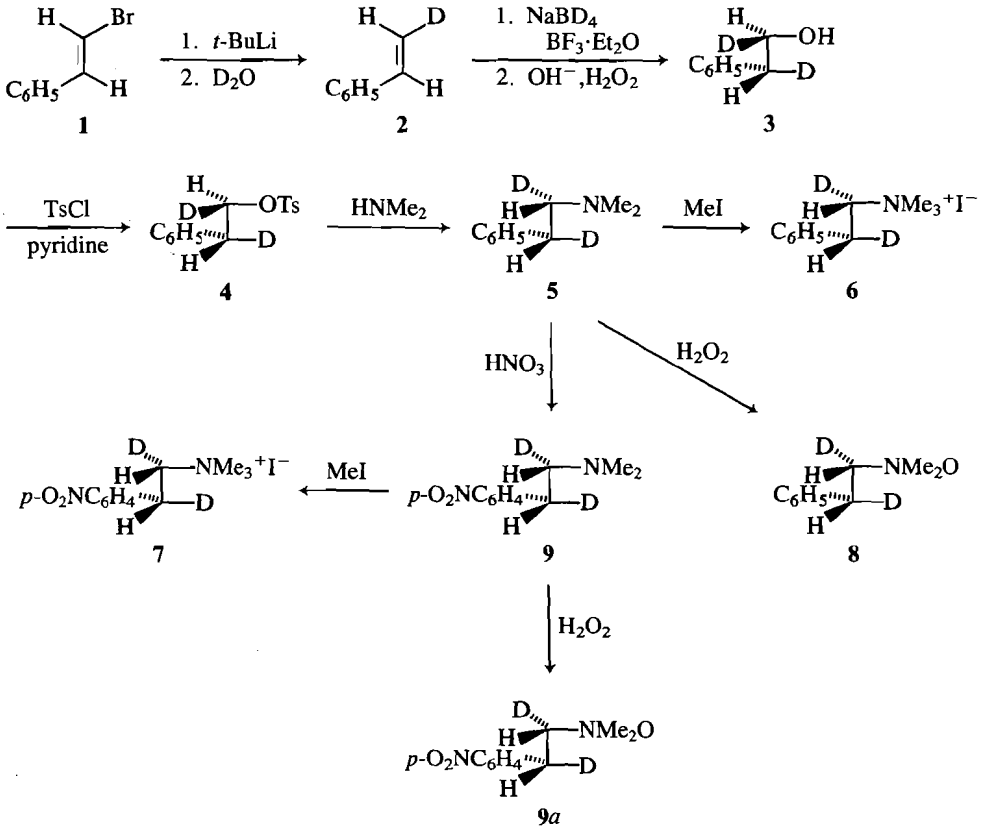
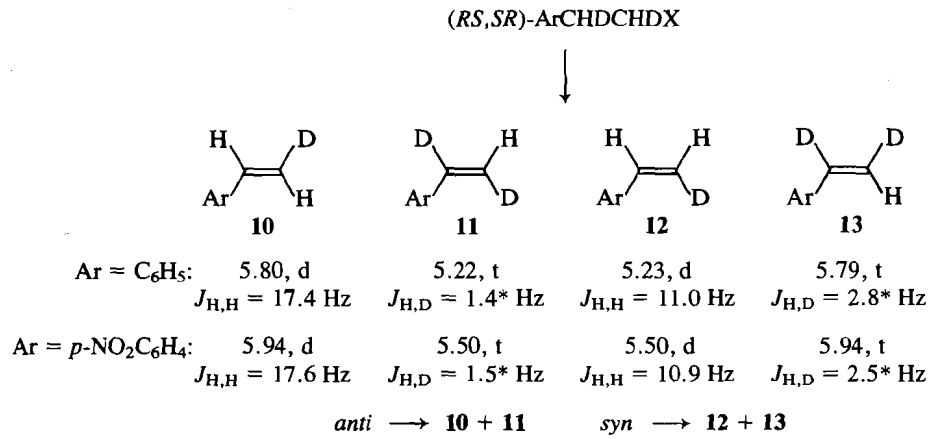


SCHEME 1. Synthesis of stereospecifically labeled 2-arylethyl-1,2-d_2-trimethylammonium salts and -dimethylamine oxides.



