# Lithium Ion Catalyzed Decompositions of Octane-2-diazotate[1]

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Abstract: Solutions of optically active octane-2-diazotate in hexamethylphosphoric triamide were slowly decomposed by excess lithium azide (chloride) with the formation of $\sim$73% (40%) net inverted 2-azido(chloro)octane, $\sim$24% net retained 2-octanol, and octenes. In a less stereoselective variation of this procedure, the diazotate was rapidly decomposed, in the presence of the nucleophilic lithium salts, by acylation or trimethylsilylation; here, azide ion captured the 2-octyl moiety with 30–50% net inversion. The mechanisms of the new reactions are discussed in terms of intermediate nitrogen separated and intimate ion pairs. They are related to the mechanisms of other deamination reactions.

The ammonolysis,[3] hydrolysis,[4] and ethanolysis[5] of alkane diazotates appear to involve nitrogen-separated ion pairs, 1,[6] which are among the archetypical

$$[R^+\ N{\equiv}N\ X^-]$$
1
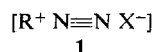
intermediates of deamination chemistry.[7,8] The solvolyses led to partition between collapse to RX, with stereochemical retention, and solvent capture of R with inversion; the latter process dominated. The results not only provided important information concerning the behavior of 1, but they related to studies made in other laboratories, which were concerned with displacement of the amino function.[9] Furthermore, we had found that substantially inverted sec-butyl acetate was formed in the acetylation of butane-2-diazotate in hexamethylphosphoric triamide (HMPA) solution,[10] which suggested that 1, or related species, could be efficiently captured by nucleophiles other than solvent. Such a result was not unprecedented,[11] but it had not been extensively investigated, particularly in solvents which potentiate nucleophilic displacements.[12]

We now report studies of the decomposition of octane-2-diazotate in the presence of nucleophilic lithium salts, which importantly augment our knowledge of the properties of 1.

(1) Alkane Diazotates. XVI. Part XV: R. A. Moss and G. M. Love, Tetrahedron Lett., 4701 (1973).

(2) Fellow of the A. P. Sloan Foundation.

(3) R. A. Moss, P. E. Schueler, and T. B. K. Lee, Tetrahedron Lett., 2509 (1973).

(4) (a) R. A. Moss, A. W. Fritz, and E. M. Emery, J. Org. Chem., 36, 3881 (1971); (b) R. A. Moss, D. W. Reger, and E. M. Emery, J. Amer. Chem. Soc., 92, 1366 (1970); (c) R. A. Moss and S. M. Lane, ibid., 89, 5655 (1967).

(5) R. A. Moss and M. J. Landon, J. Amer. Chem. Soc., 92, 5755 (1970).

(6) We agree with White that this nomenclature is preferable to "vibrationally excited ion pair;" see E. H. White, R. H. McGirk, C. A. Aufdermarsh, Jr., H. P. Tiwari, and M. J. Todd, J. Amer. Chem. Soc., 95, 8107 (1973).

(7) (a) R. A. Moss, Chem. Eng. News, 49 (48), 28 (1971); (b) E. H. White and D. J. Woodcock, "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, pp 440–483.

(8) E. H. White, T. J. Ryan, and K. W. Field, J. Amer. Chem. Soc., 94, 1360 (1972).

(9) P. J. DeChristopher, J. P. Adamek, G. D. Lyon, J. J. Galante, H. E. Haffner, R. G. Boggio, and R. J. Baumgarten, J. Amer. Chem. Soc., 91, 2384 (1969); R. S. Glass, Chem. Commun., 1546 (1971); N. H. Andersen and H. Uh, Syn. Commun., 2, 297 (1972); J. B. Hendrickson, R. Bergeson, A. Giga, and D. Sternbach, J. Amer. Chem. Soc., 95, 3412 (1973).
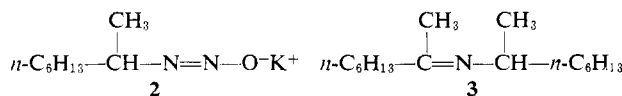
(10) R. A. Moss and K. M. Luchter, J. Org. Chem., 37, 1155 (1972).

(11) E. H. White, J. Amer. Chem. Soc., 77, 6014 (1955).

(12) Indeed, White and Woodcock advise that "... one should look for the displacement mode in polar media;" ref 7b, p 446.

Results

The Lithiolysis[13a] Reaction. A solution of octane-2-diazotate, 2, in HMPA was prepared from N-nitroso-N-2-octylurethane[13b] and treated at 25° with an HMPA solution containing 10 equiv of dried lithium azide. Nitrogen evolved slowly, amounting to 75% of theory after 20 hr; addition of water produced 16% more nitrogen.[14] Gas chromatography (gc) permitted the isolation of 2-azidooctane (17%), 2-octanol (8%), octenes (13%), and a long retention time unknown compound (7%). We had anticipated the formation of anil 3, derived from attack of 2-octyl cation (or a related

$$n\text{-}C_6H_{13}\text{—}\underset{\underset{2}{|}}{\overset{\overset{CH_3}{|}}{CH}}\text{—}N{=}N\text{—}O^-K^+ \qquad n\text{-}C_6H_{13}\text{—}\underset{\underset{3}{|}}{\overset{\overset{CH_3}{|}}{C}}{=}N\text{—}\overset{\overset{CH_3}{|}}{CH}\text{—}n\text{-}C_6H_{13}$$

electrophile) on 2-azidooctane.[15] However, the unknown (λ_{max} 226 nm, sh 270; ν_{max} 1640 cm^{-1}; M$^+$ $\sim$ 280) differed from an authentic sample of 3, prepared from 2-aminooctane and 2-octanone,[16] and could be formed in the absence of azide. It appears to represent a reaction product of 2 with a second 2-octyl moiety (mol wt 270), but its nmr spectrum is inconsistent with its formulation as azoxy-2-octane.[17] It shows no ^{31}P nmr absorptions and cannot contain a phosphoramide moiety derived from HMPA.

In the absence of LiN$_3$, an HMPA solution of 2 was stable to nitrogen loss over 19 hr; subsequent hydrolysis afforded 81% of the theoretical nitrogen evolution. The major high boiling product was the anticipated 2-octanol, accompanied by 2% of the unknown compound described above.

