m), 4.49–4.72 (3 H, m), 5.26–5.36 (2 H, m), 5.60–5.69 (1 H, m); IR (CCl_4) 1095, 1150, 1380, 1460, 1550, 2920, 2950 cm^{-1}; MS *m/z* 189 (M^+).

Reaction of 2e with 26. The conjugate addition of crotyltin to α,β-unsaturated ketones was carried out in a similar procedure as described in Table I, procedure E.

4,5-Dimethyl-6-hepten-2-one: ^{1}H NMR (CCl_4) δ of *anti*-**27** ($R^1 = R^2 =$ Me) 0.85 (3 H, d, J = 6.7 Hz), 0.99 (3 H, d, J = 7.0 Hz), 2.12 (3 H, s); δ of *syn*-**28** ($R^1 = R^2 =$ Me) 0.87 (3 H, d, J = 7.0 Hz), 0.97 (3 H, d, J = 6.4 Hz), 2.11 (3 H, s); the following signals were observed in both isomers, 1.97–2.25 (3 H, m), 2.42–2.54 (1 H, m), 4.94–5.01 (2 H, m), 5.63–5.74 (1 H, m); IR (CCl_4) 1450, 1710, 2960 cm^{-1}; MS, *m/e* 140 (M^+).

3,4-Dimethyl-1-phenyl-5-hexen-1-one: ^{1}H NMR ($CDCl_3$, 400 MHz) δ of *anti*-**27** (R^1 = Me, R^2 = Ph) 0.918 (3 H, d, J = 6.7 Hz), 1.045 (3 H, d, J = 6.7 Hz); δ of *syn*-**28** (R^1 = Me, R^2 = Ph) 0.924 (3 H, d, J = 6.7 Hz), 1.033 (3 H, d, J = 6.4 Hz); the following signals were observed in both isomers, 2.11–2.21 (1 H, m), 2.22–2.29 (1 H, m), 2.65–2.73 (1 H, m), 2.97–3.08 (1 H, m), 4.97–5.04 (2 H, m), 5.71–5.82 (1 H, m), 7.43–7.60 (3 H, m), 7.92–7.95 (2 H, m); IR (CCl_4) 680, 740, 1445, 1580, 1595, 1680, 2960 cm^{-1}; MS, *m/z* 202 (M^+).

5-Methyl-4-phenyl-6-hepten-2-one: ^{1}H NMR (CCl_4) δ of *anti*-**27** (R^1 = Ph, R^2 = Me) 0.95 (3 H, d, J = 7.0 Hz), 2.02 (3 H, s), 2.38–2.45 (1 H, m), 2.79–2.83 (2 H, m), 3.16–3.22 (1 H, m); δ of *syn*-**28** (R^1 = Ph, R^2 = Me) 0.79 (3 H, d, J = 6.7 Hz), 1.94 (3 H, s), 2.27–2.34 (1 H, m), 2.64–2.87 (2 H, m), 2.95–3.00 (1 H, m); the following signals were observed in both isomers, 4.89–5.07 (2 H, m), 5.54–5.70 (1 H, m), 7.07–7.29 (5 H, m); IR (CCl_4) 690, 905, 1160, 1355, 1450, 1715, 2960, 3040, 3080 cm^{-1}; MS, *m/z* 202 (M^+).

4-Methyl-1,3-diphenyl-5-hexen-1-one: ^{1}H NMR (CCl_4) δ of *anti*-**27** ($R^1 = R^2$ = Ph) 1.00 (3 H, d, J = 6.7 Hz), 2.51–2.56 (1 H, m); δ of *syn*-**28** ($R^1 = R^2$ = Ph) 0.84 (3 H, d, J = 6.7 Hz), 2.40–2.46 (1 H, m); the following signals were observed in both isomers, 3.19–3.46 (3 H, m), 4.91–5.10 (2 H, m), 5.59–5.77 (1 H, m), 7.11–7.57 (8 H, m), 7.81–7.91 (2 H, m); IR (CCl_4) 690, 905, 1000, 1370, 1440, 1595, 1680, 2970, 3040 cm^{-1}; MS, *m/z* 264 (M^+).