Ar = C_6H_5:	5.80, d $J_{H,H}$ = 17.4 Hz	5.22, t $J_{H,D}$ = 1.4* Hz	5.23, d $J_{H,H}$ = 11.0 Hz	5.79, t $J_{H,D}$ = 2.8* Hz
Ar = *p*-$NO_2C_6H_4$:	5.94, d $J_{H,H}$ = 17.6 Hz	5.50, t $J_{H,D}$ = 1.5* Hz	5.50, d $J_{H,H}$ = 10.9 Hz	5.94, t $J_{H,D}$ = 2.5* Hz
	anti ⟶ **10** + **11**		*syn* ⟶ **12** + **13**	

*$J_{H,D}$ values are calculated from observed H,D splittings. Slightly different (and probably more accurate) values are obtained from the formula $J_{H,D} = J_{H,H}/6.5$ (2.7 Hz for *E* and 1.7 Hz for Z orientation of H and D)

SCHEME 2. Products expected in *anti* and *syn* elimination from ArCHDCHDX.

The two samples of **6**, which can be presumed to be 79.5% *RS,SR* and 79.0% *RR,SS*, respectively, permitted us to check the results of Bourns and Frosst (4). The high-field nmr spectrometers that we used permit more precise determination of the composition of the mixture of **10**–**13** than the 60-MHz nmr instrument available for the earlier work. On treatment with sodium ethoxide in ethanol at 80°C, the 79.5% *RS,SR* sample of **6** gave 78.7% **10** and **11**, while the 79.0% *RR,SS* sample gave 79.0% **12** and **13**. These results confirm that the elimination is entirely *anti* within experimental error. Any *syn* elimination must be less than 1–2% of the overall reaction.

Nitration of **5** with fuming nitric acid at −10°C (14) afforded a mixture that was 71% *para* and 29% *ortho*, from which the pure *para* isomer, **9**, was isolated by flash chromatography (15). **9** was converted to **7**, which was then treated with sodium ethoxide in ethanol at 60°C. Analysis of the mixture of deuterated *p*-nitrostyrenes gave 52.5% of **10** and **11** and 47.5% of **12** and **13**. Conversion of **9** to **9***a*, followed by Cope

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elimination, gave 49.0% of **10** and **11** and 51% of **12** and **13**. This outcome indicates essentially complete loss of stereochemistry in *both* the base-promoted elimination of **7** and the Cope elimination of **9***a*. A random stereochemical outcome in the base-promoted elimination can be readily rationalized, but a nonstereospecific Cope elimination is, to the best of our knowledge, unprecedented. Consequently, we considered the possibility that stereochemistry was lost at some stage other than during the elimination reactions.

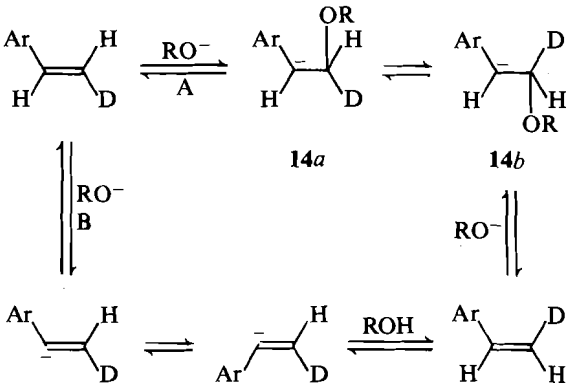
In principle, epimerization could occur during the nitration of **5** to **9**. The nmr spectra of **7** and **9** were too complex to give any information about proportions of stereoisomers, however, and the possibility of epimerization during nitration of **5** seemed farfetched in any case. A third possibility for loss of stereochemistry would be $E \rightleftharpoons Z$ isomerization of the deuterated nitrostyrenes under the conditions of the elimination reactions. This possibility was easiest to test experimentally, and was pursued first.

In order to obtain stereospecifically deuterium-labeled *p*-nitrostyrene, (*E*)-β-bromo-*p*-nitrostyrene was prepared by the method of Cristol and Norris (16), and converted to *p*-nitrophenylacetylene by treatment with sodium *tert*-butoxide in *tert*-butyl alcohol. Treatment of *p*-nitrophenylacetylene with 9-BBN (9-borabicyclo[3.3.1]nonane) (17) in tetrahydrofuran, followed by acetic-*O*-*d* acid, gave (*E*)-*p*-nitrostyrene-β-*d*. This *E* isomer showed a single nmr signal attributable to the β-proton at δ 6.01.

Treatment of the *E* isomer for 10 min with 0.1 *M* sodium ethoxide in ethanol led to a new vinyl proton nmr signal at δ 5.50, attributable to the *Z* isomer. The ratio of the signals at 6.01 and 5.50 was 47.7:52.2. Heating the *E* isomer at 80°C for 2.5 h in 80% Me_2SO – 20% H_2O containing 2-phenylethyldimethylamine oxide (Cope reaction conditions) led to a 50.0:50.0 mixture of the *E* and *Z* isomers. It is clear that complete equilibration between the *E* and *Z* isomers occurs under the conditions of both E2 and Cope eliminations.