Lithiolysis reactions were also carried out with fluoborate and chloride salts. The products and yields are displayed in Table I. The low overall yields are largely due to the difficulty of product recovery from HMPA solutions. However, the reaction pattern is clearly related to that of the octane-2-diazotate solvoly-

(13) (a) "Lithiolysis" refers to lithium ion catalyzed decompositions. (b) Details appear in ref 4a. In the present work, dicyclohexyl-18-crown-6 was found not to be essential for the solubilization of 2 and was omitted.

(14) Similar results were obtained in an experiment conducted for 41 hr.

(15) R. H. McGirk and E. H. White, J. Amer. Chem. Soc., 95, 3804 (1973).

(16) G. Stork and S. R. Dowd, J. Amer. Chem. Soc., 85, 2178 (1963); ref 2.

(17) R. A. Moss, M. J. Landon, K. M. Luchter, and A. Mamantov, J. Amer. Chem. Soc., 94, 4392 (1972).

Table I. Products of the Lithiolysis of Octane-2-diazotate[a]

LiX (equiv)[b]	2-Oct-X	Yield, %	2-Octanol, %	Octenes, %	X, %[c]
LiN₃ (10)	2-Oct-N₃	17	8	13	7
LiBF₄ (10)			15	49[d]	
{LiN₃ (10) / LiBF₄ (10)}	2-Oct-N₃	14	11	23	5
{LiN₃ (10) / n-Bu₄NN₃ (10)}	2-Oct-N₃	11	8	16	9
LiCl (10)	2-Oct-Cl	5	9	19	7[e]

[a] HMPA solution, 25°. [b] Equivalents are relative to **2**. [c] Unknown component; see text. [d] The olefin distribution was 31% 1-octene and 18% 2-octenes. [e] About 4% of an azoxyalkane was also present, formed probably by reaction of 2-Oct-Cl and **2**.[17]

was purified by gc (Pennwalt), and had α^{23}D −5.04° (neat, 1 dm), 94.6% optically pure.[21] The overall conversion of (+)-2-octanol to (−)-2-aminooctane therefore occurred with >99% stereospecificity, and the intermediate 2-azidooctane must have been formed from the 2-octyl tosylate with complete inversion in the displacement step. (See below for a relation of rotational signs and relative configuration.) Correcting for the optical purity of the 2-octanol gives α^{23}D |38.65°| (neat, 1 dm) for the rotation of optically pure 2-azidooctane.

The lithiolysis reactions of Table I were repeated with R-**2**, derived via the N-nitrosourethane from optically active (R)-(−)-N-2-octylurethane.[4c,22] The products

Table II. Stereochemistry of Formation of Substitution Products in the Lithiolysis of Octane-2-diazotate

Run	Reagents[a]	2-X-Octane αD obsd, deg[b]	2-X-Octane αD cor, deg[c]	2-X-Octane Stereochem, %[d]	2-Octanol αD obsd, deg[b]	2-Octanol αD cor, deg[c]	2-Octanol Stereochem, %[e]
1[f,g]	10LiN₃	α^{22}D +2.178	α^{22}D +28.20	72.6 net inv			
2[h]	10LiN₃	α^{21}D +2.542	α^{21}D +28.50	73.6 net inv	α^{22}D −0.183	α^{22}D −2.06	25.6 net retn
3[h]	10LiBF₄				α^{22}D −0.166	α^{22}D −1.86	23.1 net retn
4[h]	10LiBF₄ 10LiN₃	α^{23}D +1.376	α^{23}D +15.44	40.0 net inv	α^{24}D −0.171	α^{24}D −1.92	23.8 net retn
5[i]	10LiN₃ 10Bu₄NN₃	α^{22}D +1.311	α^{22}D +24.58	63.7 net inv	α^{25}D −0.019	α^{25}D −0.36	4.4 net retn[j]
6[i]	10LiN₃ 10Bu₄NN₃	α^{23}D +1.287	α^{23}D +24.10	62.3 net inv	α^{25}D −0.075[k]	α^{25}D −1.4	17 net retn
7[i]	10LiCl	α^{22}D +0.680	α^{22}D +12.7	40.4 net inv	α^{23}D −0.071	α^{23}D −1.3	17 net retn

[a] Equivalents of reagents are relative to the diazotate. The anion is the X group in product 2-X-octane (N₃ in run 4). [b] Determined with a digital read-out Perkin-Elmer Model 141 spectropolarimeter, using neat, gc-purified samples in a 0.1-dm cell. [c] Corrected for path length, to 1.0 dm, and for the optical purity of the N-2-octylurethane precursor. [d] Optically pure 2-azidooctane has α^{23}D |38.65°| (neat, 1 dm); see text. Optically pure 2-chlorooctane has α^{20}D 31.6° (neat, 1 dm).[23] [e] Optically pure 2-octanol has α^{23}D 8.04° (neat, 1 dm).[20] [f] The N-2-octylurethane from which the diazotate derived had α^{22}D −3.47° (neat, 1 dm), 77.5% optically pure. [g] Based upon α^{23}D −4.48° (neat, 1 dm) for optically pure N-2-octylurethane.[4c] Although this is the highest rotation we have observed, it is possible that it represents only 98.5% optical purity.[4c] [h] The N-2-octylurethane precursor had α^{25}D −3.99° (neat, 1 dm), 89.1% optically pure.[g] [i] The N-2-octylurethane precursor had α^{22}D −2 39° (neat, 1 dm), 53.4% optically pure.[g] [j] The low value may represent 2-octanol formed by hydrolysis of **2**. The Bu₄NN₃ was hygroscopic and difficult to dry. [k] 13.1 mg of product 2-octanol was diluted with 14.8 mg of racemic 2-octanol, affording a sample with α^{25}D −0.035° (neat, 0.1 dm). The product 2-octanol must have had α^{25}D −0.075°.

sis reactions,[3–5] with the 2-azidooctane (2-chlorooctane) replacing the normal solvolysis product.

The evolution of nitrogen from HMPA solutions of **2** and tenfold excess LiX appeared to be pseudo first order in **2**, with $k_{obsd} \sim$ 1–2 × 10⁻⁴ sec⁻¹. Occasionally, we observed initially rapid evolution, possibly due to adventitious water introduced with the lithium salt.[18a] The observed rate constants were independent of the identity and concentration of LiX. At the high lithium titers employed (0.25–1.0 M), LiX may be aggregated; indeed, the HMPA becomes quite viscous during the dissolution of the solid LiX.[18b] Interpretation of the kinetic behavior is therefore not clear.