Preparation of an Authentic Sample of 27 (R^1 = Me, R^2 = Ph). To a solution of 0.3 mmol (0.036 mL) of **12** dissolved in 3 mL of dry THF was added 5 equiv of PhMgBr dissolved in dry THF under N_2 at −78 °C. The mixture was stirred for 3 days at room temperature. The reaction was quenched with aqueous HCl, and the mixture was refluxed for 2 h. The reaction mixture was cooled, washed with a saturated aqueous $NaHCO_3$ solution, dried over $MgSO_4$, condensed, and purified by short silica gel column chromatography by using hexane–ether (20:1) as eluant. The desired ketone was obtained in 41% yield along with 41% recovered **12**.

Notes

Metal–Ammonia Reduction of Triphenylene

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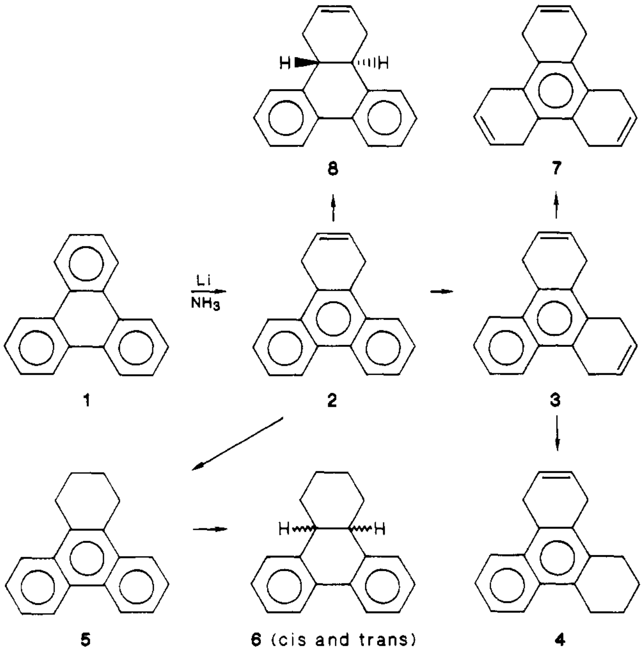
Received August 25, 1987

The reaction of polynuclear aromatic hydrocarbons with alkali metals in liquid ammonia provides a useful method for the preparation of hydroaromatics.[1] As outlined in eq 1, the aromatic, ArH, reacts with metal to form a radical

$$\mathrm{ArH} + e^- \rightleftharpoons [\mathrm{ArH}]^{\bullet -} \overset{e^-}{\rightleftharpoons} [\mathrm{ArH}]^{2-} \xrightarrow{\mathrm{NH_3}} [\mathrm{ArH_2}]^- \xrightarrow{\mathrm{H^+}} \mathrm{ArH_3} \quad (1)$$

anion which is not protonated in the absence of protic cosolvents (e.g., alcohols)[2] but goes on to furnish the considerably more basic dianion. For most two-, three-, and four-ring polynuclears, the dianion is protonated by ammonia, resulting in a monoanion which persists until the reaction is quenched with water, ammonium chloride, etc.[2,3] Regiochemistry in this reaction is dictated by the position of protonation in the dianion which is generally considered to occur at the position of highest electron density.[4] However, as we have noted previously,[5] it appears that in certain instances protonation does not occur at the (calculated) position of highest electron density but rather at a position so as to produce the most stable monoanion.[6] Herein, we report such an example which has also resulted in the isolation of a number of new and interesting hydrocarbons.

