Preparation of (Z)-2-Butanone Imines. The following procedure was used for the preparation of all (Z)-2-butanone imines. To 2 mL of a solution of 1 N "clean" LDA base[15] in THF at -78 °C in an NMR tube was added 1.8 mmol of an acetone imine (vortex stirring). Benzene-d_6 (0.2 mL) was added and the deprotonation reaction was followed by ^{13}C NMR spectroscopy at ca. -80 °C. After complete deprotonation (ca. 30 min), the NMR tube was maintained at -78 °C and the mixture was treated with 0.45 mL of 5 M iodomethane in THF (for ^{13}C NMR studies 30% ^{13}C-enriched iodomethane was used). The resulting solution of (Z)-2-butanone imine was assayed by ^{13}C NMR spectroscopy at -80 °C. The solutions were maintained at -78 °C until they were used in further studies.

Regioselectivity Studies. Solutions of LDA and LDEA in THF were prepared by adding 0.9 molar equivs of *n*-butyllithium in hexane (Aldrich) to the appropriate amine (distilled from CaH_2 and stored over 4A molecular sieves under argon) in THF (freshly distilled from potassium/benzophenone) at -78 °C followed by warming to 0 °C for 10 min. The base solutions (15-18 mL) were ca. 0.1-0.5 N in lithium dialkylamide in these various studies. Base solutions were equilibrated at the appropriate temperature, and the appropriate 2-butanone imine and a hydrocarbon standard were added via syringe. Aliquots (ca. 0.5 mL) of the reaction mixtures were transferred to flasks at -78 °C and treated with excess iodomethane. Products were identified by comparison of their GC retention times to those of authentic product imines prepared separately from the appropriate amine and ketone. GC yields were high (typically 95-105%). In several cases where the 3-pentanone imine products were formed >90% yield, the reaction mixture was treated with water, the mixture was distributed between ether and water, the resulting organic phase was dried ($MgSO_4$), and the solvent was removed at reduced pressure. The resulting residue was examined by ^1H NMR spectroscopy to confirm the identity of the 3-pentanone imine products.

Rates of Deprotonation. Clean 1 N LDA solutions were prepared[15] and then diluted to the desired concentrations. The base solutions were equilibrated at the appropriate temperature, and the 2-butanone imines and a hydrocarbon standard were added via syringe. At various times aliquots of the reaction mixtures were removed and methylated, and the resulting products were analyzed by GC by the methods described above in the regioselectivity studies. In the deprotonations which occurred over several hours, relatively smooth first-order conversions were observed from at least 20-80% completion. The results of these rate studies are given in Table I.

Isomerization Studies. Clean 1 N LDA solutions were used for the preparation of 30% ^{13}C-enriched (Z)-[4-^{13}C]-2-butanone imines at -78 °C as described above. For studies of the effects of azaallyllithium reagents **3**, an insufficient amount of iodomethane was used in the alkylation reaction. The mixtures were warmed to the desired temperatures in the probe of the NMR spectrometer and ^1H-decoupled ^{13}C NMR spectra were recorded periodically. The heights of the peaks from the labeled positions of the butanone imines were compared to determine the amounts of the *E* and *Z* isomers. The results of these experiments are presented in Table II. Because of the accumulated errors of successive volumetric transfers, we estimate that the calculated concentrations of **3** may be in error by as much as 0.1 N. The $t_{1/2}$'s reported in Table II are the times at which a 1:1 mixture of *E* and *Z* isomers was present. In none of the studies was there observed a signal from the azaallyllithium reagents **1** or **2** which would form by deprotonation of the 2-butanone imines by **3**. Separate experiments however showed that this latter deprotonation reaction is facile at room temperature and thus remains a possible mechanism for the observed isomerization catalyzed by **3** at low temperatures.

Acknowledgment. The Robert A. Welch Foundation and the National Institutes of Health (Grant GM-26268) are thanked for their support of this research.

Registry No. (*E*)-$CH_3CH_2C(CH_3)$=N-*t*-C_4H_9, 77390-50-2; (*E*)-$CH_3CH_2C(CH_3)$=N-c-C_6H_{11}, 55969-52-3; (*E*)-$CH_3CH_2C(CH_3)$=NPh, 72037-54-8; (*E*)-$CH_3CH_2C(CH_3)$=NCH_2Ph, 72037-48-0; (*E*)-$CH_3CH_2(CH_3)$=$N(CH_2)_3CH_3$, 85629-19-2; (*Z*)-$CH_3CH_2C(CH_3)$=N-*t*-C_4H_9, 77390-51-3; (*Z*)-$CH_3CH_2C(CH_3)$=N-c-C_6H_{11}, 55969-53-4; (*Z*)-$CH_3CH_2C(CH_3)$=NPh, 75250-70-3; (*Z*)-$CH_3CH_2C(CH_3)$=NCH_2Ph, 77390-49-9; (*Z*)-$CH_3CH_2C(CH_3)$=$N(CH_2)_3CH_3$, 85629-20-5; $(CH_3)_2C$=$N(CH_2)_3CH_3$, 6700-95-4; $(CH_3)_2C$=NCH_2Ph, 1197-48-4; $(CH_3)_2C$=NPh, 1124-52-3; $(CH_3)_2C$=N-c-C_6H_{11}, 6407-36-9; $(CH_3)_2C$=N-*t*-C_4H_9, 66548-20-7; $(CH_3)_2CHC(CH_3)$=$N(CH_2)_3CH_3$, 85629-21-6; $(CH_3)_2CHC(CH_3)$=NCH_2Ph, 62453-12-7; $(CH_3)_2CHC(CH_3)$=NPh, 74265-71-7; $(CH_3)_2CHC(CH_3)$=N-c-C_6H_{11}, 39139-90-7; $(CH_3)_2CHC(CH_3)$=N-*t*-C_4H_9, 57808-25-0; LDA, 4111-54-0; LDEA, 816-43-3; 3-pentanone, 96-22-0; *tert*-butylamine, 75-64-9; cyclohexylamine, 108-91-8; *n*-butyllithium, 109-72-8; diethylamine, 109-89-7; diisopropylamine, 108-18-9.