Stereochemical Studies. A reliable value for the rotation of optically pure 2-azidooctane was obtained via the reaction sequence described by Streitwieser.[19] (S)-(+)-2-Octanol, α^{23}D +7.67° (neat, 1 dm), 95.5% optically pure,[20] was converted to the corresponding tosylate and thence to 2-azidooctane by reaction with sodium azide in warm methanol. Preparative gc (Carbowax) afforded pure (R)-(−)-2-azidooctane, α^{23}D −36.56° (neat, 1 dm). The remaining, crude 2-azidooctane was reduced to (R)-(−)-2-aminooctane, which

were isolated by gc (Carbowax), and their rotations were determined. The observations and consequent stereochemical results are recorded in Table II.[23] The stereochemical courses of the conversions follow from the fact that 2-octyl-X (X = NH₂, OH, Hal) of the same rotational sign are members of the same optical series[24] and from the stereochemical relation of 2-octanol and 2-azidooctane[19] (see above). Additionally, 2-aminooctane and the corresponding urethane of similar relative configuration display identical rotational signs.[4c] Control experiments demonstrated the optical stability of 2-azidooctane (but not of 2-chlorooctane, see below) to the experimental conditions.

Trigger Reactions. An HMPA solution of **2**, doped with an excess of a potent nucleophile, was treated at 25° with either an acylating agent or trimethylchlorosilane (the "trigger"). In contrast to the very slow lithiolysis reactions, the trigger reactions were rapid; nitrogen evolution was practically quantitative, ceasing when the addition of the trigger had been completed.

(18) (a) HMPA and LiX were scrupulously dried; see the Experimental Section; (b) M. S. Puar, J. Chem. Educ., 47, 473 (1970).
(19) A. Streitwieser, Jr., and W. D. Schaeffer, J. Amer. Chem. Soc., 78, 5597 (1956).
(20) Based upon α^{23}D +16.08° (neat, 2 dm) for 100% optical purity.[19]

(21) Based upon α^{19}D −2.66° (neat, 0.5 dm) for 100% optical purity: F. G. Mann and J. W. G. Porter, J. Chem. Soc., London, 3384 (1950).
(22) This procedure does not involve racemization at the chiral center: R. A. Moss and G. M. Love, J. Amer. Chem. Soc., 95, 3070 (1973).
(23) The rotation of optically pure 2-chlorooctane is taken as α^{20}D 31.6°: H. R. Hudson, Synthesis, 1, 112 (1969), Table 5, footnote c; H. M. R. Hoffmann, J. Chem. Soc., London, 1249 (1964).
(24) M. Vogel and J. D. Roberts, J. Amer. Chem. Soc., 88, 2262 (1966); J. A. Mills and W. Klyn ·, Progr. Stereochem., 1, 195 (1954).

Table III. Products from Acylation or Silylation of Octane-2-diazotate in the Presence of Nucleophiles[a]

Run	Trigger (equiv)	Added nucleophile (equiv)	Capture prod (yield, %)	Return prod (yield, %)	Octenes, %
1	$(CH_3CO)_2O$ (2)	LiN_3 (10)	RN_3 (27)	ROAc (9), ROH (1)	9
2	$(CH_3CO)_2O$ (2)	Bu_4NN_3 (10)	RN_3 (14)	ROAc (7), ROH (1)	12
3	$(CF_3CO)_2O$ (2)	LiN_3 (10)	RN_3 (26)	$ROOCCF_2$ (5), ROH (tr)	7
4	$(CH_3)_3SiCl$ (4)	LiN_3 (10)	RN_3 (16)[b]	$ROSi(CH_3)_3$ (tr), ROH (3)	10
5	$(CH_3)_3SiCl$ (4)	None	RCl (11)	$ROSi(CH_3)_3$ (2), ROH (4)[c]	9
6	$(CH_3)_3SiCl$ (4)	LiCl (10)	RCl (23)	$ROSi(CH_3)_3$ (tr), ROH (8)[d]	8

[a] In HMPA at 25°. R = 2-octyl throughout. [b] RCl was also present in 0.5% yield. [c] $ROOCOC_2H_5$ was present in 5% yield. [d] $ROOCOC_2H_5$ was present in 10% yield.

Table IV. Stereochemistry of Formation of Capture and Return Products in Trigger Reactions of Octane-2-diazotate[a]

Run	Trigger	Nucleophile	Capture product α_D obsd, deg[b]	α_D cor, deg[c]	Stereochem, %[d]	Return product α_D obsd, deg[b]	α_D cor, deg[c]	Stereochem, %[e]
1f	$(CH_3CO)_2O$	LiN_3	RN_3: α^{23}_D +1.278	α^{23}_D +14.32	37.0 net inv	$ROOCCH_3$: α^{22}_D −0.031	α^{22}_D −0.35	5.4 net retn
2g	$(CH_3CO)_2O$	Bu_4NN_3	RN_3: α^{23}_D +1.016	α^{23}_D +19.00	49.0 net inv	$ROOCCH_3$: α^{23}_D +0.029	α^{23}_D +0.55	8.5 net inv
3f	$(CF_3CO)_2O$	LiN_3	RN_2: α^{25}_D +1.627	α^{25}_D +18.25	47.2 net inv			
4g	$(CH_3)_3SiCl$	LiN_3	RN_3: α^{23}_D +0.636	α^{23}_D +11.9	30.9 net inv			
5f	$(CH_3)_3SiCl$		RCl: α^{24}_D +0.005	α^{24}_D +0.06	0.09 net inv	ROH: α^{24}_D −0.275	α^{24}_D −3.09	38.4 net retn
6f	$(CH_3)_3SiCl$	LiCl	RCl: α^{23}_D +0.755	α^{23}_D +8.46	26.8 net inv	ROH: α^{24}_D −0.186	α^{24}_D −2.08	26.0 net retn

[a] The reactant ratios and product yields correspond in each case to those of the identically numbered run of Table III; R = 2-octyl throughout. [b] See Table II, footnote b. [c] See Table II, footnote c. [d] See Table II, footnote d. [e] See Table II, footnote e. Optically pure 2-octyl acetate has α^{20}_D +6.44° (neat, 1 dm).[25] [f] See Table II, footnotes f and g. [g] See Table II, footnote i.