Scheme I



The reaction of triphenylene (**1**) with a slight excess of lithium metal in anhydrous ammonia/THF (2:1) furnished

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(1) For reviews, see: (a) Birch, A. J. *Q. Rev. Chem. Soc.* **1950**, *4*, 69. (b) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Los Angeles, CA, 1972. (c) Harvey, R. G. *Synthesis* **1970**, *4*, 161. (d) Birch, A. J.; Subba Rao, G. *Advances in Organic Chemistry, Methods and Results*; Taylor, E. C., Ed.; Wiley-Interscience: New York, 1972.

(2) Rabideau, P. W.; Burkholder, E. G. *J. Org. Chem.* **1978**, *43*, 4283. See also: Rabideau, P. W. "The Dissolving Metal Reduction of Polynuclear Aromatic Compounds in Liquid Ammonia", *Chemistry of Polynuclear Aromatic Compounds*, ACS Advances in Chemistry Series; Ebert, L. B., Ed.; American Chemical Society: Washington, DC, 1987. *Prepr.-Am. Chem. Soc., Div. Pet. Chem.* **1986**, *31* (4), 791.

(3) Müllen, K.; Huber, W.; Neumann, G.; Schnieders, C.; Unterberg, H. *J. Am. Chem. Soc.* **1985**, *107*, 801.

(4) (a) Streitwieser, A., Jr.; Suzuki, S. *Tetrahedron* **1961**, *16*, 153. (b) Zimmermann, H. E. *Ibid.* **1961**, *16*, 169. (c) Birch, A. J.; Hinde, A. L.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 3370.

(5) Rabideau, P. W.; Peters, N. K.; Huser, D. L. *J. Org. Chem.* **1981**, *46*, 1593.

(6) Barton, D. H. R.; Robinson, C. H. *J. Chem. Soc.* **1954**, 3045.

0022-3263/88/1953-3603$01.50/0

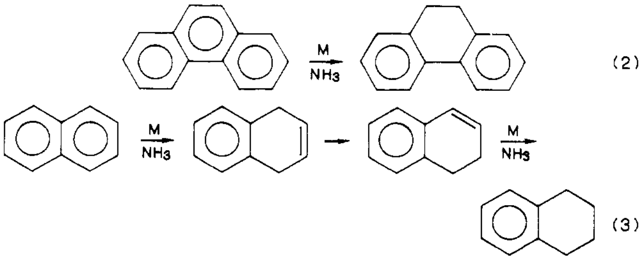
Table I. MNDO Calculated Charge Densities for the Triphenylene Dianion 1^{2-} [a]

		singlet states	
position[b]	triplet state (H_f = 104.8 kcal/mol)	$^1A_2$ symmetry (H_f = 117.4 kcal/mol)	$^1B_2$ symmetry (H_f = 117.9 kcal/mol)
C-1	0.02	0.04	-0.20
C-2	-0.23	-0.20	-0.11
C-1a	-0.17	-0.21	0.09
C-9a	-0.07	-0.09	-0.05
C-9	-0.16	-0.03	-0.12
C-10	-0.07	-0.31	-0.04
C-11	-0.19	0.0	-0.35
C-12	-0.19	-0.26	0.07
C-12a	0.08	0.09	-0.24

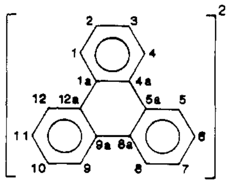
[a] See 1^{2-} in text for numbering system. [b] Values provided for left half of the structure only since right half are identical.

the dihydro (GC/MS) compound **2** as the major product. It was easily identified from its "phenanthrene like" UV spectrum, and the proton NMR spectrum which showed allylic (4 H) and vinylic (2 H) singlets (spin coupling between allyl and vinyl signals is often not observed under ordinary conditions in 1,4-dihydronaphthalenes).[7]