Two possible mechanisms for the isomerization are outlined in Scheme 3. Here RO^- is EtO^- (base-promoted reaction) or $ArCH_2CH_2N^+Me_2O^-$ (Cope reaction). While path A seemed more likely than path B, we felt it necessary to distinguish between them, and chose an experiment which shed further light on path A as well. Reduction of *p*-nitroacetophenone by sodium borodeuteride, followed by tosylation and treatment of the resulting tosylate with sodium *tert*-butoxide in *tert*-butyl alcohol, afforded *p*-nitrostyrene-α-*d*. Neither under the E2 nor the Cope elimination conditions was there any observable loss of the α-deuterium, a fact which excludes path B. The method of synthesis also excludes path B for reaction with *tert*-butoxide in *tert*-butyl alcohol. Finally, the experiment excludes any significant *reversible* protonation of the carbanion **14**, resulting from addition of RO^- to *p*-nitrostyrene, for this, too, would lead to loss of α-deuterium. Irreversible protonation of **14** would give 2-(*p*-nitrophenyl)ethyl ethyl ether in the ethoxide-promoted isomerization, but no lines attributable to this compound appeared in the nmr spectrum of the isomerization product.

That nucleophilic addition to *p*-nitrostyrene occurs readily is not surprising, and there are literature precedents. Secondary amines give isolable adducts (18), and *N*-methyl-*C*-phenylnitrone (a model for the amine oxide) undergoes 1,3-dipolar addition, the nucleophilic oxygen going to the β-carbon of the *p*-nitrostyrene (19). Even more pertinent is the report of Alunni and Jencks that eliminations from 2-(*p*-nitrophenyl)ethyl quaternary ammonium salts are reversible (20), which means that tertiary amines as well can add to *p*-nitrostyrene.



SCHEME 3. Possible mechanisms for stereoisomerization of (*E*)-*p*-nitrostyrene-β-*d*.

The data of Alunni and Jencks provide a means of estimating this rate of addition. The overall equilibrium (eq. [1]) is the sum of the two reactions of eqs. [2] and [3].

[1] $ArCH{=}CH_2 + HNMe_3^+ \leftrightharpoons ArCH_2CH_2NMe_3^+$

[2] $ArCH{=}CH_2 + NMe_3 \leftrightharpoons ArCHCH_2NMe_3^+$

[3] $ArCHCH_2NMe_3^+ + HNMe_3^+ \leftrightharpoons ArCH_2CH_2NMe_3^+ + NMe_3$

The equilibrium constant K_1 is not given by Alunni and Jencks, but there is a good linear correlation between log K_1 and $pK_a(R_3NH^+)$ for the other quaternary salts, which permits estimation of K_1 as 0.05. The equilibrium constant for eq. [3] is given by the ionization constant of Me_3NH^+ divided by the ionization constant of $ArCH_2CH_2NMe_3^+$. The former is quoted by Alunni and Jencks as $10^{-9.85}$, and the latter estimated by Keeffe and Jencks (7) as $10^{-15.5}$. With these numbers in hand, we can estimate K_2 to be $10^{-4.35}$. In turn, $K_2 = k_{addn}/k_{elim}$, and Keeffe and Jencks estimate k_{elim} to be 15 s^{-1}, which makes k_{addn} 7×10^{-4} M^{-1} s^{-1}. This compares with an *overall* rate of elimination reaction of 10^{-3} M^{-1} s^{-1} at 25°C in water.

Thus, even the back addition of trimethylamine to *p*-nitrostyrene is comparable in rate to the overall elimination, and the addition of the stronger hydroxide ion can be expected to be faster still. These conclusions apply to aqueous solution at 25°C, of course, rather than to our conditions of ethanolic solution at 60°C. It is probably safe, however, to assume that the difference in solvent and temperature does not drastically change the qualitative picture. Definitive evidence would require determination of the rates of both elimination and stereoisomerization. We did not consider this practicable, because both reactions are complete in less than ten minutes under our conditions. The available evidence strongly suggests that it will be difficult if not impossible to determine the stereochemistry of elimination from 2-(*p*-nitrophenyl)ethyltrimethylammonium ion without interference from stereoisomerization of the product.

