Direct Proton-Transfer Reaction via a Transient Hydrogen Bond Bridged Allyl Anion System on the Models of Cycloheptatrienes and Propene

Kazuko Takahashi,* Tsuyoshi Suzuki, Hideo Toda, Kahei Takase, Shiro Koseki, and Takeshi Nakajima

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

Received October 7, 1986

The base-catalyzed intramolecular proton transfer in cycloheptatriene derivatives and propene has been investigated both theoretically and experimentally. A direct 1,3-intramolecular proton shift was observed in cycloheptatriene derivatives, the shift proceeding through a 1,3-hydrogen bond bridged carbanion that is a transition state rather than an intermediate. Confirmation of the direct 1,3-proton shift in cycloheptatrienes was provided by MNDO calculations. Calculations on the ammonia-catalyzed hydrogen migration in propene indicate that it also proceeds by a direct 1,3-shift. The optimized geometry of the transition states for the 1,3-hydrogen shifts in cycloheptatrienes and propene has been calculated.

Introduction

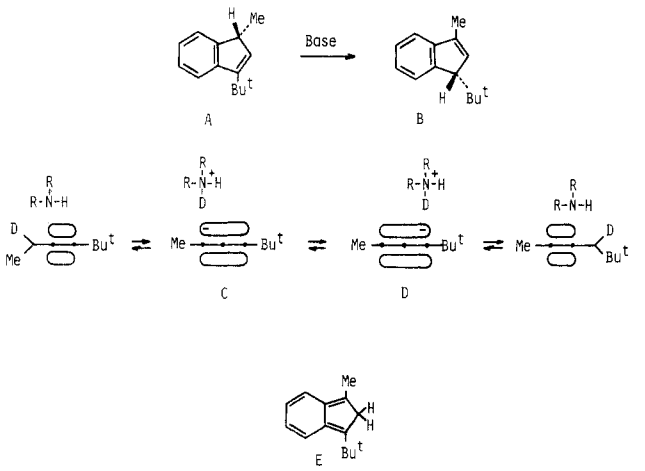
Base-catalyzed double bond rearrangements of carbon acids were first investigated by Cram et al. and Bergson et al.,[1a-e] who demonstrated that the weak base catalyzed rearrangements of 3-phenyl-1-butene[1b] or 3-*tert*-butyl-1-methylindene[1c-e] (A) occur through an intramolecular and suprafacial hydrogen shift. For this hydrogen shift, Cram has proposed an ion pair conducted tour mechanism[1d] where the proton in the form of a protonated base moves faster to the new site across the π cloud of the carbanion than the cationic ligand is exchanged in the ion pair (Scheme I). In the conducted tour mechanism, it has been proposed that (i) the C–H covalent bond of a starting material first becomes hydrogen bonded at the original carbon site by the base catalyst, then (ii) the protonated base moves successively from its original residence to other carbon sites without wandering out into the medium, and finally (iii) recapture of the proton by the carbanion (collapse to the product) occurs when the hydrogen-bonding tour arrives at the carbon capable of forming a stable covalent bond. Therefore in the conducted tour mechanism, hydrogen transfer occurs essentially in successive 1,2-shifts, although covalent intermediates do not always intervene in each step. For the 1,3-hydrogen transfer in the indene system (A → B), another explanation was given, which avoids a covalent state at C_2 involving the nonaromatic intermediate E.

In the rearrangement of 3-phenyl-1-butene to 2-phenyl-2-butene Cram and Uyeda have described their concept of a discrete intermediate, in which the allylic anion moiety might form a better hydrogen bridge at the terminal carbon atoms if the hybridization is not pure sp^2 but something like $sp^{2.3}$ and the C_1–C_2–C_3 bond angle might be less than 120°. Possibly the allylic carbanion might have some three-membered ring character placing some negative charge on the central carbon so as to overlap with the migrating hydrogen atom and bringing three carbon atoms and one hydrogen atom close together.[1b,h]

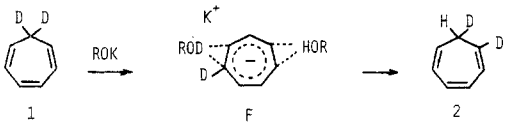
Doering and Gasper[2] found that the base-catalyzed isotope exchange of 7,7-dideuteriocycloheptatriene (1) occurs randomly on each ring carbon atom in 1,1-diethylpropanol and its potassium salt. Cram has discussed this random deuterium distribution, proposing intermediate F (Scheme II) in which the deuteriated ligand moves in successive 1,2- or 1,7-shifts before the carbanion incorporates the deuterium.[3] Since then, no systematic investigation on the mechanism of the base-catalyzed isomerization has been described in the literature.[4]

Although the stereospecificity and intramolecularity in the isomerization of A and butenes have been demonstrated experimentally by Cram[1b,d] and Bergson,[1e,f] many ambiguities remain about the reaction intermediates or the transition states of these reactions. Actually, there are many examples of overall 1,3-rearrangements proceeding via two successive 1,2-shifts in reactions of organometallic compounds or in thermally induced reactions.[5,6] However,

Scheme I



Scheme II



(1) (a) Cram, D. J.; Uyeda, R. T. *J. Am. Chem. Soc.* **1962**, *84*, 4358; (b) **1964**, *86*, 5466. (c) Almy, J.; Uyeda, R. T.; Cram, D. J. *Ibid.* **1967**, *89*, 6768. (d) Almy, J.; Cram, D. J. *Ibid.* **1969**, *91*, 4459. (e) Bergson, G.; Weidler, A. *Acta Chem. Scand.* **1963**, *17*, 1798. (f) Weidler, A.; Bergson, G. *Ibid.* **1964**, *18*, 1487. (g) Almy, J.; Hoffman, D. H.; Chu, K. C.; Cram, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 1185. (h) Cram, D. J. *Fundamentals of Carbanion Chemistry*; Academic: New York, 1965; p. 178.

(2) Doering, W. von E.; Gasper, P. P. *J. Am. Chem. Soc.* **1963**, *85*, 3043.

(3) Cram, D. J. *Fundamentals of Carbanion Chemistry*; Academic: New York, 1965; p 182.

(4) The double bond isomerizations of cycloheptatriene derivatives and related compounds in basic media have been reported without mechanistic description: (a) Buchner, E. *Chem. Ber.* **1898**, *31*, 2241. (b) Nozoe, T.; Mukai, T.; Tezuka, T.; Osaka, K. *Nippon Kagaku Zasshi*, **1963**, *84*, 662. (c) Swentons, J. S.; Burdett, K. A.; Madigan, D. M.; Rosso, P. D. *J. Org. Chem.* **1975**, *40*, 1280. (d) Vogel, E.; Brocker, U.; Junglas, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1015. (e) Vogel, E.; Altenbach, H. J.; Drossard, J. M.; Schmickler, H.; Stegelmeier, H. *Ibid.* **1981**, *19*, 1016.

(5) For example: Cotton, F. A.; Ciappenelli, D. J. *Synth. Inorg. Met. Org. Chem.* **1972**, *2*, 197. Davison, A.; Rakita, P. E. *J. Organomet. Chem.* **1970**, *23*, 407.

(6) Minato, T.; Inagaki, S.; Fujimoto, H.; Fukui, K. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1651 and references cited therein.

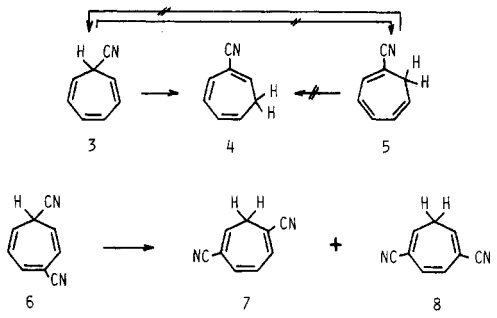
0022-3263/87/1952-2666$01.50/0

Table I. Isomerization of 7-Cyanocycloheptatriene (3) to 2-Cyanocycloheptatriene (4)[a]

run	[3], M[b]	[base], M[b]	temp	time, h	yield, %[e] 3	4
1	0.51[c]	1:1.03	A	5	49	51
2	0.51[c]	1:2.06	A	6	50	50
3	0.51[c]	1:2.06	A	10	37	63
4	0.51[c]	1:2.06	A	21.5	8	92
5	0.51[c]	1:2.06	A	44.5	0	100
6	0.067[d]	2:0.58	B	22.5	45.5	54.5
7	0.067[d]	2:0.58	B	30.5	33.3	66.7
8	0.067[d]	2:0.58	B	48.5	14.0	86.0
9	0.067[d]	2:0	B	24.0	100	0

[a] Base: 1, DIPEA; 2, NPr_3. Temperature: A, 44 ± 0.2 °C; B, 72 ± 0.2 °C. [b] Molar concentration. [c] Solvent: MeCN. [d] Solvent: THF. [e] Rate constants: $K = 3.16 \times 10^{-5}$ s^{-1} (in the reaction conditions of runs 2–5); $K = 1.23 \times 10^{-5}$ s^{-1} (in the reaction conditions of runs 6–8).