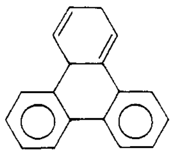
Careful chromatography on silica gel impregnated with tetranitrofluorenone[8] allowed the isolation of additional tetra- and hexahydro isomers and the order of elution corresponded to the level of unsaturation/aromaticity. The origin of each of these products is indicated in Scheme I and is easily rationalized on the basis of the behavior of phenanthrene (eq 2) and naphthalene (eq 3). Thus we may consider the reduction of triphenylene, as well as its dihydro and tetrahydro isomers, in terms of the reduction behavior of the phenanthrene and/or naphthalene subunits. As shown in eq 2, phenanthrene reduces across its 9,10 positions and this accounts for reactions **2** → **8** and **5** → **6**. Naphthalene (eq 3) reduces 1,4 and can also provide tetrahydronaphthalene by rearrangement to the 1,2-dihydro isomer which is quite susceptible to reduction under the reaction conditions if any excess metal is present (in contrast to the 1,4 isomer). These latter two processes explain the remaining products.



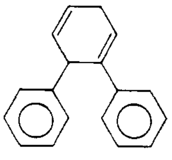
The formation of **2** from **1** must result from (initial) protonation of the triphenylene dianion (1^{2-}) at the 1 position (an α position). This result is not expected on the basis of theory. It has been known for some time that, for reasons of symmetry, the triphenylene dianion is expected to be a ground-state triplet, and this has been confirmed by experiment.[9] MNDO calculations[10] (Table I) also predict a triplet to be lowest energy with two singlets around 13 kcal/mol higher. In any event, charge densities for all three have been calculated (Table I), and, in every case, protonation at the β position to produce **9** (ultimately) would be expected on this basis. In fact, *o*-terphenyl does produce **10** which is consistent with a biphenyl-like reduction.[1]



1^{2-}

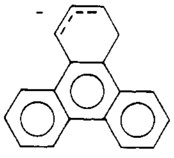


9

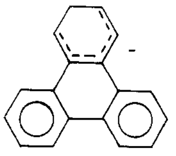


10

An early proposal by Barton and Robinson[6] suggested that dianions will be protonated at sites such as to produce the most stable monoanion. This approach has not received much recent attention, however, and appears to have been replaced by the concept that protonation will occur at the site of highest electron density (or largest HOMO coefficient) in the dianion.[4] We have had cause to question the generality of this approach before,[5] and indeed triphenylene appears to be another example given our calculated results. Hence we suggest that monoanion stability is the driving force with the reduction of **1**. The monoanion resulting from protonation at an α position (**11**) is more phenanthrene-like since a higher bond order is expected for C_{1a}–C_{4a} as compared with **12**.

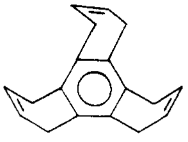


11

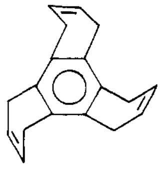


12

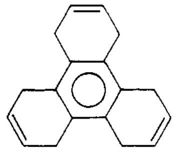
The geometries of the reduced products are also intriguing. For example, Dreiding mechanical models suggest two structures for **7**, one with all outside rings up (**7a**) and the other with one down and two up (**7b**). The former would appear to be the less stable, however, due to nonbonded interactions between the allylic hydrogens. Interestingly, the computer model (MMP2 force field)[11,12] does not favor either of these geometries but rather provides the completely planar system (**7c**) as the global minimum. This is not surprising, however, since 1,4-dihydronaphthalene itself shows the same discrepancy be-



7a



7b



7c

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[7] For a review of 1,4-dihydroaromatics, see: Rabideau, P. W. *Acc. Chem. Res.* **1978**, *11*, 141.

[8] Harvey, R. G.; Haloren, M. *J. Chromatogr.* **1966**, *25*, 294.

[9] Szwarc, M., Ed. *Ions and Ion Pairs in Organic Reactions*, Vol. 1; Wiley: New York, 1972; p 366 and references therein.

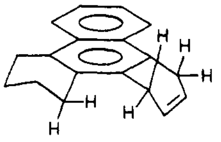
[10] Stewart, J. P. *QCPE Bull.* **1983**, *3*, 455.

[11] (a) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982. (b) Allinger, N. L.; Yuh, Y. H. *QCPE* **1980**, *12*, 395.