(30) **Note Added in Proof**: Methods for obtaining high regioselectivity in deprotonations of highly substituted ketimines have been established: Smith, J. K.; Newcomb, M.; Bergbreiter, D. E.; Williams, D. R.; Meyers, A. I. *Tetrahedron Lett.*, submitted for publication.

Cyclopropylidene Rearrangement in the Reduction of 1,2:3,4-Bis(dihalomethano)-1,2,3,4-tetrahydropolymethylnaphthalenes by Naphthalenides

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Contribution from the Department of Chemistry, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan. *Received April 19, 1982*

Abstract: The reduction of octamethyl-substituted title compound (**1a**) with Na naphthalene in THF at -70 °C afforded 1,2:3,4-diethylideno-1,2,3,4-tetrahydro-2,3,5,6,7,8-hexamethylnaphthalene (**2a**, 75%), whereas at 25 °C a mixture of 1,2,3,4,5,7,8,9-octamethylbenzocyclooctene (**5a**) and 2,3,5,6,7,8,9-heptamethyl-1-ethylideno-1*H*-benzocycloheptene (**4a**) but not **2a** was formed. The structure of **2a** was determined by its oxidation with OsO_4 to 1,2,3,4,6,7-hexamethylnaphthalene. The formation of **2a** is explained in terms of a cyclopropylidene rearrangement. The reaction was facilitated at low temperatures by the use of Na or K naphthalene and was also dependent upon the change of solvent, halogen, and more significantly the substituents of the starting compound. Title compounds bearing methyl groups at 1,2,3,4,5,6,7,8-, 1,2,3,4,5,8-, 1,2,3,4,5,6-, and 1,2,3,4,5-positions underwent the rearrangement whereas those bearing methyl groups at 1,4,5,6,7,8-, 1,2,3,4,6,7-, 1,2,3,4-, and 1,4,5,8-positions did not. Thus, structural requisites for the rearrangement are the presence of two methyl groups at paired peri positions and also the presence of cyclopropane *cis*-dimethyl substitutents, which as discussed with the aid of crystallographic analysis, accumulate steric strain around the peri position but release it by shifting the aryl group to a carbene center. The formation of **4** and **5** is explained in terms of ring opening of the intervening α-halocyclopropyl anion followed by carbene rearrangements.

It has commonly been held that the electron-transfer reduction of organic halides RX proceeds by a stepwise mechanism via the free radical R· and its anion $R:^-$.[1] When this general mechanism is applied to *gem*-dihalides, the indispensable intermediate is an

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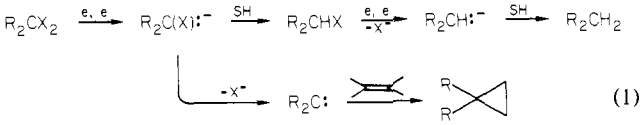
α-halocarbanion. Here, if the protonation (or hydrogen abstraction) takes place in the same way as in the case of the monohalides, the first intermediate produced should be a monohalide (eq 1). One also expects the competitive generation of carbene



(1)

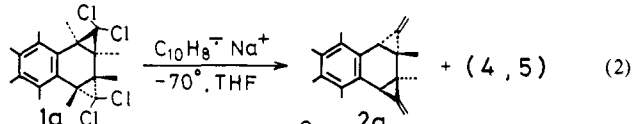
from the halocarbanion. In fact, several examples of the generation of carbenes from *gem*-dihaloalkanes under aprotic conditions have been reported.[2] However, the generation of a cyclopropylidene intermediate has only recently been reported by us in the naphthalenide reduction of *gem*-dihalocyclopropanes.[3]

A literature survey of carbene rearrangements shows that none of the aryl or alkyl migrations to the adjacent electron-deficient cyclopropylidene center has been reported,[4] probably due to the formation of a highly strained cyclopropene skeleton and also due to the rapid isomerization to allenes. In the course of studying the electron-transfer reduction of organic halides with aromatic radical anions or solvated electrons in amines, we have found a novel cyclopropylidene rearrangement that takes place in bis(*gem*-dihalocyclopropane) systems. This rearrangement is noteworthy in that it is sensitive to the change of medium polarity as well as acidity, to the change of cations as well as temperature, and also to the structural change of the substrate, thus informing us about the general character of α-halocyclopropyl anions. Also worthy of mention is that the driving force of the rearrangement has been proved attributable not simply to the carbene generation but also to the steric effect accumulated in the substrate structure.