Scheme III



further study of the weak base catalyzed hydrogen-transfer reaction is needed to determine whether it occurs by a direct 1,3-shift or via two successive 1,2-shifts and whether the interaction between the central carbon of the allylic system and the migrating hydrogen atom is attractive or repulsive in the transition state.

Indene and butene systems are of limited value for experimental study of these problems, because the double bond reorganization is significantly restricted. We have undertaken an investigation of the base-catalyzed intramolecular hydrogen transfer in 7-substituted cycloheptatrienes to distinguish between two successive 1,2-shifts and a direct 1,3-shift. In contrast to the nonaromatic isomer E of indenes, 1-substituted cycloheptatrienes resulting from a 1,2-(1,7-)shift are thermodynamically stable and easily isolated. We have now investigated[7] the mechanism of base-catalyzed hydrogen shifts of cycloheptatrienes and have optimized the geometry of the transition state of the isomerization by MNDO calculations in order to distinguish between direct 1,3- and double 1,2-shifts. We have also studied the mechanism of the base-catalyzed hydrogen shift of propene at the 6-31G level by use of the Gaussian 82 series of programs to get a detailed insight into the electronic control of the intramolecular hydrogen migration path of this reaction.

Results and Discussion

Isomerization of 7-Substituted Cycloheptatrienes. 7-Cyanocycloheptatriene (**3**) was first treated with a nonproton-donating base, diisopropylethylamine (DIPEA) or tri-*n*-propylamine, in an aprotic solvent, acetonitrile or THF (Table I). After 44.5 h at 44 °C (run 5), **3** was completely rearranged to **4**, no other isomer being detected[8] (Scheme III). The first-order kinetic parameters for the isomerization of **3** to **4** in acetonitrile with DIPEA are summarized in Table II. When 1-cyanocycloheptatriene (**5**), obtained from **3** by consecutive 1,5-thermal hydrogen shifts,[9] was treated with DIPEA in acetonitrile, it remained practically unchanged at around 50 °C for 30 h or at around 80 °C for 6 h. The treatment of 3,7-dicyanocycloheptatriene (**6**)[10] with DIPEA in acetonitrile at 44 °C for 1 h afforded a mixture of two isomerization products, **7** (55%) and **8** (45%), and no 1,4-dicyano isomer, in accord with the usual 1,3-hydrogen transfer in polysubstituted

Table II. Kinetic Parameters for the Isomerization of 7-Cyanocycloheptatriene (3) to 2-Cyanocycloheptatriene (4)[a]

E_a, kcal/mol	log A, s^{-1}	$\Delta F^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
11.9	3.85	25.5	11.2	−43.1

[a] With DIPEA in MeCN at the following molar concentrations: **3**, 0.32 M; DIPEA, 1.40 M.

Table III. Isomerization of Cycloheptatriene-7-carboxylic Acid (9) (0.058 M) to Cycloheptatriene-2-carboxylic Acid (10) with Tri-*n*-propylamine in THF[a]

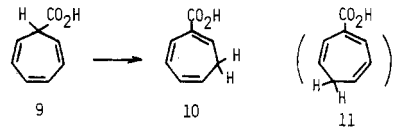
run	$[NPr_3]$, M	temp, °C	time, h	yield, % 9	10	11
1	0.58	72[b]	30	100		
2	0.58	110[c]	6	77	22	1
3	0.58	110	8	63	36	1
4	0	110	8	96		4
5	0.58	110	20	29	67	4
6	0.58	110	29	9	78	13
7	0	110	29	81		19

[a] Rate constant: $K = 1.89 \times 10^{-5}$ s^{-1} at 110 ± 0.2 °C. [b] 72 ± 0.2 °C. [c] 110 ± 0.2 °C.

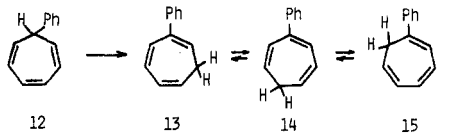
Table IV. Isomerization of 7-Phenylcycloheptatriene (12) (0.232 M) with *t*-BuOK in *t*-BuOH at 44 ± 0.2 °C

run	[*t*-BuOK], M	time, h	yield, % 12	13	14	15
1	0.199	19	75	15	10	
2	0.399	4	58	25	17	
3	0.399	8	33	33	22	11
4	0.399	17.5	20	37	24	19
5	0.399	67		51	35	14
6	0	52	100			

Scheme IV



Scheme V



(7) Takahashi, K.; Yamamoto, H.; Nozoe, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 200. The preceding paper, reviewed by Brown (Brown, J. M. *Organic Reaction Mechanisms*; Wiley: London, 1970; p 133), is where we proposed non-hydrogen-bonded carbanion G for an intermediate of the base-catalyzed isomerization of 7-substituted cycloheptatrienes, since no evidence of intramolecular hydrogen transfer was then detected by using highly polar solvents such as water and/or methanol.

(8) In the isomerization of **3**, the first step (**3** → **4**) is irreversible and much faster than the second step (**4** → 4-cyanocycloheptatriene); therefore **4** is more stable than **3** under the conditions listed in Table I.

(9) (a) ter Borg, A. P.; Kloosterziel, H.; van Meurs, N. *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 717. (b) ter Borg, A. P.; Kloosterziel, H. *Ibid.* **1963**, *82*, 741; (c) **1963**, *82*, 1189. (d) Nozoe, T.; Takahashi, K. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 665.

(10) (a) Ciganek, E. *J. Am. Chem. Soc.* **1967**, *89*, 1454; (b) **1967**, *89*, 1458.

Table V. Tri-*n*-propylamine(0.58 M)-Catalyzed Isomerizations of 3 (0.066 M) and 3d (0.066 M) at 72 ± 0.2 °C for 19.5 h

run	substrate	solv	isotopic pool (conc, M)	product, % 3	3d	4	4d	isomeriz, %	intramolity, %
1	3d[a]	THF	*t*-BuOH (1.48)/Pr_3NHI (0.066)	18	14	24	45	69	65
2	3d	THF	*t*-BuOH (1.48)	8	33	5	54	59	92
3	3	THF	*t*-BuOD (1.48)/Pr_3NHI (0.066)	19	2	68	10	78	87
4	3	THF	*t*-BuOD (1.48)	36	0	64	0	64	100
5	3	THF	*t*-BuOD (1.48)/Pr_3NDI (0.066)	15	5	67	13	80	84
6	3d	MeCN	*t*-BuOH (1.48)/Pr_3NHI (0.066)	0	0	62	38	100	38
7	3d	*t*-BuOH	*t*-BuOH/Pr_3NHI (0.066)	1	6	47	45	92	49

[a] 0.92 atom per molecule of deuterium.

cycloheptatriene derivatives. The isomerization of cycloheptatriene-7-carboxylic acid (**9**) proceeded more slowly than the cyano derivatives, affording **10** at higher temperatures (Table III, Scheme IV). The appearance of a small amount of cycloheptatriene-3-carboxylic acid (**11**) is due to a thermal 1,5-hydrogen shift of **9** since **11** was also detected in runs 4 and 7 in which tri-*n*-propylamine was absent (Table III). The isomerization of 7-phenylcycloheptatriene (**12**) did not occur with a trialkylamine base even at 120 °C but occurred with potassium *tert*-butoxide in *tert*-butyl alcohol at 44 °C where **12** was converted consecutively to **13**, **14**, and **15**, an equilibrium among them being finally attained (Table IV, Scheme V). A thermal 1,5-hydrogen shift did not accompany this rearrangement because of the low reaction temperature. The consecutive isomerizations of the phenylcycloheptatrienes are attributable to their having similar pK_a values, thus allowing the hydrogen shifts at comparable rates.