[12] For previous application to these systems, see: (a) Lipkowitz, K. B.; Rabideau, P. W.; Raber, L. E.; Hardee, L. E.; Schleyer, P. v. R.; Kos, A. J.; Kahn, R. A. *J. Org. Chem.* **1982**, *47*, 1002. (b) Raber, D. J.; Hardee, L. E.; Rabideau, P. W.; Lipkowitz, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 2843.

tween mechanical and computer models.[12] The proton NMR spectrum of 7 shows equivalent allylic protons even at low temperature (-40 °C), and this is consistent with the planar structure but does not rule out rapid ring inversions of puckered structures. The MMP2 force field also predicts planar geometries for 2 and 3.

Mechanical models also suggest a puckered 1,4-cyclohexadiene ring in 4. In the illustrated geometry, it would

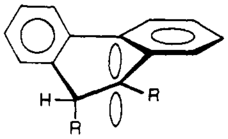


4

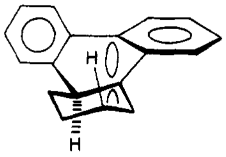
appear that the pseudoequatorial allylic hydrogen can "fit" between the two nearby benzylic hydrogens. However, this puckering would also bring the opposite pseudoequatorial hydrogen in closer proximity to its ortho aryl neighbor. Perhaps these effects balance out because MMP2 calculations suggest a planar 1,4-cyclohexadiene ring (and a normally puckered cyclohexene ring). The proton NMR spectrum of 4 does not show separate resonances for pseudoaxial and pseudoequatorial allylic hydrogens. They appear as a pair of triplets arising from the long-range homoallylic coupling (^5J) between the allylic pairs. The lack of resolvable coupling between the allylic and vinylic protons does support a planar ring since, in this geometry, each of the respective vinyl hydrogens bisects its neighboring allylic pair. The cyclohexene-like ring shows two broad signals indicative of rapid inversion as might be expected.

Compounds 6 and 8 can exist as either cis or trans isomers, and in the case of 6, both isomers were produced. In contrast, 8 was found to be a single isomer, and the trans assignment was made on the basis of its temperature-independent NMR spectrum (*cis*-9,10-dialkyl-9,10-dihydrophenanthrenes show temperature-dependent NMR behavior due to a ring inversion process; this is not true for the trans isomers).[13]

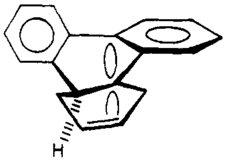
This reduction behavior exhibiting a tendency toward trans products may at first seem surprising since 9,10-dialkylphenanthrenes are known to provide cis (only) products. However, we feel that this can be radionalized as follows. Protonation of the monoanion 13 is expected



13



14



15

to take place on the side opposite to the axial R group (axial preference has been demonstrated for 9,10-dihydrophenanthrenes by NMR).[14] This results in cis products. With 14, however, the system is constrained so that the axial ("blocking") group is hydrogen (H_{10}). However, the axial hydrogen(s) of the cyclohexane moiety also provides steric interference so that attack occurs from either side affording *cis*- and *trans*-6. In the case of 15, these axial cyclohexyl hydrogens are missing and so the major steric interference comes from H_{10} resulting in protonation from the top side. This, of course, produces the trans product.

Experimental Section

Proton NMR spectra were recorded at 90 MHz on a Varian EM-390 spectrometer with tetramethylsilane as reference and $CDCl_3$ as solvent. Mass spectra were determined on a HP 5988A GC/MS spectrometer at an ionization potential of 30 eV. Microanalyses were obtained for all new compounds by Galbraith Laboratories, Inc. R_f values of hydroaromatic triphenylenes on impregnated silica gel plates (with 2% TNF)[8] are given for a 1:1 benzene/hexane solvent mixture.