Experimental

Solvents

Ether and tetrahydrofuran were refluxed over sodium, with benzophenone used as an indicator of dryness (21). They were then distilled. Dimethyl sulfoxide was stirred over calcium hydride for 2 days. It was distilled under reduced pressure and the first 10% discarded. Distilled water was refluxed over potassium permanganate for 2 h and distilled. Absolute ethanol was refluxed over magnesium turnings for 8 h and distilled. The first 10% of distillate was discarded.

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General

All melting and boiling points are uncorrected. Most of the nmr spectra were recorded on a Bruker WH-400 or a Nicolet QE 300 nmr spectrometer. In a few cases a Varian EM-390 instrument was used. Chloroform-*d* and dimethyl-d_6 sulfoxide were used as nmr solvents.

(E)-Styrene-β-d was obtained from β-bromostyrene (Aldrich: 78.6% *E*, 21.4% *Z*) by the procedure used to prepare (*E*)-1-phenyl-1-(*p*-methoxyphenyl)ethylene-2-*d* (5). The product was extracted into ether and kept in solution to minimize possible polymerization or isomerization.

(RR,SS)-2-Phenylethanol-1,2-d_2

Deuteroborane was generated by the addition of boron trifluoride etherate (0.029 mol) to a solution of sodium borodeuteride (0.022 mol) in 200 mL of tetrahydrofuran at 0°C. (*E*)-Styrene-β-*d* was then converted to the desired product by the procedure used to prepare (*RR,SS*)-3-methyl-2-phenyl-1-butanol-1-*d* (5), except that ether was used to extract the product and the extract washed with aqueous ferrous sulfate before drying over magnesium sulfate.

(RR,SS)-2-Phenylethyl-1,2-d_2 *tosylate* was prepared by a standard procedure (22) and used without recrystallization.

(RS,SR)-2-Phenylethyl-1,2-d_2*-dimethylamine* was obtained from (*RR,SS*)-2-phenylethyl-1,2-d_2 tosylate and dimethylamine by the procedure used to prepare (*RS,SR*)-3-methyl-2-phenyl-1-(butyl-1-*d*)dimethylamine (5). It was shown to be 78% *RS,SR* isomer by analysis of its Cope elimination products (see below); ^{1}H nmr δ: 2.31 (s, 6H), 2.52 (d, 1H), 2.80 (d, 1H), 7.2–7.4 (m, 5H).

(RS,SR)-2-Phenylethyl-1,2-d_2*-trimethylammonium iodide*

Treatment of the above product with methyl iodide (5) gave material of mp 230–233°C; ^{1}H nmr δ: 3.02 (d, 1H), 3.12 (s, 9H), 3.50 (d, 1H), 7.35 (m, 5H).

(RR,SS)-2-Phenylethyl-1,2-d_2*-amine*

Deuteroboration of (*E*)-styrene-β-*d* was carried out as in the preparation of (*RS,SR*)-2-phenylethanol-2,3-d_2 (above), but instead of treating the borane with hydrogen peroxide, NH_2OSO_3H (1.1 equiv.) was added slowly and the reaction mixture heated to 95°C for 4 h. The reaction mixture was treated with concentrated hydrochloric acid, made basic, and the amine extracted with ether. The crude product was obtained in 14% yield.

(RR,SS)-2-Phenylethyl-1,2-d_2*-dimethylamine* was obtained by methylation of the above amine with formaldehyde and formic acid (13) and was shown to be 79% *RR,SS* by analysis of its Cope elimination products (see below).

(RR,SS)-2-Phenylethyl-1,2-d_2*-trimethylammonium iodide* was prepared by the same procedure as for the *RS,SR* isomer (above) and had mp 228–232°C.

(RS,SR)-2-(p-Nitrophenyl)ethyl-1,2-d_2*-dimethylamine* was prepared by adding (*RS,SR*)-2-phenylethyl-1,2-d_2-dimethylamine dropwise to fuming nitric acid at −10°C (14). The reaction mixture was allowed to warm to 0°C, made basic with sodium hydroxide, and the product extracted into ether. After removal of the ether, it was shown by nmr to be 71% *para* and 29% *ortho*. Separation was effected by flash chromatography (15). The solvent consisted of 120 mL of pentane, 30 mL of trimethylamine, and 100 mL of ether. A 230–240 mesh silica gel 60 column was used. The *ortho* isomer (R_f=0.36) preceded the *para* isomer (R_f=0.28), which was obtained in 56% yield; ^{1}H nmr δ: 2.31 (s, 6H), 2.51 (d, 1H), 2.80 (d, 2H), 7.80 (dd, 4H).