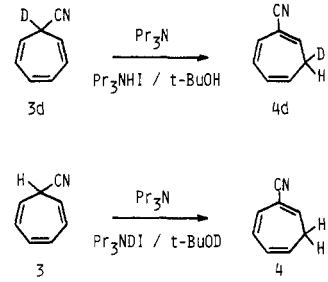
The facile isomerizations of **3**, **6**, **9**, and **12** with a trialkylamine[11] or *tert*-butoxide[12] base in a medium of relatively low dielectric constant such as THF or *tert*-butyl alcohol, together with the large negative value of $\Delta S^{\ddagger}$ (Table II), strongly suggest that the isomerizations proceed through a hydrogen-bonded carbanion intermediate rather than a non-hydrogen-bonded carbanion intermediate such as G.[7]

G

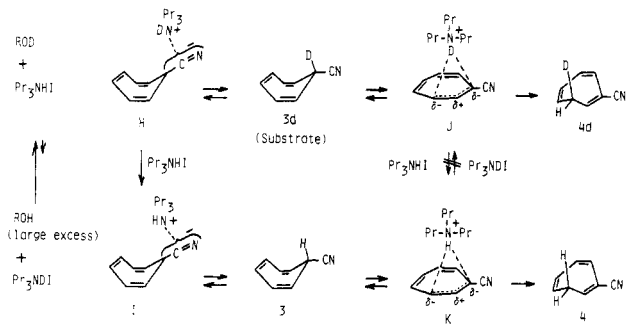
Intramolecular Hydrogen Transfer. In order to obtain further evidence for a hydrogen-bonded carbanion mechanism, we investigated the hydrogen–deuterium exchange in **3**, using tri-*n*-propylamine as a base and *tert*-butyl alcohol–tri-*n*-propylammonium iodide as an isotropic pool, because **3** is acidic enough to isomerize with this base at relatively low temperatures[13] in a low dielectric solvent such as THF. The estimated pK_a difference (ΔpK_a) between tri-*n*-propylammonium ion (a proton donor) and **3** (about 11–12)[11] is probably enough to make the hydrogen-capturing process faster than the hydrogen-bond dissociation. Table V indicates that the isotopic exchange and the hydrogen shifts of the starting material occur at comparable rates.

The distribution of the products in run 3 (Table V) involving tri-*n*-propylammonium hydrogen iodide is similar to that in run 5 involving tri-*n*-propylammonium deuterium iodide. This result demonstrates that the isotope

Scheme VI



Scheme VII. Schematic Expression of Run 1 in Table V



exchange between the ammonium salt and *tert*-butyl alcohol is many powers of ten faster than that between the cycloheptatrienes and the isotopic reservoirs.[14] Thus there were opportunities for the carbanion intermediates to exchange the cationic ligand with that containing the other isotope, which exists in constant concentration in the medium throughout the reaction. Nevertheless, **3d** in run 1 and **3** in run 5 gave 65% and 84% intramolecularities, respectively, in THF.[15] Intramolecularity (%) in Table V represents a direct intramolecular isomerization (e.g., **3d** → **4d**, Scheme VI). Alternatively, the starting compound may undergo to some extent first deuterium exchange and then intramolecular isomerization (e.g., **3d** ⇌ H → I ⇌ **3** → **4**, Scheme VII), which is not included in the intramolecularlity given in Table V. All runs in Table V were carried out in the presence of a large excess (at least 21 molar equiv based on the substrate) of *tert*-butyl alcohol, so that any significant isotope reincorporation into the once isotrope-exchanged starting material (e.g., I → H) could be disregarded.

These intramolecular hydrogen shifts in the presence of an external isotope donor strongly support the hydrogen-bonded carbanion mechanism, in which the hydrogen shift occurs faster than the dissociation. It is of particular importance that the intramolecular hydrogen shift via a hydrogen-bonded carbanion is demonstrated in a 1,3-mode, not in a 1,2-mode, in the cycloheptatriene system where

(11) Trialkylammonium ion (pK_a = 10.6), a proton source of the isomerization reaction, is more acidic by about six powers of ten than methanol. The pK_a differences between proton donors and substrates are about 11 (for **3**) to 15 (for **9**).

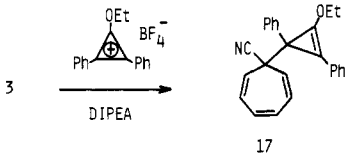
(12) The pK_a of *tert*-butyl alcohol in THF is about 25. Thus the ΔpK_a between **12** and the proton donor is about 7.

(13) At higher temperatures a thermal 1,5-hydrogen shift would be blended.

(14) Grunwald, E. *J. Phys. Chem.* **1967**, *71*, 1846 and references cited therein.

(15) No dideuteriated cyanocycloheptatriene was detected in all runs.

Scheme VIII



there is not significant restriction on double bond reorganization.

The isomerization rate of **3** was higher than that of **3d**, as shown by comparing runs 1 and 5 or runs 2 and 4. Moreover, the intramolecularity in the isomerization of **3** is greater than that of **3d**, as seen by comparing runs 1 and 5 or runs 1 and 3. Since isomerized products **4** and **4d** were insensitive to isotope exchange under these conditions,[16,17] the greater intramolecularity in **3** compared with **3d** is mainly attributable to the more facile isomerization of **3** to **4** compared with that of **3d** to **4d**. Therefore, it follows that in the isotope exchange during isomerization, the interchange J ⇌ K did not take place, at least in runs 1–5. Thus J and K are not intermediates but rather transition states too short-lived to allow isotope exchange.

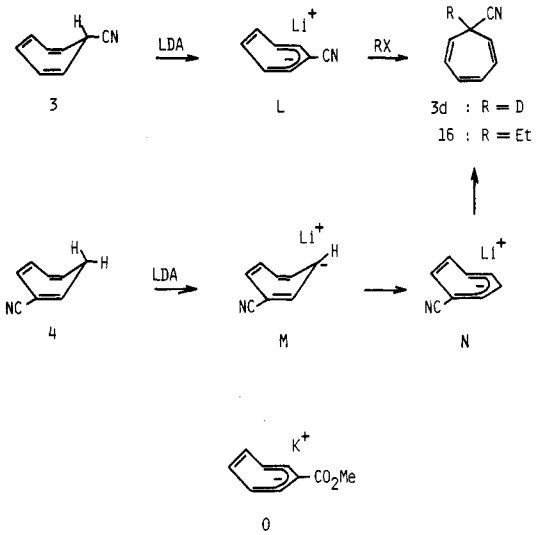
The formation of **4d** in runs 3 and 5 and of **4** in runs 1, 6, and 7 can be ascribed to isotope exchange (**3** → **3d**, **3d** → **3**) followed by isomerization (**3d** → **4d**, **3** → **4**). The estimated pK_a of **3** is close to that of 2-phenylbutyronitrile (~21), and the solvent–base combination listed in Table V is almost identical with that in which the latter compound undergoes an isoracemization reaction.[18] Therefore, deuterium–hydrogen exchange at the C_7 position of **3d** or **3** should proceed via a carbanion paired with an ammonium ion.[19] Whereas no incorporation of an ethyl group was observed on addition of ethyl iodide to the reaction medium in run 1 (Table I) or run 4 (Table V), the C_7-cyclopropenylated compound **17**[20] was obtained together with **4** when **3** was treated with DIPEA in the presence of 1-ethoxy-2,3-diphenylcyclopropenium ion in acetonitrile (Scheme VIII). No product cyclopropenylated at any position other than C_7 was detected. This fact suggests that the interchange of the cationic ligand takes place in H but is difficult in J (Scheme VII) presumably because J has a shorter lifetime than H.

The isomerization was accelerated in more polar solvents (runs 1, 6, and 7, Table V) or by addition of a trialkylammonium salt (runs 1 and 2, runs 5 and 4, Table V). This evidence indicates that the transition state of the isomerization (J or K) is ionic rather than covalent.