Metal–Ammonia Reduction Procedure. Triphenylene (912 mg, 4 mmol) was dissolved in 40 mL of THF (freshly distilled from sodium benzophenone ketyl) and added to 80 mL of anhydrous ammonia, under argon, at -78 °C, followed by the addition of lithium (20 mmol) in pieces, and stirring was continued for 30 min. The mixture was then pumped (with argon pressure) through a glass tube into a large excess of aqueous NH_4Cl and products were isolated by ether extraction. The white solid (910 mg) was separated by careful chromatography on 230–400-mesh silica gel (Merck) impregnated with 2% TNF; other commercial grades proved less satisfactory. Elution with 5% solution of benzene in hexane gave (in order of elution) the following.

***cis*-1,1a,2,3,4,4a-Hexahydrotriphenylene (*cis*-6) (*R_f* 0.86):**[15] 130 mg (14%); oil;[16] NMR ($CDCl_3$) δ 1.3–2.1 (m, 8 H), 3.0 (m, 2 H), 7.3 (m, 6 H), 7.7–7.9 (m, 2 H); mass spectrum, *m/e* 234 (M^+).

***trans*-1,1a,2,3,4,4a-Hexahydrotriphenylene (*trans*-6) (*R_f* 0.83):** 45 mg (5%); mp 79–80 °C (lit.[16] mp 90 °C); NMR ($CDCl_3$) δ 1.43 (m, 4 H), 1.95 (m, 2 H), 2.4 (m, 4 H), 7.27 (m, 6 H), 7.6–7.85 (m, 2 H); mass spectrum, *m/e* 234 (M^+).

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 91.97; H, 7.85.

***trans*-1,1a,4,4a-Tetrahydrotriphenylene (8) (*R_f* 0.80):** 25 mg (3%); mp 127–128 °C (ethanol); NMR ($CDCl_3$) δ 2.1–3.1 (m, 6 H), 5.9 (br s, 2 H), 7.27 (m, 6 H), 7.65–7.9 (m, 2 H); mass spectrum, *m/e* 232 (M^+).

Anal. Calcd for $C_{18}H_{16}$: C, 93.05; H, 6.95. Found: C, 92.92; H, 6.94.

1,4,5,6,7,8-Hexahydrotriphenylene (4) (*R_f* 0.56): 80 mg (9%); mp 133–134 °C (ethanol); NMR ($CDCl_3$) δ 1.9 (m, 4 H), 2.7 (m, 2 H), 3.1 (m, 2 H), 3.3 (t, 2 H), 3.7 (t, 2 H), 6.0 (br s, 2 H), 7.3–7.6 (m, 2 H), 7.8–8.1 (m, 2 H); mass spectrum, *m/e* 234 (M^+).

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.33; H, 7.72.

1,4,5,8,9,12-Hexahydrotriphenylene (7) (*R_f* 0.55): 30 mg (3%); mp 199–201 °C (ethanol); NMR ($CDCl_3$) δ 3.2 (br s, 12 H), 5.83 (br s, 6 H); mass spectrum, *m/e* 234 (M^+).

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.58; H, 7.75.

1,2,3,4-Tetrahydrotriphenylene (5) (*R_f* 0.40): 20 mg (2%); mp 121–122 °C (lit.[17] mp 120–121 °C); NMR ($CDCl_3$) δ 2.0 (m, 4 H), 3.12 (m, 4 H), 7.5–7.75 (m, 4 H), 7.95–8.20 (m, 2 H), 8.60–8.85 (m, 2 H); mass spectrum, *m/e* 232 (M^+).

1,4,5,8-Tetrahydrotriphenylene (3) (*R_f* 0.39): 120 mg (13%); mp 199–200 °C (ethanol); NMR ($CDCl_3$) δ 3.32 (t, 4 H), 3.78 (t, 4 H), 6.05 (br s, 4 H), 7.4–7.62 (m, 2 H), 7.85–8.1 (m, 2 H); mass spectrum, *m/e* 232 (M^+).

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(13) Rabideau, P. W.; Harvey, R. G.; Stothers, J. B. *J. Chem. Soc. D* **1969**, 1005.