The total reaction time was less than 15 min, and products were conveniently isolated by gc.
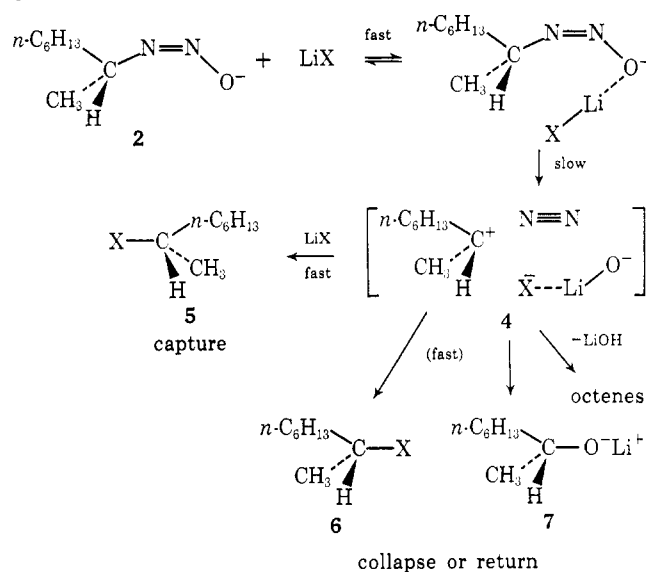
The large rate differential between the trigger procedure and the lithiolysis reaction ensured that the nucleophile-capture product of the trigger reaction was not formed by lithiolysis of the diazotate, even though the capturing nucleophile was usually present in the form of its lithium salt. Moreover, controls established that return products derived from the trigger reagents (e.g., 2-octyl trifluoroacetate) were not converted to capture products (e.g., 2-azidooctane) by reaction with LiX under the conditions of the trigger procedure. These controls also imply that neither 2-azidooctane nor 2-chlorooctane could be racemized by azide or chloride ion under the trigger reaction conditions. Products and yields appear in Table III.

The stereochemistry of the trigger reactions was investigated using (R)-2 derived from (R)-(−)-N-2-octyl-urethane.[4c] The maximum rotations and relative configurations of most of the reaction products are discussed above. We add that 2-octanol and 2-octyl acetate are also of the same optical series when they display like rotational signs.[25] Results appear in Table IV.

Discussion

The Lithiolysis Reaction. A consistent *schema* for the lithiolysis reaction appears in Chart I. A rapid association of LiX with **2** is followed by a rate-determining formation of the nitrogen-separated ion triplet, **4**. Probably, in the polar solvent HMPA, the C–N and N–O bonds of **4**'s precursor fission concertedly, bypassing a 2-octyldiazonium lithoxide ion pair.[26,27]

Chart I

collapse or return

Species **4** can collapse with return of lithoxide, affording, after hydrolysis, 2-octanol with configurational retention. We observe $\sim$62% *overall* retention (Table II, runs 2–4), which compares reasonably well with the formation of 2-octanol by *collapse* of 2-Oct-N=NOH in $H_2^{18}O$–HMPA (73% overall retention[4a]) or in NH_3–HMPA (65% overall retention[3]). The related collapse of 2-BuN=NOOCC₆H₅ in acetic acid affords sec-butyl benzoate with 68% overall retention.[11]

Note that, in accord with current understanding of the mechanism of the generation of alkane diazotates by the basic cleavage of N-nitrosourethanes, we have considered only the syn configuration for octane-2-diazotate

(25) E. D. Hughes, C. K. Ingold, and S. Masterman, *J. Chem. Soc., London*, 840 (1939). The rotation of optically pure 2-octyl acetate is given as $[\alpha]^{20}_D$ +7.48° or α^{20}_D +6.44° (neat, 1 dm). See also R. H. Pickard and J. Kenyon, *ibid.*, 830 (1914).

(26) M. C. Whiting, *Chem. Brit.*, 2, 482 (1966); H. Maskill, R. M. Southam, and M. C. Whiting, *Chem. Commun.*, 496 (1965).

(27) See ref 7b, p 453.

(2) in Chart I. Relevant evidence and references have been considered in detail by White, Ryan, and Field.[8]

Two potential complications should be noted. (a) Hydrolysis of 2 by adventitious water carried along with the LiX reagent could contribute to the lithiolysis. This would not alter the fundamental idea of Chart I; Li would be replaced, in part, by a proton, but the behavior of RN=NOLi and RN=NOH in the partition process should be comparable under these reaction conditions. (b) A small part of the product 2-octanol could arise by hydrolysis of undecomposed 2 during work-up. Since the overall stereochemistry of 2-octanol formation *via* the hydrolysis of 2 is inversion,[4] hydrolysis of residual 2 would, in the present case, lead to somewhat lower retention in the 2-octanol product than would be truly characteristic of the collapse of 4 to 7. The attention given to the drying of LiX and the observed similarity of 2-octanol stereochemistry here and in related collapse reactions suggest that complications "a" and "b" play a minor role.

A major fate of 4 is inverting capture by LiX. 2-Azidooctane forms with ~73% net or 86% overall inversion in the lithiolysis of 2 with LiN₃ (Table II, runs 1 and 2). This rivals the formation of *o-sec*-butylphenol *via* the phenolysis of butane-2-diazotate[28] as the most stereoselective intermolecular deaminative inversion described for an acyclic amine derivative. The extent of overall inversion is considerably greater than in the formation of *sec*-butyl acetate by reaction of acetate ion with 2-BuN=NOAc in HMPA (71%)[10] or by reaction of acetic acid with 2-BuN=NOOCC₆H₅ in pentane-acetic acid.[11] Indeed, LiX capture of 4 occurs with overall inversion similar to that of *solvolyses* of 2-Oct-N=NOH: 76% in the formation of 2-octanol $(H_2{}^{18}O–HMPA)$[4a] and 85% in the formation of 2-aminooctane $(NH_3–HMPA)$.[3]

Nevertheless, azide formation by the capture process occurs *after* the rate-determining formation of reactive intermediate 4, because doubling the azide ion concentration (relative to 2), without increasing the lithium ion concentration, leads to a decrease rather than an increase in overall inversion (Table II, runs 5 and 6 *vs.* 1 and 2).[29] This precludes SN2 mechanisms which feature rate-determining attack of azide on a covalent precursor of 4. Moreover, it is the absence of a nucleophilic solvent which permits azide to capture the 2-octyl moiety of 4 at all; hydrolysis of 2 with 7 *M* aqueous sodium azide solution leads mainly to 2-octanol and to very little 2-azidooctane.[4c,30] Note that 5 (Chart I) could also be formed from 4 by rotation of 2-octyl cation *within* 4, followed by collapse (see below) with the counterion (X = N₃). The "intramolecular inversion" pathway[7b] is a minor contributor in the hydrolysis of 2 (6.0%)[4a] and probably here, too.