The lower intramolecularities in runs 6 and 7 (Table V) reflect the higher polarity of the solvents (runs 6 and 7) and the extremely high concentration of the proton pool (run 7), both of which accelerate the ion-pair dissociation (H → I).

Non-Hydrogen-Bonded Cycloheptatrienide Anion. To obtain additional information on the reactivity of the ion-paired but non-hydrogen-bonded cycloheptatrienide anions derived from **3** and **4**, compound **3** was allowed to react with the strong base LDA in THF, affording a deep green solution which on quenching with deuterium oxide gave **3d** uncontaminated with any double bond isomer such as **4** (Scheme IX). Quenching of the solution with ethyl iodide at room temperature gave 7-cyano-7-ethylcycloheptatriene (**16**) as a sole product.

Scheme IX



In addition, **4** was alllowed to react with LDA in THF, and the resulting reddish orange solution was quenched with deuterium oxide, water, or ethyl iodide to give **3d**, **3**, or **16**, respectively. These facts demonstrate that the negative charge of the carbanions L and N (Scheme IX) is largely concentrated on the carbon carrying the cyano group and/or on the cyano nitrogen and less on the other ring carbons and that carbanion M rearranges to the more stable carbanion N faster than it captures the electrophiles. Zwaard and Kloosterziel[21] have recently proposed the pentadienyl structure O for the carbanion formed in the reaction of 7-(methoxycarbonyl)cycloheptatriene with potassium amide. N and L should have similar structures,[22] and the rearrangement of M to N is quite plausible by the easy flipping of the seven-membered ring.[23]

It is apparent that neither the non-hydrogen-bonded ion-paired carbanions L, N, and M nor the allylic anion G is involved in the 1,3-hydrogen transfer in cycloheptatrienes and that the incorporation of hydrogen at C_2 in the isomerization of **3** to **4** is not attributable to the higher electron density at this position. Hence in the hydrogen transfer a vacant orbital of the trialkylammonium ion ($HNPr_3^+$) must interact with the π orbital of C_2 before the C_7–H bond breaking is complete. Thus the hydrogen atom of the trialkylammonium ion is loosely bonded to both of the allylic termini to form a transition state, which then collapses via a suprafacial route to the isomerized product.[24] This consequence of the 1,3-hydrogen bond bridged transition state is in excellent

(16) On further treatment of **4** or **4d** with fresh batches containing the same media as in Table V, there was detected neither isotope incorporation nor reverse reaction from **4** to **3**.

(17) On the collapse of the hydrogen-bonded transition-state J or K, thermodynamically more stable isomer **4** is produced prior to thermodynamically less stable but kinetically more acidic isomer **3**.

(18) In an isoracemization mechanism, ion-pair racemization and collapse to the covalent state occur faster than the isotopic exchange of the ion-pair cation: (a) Cram, D. J.; Gosser, L. *J. Am. Chem. Soc.* **1964**, *86*, 5457; (b) **1964**, *86*, 2950.

(19) The hydrogen bond bridged transition state J or K is not involved in the exchange process because such a transition state would collapse to provide a kinetically less acidic (thermodynamically more stable) olefin.

(20) The norcaradiene–cycloheptatriene equilibrium of **17** has been reported: Takahashi, K.; Takase, K; Toda, H. *Chem. Lett.* **1981**, 979.

(21) Zwaard, A. W.; Kloosterziel, H. *Recl. Trav. Chim.* **1981**, *100*, 126.

(22) Direct ^1H NMR spectral detection of the cyanocycloheptatrienide anion was attempted in vain, because the ion disappears rapidly evan at −80 °C in deuteriated liquid ammonia. This fact has also been reported by Zwaard et al.[23] However, the carbanion derived from 7-(benzylsulfonyl)cycloheptatriene also has a similar structure to that of O: Zwaard, A. W.; Kloosterziel, H. *J. Chem. Soc., Chem. Commun.* **1982**, 391.

(23) Direct observation of carbanion O by NMR spectroscopy at −40 °C suggests that the conversion of L to thermodynamically more stable anion N is not attained at such a lower temperature as −78 °C at which L and N were generated and quenched.

(24) A simulataneous bonding to both of the allylic terminals in an antarafacial mode is sterically forbidden.

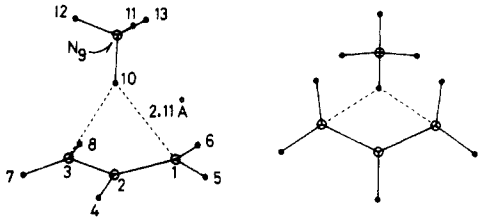


Figure 1. Geometric drawing for the transition state of the reaction of propene with ammonia.

agreement with the actual stereospecific suprafacial mode observed in the 1,3-hydrogen shift of optically active (−)-3-*tert*-butyl-1-methylindene.[1c,d] Thus the base-catalyzed rearrangement of the cycloheptatrienes proceeds by the same mechanism as the indenes and the butenes, involving a direct 1,3-hydrogen shift rather than two successive 1,2-shifts.

Theoretical Treatment. Although many molecular orbital studies[6,25] have been reported on the mechanism of the 1,3-sigmatropic reaction, the reaction paths of the base-catalyzed intramolecular hydrogen migration in carbon acids have not been discussed in detail. In order to clarify the course of the migration, we have optimized the geometry of the transition state of the ammonia-catalyzed hydrogen shift of propene by ab initio computations at the 6-31G basis set[26] of split valence on the Gaussian 82 series of programs. After structural optimizations followed by vibrational analyses for several plausible paths, we obtained the best geometry of the true transition state (Figure 1). There are large negative changes at C_1 and C_3, and the migrating hydrogen atom H_m has a positive charge. While C_2 is slightly negative (−0.06 e), H_m is located far away (0.584 Å) from the center of the C_1–C_3 line in the direction away from C_2. Thus H_m migrates in such a way as to minimize the overlap with C_2 of the allyl framework. The distances H_m–N (1.048 Å) and H_m—C_1 (or C_3) (2.108 Å) are reasonable values for NH_4^+ as the migrating species and for the hydrogen-bonded carbanions, respectively. The C_1–C_2 (C_2–C_3) bond length (1.394 Å) is similar to that of the free allyl anion structure calculated by Streitwieser et al. at the 4-31G level,[27] whereas the C_1–C_2–C_3 bond angle (129.8°) is 2.4° smaller than that for the free anion (132.2°). This contraction of the bond angle might be caused by a decrease in the antiaromatic character of the free allyl anion by the formation of the 1,3-bridged hydrogen bond. The methylene proteon H_6 (H_8) lies 0.359 Å out of the plane defined by the $C_1C_2C_3$ skeleton in the direction away from H_m, thus giving a $C_3C_2C_1H_6$ dihedral angle of 18.36°, which is about twice as large as that for the free anion. The optimized C's symmetrical structure has an orbital symmetry which does not allow bonding interaction between the transferring hydrogen and the HOMO of the carbanion. In this sense, the base-catalyzed 1,3-hydrogen shift can be specified as a forbidden reaction. The 1,3-shift is significantly accelerated by the presence of a base, since, according to our calculations, the activation energy of the 1,3-hydrogen shift (about 5.0 eV) is reduced to about 3.6 eV in the presence of ammonia.

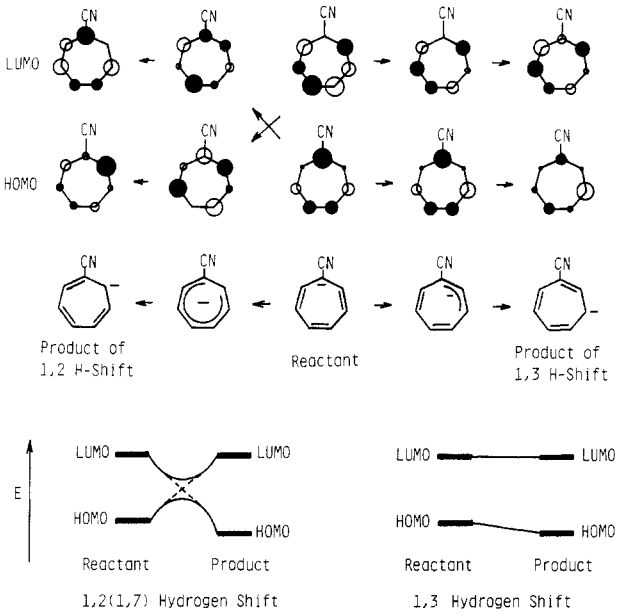
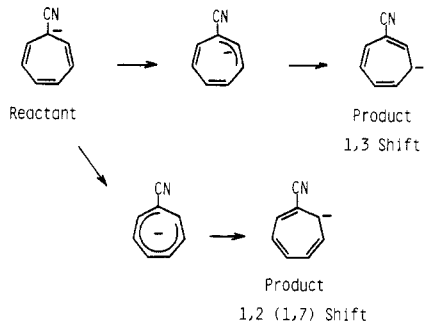


Figure 2. Correlation diagram of the 1,3- and 1,2-(1,7-)hydrogen shifts.

