

SO₄⁻-aromatic reactions.¹² Further, in such a strongly alkaline solution conversion of SO₄⁻ to HO· should compete with attack on aromatic substrates,²¹ and the HO·-O· equilibrium becomes significant.

Experimental Section

Reagents. Potassium peroxydisulfate was recrystallized twice from water, purity by titration >98%. Hydrogen peroxide was vacuum distilled before use. Other inorganic reagents (usually reagent grade perchlorates) were used as received. Purity of organic substrates was checked by gas-liquid chromatography (GLC) and they were distilled if necessary. Standard solutions were made up and used to prepare reaction mixtures.

Reactions were carried out by adding peroxide solutions dropwise to stirred mixtures of other reactants, (N) in tables, or by inverse addition (I) of Fe²⁺ solutions to substrate-peroxide solutions, all well stirred and thermostated under N₂ as described previously.²² Thermal reactions were carried out by mixing reagents, flushing with N₂, and heating in stoppered flasks in a thermostat.

Analyses of reaction mixtures were carried out as previously²² by GLC using previously calibrated internal standards and known reference materials. Phenols and alcohols were extracted, silylated, and analyzed. Best results were obtained by temperature programming on 5% SE-30 or 10% OV-1 on Chromosorb W or with nitrophenols, on 10% XE-60 on Chromosorb W. Benzaldehydes were separated on 5% Carbowax 20M or 10% OV-17 on Chromosorb W.

***p*-Nitrophenyl sulfate** was identified from nitrobenzene reactions by two techniques. First, phenols and other organics were extracted from the reaction mixture; the aqueous fraction was made 1 N in acid and refluxed for 1 h, and liberated nitrophenols were extracted and analyzed by GLC. Only *p*-nitrophenol was detected, and no phenols were obtained from hydrolysis of similar benzene oxidations. This technique was used to determine sulfate yields. Next, a nitrobenzene reaction, after extraction of phenols and other organic-soluble material, was made alkaline with KOH, precipitated Fe and Cu salts were removed by centrifuging, and the supernatant liquid was evaporated. Acetone extracts of the residue were spotted on Whatman no. 1 filter paper, dried, and developed using 2-butanone-water-diethylamine (92:1:77:2).²⁶ Both the sample and authentic potassium *p*-nitrophenyl

sulfate²⁷ gave spots, *R_f* 0.63, blue under UV illumination, which, when spotted with HCl and warmed, turned pale yellow, and darkened on exposure to NH₃.

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Regioselectivity as a Criterion for Mechanism in the Base-Promoted Opening of Methylbicyclo[6.1.0]nona-2,4,6-trienes

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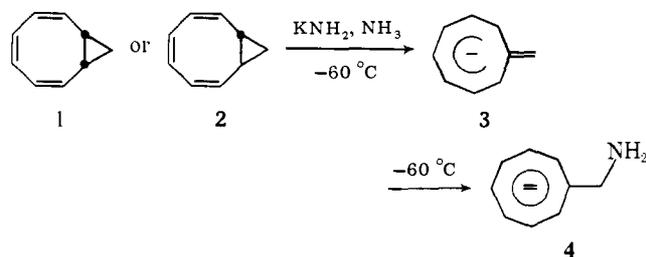
Abstract: Treatment of 1-, 2-, 3-, and 4-methyl-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (**10–13**, respectively) and 2-methyl-*trans*-bicyclo[6.1.0]nona-2,4,6-triene (**14**) with potassium amide in liquid ammonia at 25 °C afforded various methyl-substituted aminomethylcyclooctatetraene dianions. Determination of the regioselectivities of these reactions, along with an absence of deuterium exchange in *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**1**) on treatment with potassium *tert*-butoxide-dimethyl-*d*₆ sulfoxide, has led to the conclusion that the rate-limiting transition state for the overall reaction involves the deprotonation of **1** and its derivatives with little distortion from its tublike ground state conformation.