In 4, there is probably an azide ion associated with the lithium cation at the front side of the 2-octyl moiety; some front side collapse to 6 should therefore occur competitively with inverting azide capture, yielding 2-

azidooctane with retention, and preventing the stereospecific formation of inverted 2-azidooctane (5, X = N₃). Also, nitrogen could leave before collapse leading, after relaxation, to 2-octyl cations which are symmetrically sandwiched between pairs of azide anions and which must give racemic 2-azidooctane. Indeed, White, *et al.*,[6] suggested that "varieties of intimate ion pairs" could cascade from species like 4. These could lead to varying blends of 5 and 6.

2-Octyl cations may occasionally "escape" from 4, later giving racemic 2-azidooctane. Run 4 (Table II), in which [Li⁺] is doubled relative to [N₃⁻] and net inversion in 2-azidooctane formation is nearly halved compared to runs 1 and 2, may represent the consequences of deliberately enhancing 2-octyl cation escape. In run 4, 4 can be formed with either fluoborate or azide counterions. "Escape" could take the forms of either inverting capture of 2-octyl cation by fluoborate, followed by reinversion with azide (*i.e.*, formation of 2-azidooctane with retention), or of the ultimate production of achiral 2-octyl cations symmetrically disposed toward fluoborate anions. The latter process could occur readily if 4 (X = BF₄) loses nitrogen and lithoxide while a fluoborate ion is near the rear face of the 2-octyl moiety.

The rates of the various competing processes must be very fast, because the 2-octyl cation selects between water and azide ion in a nearly statistical manner when 2 is treated with 7 *M* aqueous sodium azide solution[4c] (see above). This implies that [2-Oct⁺N≡N⁻OH] in water is extremely unselective and that its quenching must be very rapid. A similar situation is likely to prevail in HMPA. This behavior is quite different from that of more stable cations, which strongly select azide over water.[31]

In the absence of a good nucleophile (Table II, run 3), 4 (X = BF₄) collapses to 7, eventually giving 2-octanol, or loses a proton from the octyl moiety, affording octenes. 2-Octyl fluoborate ion pairs may be transients in the latter process, but elimination could occur *within* 4, *cf.* 8. Intraion pair eliminations in

$$\left[\begin{array}{cc} \overset{\diagdown}{\underset{\diagup}{C^+}}\overset{N≡N}{\underset{C–H}{\diagdown}} & \overset{\bar{O}–Li}{\underset{X^-}{\diagup}} \end{array} \right]$$

8

deaminations have been discussed by White[11] and Cohen;[32] they may also occur during the decomposition of *sec*-Bu-N=N-OOCCH₃.[10] In the latter case, 1-/2-butene ratios as high as 2.4 have been observed;[10] lithiolysis of 2 with LiBF₄ affords 49% of octenes with 1-/2-octene = 1.7 (Table I).

Lithiolysis of 2 with excess LiCl leads to inverted 2-chlorooctane, in accord with the mechanism of Chart I. Inversion is not as pronounced as in the corresponding azide reactions (Table II, run 7 *vs.* runs 1 or 2). This difference is not mechanistically meaningful, however, because 2-chlorooctane is partially racemized by lithium chloride under the reaction conditions.[33]

(28) R. A. Moss and G. H. Temme, III, *Tetrahedron Lett.*, 3219 (1968).

(29) The decreased inversion could be due to a salt effect, "looser" ion pairs forming in the medium of greater ionic strength and leading to products less stereospecifically.
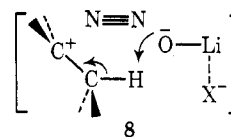
(30) Because 2-azidooctane can be efficiently reduced to 2-aminooctane,[19] lithiolysis of 2 with LiN₃ represents a second method of "inverting" an amine.[3] However, the low yields of displacement product make it doubtful that the new reaction will find synthetic use.

(31) C. D. Ritchie, *Accounts Chem. Res.*, 5, 348 (1972).

(32) T. Cohen, A. R. Daniewski, G. M. Deeb, and C. K. Shaw, *J. Amer. Chem. Soc.*, 94, 1786 (1972); T. Cohen and A. R. Daniewski, *ibid.*, 91, 533 (1969).

(33) 2-Azidooctane, however, is not racemized by LiN₃ in HMPA; see the Experimental Section.

Deaminative reactions which proceed through alkyl diazo esters, or related derivatives of alkane diazotates, generally afford ion pairs which differ from the formally identical ion pairs generated by solvolysis reactions.[7b,34] At least initially, the former ion pairs are nitrogen separated, and the spatial relation forced upon R^+ and X^- by the intervening nitrogen molecule may subsequently govern their chemistry. This "counterion hypothesis" has been eloquently stated by White and Woodcock.[35] Recent studies have applied the flexible interpretive power of the ion pair concept to deaminations of such disparate systems as steroidal amines,[36] norbornylamines,[37] bicycloalkyl- and bi- and tricycloalkylcarbinamines,[38] bridgehead amines,[6,8] decalylamines and derivatives,[32,39] an acyclic tert-carbinamine,[40] α-phenylethylamine and its derivatives,[3,5,41] 2-aminoalkanes and derivatives,[3,4,10] and neryl- and geranyl- (allylic) amines.[42]

The present results amplify the utility of the deaminative ion pair mechanism by focussing on the ability of added nucleophile to intercept the cationic moiety with high stereoselectivity. The closest analogy is the report, by Kirmse and Arold,[41] of the azide capture of α-phenylethyl cation, with 74% overall inversion, during the basic cleavage of N-nitroso-(1-phenylethyl)-carbamate in dimethoxyethane–methanol. Our results also suggest that SN2 capture of a covalent precursor of the ion pair does not occur during the deamination of an acyclic sec-carbinamine in polar solvents. We prefer to reinterpret the observation of inverted sec-butyl acetate formation in the acetylation (HMPA) of butane-2-diazotate[10] as inverting acetate ion interception of a nitrogen-separated sec-butyl acetate ion pair. More recently, new evidence has appeared supporting SN2 like capture of diazonium ions derived from allylic primary carbinamines.[42,43]