Scheme X



In order to rationalize the experimentally observed high regioselectivity of the base-catalyzed isomerization of cycloheptatrienes, the mechanistic differences between the suprafacial 1,3- and 1,2-(1,7-)hydrogen shifts in 7-cyanocycloheptatriene and cycloheptatriene itself were assessed by Hückel MO calculations.[28]

For qualitative purposes, the Hückel calculations were carried out with the assumption that the cyanocycloheptatrienide anion produced by removing the proton (H_m^+) from the C_7 position of **3** has a planar ring. In both 1,3- and 1,2-(1,7-)hydrogen migrations, the negative charge in this ring should shift along the reaction path as shown in Scheme X. The Hückel MO calculations suggest that in the 1,2-(1,7-)migration reaction the HOMO and the LUMO of the reactant correlate with the LUMO and the HOMO of the product, respectively. However, in the actual situation the HOMO of the reactant correlates with that of the product because of the avoided crossing as shown schematically in Figure 2, with the result that the reaction must pay the price in activation energy and is thermally forbidden. On the other hand, in the 1,3-migration reaction the HOMO and the LUMO of the reactant correlate with the HOMO and the LUMO of the product, respectively (Figure 2). Therefore, the reaction should be thermally allowed. These results are in qualitative agreement with the experimental observations.

Hückel MO calculations were also carried out on cycloheptatrienide anion. In this anion, the energy levels of

(25) (a) Castenmiller, W. A. M.; Buck, H. M. *Tetrahedron* **1979**, *35*, 397. (b) Bouma, W. J.; Vincent, W. A.; Radom, L. *Int. J. Quantum Chem.* **1978**, *14*, 767. (c) Rodwell, W. R.; Bouma, W. J.; Radom, L. *Ibid.* **1980**, *18*, 107. (d) Niemeyer, H. M.; Ahlberg, P. *J. Chem. Soc., Chem. Commun.* **1974**, 799. (e) Neimeyer, H. M.; Goscinski, O.; Ahlberg, P. *Tetrahedron* **1975**, *31*, 1699. (f) Bernardi, F.; Epiotis, N. D.; Yates, R. L. *J. Am. Chem. Soc.* **1975**, *97*, 1334. (g) Epiotis, N. D. *Ibid.* **1973**, *95*, 1206.

(26) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(27) Boerth, D. W.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 750.

(28) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899; *QCPE No. 353.*

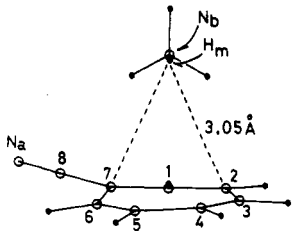


Figure 3. Geometric drawing for the transition state of the 1,3-migration in 7-cyanocycloheptatriene.

the HOMO and the LUMO in the transition state of the 1,2-(1,7-)hydrogen migration approach closely or degenerate each other, whereas such an approach of the HOMO–LUMO levels in the transition state of a 1,3-migration does not occur. Therefore, a 1,2-(1,7-)hydrogen migration in cycloheptatrienide anion should proceed via an avoided crossing mechanism, like the cyanocycloheptatrienide anion, requiring a higher activation energy than the 1,3-migration. Thus Cram's 1,2-hydrogen migration mechanism for cycloheptatriene is not supported by these calculations.

For the 1,3-migration in 7-cyanocycloheptatriene, the optimization of the geometrical structure of the true transition state was performed by the MNDO method with the assumption that the migrating proton (H_m) attached to the nitrogen atom (N_b) of the ammonia molecule[29] is located in the plane that includes C_1 and the midpoint of the C_4–C_5 bond and is perpendicular to the molecular plane. The MNDO calculations show that the optimized hydrogen-bond-bridged cyanocycloheptatrienide anion is planar (Figure 3). The distance between H_m and N_b is calculated to be 1.07 Å, so the migrating unit can be considered to be NH_4^+.

The π electrons are localized on the C_3–C_4 and C_5–C_6 bonds and the negatively charged allyl fragment C_7–C_1–C_2. The C_2 and C_7 carbon atoms have a large negative charges (−0.384 and −0.433 e, respectively). The distance of H_m from C_1 (2.82 Å) is slightly shorter than those from C_2 and C_7 (3.05 Å), but the interaction between H_m (+0.235 e) and C_1 is repulsive because the C_1 atom has a positive charge (+0.154 e). Therefore the reaction cannot involve two successive 1,2-(1,7-)hydrogen shifts.

The geometrical structure of the transition state in the 1,2-(1,7-)migration reaction was optimized with the assumption that H_m and N_b are arranged in the plane including C_4 and the midpoint of the C_1–C_7 bond and perpendicular to the molecular plane (Figure 4). The π electrons are significantly delocalized over the ring except for the C_1–C_7 bond. The bond length C_1–C_7 is calculated to be 1.476 Å and those of the remaining bonds are in the range 1.397–1.422 Å. The bond lengths of C_1–H_m and C_7–H_m are both 1.41 Å. The distance between H_m and the ammonia molecule is very large (4.4 Å), indicating that in this case the base catalyst can play only a very minor role in the migration reaction. The C_1, C_7 and H_m atoms have very small positive charges (+0.080, +0.142, and +0.039 e, respectively) so that the C_1–H_m and C_7–H_m bonds are largely covalent rather than hydrogen-bonded ion pairs. The transition state is calculated to be less stable than that in the 1,3-migration reaction by about 10 kcal mol^{-1}.[30]

If a very short length is assumed for the N_b–H_m bond as a starting geometry of the transition state in the 1,2-(1,7-)migration reaction, geometry optimization under the same assumption leads to the ion pair shown in Figure 5. The C_1–H_m and C_7–H_m bonds become much longer (4.1 Å) and the transition state becomes less stable (by about 2 kcal mol^{-1}). In the ion pair the cyanocycloheptatrienide anion has almost the same C–C bond lengths except for the C_1–C_7 bond. The C_7 atom has a large negative charge (−0.390 e), and the C_1 atom has a positive charge (+0.028 e), being repulsive to H_m (+0.247). Thus the obtained geometry does not correspond to the transition state.

It should be noted that the optimized transition-state geometry in the direct 1,3-migration reaction is energetically the more favorable and is essentially a hydrogen bond bridged ion pair ($C_7H_6CN^-NH_4^+$) in which H_m associates with both C_2 and C_7 at equal distances of 3.05 Å.

In agreement with the prediction from the Hückel MO method, the 1,2-(1,7-)migration reaction should be thermally forbidden, because if we assume that the reaction proceeds via the transition state shown in Figure 4, the HOMO of the reactant (7-cyanocycloheptatriene) correlates not with the HOMO but with the LUMO of the product (1-cyanocycloheptatriene).

We conclude that the 1,3-hydrogen shift does occur directly rather than via two successive 1,2-shifts and that the interaction between the migrating hydrogen atom and the central C_2 of an allyl system is repulsive, preventing the formation of a C_2 hydrogen-bonded intermediate.

Experimental Section

^{1}H NMR spectra were recorded on Varian HA-100 and Varian XL-200 instruments; chemical shifts (δ) and coupling constants (J) are expressed in parts per million relative to Me_4Si and in Hz, respectively. IR spectra were recorded on a Schimazu IR-27G spectrophotometer. Mass spectra were recorded on a Hitachi M-52 spectrometer. Some reaction product mixtures were separated by HPLC on a Japan Analytical Industry R1-3H (Lichrosorb) liquid chromatograph and analyzed by the 200-MHz ^{1}H NMR spectrometry. Elemental analyses were performed at Instrumental Analysis Center for Chemistry, Tohoku University. All temperatures were uncorrected.