The methylenecyclooctatrienyl anion (**3**) is formed by the base-promoted ring opening of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**1**) or its *trans* isomer (**2**).^{1,2} The lithium salts of **3** and various derivatives of **3** are stable in liquid ammonia at -30 °C. In contrast, the potassium salts can be detected by NMR spectroscopy at -65 °C, but rapidly suffer amide attack at C₉ to afford aminomethylcyclooctatetraene dianions (**4**).^{2,3}

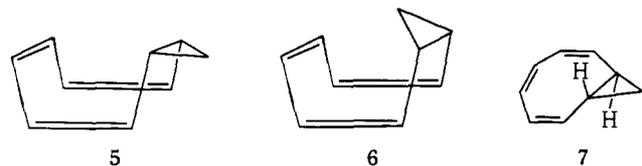
In this paper we employ the novel probe of regioselectivity in the ring opening of unsymmetrically substituted methyl derivatives of **1** and **2** in order to define the charge distribution in and therefore the geometry of the rate-limiting transmission state of the reaction.

Analysis of the Problem

cis-Bicyclo[6.1.0]nona-2,4,6-trienes were first proposed to



exist in the "extended" conformation (**5**) rather than the "folded" conformation (**6**) on the basis of relative rates and



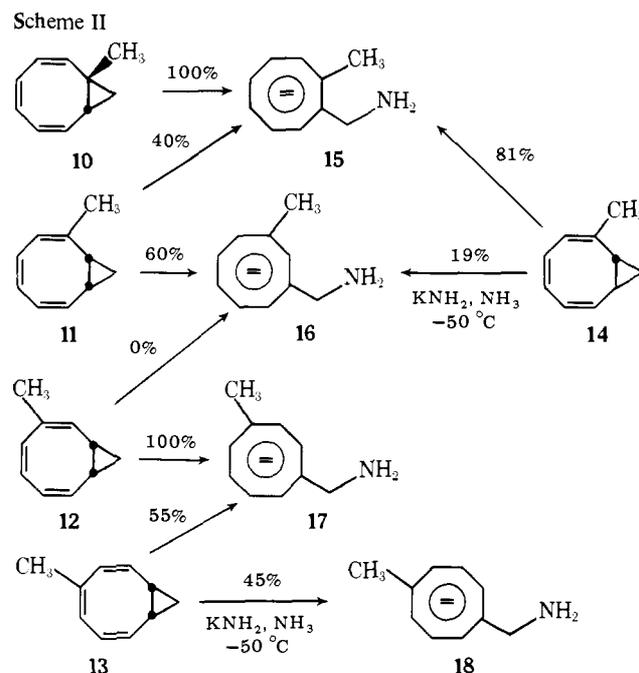
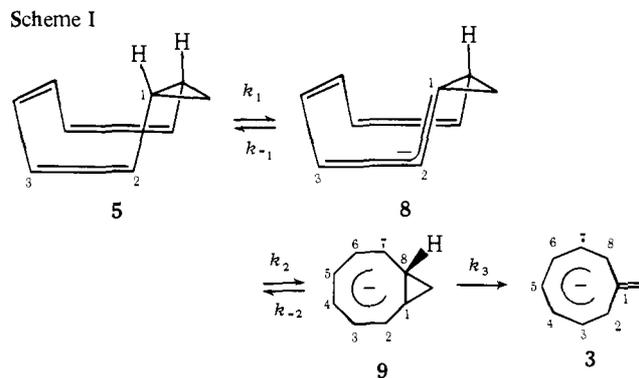
product compositions in the thermal rearrangements of **1** and its 9,9-dimethyl derivative.^{4,5} This point has recently been confirmed by lanthanide-induced shift NMR studies of various 9-substituted derivatives of **1** as well as by x-ray crystallographic studies of the *anti*-9-(*p*-bromophenylcarboxylate) derivative of **1**.⁶ Furthermore, the vicinal proton-proton coupling constants of the lithium salt of **3** in liquid ammonia ($J_{12} = 12.5$, $J_{23} = 10.2$, $J_{34} = 10.8$ Hz) indicate that this anion is planar or nearly planar.¹ Thus the following steps must occur, either sequentially or concertedly, in the course of the conversion of **1** to **4**: (a) removal of a bridgehead proton, (b) flattening of the eight-membered ring, and (c) ring opening of the cyclopropyl anion. These individual processes are illustrated in Scheme I and are designated as k_1 , k_2 , and k_3 , respectively. Note that the numbering in anion **3** does not reflect standard rules of nomenclature (in which case the methylene group would be at C₈), but is done as indicated so that each carbon atom will keep the same number on going from **5** to **3**.