Nitrogen-separated ion pairs could lead to intimate ion pairs similar to those associated with solvolysis reactions, if the former could survive long enough to lose nitrogen and adjust their interionic separation. With simple, sec-alkyl examples, we do not know what fraction of nitrogen-separated ion pairs survives to reach the intimate ion pair state. Certainly, in the case of $[R^+N_2X^-]$ with X = OH, OR', and OLi, an "intimate ion pair" would collapse to product rapidly and ir-

reversibly. One could not generate such ion pairs from alcohols, ethers, or lithium alkoxides, and their inclusion in Chart I seems unnecessary. When X = OOCR (diazo ester decomposition), intimate ion pairs would be a more likely second state. Although the intermediacy of ion pairs in the solvolysis of simple sec-alkyl derivatives is still contentious,[44] it is worth noting that azide capture of solvolytically generated 2-octyl methanesulfonate intimate ion pairs (1 : 3 dioxane–water, 3–4 : 1 [azide]:[substrate]) gave ∼80% net inverted 2-azidooctane,[44m] a very similar result to the 73% net inversion which we observed in the lithium azide capture of 4.

The Trigger Reactions. Reactions 1–3 (Tables III and IV) can be understood with reference to Chart II.

Chart II
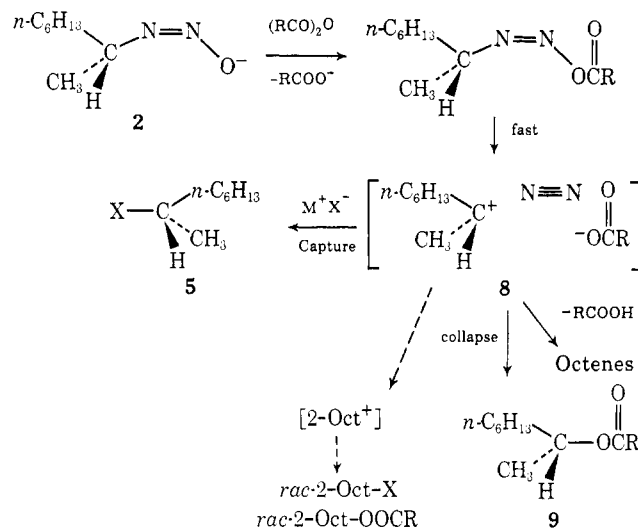
In runs 4–6, the trimethylsiloxide anion replaces the carboxylate counterion. The reaction generates the nitrogen-separated ion pair **8**, which can be captured by an added nucleophile to afford inverted substitution product, **5**. Products derived by reaction with the counterion **9** or the corresponding trimethylsilyl ether are also anticipated.

The overall reaction is analogous to the lithiolysis reaction, and only a few points require comment. Comparison of Table IV (runs 1–3) with Table II (runs 1 and 2) shows that the trigger reactions are less stereoselective than the lithiolysis reactions. The counterions of the trigger reactions, carboxylate or trimethylsiloxide, are better leaving groups than the lithoxide ion of the lithiolysis. This accounts for the much faster rate of diazotate destruction in the trigger reaction as compared with the lithiolysis reactions. Furthermore, 2-octyl cation can more readily escape from "looser" ion pair **8** (Chart II) than from ion pair **4** (Chart I). Because the substitution and collapse products formed from escaped octyl cation would be largely racemic, they would

(34) For a specific example, see E. H. White and C. A. Elliger, J. Amer. Chem. Soc., 89, 165 (1967).

(35) See ref 7b, pp 463–466.

(36) F. W. Bachelor and E. H. White, Can. J. Chem., 50, 364 (1972); C. W. Shoppee, J. G. Feher, R. M. Hall, R. E. Lack, and L. Tarasoff, Jr., J. Chem. Soc. C, 2211 (1968).

(37) C. J. Collins, I. T. Glover, M. D. Eckart, V. F. Raaen, B. M. Benjamin, and B. S. Benjaminov, J. Amer. Chem. Soc., 94, 899 (1972). C. J. Collins and B. M. Benjamin, J. Org. Chem., 37, 4358 (1972); C. J. Collins, Accounts Chem. Res., 4, 315 (1971); C. J. Collins, V. F. Raaen, and M. D. Eckart, J. Amer. Chem. Soc., 92, 1787 (1970).

(38) S. J. Cristol, J. R. Mohrig, and G. T. Tiedeman, J. Org. Chem., 37, 3239 (1972); S. J. Cristol, G. C. Schloemer, D. R. James, and L. A. Paquette, ibid., 37, 3852 (1972); S. J. Cristol and D. K. Pennelle, ibid., 35, 2357 (1970).

(39) T. Cohen and E. Jankowski, J. Amer. Chem. Soc., 86, 4217 (1964).

(40) E. H. White and J. E. Stuber, J. Amer. Chem. Soc., 85, 2168 (1963).

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(42) C. A. Bunton, D. L. Hachey, and J. P. Leresche, J. Org. Chem., 37, 4036 (1972).

(43) W. Kirmse and H. Schütte, Chem. Ber., 105, 824 (1972); W. Kirmse and H. Urbach, ibid., 105, 832, 840 (1972); see also A. Streitwieser, Jr., and W. D. Schaeffer, J. Amer. Chem. Soc., 79, 2888 (1957).

(44) Selected recent examples include (a) J. B. Lambert and G. J. Putz, J. Amer. Chem. Soc., 95, 6313 (1973); (b) R. A. Sneen, Accounts Chem. Res., 6, 46 (1973); (c) R. A. Sneen and H. M. Robbins, J. Amer. Chem. Soc., 94, 7868 (1972); (d) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, ibid., 93, 4821 (1971); (e) B. J. Gregory, G. Kohnstam, M. Paddon-Row, and A. Queen, Chem. Commun., 1032 (1970); (f) V. J. Shiner, Jr., and W. Dowd, J. Amer. Chem. Soc., 91, 6528 (1969); (g) H. L. Goering and R. F. Myers, ibid., 91, 3386 (1969); (h) R. A. Sneen and J. W. Larsen, ibid., 91, 362 (1969); (i) W. G. Dauben and J. L. Chitwood, J. Org. Chem., 34, 726 (1969); (j) R. A. Sneen and J. W. Larsen, J. Amer. Chem. Soc., 88, 2593 (1966); (k) R. A. Sneen, J. V. Carter, and P. S. Kay, ibid., 88, 2595 (1966); (l) A. Streitwieser, Jr., and T. D. Walsh, ibid., 87, 3686 (1965); (m) H. Weiner and R. A. Sneen, ibid., 87, 287, 292 (1965).

decrease the stereoselectivity enjoyed by these products when they are formed at the ion pair stages. The absence of rapid ion pair collapse in the trigger reactions is demonstrated by the formation of minimally retained *or* inverted counterion product **9** (Table IV, runs 1 and 2).