(RS,SR)-2-(p-Nitrophenyl)ethyl-1,2-d_2*-trimethylammonium iodide* was obtained by treatment of the above product with methyl iodide (5) and had mp 207–208°C; ^{1}H nmr δ: 3.13 (s, 9H), 3.31 (d, 1H), 3.58 (d, 1H), 7.95 (dd, 4H).

(E)-β-Bromo-p-nitrostyrene was prepared by the procedure of Cristol and Norris (16). It had mp 155–157°C (lit. (16) mp 156–157°C); ^{1}H nmr δ: 6.69 (s, 1H), 7.03 (s, 1H), 7.70 (dd, 4H).

p-Nitrophenylacetylene

(*E*)-β-bromo-*p*-nitrostyrene (0.044 mol) was dissolved in 250 mL of 0.1 *M* sodium *tert*-butoxide in *tert*-butyl alcohol and stirred at 30°C for 35 h. The reaction mixture was poured into water and the product extracted with ether. The ether extract was dried over magnesium sulfate and the ether removed to give 88% of the crude product; ^{1}H nmr δ: 3.30 (s, 1H), 7.85 (dd, 4H).

(E)-p-Nitrostyrene-β-d

p-Nitrophenylacetylene (0.0034 mol) in anhydrous tetrahydrofuran was added to a solution of 9-BBN (17) (0.0017 mol) in tetrahydrofuran at 0°C. The mixture was stirred for 1 h at 0°C and 2 h at room temperature. Acetic-*O*-*d* acid (0.034 mol) was added and the mixture stirred for 2 h. The mixture was poured into water and the product extracted with ether. It was stored in ether solution to minimize possible polymerization or isomerization. ^{1}H nmr δ: 6.01 (d, 1H), 6.65 (d, 1H), 7.81 (dd, 4H).

1-(p-Nitrophenyl)ethanol-1-d

To 0.0055 mol of *p*-nitroacetophenone in ethanol was added 0.0055 mol of sodium borodeuteride and the mixture stirred for 1 h at room temperature. The reaction mixture was poured into water and the product extracted with ether. The ether solution was dried over magnesium sulfate and evaporated to give 58% of crude product; ^{1}H nmr δ: 1.50 (s, 3H), 3.44 (s, 1H), 7.80 (dd, 4H).

1-(p-Nitrophenyl)ethyl-1-d *tosylate* was obtained from 1-(*p*-nitrophenyl)ethanol-1-*d* by a standard procedure (22). The crude product was used in the next step; ^{1}H nmr δ: 1.49 (d, 3H), 2.49 (s, 3H), 4.99 (q, 1H), 7.60 (dd, 4H), 7.80 (dd, 4H).

p-Nitrostyrene-α-d was obtained by heating 1-(*p*-nitrophenyl)ethyl-1-*d* tosylate (0.0032 mol) in excess 0.1 *M* sodium *tert*-butoxide in *tert*-butyl alcohol at 60°C for 12 h. The mixture was cooled, poured into water, and the product extracted with ether. It was kept in ether solution to minimize possible polymerization; ^{1}H nmr δ: 5.53 (t, 1H), 6.09 (t, 1H), 7.81 (dd, 4H).

Cope elimination reactions (23) of 2-arylethyldimethylamine oxides

The amine (0.00051 mol) was dissolved in 10 mL of methanol, cooled at 0°C, and 30% hydrogen peroxide (0.0015 mol) added dropwise. The mixture was warmed to room temperature, stirred for 24 h, and the excess peroxide decomposed by adding 5 mg of 10% platinum on carbon and stirring for 5 h. The mixture was filtered, the solvent removed under reduced pressure, and the residue dissolved in 80% dimethyl sulfoxide – 20% water and heated for 2.5 h (>5 half lives for 2-phenylethyldimethylamine oxide (24)). The solvent was removed and the mixture of mono- and di-deuterated styrenes analyzed by 300- or 400-MHz nmr (see Discussion).

Stereochemistry of base-promoted reactions of 2-arylethyl-1,2-d_2*-trimethylammonium iodides with sodium ethoxide in ethanol*

The substrate (ca. 20 mg) was dissolved in 5 mL of 0.1 *M* sodium ethoxide in ethanol at 80°C (unsubstituted) or 60°C (*p*-nitro substituted). The reaction was followed to completion by tlc (thin-layer chromatography). The reaction mixture was poured into water and the product was extracted with petroleum ether. The petroleum ether solution was dried over magnesium sulfate, filtered, 2 mL of dimethyl-d_6 sulfoxide added, and the petroleum ether removed on a rotary evaporator. The mixture of mono- and di-deutero styrenes was analyzed by 300- or 400-MHz nmr.

Acknowledgment

This work was supported by the U.S. National Science Foundation.

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