There is precedent for having deprotonation precede ring opening,⁷⁻⁹ but the ring flattening step could, in principle, occur at any point. These possibilities will be dealt with at a later point. In contrast, the π system of **2** is more nearly planar, as indicated by its UV spectrum (λ_{max} (ethanol) 311 nm compared with 247 nm for **1**).⁵ Molecular models suggest that the π system of this isomer adopts a helical arrangement around the trans-ring fusion (**7**). This structure closely approximates that of anion **9** and one therefore expects a minimum of ring flattening during conversion of **7** to **9**.

If **1** is substituted with a group which will stabilize or destabilize the negative charge in the rate-limiting transition state (such as k_1 , k_2 , or k_3 , or some combination thereof) then removal of one or the other of the bridgehead protons in **1** will no longer be equivalent processes. It seemed to us that, in principle, one could learn a great deal about the charge distribution and therefore about the transition state of the reaction by examining the regioselectivity of opening of monosubstituted derivatives of **1**. This approach has proven successful and has led us to conclude that, at least in the present case, this type of study can give remarkably detailed information regarding charge distribution in transition states.

Results

Compounds **10**–**13** were prepared in 70% combined yield by the addition of methylene chloride to a solution of dilithium methylcyclooctatetraene in liquid ammonia at ca. -33°C .⁴ The isomers were separated by GLC and identified by comparison of their NMR data with those previously reported.¹⁰ Data for **12** were not available and are given in the Experimental Section. The *trans* isomer of **13** (**14**) was obtained as 43% (by GLC) of the product mixture on irradiation (2537 Å)



of dilute solutions of **13** in hexane through quartz.¹¹

Treatment of **10**–**14** with excess potassium amide in liquid ammonia in sealed NMR tubes at 25°C afforded various methyl-substituted aminomethylcyclooctatetraene dianions (**15**–**18**). NMR spectral data for the latter compounds are given in Table I. The signals for the $-\text{NH}_2$ group are presumably obscured by the broad ammonia peak at ca. δ 0.8. Owing to the rather small differences in the chemical shifts measured for the corresponding signals for **10**–**13**, additional spectra were generated from 1:1 mixtures of **11** and **12** and of **12** and **13**. In each case the number and area of NMR signals expected from Scheme II and Table I were observed. The structures of **15**–**18** were readily assigned on the basis of their NMR spectra (Table I) and the structures of their precursors (Scheme II). Thus, **10** can only open to **15** and **18** can only be derived from **13**. Similarly, **17** can be derived from both **12** and **13** and **11** can afford both **15** and **16**, as was observed. Thus, the fact that **12** gave only **17** (no **16** was observed) did not hinder the product analysis.

Finally, treatment of **1** with an excess of potassium *tert*-butoxide in dimethyl sulfoxide (Me_2SO) has been shown to give **3** (δ 5.14 (apparent t (d of d)), $\text{H}_{2,6}$), 4.98 (t, H_4 , $J_{34} = 11$ Hz), 4.82 (s, 2 H, H_9), and 4.22 (unsymmetrical d, $\text{H}_{1,7}$, $J_{12} = 12.6$ Hz); the signals for $\text{H}_{3,5}$ were obscured by a large peak at δ 3.6). When **1** was treated with a deficiency of potassium *tert*-butoxide in $\text{Me}_2\text{SO}-d_6$, an analysis of recovered **1** (by mass spectrometry) indicated that no deuterium exchange had occurred.

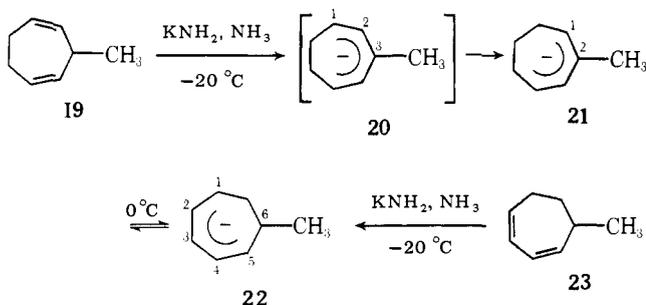
Table I. Chemical Shift Data for Methyl-Substituted Aminomethylcyclooctatetraene Dianions (Potassium Salts) in Liquid Ammonia at 25 °C

Dianion	Source	Chemical shift, δ^a		
		Ring protons	-CH ₂ -	-CH ₃
4	1	5.58-5.92	4.00	
15	10, 11, 14	5.30-5.68	4.07	2.95
16	11, 14	5.35-5.77	3.94	2.90
17	12, 13	5.33-5.72	3.92	2.83
18	13	5.38-5.78	3.92	2.81

^a Relative to Me₄Si; trimethylamine ($\delta_{\text{Me}_4\text{Si}}$ 2.135) was used as an internal standard.