A referee has suggested that **9** (R = CH₃) could be contaminated with the isomeric 3-octyl acetate (hydride shift product), thus accounting for its low activity. However, 2- and 3-octyl acetate were separable under our gc isolation conditions. (See the Carbowax column described in the Experimental Section.) Moreover, the isolated 2-octyl acetate was identical with an authentic sample in both gc and ir comparisons.

Operation of the escape process is illustrated by run 5, Table IV. In the absence of added nucleophile, 2-octyl cation escapes from its trimethylsiloxide counterion and, by scavenging chloride ion released in the silylation step, affords 11% of essentially racemic 2-chlorooctane. When chloride is present in substantially larger concentration (run 6), the 2-octyl cation can be intercepted at the ion pair stages, although escape still competes and there is less inversion than in the corresponding lithiolysis reaction (Table II, run 7), *despite* the increased opportunity for product racemization in the latter case.

As mentioned above, 2-octyl trifluoroacetate and 2-octyl trimethylsilyl ether are stable to LiX under the conditions of the trigger reactions; they are not converted to 2-Oct-X. Moreover, the silyl ether is not significantly hydrolyzed during work-up nor is it attacked by octane-2-diazotate. The presence in the trimethylsilyl chloride runs (Tables III and IV, runs 5 and 6) of small amounts of moderately retained 2-octanol is therefore puzzling. Small quantities of water, perhaps from the conversion of trimethylsilyl-carbinol to trimethylsilyl ether, appear to be present during the silylation reactions. This would afford octane-2-diazotic acid, which would ultimately give 2-octanol with retention. The 2-octyl ethyl carbonate (Table III, runs 5 and 6) may represent the product of attack by the 2-octyl cation on the ethyl *tert*-butyl carbonate produced during the diazotate generation step and carried along thereafter.[4c] The 2-octyl ethyl carbonate is not formed when a good nucleophile (azide) is present in quantity (cf., run 4, Table III).

Experimental Section

Methods and Materials. Optical rotations were determined on gc-purified neat liquids, using a Perkin-Elmer Model 141 digital spectropolarimeter and a 1-cm Rudolph cell. Averages of 3–5 readings are reported; reproducibility was ±0.002°. The rotation data are tabulated in Tables II and IV.

Most preparative and analytical gc procedures employed a Varian Aerograph Model A90-P3 instrument, fitted with a 12 ft × 0.25 in. 5% Carbowax 20M on 80–100 Gas Chrom R column. Octenes were analyzed with a 10 ft × 0.125 in. 5% Carbowax 20M on 80–100 Gas Chrom R column. Absolute yields were determined either by cut-and-weigh of Xerox copies of the traces or with a Varian Model 481 electronic integrator. In both cases, detector response was calibrated with authentic samples and peak areas were taken as averages of at least three traces.

2-Aminooctane (Norse) was resolved by repeated recrystallization of its tartrate salt from methanol.[45] The active amine was distilled from sodium, and polarimetric samples were further purified by gc on a 5 ft × 0.25 in. 28% Pennwalt 223, 4% KOH on 80–100 Gas

Chrom R column immediately prior to reading. In general, however, optical purity was determined on the 2-octylurethane derivative of the amine (see Table II).

Ether was distilled from LiAlH₄ and stored over Linde 4A sieves. **HMPA** (Aldrich) was distilled from CaH₂ and stored over Linde 13X sieves. **Lithium azide, fluoborate, and chloride** salts (Alfa Inorganics) were dried over P₂O₅ at 80° (0.1 mm) for >15 hr and used without further purification.

Tetrabutylammonium azide was prepared from hydrazoic acid and tetrabutylammonium hydroxide[46] and dried over P₂O₅ (0.1 mm) for 5 days. The crystalline material had mp 80–85° (lit.[46] mp 83–85°).

2-Azidooctane was prepared by the method of Streitwieser and Schaeffer.[19] The stereochemical details are discussed in the text.

Potassium octane-2-diazotate (2) was prepared from *N*-nitroso-*N*-2-octylurethane as previously described.[4c] Optically active **2** was prepared analogously, and its optical purity was based on the precursor *N*-2-octylurethane; see Tables II and IV. HMPA solutions of **2** were prepared as described,[4a] except that dicyclohexyl-18-crown-6 was not necessary for the solubilization of **2**. Thus, 10 mmol of **2**, freed from ether at 5 mm, dissolved in 20 ml of HMPA after 15 min of stirring (under N₂) to yield a clear light-orange solution.

Active **2-octanol** (see text) was purchased from Norse Laboratories. Derivatives of 2-octanol, such as 2-octyl trifluoroacetate and 2-octyl trimethylsilyl ether, were prepared by standard methods,[47] purified by gc (Carbowax at 65°, SE-30 at 100°, respectively), and characterized by satisfactory nmr and ir spectra. The ester showed $\nu_{C=O}$ 1790 cm⁻¹, and the ether exhibited a trimethylsilyl singlet at δ 0.03 in the nmr. All other reagents were purchased from typical suppliers.

Lithiolysis Reactions. The general procedure involved the preparation of an HMPA solution of **2**,[4a] under dry N₂, in a three-neck flask which was fitted with a magnetic stirrer, pressure-equalized dropping funnel, and a gas evolution tube leading to a gas buret. An HMPA solution of the appropriate lithium or tetrabutylammonium salt was prepared and rapidly added through the addition funnel. The reaction mixture was stirred at 25°, while gas evolution was followed until cessation, usually ~20 hr. Water was added dropwise, while any additional gas evolution was monitored. Addition of 100 ml of water followed, and the organic products were then extracted with 4 × 100 ml of ether. The combined ethereal extract was back-washed with 3 × 200 ml of water, followed by brine, dried over K₂CO₃, and stripped of solvent. The residue was analyzed by gc on the Carbowax columns described above. Analytical temperatures were 30° for the octenes and 120° for substitution products.