(14) Harvey, R. G.; Fu, P. P.; Rabideau, P. W. *J. Org. Chem.* **1976**, *41*, 3722.

(15) The Chemical Abstracts name for the triphenylene compounds would label the authors position 1a as 12b, 5a as 4b, and 9a as 8b.

(16) Lapouyade, R.; Manigand, C.; Nourmamode, A. *Can. J. Chem.* **1985**, *63*, 2192. Our data (mp, NMR) for *trans*-6 do not agree with those given for that compound in this paper. So, we prepared *trans*-6 in another way, by hydrogenation of *trans*-8 with 10% $Pd/CaCO_3$ in a Parr hydrogenation vessel under 50-psi hydrogen atmosphere at 20 °C for 24 h. Product, after crystallization from methanol, was identical (NMR, mp) with our data for *trans*-6.

(17) Bergmann, E.; Blum-Bergmann, O. *J. Am. Chem. Soc.* **1937**, *59*, 1441.

Anal. Calcd for $C_{18}H_{16}$: C, 93.05; H, 6.95. Found: C, 92.86; H, 6.76.

1,4-Dihydrotriphenylene (2) (R_f 0.28): 425 mg (47%) (67% of 2 was isolated by column chromatography from the crude products of the metal–ammonia reduction of 1 using 2.5 mmol of lithium per 1 mmol of substrate); mp 203–204 °C (ethanol); NMR ($CDCl_3$) δ 3.80 (s, 4 H), 6.1 (br s, 2 H), 7.5–7.8 (m, 4 H), 7.9–8.1 (m, 2 H), 8.6–8.9 (m, 2 H); mass spectrum, m/e 230 (M^+).

Anal. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.32; H, 6.18.

Finally, elution with benzene gave recovered triphenylene (15 mg, 2%).

Acknowledgment. We gratefully acknowledge support of this work by the U.S. Department of Energy, Office of Energy Research.

Registry No. 1, 217-59-4; 2, 39935-60-9; 3, 114249-91-1; 4, 114221-72-6; 5, 5981-10-2; *cis*-6, 99144-04-4; *trans*-6, 99144-01-1; 7, 114221-73-7; 8, 114221-74-8; NH_3, 7664-41-7; Li, 7439-93-2.

Kinetic Effects of Pressure on Thermal *Z*-*E* Isomerization of a Stilbazolium Betaine. Dependence of Activation Volume on Reaction Conditions

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Received December 30, 1987

Stilbazolium betaines continue to attract attention because of their extreme solvatochromism.[1] 1-Methyl-4-(4-hydroxystyryl)pyridinium betaine (1) has been studied especially extensively. The *Z*–*E* photoisomerization and thermal isomerization of 1 and its conjugate acid were first confirmed by Steiner and his co-workers.[2] Their study revealed that thermal *Z*–*E* isomerization of 1 takes place relatively slowly in water. Rotation about the central carbon–carbon bond in its quinoid form 2 is the only plausible route in this isomerization (Scheme I); this reaction provides us with an opportunity to examine whether the solvent molecules recognize the oxygen and nitrogen atoms as independent charge centers in the *Z* configuration and whether the formal charge disappearance in the activation step results in a large positive activation volume. If this turns out to be the case, it may be taken as yet another fact supporting the rotational mechanism of *Z*–*E* isomerization of aminoazobenzenes. Large *negative* activation volumes were previously interpreted to be the result of electrostriction of solvent caused by intramolecular charge separation during the activation step.[3] This paper describes the kinetic effect of pressure on the thermal *Z*–*E* isomerization of 1 and its dependence on the reaction conditions.