Materials. Acetonitrile was distilled from calcium hydride and then from phosphorus pentoxide. The middle 80% fraction was finally distilled from calcium hydride. *tert*-Butyl alcohol was distilled from calcium hydride and stored in a sealed bottle. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride freshly prior to use. *t*-BuOD (99.7% deuterium content) was commercially available. Tri-*n*-propylamine was refluxed successively with *p*-toluenesulfonyl chloride and with potassium hydroxide and then fractionally distilled. The distillate, after addition of about 2% phenyl isocyanate, was redistilled, and the middle fraction was finally distilled from metallic sodium. Diisopropylethylamine (DIPEA) was purified essentially in the same manner as tri-*n*-propylamine. Cycloheptatriene derivatives **3**, **9**, and **12** were prepared by the procedure reported by us.[7] The following ^{1}H NMR data ($CDCl_3$) were used for the references. **3**: δ 3.00 (1 H, tt, J = 6.1 and 0.8, H-7), 5.37 (2 H, ddt, J = 9.0, 6.1, and 0.8, H-1,6), 6.32 (2 H, m, H-2,5), 6.73 (2 H, tt, J =3.0 and 0.7, H-3,4). **9**: δ 2.48 (1 H, tt, J = 5.5 and 1.1, H-7), 5.34 (2 H, ddt, J = 8.0, 5.5, and 1.0, H-1,6), 6.28 (2 H, m, H-2,5), 6.63 (2 H, m, H-3,4). **12**: δ 2.73 (1 H, tt, J = 5.5 and 1.0, H-7), 5.41 (2 H, dt, J = 9.0, and 5.5, H-1,6), 6.24 (2 H, m, H-2,5), 6.72 (2 H, m, H-3,4), 7.33 (5 H, Ph).

2-Cyanocycloheptatriene (4). A solution of **3** (500 mg, 4.27 mmol) and DIPEA (2.322 g, 18 mmol) in acetonitrile (8 mL) was stirred for 30 h at 45 °C under N_2. After cooling, the reaction mixture was quenched with water (130 mL) and extracted with ether. The combined extracts were washed with 1 N H_2SO_4 (125 mL × 2) and with saturated aqueous $NaHCO_3$ and dried. Removal of the solvent afforded crude **4** (480 mg, 96%), which was chromatographed on silica gel by eluting with benzene–hexane (1:1) to give a colorless oil: IR (neat) 3050, 3000, 2900, 2850, 2225, 1600, 1519, 1437, 1372, 1291 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.39 (2 H, td, J = 7.0 and 0.5, H-7), 5.43 (1 H, tdd, J = 7.0, 9.1, and 1.0, H-6), 6.07 (1 H, td, J = 7.0 and 1.0, H-1), 6.28 (1 H, dd, J = 9.1, 5.0,

(29) For convenient manipulation, the trialkyl amine base used in experiments is replaced by ammonia molecule in MO calculations.

(30) This absolute value is not precise because the solvation energies and entropy factors are disregarded.

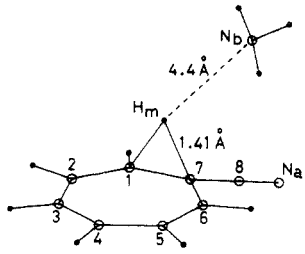


Figure 4. Geometric drawing for the transition state of the 1,2-(1,7-)migration in 7-cyanocycloheptatriene.

0.5, and 1.0, H-5), 6.59 (1 H, dt, J = 11.0 and 1.0, H-3), 6.79 (1 H, ddd, J = 11.0, 0.5, and 1.0, H-4). Anal. Calcd for C_8H_7N: C, 82.02; H, 6.02; N, 11.96. Found: C, 82.20; H, 6.14; N, 11.75.

Kinetics of the Isomerization of 3 to 4. An acetonitrile solution of **3** (0.749 g) and DIPEA (3.612 g) was placed in a 20-mL volumetric flask, and the final volume was exactly adjusted with additional acetonitrile (**3**, 0.32 M; DIPEA, 1.4 M). After being vigorous shaken, 2-mL samples of the solution were placed in small ampules under N_2, which were sealed and then allowed to stand in a constant-temperature oil bath. The ampules were opened at convenient intervals, and the reaction mixtures were worked up as above and then chromatographed on silica gel to give a mixture of **3** and **4**. The ^{1}H NMR spectrum was recorded and electrically integrated. The areas of signals for H-7 of **3** (δ 3.00) and for H-7 of **4** (δ 2.39) were separately measured from the average of the several repeated integrations to provide the concentration of the isomers. The rate constants of isomerization of **3** to **4** (concentration: substrate, 0.32 M; base, 1.4 M, in acetonitrile) were as follows: 1.84×10^{-5} s^{-1} (30 ± 0.2 °C), 3.27×10^{-5} s^{-1} (35 ± 0.2 °C), 3.64×10^{-5} s^{-1} (40 ± 0.2 °C), 6.34×10^{-5} s^{-1} (50 ± 0.2 °C). A plot of the log K values against $1/T$ was found to be linear, giving values for the parameters listed in Table II. The results shown in Table I were obtained in similar procedures.

Attempted Isomerization of 1-Cyanocycloheptatriene (5) with DIPEA. A solution containing **5** (300 mg, 2.56 mmol) and DIPEA (1.393 g, 10.8 mmol) in acetonitrile (4.8 mL) was warmed to 50 °C for 30 h or refluxed (80 °C) for 6 h. Subsequent workup afforded a colorless oil, which was identified by ^{1}H NMR spectral examination to be pure **5** uncontaminated with any other isomer.

Preparation of 3,7-Dicyanocycloheptatriene (6). 7,7-Dicyanonorcaradiene was prepared by reaction of benzene with dicyanocarbene according to the procedure of Ciganeck.[12] To a solution of 7,7-dicyanonorcaradiene (6.90 g) in toluene (170 mL) was introduced N_2 gas for 30 min, and the solution was placed in a toluene vapor bath for 115 h under N_2. The resulting solution was distilled off, and the residue was chromatographed on Florisil (170 g) by eluting successively with benzene–petroleum ether (1:1), benzene–dichloromethane (1:1), and finally dichloromethane. The chromaotgraphic fractions from benzene–dichloromethane and from dichloromethane were rechromatographed on Florisil to give **6** (853 mg): ^{1}H NMR ($CDCl_3$) δ 3.15 (1 H, br t, J = 6.6 and 1.0, H-7), 5.59 (1 H, dd, J = 9.8 and 6.6, H-6), 5.73 (1 H, dd, J = 6.6 and 9.8, H-1), 6.54 (1 H, br d, J = 9.8, H-2), 6.62 (1 H, dd, J = 9.8 and 6.2, H-5), 7.42 (1 H, d, J = 6.2, H-4); IR (neat) 3070, 2970, 2910–2860, 2250, 2220, 1625, 1525, 1380 cm^{-1}.

Isomerization of 3,7-Dicyanocycloheptatriene (6). A solution containing **6** (100 mg, 0.7 mmol) and DIPEA (208 mg, 1.6 mmol) in acetonitrile (3.5 mL) was heated at 44 ± 0.2 °C for 1 h in a sealed tube under N_2. The reaction mixture was diluted with water and extracted with ether. The ether extracts were washed successively with 2 N H_2SO_4 and aqueous $NaHCO_3$ and then dried. Removal of the solvent and column chromatography (Florisil, benzene) of the residue gave a colorless crystalline solid (43 mg). The ^{1}H NMR spectral examination through double irradiation technique revealed this product to be a mixture of 1,5-dicyanocycloheptatriene (**7**) and 2,5-dicyanocycloheptatriene (**8**). **7**: ($CDCl_3$) δ 2.72 (2 H, d, J = 7.5 H-7), 6.42 (1 H, t, J = 7.5, H-6), 6.98 (1 H, d, J = 5.5, H-2), 6.92 (2 H, m, H-3,4). **8**: ($CDCl_3$) δ 2.63 (2 H, t, J = 7.2, H-7), 6.30 (2 H, t, J = 7.2, H-1,6), 6.92 (2 H, m, H-3,4). The concentration of each component was calculated from the averages of the repeated integrations of the regions of δ 2.8–2.45 (H-7's of **7** and **8**) and 6.6–6.1 (H-1,6's of **7** and **8**), giving $(2x + 2y)/(x + 2y) = 24.4/17.8$, where x and y are the molar percentages of **7** and **8**, respectively: **7**, 55%; **8**, 45%.