The experiments were usually conducted with 5 mmol of **2**; reagent ratios, products, and yields are indicated in Table I. An unknown long retention time product was isolated from the lithiolysis reactions by gc on the 12 ft Carbowax column at 155° (see text). Its ir and uv spectra are described above; the nmr spectrum (CCl₄) showed δ 2.22 (m), 1.93 (s), 1.77 (s), 1.31 (narrow m), and 0.88 (crude t). Approximate integral ratios were 2.5:1:2.25:10.5:3.75, respectively.

Trigger Reactions. The same apparatus was used as in the lithiolysis reactions. Trigger reagent (acetic or trifluoroacetic anhydride or trimethylsilyl chloride) was placed in the addition funnel. The HMPA solution of lithium or tetrabutylammonium salt was rapidly injected through a septum into a magnetically stirred HMPA solution containing 2–10 mmol of **2**. Then, the trigger reagent was added dropwise. Gas evolution was immediate, quantitative, and complete when the addition of the trigger had been completed (~15 min). Work-up and analytical procedures were identical with those of the lithiolysis reactions; reagent ratios, products, and yields appear in Table III.

Control Experiments. (a) A solution of 2-azidooctane (0.104 g, 0.670 mmol), tetradecane (gc standard, 0.105 g, 0.530 mmol), potassium *tert*-butoxide (0.167 g, 1.49 mmol), and lithium azide (0.392 g, 8.00 mmol) in 10 ml of HMPA was stirred at 25° for 19 hr. The usual work-up (see above), followed by gc analysis, showed that 91% of the 2-azidooctane remained. (b) This experiment was repeated with 2-azidooctane, $\alpha^{28}D$ −36.43° (neat, 1 dm). The gc-isolated azide showed $\alpha^{19}D$ −37.02° (neat, 1 dm) after the experiment. (c) The optical stability of 2-chlorooctane was also tested.

(45) F. G. Mann and J. W. G. Porter, *J. Chem. Soc., London*, 456 (1944).

(46) H. L. Goering, R. G. Briody, and G. Sandrock, *J. Amer. Chem. Soc.*, **92**, 7401 (1970).

(47) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, pp 1221 *f* and 1232.

The above experiment was repeated with 2-chlorooctane (0.10 g, 0.67 mmol), potassium *tert*-butoxide (0.167 g, 1.49 mmol), and LiCl (0.34 g, 8.0 mmol) in 10 ml of HMPA. Initially, the chloride had α^{27}D −28.79° (neat, 1 dm); recovered, purified 2-chlorooctane had α^{13}D −3.89° (neat, 1 dm). Racemization had proceeded to more than 86%. (d) To a solution of lithium azide (1.00 g, 20.4 mmol) in 15 ml of HMPA was added 2-octyl trifluoroacetate (0.11 g, 0.486 mmol) in 2 ml of HMPA. The mixture was stirred at 25° for 15 min and then worked up in the manner described above. Gc analysis showed the absence of 2-azidooctane. 2-Octyl trifluoroacetate and a trace of 2-octanol were the only products. (e) 2-Octyl trimethylsilyl ether (0.044 g, 0.22 mmol) and lithium chloride (0.10 g, 2.4 mmol) were stirred at 25° in 10 ml of HMPA for 15 min. Normal work-up afforded a residue which, on gc analysis, showed that only 2–3% of hydrolysis to 2-octanol had occurred. 2-Chlorooctane was absent. (f) A solution of 5.0 mmol of 2 in 30 ml of HMPA was doped with 2.5 g (17 mmol) of 2-butyl trimethylsilyl ether and stirred for 1 hr at 25°. No gas evolution was observed. Addition of water then produced 117 ml (95%) of the theoretical nitrogen evolution.

Structure of Transition States. III. A MINDO/2 Study of the Cyclization of 1,3,5-Hexatriene to 1,3-Cyclohexadiene

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Abstract: The disrotatory closure of 1,3,5-hexatriene to 1,3-cyclohexadiene is investigated using the MINDO/2 molecular orbital method. Minimum energy geometries of reactant and product are in moderately good agreement with the geometries determined by electron diffraction, although the enthalpy of reaction is calculated to be 17.4 kcal larger than the experimental value. The calculated transition state was found to be a C_s symmetry structure resembling a distorted hexatriene. The calculated enthalpy and entropy of activation, relative to hexatriene, are also in moderately good agreement with experiment.

The cyclization of 1,3,5-hexatriene to 1,3-cyclohexadiene is the prototype of thermal, disrotatory, electrocyclic reactions and is thus a textbook example of the application of the Woodward–Hoffmann rules.[2] In addition to its theoretical interest, this type of reaction is of some biochemical significance due to its involvement in the chemistry of vitamins A and D.[3]

Experimentally, the parent reaction has been fairly well characterized; the kinetic parameters have been determined by two independent groups of workers[4,5] and electron diffraction studies have yielded the geometrical parameters of reactant[6] and product.[7] The detailed geometry of the transition state is, as usual, experimentally unavailable.

This experimentally well understood reaction thus appears ideal for a theoretical-computational study on a model potential energy surface; the extent to which the predictions of the model agree with the experimentally known structural, thermodynamic, and kinetic parameters helps to establish the limits of reliability of the model, and if successful in this respect, additional predictions of the model can help clarify our detailed understanding of the reaction. This particular reaction seems well suited for a computational study using the semiempirical MINDO/2 molecular orbital method[8] as the model of the potential energy, since this method works best for unstrained hydrocarbons[8,9] and since it can be applied to a system of this size at only a moderate computational expense. We are unaware of any previous computational study of this reaction.

We reported herein the MINDO/2 calculated geometries of both *cis*- and *trans*-1,3,5-hexatriene, the equilibrium geometry of 1,3-cyclohexadiene, the geometry of the transition state in the thermal cyclization, and the enthalpies and entropies of activation and reaction.

Computational Methods

Given the MINDO/2 potential surface, the problem of the kinetics and thermodynamics of the hexatriene closure was treated by first locating the minima corresponding to the reactant and product geometries and the saddle point corresponding to the transition state. The calculated harmonic force constants of these structures were then used to estimate the vibrational partition functions. These, together with the calculated energies, were then used to obtain the thermodynamic and, using the formalism of transition state theory, kinetic parameters.

Geometries which were believed to be potential

(1) Samuel B. Silbert, Graduate Fellow, 1972–1973.

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(7) (a) M. Traetteberg, *Acta Chem. Scand.*, **22**, 2305 (1968); (b) H. Oberhammer and S. H. Bauer, *J. Amer. Chem. Soc.*, **91**, 10 (1969).

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