Discussion

There is ample precedent to indicate that methyl groups destabilize carbanions in solution when they are connected to charge-bearing carbons. The most pertinent data with regard to our present results are the observations that **21** and **22** are rapidly produced on deprotonation of **19** and **23**, respectively,



and that these two anions equilibrate to a 2:3 mixture, respectively, at 0 °C.¹² Since **20** should be produced on initial deprotonation, this indicates that the latter anion is substantially less stable than **21**; i.e., the methyl group on the negatively charged carbon (C₃) in **20** is destabilizing relative to a methyl group on a relatively uncharged carbon (C₂) in **21**. Furthermore, the equilibrium results indicate that a C₂ methyl is slightly destabilizing relative to a methyl group on an adjacent sp³ carbon (C₆). Since methyl groups on sp² carbons are normally stabilizing relative to methyl groups on sp³ carbons (cf. ΔH_f of *trans*-2-butene (-8.15 kcal/mol) and 1-butene (-5.12 kcal/mol)),¹³ it is clear that the C₂ methyl group is also exerting a small destabilizing effect in **21**. The origin of this effect is unclear. However, if it arises from steric inhibition of solvation or ion pairing,¹⁴ then it is understandable that a C₂ methyl group is destabilizing since it is adjacent to two charged carbons (C₁ and C₃).

We expect the negative charge to be located at C₁ and C₃ in **8**, at C₁, C₃, C₅, and C₇ in **9**, and at C₂, C₄, C₆, and C₈ in **4** (Scheme I). The charge distributions expected in various transition states in the context of Scheme I are given in Table II.

Our results allow us to reach the following conclusions, based, in part, on the assumption that processes which place methyl groups on negatively charged carbon atoms in the transition state will be retarded. First, since anion **9** is common to the opening of both *cis*- and *trans*-bicyclo[6.1.0]nona-2,4,6-trienes, the fact that **11** and **14** exhibit opposite regioselectivities indicates that step **3** is not the rate-limiting step. That is, the stereochemical differences between **11** and **14** must be reflected in the corresponding transition states. The lack of deuterium exchange in recovered **1** indicates that $k_2 + k_3 \gg k_{-1}$ and therefore that k_2 , or k_3 , or k_{2+3} are not the slow steps. Although this experiment was done in Me₂SO-*d*₆ and not in liquid ammonia, our conclusion is strongly supported by the regioselectivity data for **13**. The latter indicate that the charge

Table II. Negative Charge Distributions Expected for the Transition States in Scheme I

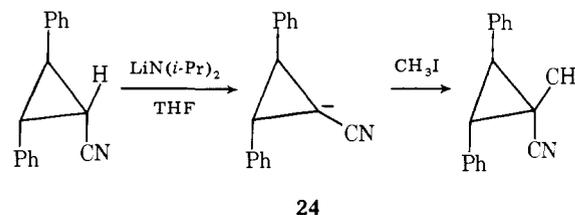
Transition state	Charge distribution		
	Reactant	Transition state ^a	Product
<i>k</i> ₁	Uncharged	C ₁ , C ₃	C ₁ , C ₃
<i>k</i> ₂	C ₁ , C ₃	C ₁ , C ₃ , C ₅ , C ₇	C ₁ , C ₃ , C ₅ , C ₇
<i>k</i> ₃	C ₁ , C ₃ , C ₅ , C ₇	C ₁ -C ₈	C ₂ , C ₄ , C ₆ , C ₈
<i>k</i> ₁₊₂	Uncharged	C ₁ , C ₃ , C ₅ , C ₇	C ₁ , C ₃ , C ₅ , C ₇
<i>k</i> ₂₊₃	C ₁ , C ₃	C ₁ , C ₂ , C ₃ , C ₄ -C ₈	C ₁ , C ₄ , C ₆ , C ₈
<i>k</i> ₁₊₂₊₃	Uncharged	C ₁ , C ₂ , C ₃ , C ₄ -C ₈	C ₂ , C ₄ , C ₆ , C ₈

^a The italicized positions are expected to bear the greatest amount of charge.

densities (*Q*) on C₄ and C₅ are about equal, thus eliminating k_2 or k_{1+2} as the rate-limiting steps.