Isomerization of Cycloheptatriene-7-carboxylic acid (9) to Cycloheptatriene-2-carboxylic acid (10) was carried out in a similar manner to that described for the isomerization of **3** to **4**, but by using the combination of substrate and base shown in Table III, and the reaction products were analyzed by the ^{1}H NMR spectrum. In the typical run 2 in Table III, the averages of the integrations obtained from several scans at the region of δ 2.1–2.7 (H-7's of **9**, **10**, and **11**) and at the region of the signals for the olefinic protons gave $[x + 2(y + z)]/[6x + 5(y + z)] = 15.5/72.5$, where x, y, and z are molar percentages of **9**, **10**, and **11**, respectively: **9**, 76.7%; **10** + **11**, 23.3%. The areas of signals H-3 of **10** (δ 7.15) and H-4 of **11** (δ 7.70) were separately measured from the average of the integrations, giving $y/z = 3.7/0.2$: **10**, 22%; **11**, 1%. ^{1}H NMR data used as internal standards are as follows. **10**: ($CDCl_3$) δ 2.37 (2 H, t, J = 7.0, H-7), 6.58 (1 H, t, J = 7.0, H-1), 7.15 (1 H, dd, J = 11.5 and 0.7, H-3), 6.65 (1 H, dd, J = 11.5 and 5.3, H-4), 6.24 (1 H, dd, J = 9.0 and 5.3, H-5), 5.37 (1 H, dt, J = 9.0 and 7.0, H-6). **11**[7]: ($CDCl_3$) δ 2.29 (2 H, t, J = 6.8 , H-7), 5.60 (1 H, dt, J = 9.3 and 6.8, H-1), 6.69 (1 H, d, J = 9.3 , H-2), 7.70 (1 H, d, J = 6.0, H-4), 6.28 (1 H, dd, J = 9.3 and 6.0, H-5), 5.37 (1 H, dt, J = 9.3 and 6.8, H-6).

Isomerization of 7-Phenylcycloheptatriene (12) to 2-Phenylcycloheptatriene (13). Substrate **12** (779.5 mg, 4.64 mmol) was added to *tert*-butyl alcohol containing potassium *tert*-butoxide (34.3 mmol) in a 20-mL volumetric flask, and the volume was exactly adjusted. The solution was shaken and then transferred under N_2 to six small ampules. The ampules were sealed under N_2, warmed to 44 ± 0.2 °C, and then opened at convenient intervals. Each of the reaction mixtures was worked up as usual and chromatographed on silica gel by using petroleum ether–benzene (1:1), and the colorless oil obtained was analyzed on a 200-MHz ^{1}H NMR spectrometer measuring the areas of the signals of H-7 of **12** [δ 2.73 (t, J = 5.5)], H-7 of **13** [δ 2.36 (t, J = 6.9)], H-7 of **14** [δ 2.33 (t, J = 6.8)], and H-7 or **15** [δ 2.61 (d, J = 7.0)].

When warmed to 44 °C for 55 h in *tert*-butyl alcohol, **12** remained completely unchanged.

A solution of **12** (454 mg, 2.7 mmol) and DIPEA (1.39 g, 10.8 mmol) in dry acetonitrile (4.8 mL) was heated to 72 °C for 77 h, and the reaction product was subjected to ^{1}H NMR spectral examination, showing that **12** remained unchanged, except for a faint appearance of a triplet at δ 2.33 arising from H-7 of the thermal isomerization product, **14**.

Deuteriation of Cyanocycloheptatrienide Anion Prepared from 3 and LDA. 7-Cyanocycloheptatriene-7-d_1 (3d). To a stirred solution of diisoproylamine (1.776 g, 17.58 mmol) in THF (15 mL) was added dropwise a solution of *n*-butyllithium in dry ether (17.6 mmol/15 mL of ether) at −30 °C under N_2. After being stirred for 30 min at −30 °C and then for 30 min at 0 °C, the solution was cooled again to −78 °C followed by the addition of a solution of **3** (1.714 g, 14.65 mmol) in THF (2 mL). The resulting green solution was stirred for 1 h at −78 °C, quenched with a mixture of D_2O and THF (1:1), and then further stirred for 1.5 h. The resulting mixture was neutralized with 5% HCl, extracted with ether, and the ether extracts were washed with brine and dried over $MgSO_4$. Solvent evaporation and chromatography of the residue on silica gel by eluting with petroleum ether–benzene (1:1) gave a colorless oil (1.21 g, 70%). The ^{1}H NMR spectrum of this oil showed a very small triplet at δ 3.00 arising from H-7 of **3** and the signals for olefinic hydrogens of **3d**: ($CDCl_3$) δ 5.38 (dd, J = 9.5 and 1.2, H-1,6), 6.28 (ddd, J = 9.5, 3.0, and 1.2, H-2,5), 6.74 (dd, J = 3.0, 2.5 (J(4,2) and J(3,5)), and 1.2 (J(1,3) and J(4,6)), H-3,4). From the averages of the several integrations of these regions, the deuterium content of **3d** was determined to be 0.85 atom of deuterium per molecule. The deuterium content was also calculated on a mass spectrometer from the relative peak intensities of m/e 117 and 118 at 8 eV, giving **3d** (85%) and **3** (15%). A higher deuterium concentration of **3d**, 0.92–0.99 atom of deuterium per molecule, was achieved by the repeated deprotonation with LDA followed by quenching with D_2O.

Ethylation of Cyanocycloheptatrienide Anion Prepared from 3 and LDA. 7-Cyano-7-ethylcycloheptatriene (16). To a stirred solution of LDA prepared from diisopropylamine (12.8 mmol), *n*-butyllithium (12.8 mmol), and THF (8.6 mL) was added a solution of **3** (1.251 g, 10.69 mmol) in THF (3.7 mL) at −48 °C,

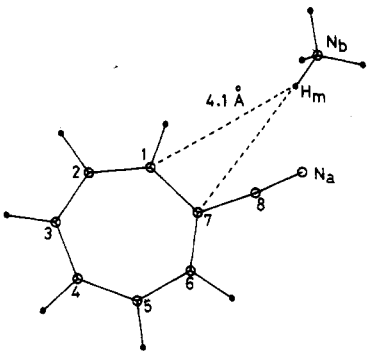


Figure 5. Geometric drawing for the ion-paired carbanion in the 1,2-(1,7-)migration in 7-cyanocycloheptatriene.

the resulting solution was stirred for 1.5 h at −48 °C, HMPA (2.2 mL) and ethyl iodide (4.99 g, 32.1 mmol) were added, and the resulting solution was again stirred for 30 min at −28 °C and then for 5 h at room temperature. The reaction mixture was worked up as usual to give a colorless oil, **16** (724 mg, 47%), which was purified for an analytical sample by vacuum distillation: bp 55–56 °C (1.5 mmHg); IR (neat) 3025, 2975, 2935, 2225, 1460, 1438, 1380, 1141, 1130, 1000, 950, 743, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (3 H, t, Me), 1.95 (2 H, q, CH_2), 4.84 (2 H, d, J = 8.0, H-1,6), 6.28 (2 H, ddd, H-2,5), 6.70 (2 H, dd, H-3,4); mass spectrum, m/e (relative intensity) 145 (23), 117 (62), 116 (100), 103 (39), 91 (46), 90 (13.5); UV λ_{max} (MeCN) 259 nm (ϵ 4270). Anal. Calcd for $C_{10}H_{11}N$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.91; H, 8.47; N, 9.49.