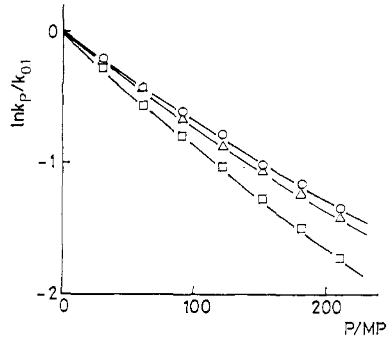
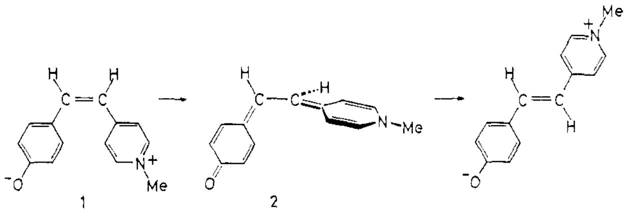


Figure 1. Effect of pressure on the isomerization rate of (*Z*)-1-methyl-4-(4-hydroxystyryl)pyridinium betaine in water and aqueous methanol at 25 °C: (○) water; (△) 20 wt % methanol; (□) 40 wt % methanol.

Scheme I



1 2

Table I. First-Order Rate Constants ($10^5k/s^{-1}$) and Activation Volumes ($cm^3\ mol^{-1}$) for *Z*–*E* Isomerization of 1 in Water

	T/°C				
P/MPa	10	15	25	35	45
0.1	0.499	1.17	5.74	24.6	101
30.0		0.967	4.64	20.2	81.7
60.0		0.779	3.73	16.7	65.0
90.0		0.661	3.12	13.7	55.7
120.0		0.534	2.61	11.5	46.2
150.0		0.419	2.04	9.86	39.8
180.0		0.335	1.79	8.09	33.9
210.0			1.48	7.10	29.8
$\Delta V_0^{\ddagger}$		16.5 ± 0.4[a]	17.7 ± 1.4	18.1 ± 1.7	20.0 ± 1.2

[a] The pressure independence of the activation volume was assumed in the calculation.

Experimental Section

Materials. 1-Methyl-4-(4-hydroxystyryl)pyridinium betaine was prepared as described.[4] After several recrystallizations from water, the blue-red crystals were dried in vacuo.

Anal. Calcd for $C_{14}H_{13}ON\cdot{}^1/_2H_2O$: C, 76.34; H, 6.41; N, 6.36. Found: C, 76.43; H, 6.57; N, 6.52.

Water was deionized and distilled. Methanol was used after distillation from magnesium.

Kinetic Measurements. To 10 mL of a (1–1.4) × 10^{-4} mol L^{-1} solution of 1 was added 1 mL of 1 × 10^{-3} mol L^{-1} hydrochloric acid, and the mixture was diluted to ca. 30 mL. After irradiation by a UV lamp (Toshiba FL20S-BLB), the solution was basified by adding 10 mL of 0.1 mol L^{-1} sodium hydroxide solution and diluted to 50 mL. It was transferred to a modified hypodermic syringe. The syringe was connected to a sampling valve and pressurized in a thermostated pressure vessel. Samples were withdrawn at regular intervals after the compression heat was dissipated. The reaction was followed by monitoring the absorption increase in the visible region.[2] Measurements were made at every 30 MPa up to 210 MPa. It was confirmed that the reaction rate was independent of the base concentration; the reproducibility of the rate constant was 2–4%.

Results and Discussion

The reaction follows a first-order rate law under all conditions studied and it was retarded greatly by increasing the pressure. For example, at 25 °C in water, the half-life was 3.35 h at 0.1 MPa and 13 h at 210 MPa. The rate constants in water are listed in Table I along with the

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[1] Jacques, P. *J. Phys. Chem.* **1986**, *90*, 5535.

[2] Steiner, U.; Abdel-Kader, M. H.; Fischer, P.; Kramer, H. E. A. *J. Am. Chem. Soc.* **1978**, *100*, 3190.

[3] Asano, T.; Okada, T. *J. Org. Chem.* **1986**, *51*, 4454 and earlier papers.

[4] Minch, M. J.; Sadiq Shah, S. *J. Chem. Educ.* **1977**, *54*, 709.

0022-3263/88/1953-3606$01.50/0