On balance, the evidence leads one to the conclusion that the rate-limiting transition state for the overall reaction involves proton removal from **1** in its tub conformation (**8**) with little ring flattening; i.e., the C₄-C₅ and C₆-C₇ double bonds are more or less isolated from the negative charge being transferred to **1** on deprotonation. This is supported by the results for **12** ($Q_3 \gg Q_6$) and for **11** ($Q_2 \approx Q_7$). The observation that a methyl group at C₂ is slightly destabilizing relative to one at C₇ is consistent with the fact that even though C₂ is not a "charged" position, it is adjacent to the two sites of highest charge density (C₁ and C₃).

Finally, we note that the regioselectivity observed in the opening of **14** supports this interpretation. Since there is significant interaction between adjacent double bonds in this compound, the charge is delocalized throughout the π system on deprotonation, so that $Q_7 > Q_2$. We cannot exclude the possibility that some ring opening accompanies deprotonation, but the observed regioselectivities suggest that this does not occur to a large extent. In this regard, we note that previous investigators have established that, in certain cases (such as **24**) where the negative charge can be delocalized, cyclopropyl

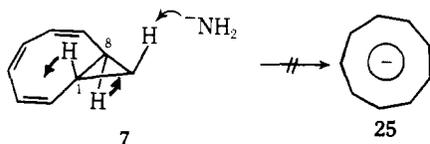


anions are stable and can be trapped with methyl iodide⁸ or deuterium oxide.⁹

Summary

The picture which emerges from these regioselectivity studies is of a rate-limiting removal of a bridgehead proton in which the structure of the transition state resembles that of the hydrocarbon precursor. Deprotonation is rapid, even at ca. -70 °C, for several reasons. First, models indicate that the bridgehead C-H bonds are nearly parallel to the axes of the p orbitals on the adjacent double bonds, so that delocalization of the developing negative charge can occur with a minimum of structural reorganization. Second, cyclopropyl hydrogens are well known to have enhanced acidity relative to other alkyl protons because they are bonded via an approximately sp² orbital on carbon.¹⁵

The importance of least motion considerations is cogently illustrated by the fact that the aromatic cyclononatetraenyl anion (**25**), which could, in principle, be formed from **7** via deprotonation at C₉ coupled with an allowed conrotatory opening of the C₁-C₈ bond, is not observed. Apparently enough of the stabilization of the product cannot be incorporated into



the transition state to cause this to be the favored pathway. The proposed mechanism is also supported by the observation that **1** does not suffer deuterium exchange (in competition with ring opening) on treatment with potassium *tert*-butoxide in $\text{Me}_2\text{SO}-d_6$. The latter experiment represents the classical approach to determining whether the deprotonation step is rate limiting or merely the forward step in a rapid preequilibrium process, but it cannot give the detailed information regarding charge distribution in the transition state that is provided by the regioselectivity studies.

Experimental Section

Infrared (IR) spectra were recorded on a Perkin-Elmer Model 337 grating infrared spectrometer with 0.1-cm NaCl cells. Only major bands are given. Nuclear magnetic resonance (NMR) spectra were obtained on deuteriochloroform solutions with tetramethylsilane (Me_4Si) as an internal standard or on liquid ammonia solutions with trimethylamine ($\delta_{\text{N},\text{H}_3}$ (Me_4Si) 2.135) as an internal standard on a Varian A-60D spectrometer. A technique for obtaining NMR spectra of liquid ammonia solutions has been previously described.¹⁶ Mass spectra were obtained by Dr. T. Hobo on a Du Pont 21-492 mass spectrometer. GLC separations were effected on a Varian A-90P3 thermal conductivity instrument equipped with 0.25-in copper columns packed with 100/120 mesh acid-washed, dimethyldichlorosilane-treated Chromosorb P as support for various stationary phases. Microanalyses were performed by Dr. Franz Kasler of the Department of Chemistry, University of Maryland.