Deuteriation of Cyanocycloheptatrienide Anion Prepared from 4 and LDA. To a stirred LDA solution prepared from diisopropylamine (719 mg, 7.12 mmol), *n*-butyllithium (7.12 mmol/6.0 mL of ether), and THF (4.5 mL) was added a solution of **4** (694 mg, 5.9 mmol) in THF (2 mL) at −78 °C. After 30 min, the resulting reddish orange solution was quenched with 2 mL of a mixture of D_2O and THF (1:1). The reaction mixutre was maintained at −78 °C for 1 h, allowed to warm to room temperature, and then worked up in a similar manner to that described above to produce a colorless oil (200 mg, 29%). The ^1H NMR (200 MHz) spectral examination proved that this oil was a mixture of **3d** and **4** (recovery), not being contaminated with **4d**, in which the integration ratio at the region of a triplet at δ 2.47 (H-7 of **4**) to that at δ 6.11 (H-1 of **4**) was 2.0:1.0. The averages of the integrations obtained from several scans at the regions of the signals for H-7 of **4** and for olefinic hydrogens of **4** and **3d** gave $2y/(6x + 5y) = 24/95.5$, where x and y are the molar percentages of **3d** and **4**, respectively: **3d**, 33%; **4**, 67%.

Protonation of Cyanocycloheptatrienide Anion Prepared from 4 and LDA. To a stirred LDA solution prepared from diisopropylamine (104 mg, 1.03 mmol), *n*-butyllithium (1.03 mmol/0.6 mL of hexane), and THF (2.0 mL) was added a solution of **4** (100 mg, 0.85 mmol) in THF (2.0 mL) at −78 °C, and after 1 h, the solution was quenched with 2 mL of a mixture of H_2O and THF (1:1). A colorless oil (22 mg, 22%) was obtained by a similar workup to that given above. In the ^1H NMR spectrum of this oil, the areas of signals for δ 3.00 (H-7 of **3**) and 2.39 (H-7 of **4**) were 10.0 and 18.0, respectively, thus giving the following: **3**, 36%; **4**, 64%.

Ethylation of Cyanocycloheptatrienide Anion Prepared from 4 and LDA. To a solution of lithium cyanocycloheptatrienide, prepared in the same method as above using **4** (926 mg, 7.91 mmol) and LDA (9.5 mmol), were added HMPA (2 mL) and then ethyl iodide (3.72 g, 23.7 mmol) at −78 °C. After being stirred for 30 min, the resulting solution was warmed to room temperature and then worked up as usual to give a colorless oil. Purification on silica gel (petroleum ether–benzene) gave **16** (111 mg, 12%) together with the recovery of **4** (174 mg).

Intramolecularity in a Base-Catalyzed Isomerization of 3d to 4d. Run 1 in Table V. A solution of **3d** (237 mg, 2.0 mmol), tri-*n*-propylamine (3.3 mL, 17.4 mmol), *t*-BuOH (4.12 mL, 43.7 mmol), and tri-*n*-propylammonium iodide (542.36 mg, 2.0 mmol) in THF was placed in a volumetric flask, and the volume was adjusted to 30 mL with addition of THF. After the volumetric flask had been shaken, the mixture was placed in an ampule and frozen in a liquid N_2 bath under vacuum (5×10^{-4} mmHg). Melting and freezing were repeated until a volatile solute was no longer detectable. The ampule was then sealed, warmed to 72 ± 0.2 °C, and kept at this temperature for 19.5 h. The reaction products obtained by the usual workup were submitted to ^1H NMR measurement. From the integrated areas of the signals of H-7 of **3** (δ 3.00) and H-7's of **4** and **4d** (δ 2.39), $y/(z + 2w)$ = 5.8/35.7 were obtained, where y, z, and w are the molar percentages of **3**, **4d**, and **4**, respectively. Then the mixture of **3** and **3d** was separated from the mixture of **4** and **4d** by HPLC (Lichrosorb–hexane) and each of the mixtures was submitted again to the 200-MHz ^1H NMR measurement. The integrated areas of the signals for H-7 and all olefinic protons of the mixture **3** + **3d** were recorded to be 32.6 and 373.5, respectively, giving $y/(6x + 6y) = 32.6/373.5$, where x is the molar percentages of **3d**. The integrated areas of the signals for H-7 and H-1 of the mixture **4** + **4d** were recorded to be 82.0 and 60.8, respectively, giving $(z + 2w)/(z + w) = 82.0/60.8$. Thus the following obtains: **3d**, 14%; **3**, 18%; **4**, 24%; **4d**, 45%. Intramolecularity: $4d/(4 + 4d) \times 100$ = 65%.

Other runs in Table V were carried out, and the content of the components was determined in a similar manner to that described above, but the deuterium concentration of substrate **3d** (0.92% of 1 atom of deuterium per molecule) was not corrected for the calculation. Therefore the corrected intramolecularities should be slightly higher than the values listed in the table. The intramolecularity was also observed when D_2O or H_2O was used as an isotopic pool instead of *t*-BuOD or *t*-BuOH in run 5 or 1 in Table V but in a lower extent.

Treatment of 3 with DIPEA in the Presence of Ethyl Iodide. An acetonitrile solution of **3** (0.597 g), DIPEA (1.329 g), and ethyl iodide (0.796 g) was placed in a 10-mL volumetric flask, and the volume was exactly adjusted with additional acetonitrile. The resulting solution was warmed to 72 °C for 12 h under N_2 without any detectable formation of cycloheptatriene derivative except for **4**. Ethyl iodide (1.5 M) was dissolved in the same medium as that of run 4 in Table V, and the resulting mixture was stirred at 72 °C for 20 h. But any compound other than **3** and **4** was not detected on ^1H NMR spectrum or on HPLC.

Treatment of 3 with DIPEA in the Presence of 1-Ethoxy-2,3-diphenylcyclopropenium Ion. To a solution of **3** (300 mg, 2.56 mmol) and 1-ethoxy-2,3-diphenylcyclopropenium fluoroborate (879 mg, 2.7 mmol) in acetonitrile (3 mL) was added a solution of DIPEA (697 mg, 5.4 mmol) in acetonitrile (1 mL), and the resulting mixture was stirred at room temperature for 10.5 h under N_2. The solvent was evaporated, benzene (14 mL) was added, the percipitate formed was removed by filtration, the filtrate was evaporated, and the residual oil was chromatographed on silica gel by using petroleum ether–benzene (1:1) to give a mixture of **3** + **4** (5:2) and 7-cyano-7-(2-ethoxy-1,3-diphenylcycloprop-2-en-1-yl)cycloheptatriene **17** (96 mg, 21%): a pasty oil; IR (neat) 3080, 3040, 2225, 1865, 1600, 1478, 1049, 752, 731, 672 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.04 (2 H, br t, J = 3.0, H-1,6), 6.19 (2 H, m, H-2,5), 6.35 (2 H, m, H-3,4), 1.40 (3 H, t, J = 7.0, Me), 4.36 (2 H, q, J = 7.0, CH_2), 7.10–7.60 (10 H, m, Ph); mass spectrum, m/e (relative intensity) 351 (45), 322 (46), 244 (59), 216 (100); UV λ_{max} (MeOH) 267 nm (ϵ 12 400). Anal. Calcd for $C_{25}H_{21}NO$: C, 85.44; H, 6.02; N, 3.99. Found: C, 85.18; H, 6.24; N, 3.82.

Acknowledgment. This work was supported by a Grant-in-aid from the Ministry of Education, Science and Culture, Japan. We thank Kazuo Sasaki of Tohoku University, Instrumental Analysis Center for Chemistry, for measurement of ^1H NMR spectra at 200 MHz.

Registry No. **3**, 13612-59-4; **4**, 19052-84-7; **6**, 13612-31-2; **7**, 108418-31-1; **8**, 108418-32-2; **9**, 4440-40-8; **10**, 26902-51-2; **12**, 1541-11-3; **13**, 1541-15-7; **16**, 79574-40-6; **17**, 79574-43-9; propene, 115-07-1.

Supplementary Material Available: Optimized geometry, net atomic charges at the 6-31G level (Table VI), and atomic coordinates for the transient hydrogen bond bridged allyl anion (Table VII) and atomic coordinates for the transition state of the 1,3-hydrogen shift in 7-cyanocycloheptatriene (Table VIII) (3 pages). Ordering information is given on any current masthead page.