1-, 2-, 3-, and 4-Methyl-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (10–13). These isomers were prepared (in 70% yield) as previously described.¹⁰ GLC analysis (1.5-m 8% 1,2,3-tris(2-cyanoethoxy)propane column at 60 °C) showed four major components in the ratio 14:28:30.5:27.5 with relative retention times of 1.00, 1.77, 2.14, and 2.80, corresponding to **10**, **12**, **13**, and **11**, respectively. Repeated preparative GLC (1-m 15% Carbowax 20M column at 65 °C) gave samples of the pure isomeric hydrocarbons, the NMR spectra of which were identical with those reported previously. Data for **11** had not been reported: IR (CCl_4) 3075, 3015, 2985, 2945, 2920, 2890, 2855, 1650, 1615, 1450, 1430, 1370, 1028, 882, 843, 838, and 692 cm^{-1} ; NMR (CDCl_3) δ 5.30–6.06 (major peaks at 5.87 and 5.97, 5 H, olefinic), 1.92 (s, 3 H, methyl), 0.75–1.60 (m, major peaks at 1.30 and 1.42, 3 H, cyclopropyl), 0.00 (d of t, 1 H, *exo*-9-cyclopropyl proton, $J_{99} = 3.0$, $J_{19} = J_{89} = 6.0$ Hz).

Anal. Calcd for $\text{C}_{10}\text{H}_{12}$: C, 90.84; H, 9.16. Found: C, 90.67; H, 9.31.

2-Methyl-*trans*-bicyclo[6.1.0]nona-2,4,6-triene (14). Dilute solutions of 2-methyl-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (**11**, 0.5%, 25 μL in 5 mL) in spectrograde *n*-hexane were placed in 8-mm quartz tubes sealed with rubber serum caps and degassed with nitrogen. The tubes were supported in a carousel revolving in a circular array of ten low-

pressure mercury-arc lamps (2537 Å). The progress of the reaction was monitored by GLC (0.5-m 7% tetracyanoethylated pentaerythritol column at 25 °C). After 1.5 h of irradiation analysis showed three unidentified peaks (6, 17, and 15%), **11** (19%), and **14** (43%) with relative retention times of 1.00, 1.36, 2.03, 2.80, and 3.94, respectively. Concentration by rotary evaporation followed by preparative GLC on a 0.5-m 15% 1,2,3-tris(2-cyanoethoxy)propane column at 60 °C afforded pure **14**: IR (CCl_4) 3075, 3030, 3005, 2975, 2935, 2910, 2875, 1610, 1450, 1425, 1385, 1045, 875, and 848 cm^{-1} ; NMR (CDCl_3) δ 5.83 (broadened s, fwhm = 5 Hz, 5 H, olefinic), 1.74 (s, 3 H, methyl), and 0.65–2.22 (complex m, 4 H, cyclopropyl).

2-, 3-, 4-, and 5-Methyl-1-aminomethylcyclooctatetraenyldipotassium (15–18). Treatment of ca. 25 μL of **10**, **11**, **12**, **13**, or **14**, or of a 1:1 mixture of **11** and **12** or **12** and **13**, with the excess of potassium amide (generated from 70 mg (1.8 mg-atoms) of potassium) in ca. 0.5 mL of anhydrous liquid ammonia gave NMR spectra which are summarized in Table I.

Reaction of *cis*-Bicyclo[6.1.0]nona-2,4,6-triene (1) with Potassium *tert*-Butoxide in Dimethyl- d_6 Sulfoxide. *cis*-Bicyclo[6.1.0]nona-2,4,6-triene (25 mg, 0.27 mmol) was rapidly (ca. 1 s) mixed with 30 mg (0.27 mmol) of potassium *tert*-butoxide in 0.5 mL of $\text{Me}_2\text{SO}-d_6$ and quenched with water after 5 min. Unchanged **1** (35% by GLC) was extracted with pentane and isolated on a 0.3-m 15% 1,2,3-tris(2-cyanoethoxy)propane column at 45 °C. The mass spectrum of the recovered material had M^+ at m/e 118 and showed no evidence for deuterium incorporation.

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