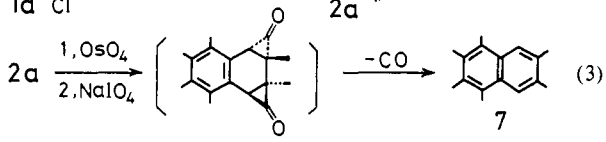
In the present report, the novel character of this rearrangement will be clarified in detail in terms of structural effects and α-halocyclopropyl anion chemistry.

Results

When compound **1a**, which can be prepared through the reaction of octamethylnaphthalene with dihalocarbene,[5] was treated with sodium naphthalene in tetrahydrofuran (THF) at −70 °C, rearrangement product **2a** was obtained (75%) besides small amounts of byproducts **4** and **5** (eq 2).



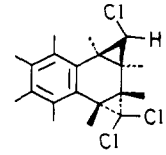
(2)



(3)

The NMR spectrum of **2a** simply shows the existence of one aliphatic and two aromatic methyl groups and also methine and vinylic *exo*-methylene protons. We assumed structure **2a** and confirmed this by oxidation with osmium tetraoxide followed by treatment with sodium periodate to yield 1,2,3,4,6,7-hexamethylnaphthalene (**7**, 35%; eq 3). Since the isomerization of 1,2,3,4,5,8-hexamethylnaphthalene to **7** did not take place under the same conditions,[6] the structure **2a**, as opposed to its 1,4,5,6,7,8-hexamethyl isomer, is proven to be correct. In producing structure **2a**, it must be noted that four chlorine atoms are removed from **1a** without introducing any additional hydrogen atom and that the amount of reductant necessary to complete this rearrangement was about 4–6 mol equiv. These observations are compatible with a carbene mechanism for the removal of chlorines.

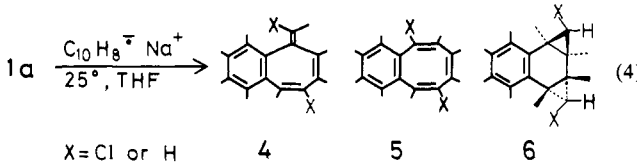
When the reduction mixture was quenched by water after 1 mol equiv of the reductant was added, compound **3** (formed from



3

the corresponding exo carbanion) was isolated as the initially formed intermediate before the formation of **2a** became detectable: the amount of **3** decreased as **2a** increased with the addition of further reductant (Experimental Section).

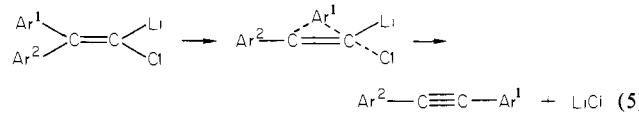
The reaction behavior of **1a** is influenced significantly by the temperature. When the reaction was carried out at ambient temperature, ring-enlarged products **4a** (X = H, 55%) and **5a** (X = H, 35%) were formed, but **2a** was not detected (eq 4). Products



(4)

4a and **5a** (X = Cl) were also isolated from the reaction at −70 °C and treated independently with naphthalenide to give final products **4** and **5** (X = H).

In carbenoid chemistry, the reaction that is called Fritsch–Buttenberg–Wiechell rearrangement (F–B–W)[7] has been known to involve a carbene-like rearrangement (eq 5). In this reaction



(5)

the aryl group bearing an electron-donating group rearranges faster onto the carbenoid carbon to give an acetylenic product via a S_N-type transition state.[8] If the rearrangement we have found proceeds like the F–B–W mechanism, we would expect that aryl methyl groups at the ortho or para positions to the migrating bond will favor the rearrangement but the meta methyl will not. To verify this possibility, several compounds where methyl groups are properly situated for this examination were prepared.

Among eight polymethylnaphthalene–dichlorocarbene adducts examined, four compounds—octamethylnaphthalene–, 1,2,3,4,5,8- and 1,2,3,4,5,6-hexamethylnaphthalene-, and 1,2,3,4,5-pentamethylnaphthalene–dichlorocarbene adducts (**1a–d**)—treated with naphthalenide gave the corresponding rearrangement products,[9] whereas 1,2,3,4,6,7- and 1,4,5,6,7,8-hexamethylnaphthalene and 1,2,3,4- and 1,4,5,8-tetramethylnaphthalene adducts (**1e–h**) did not. Thus, the aromatic methyl substitution that facilitates the rearrangement does not necessarily exist at the para position to the shifting bond, and a greater number of methyl substituents are not necessarily required for the rearrangement.

The reaction is affected by the change of solvent polarity and kinds of halogen and alkali metals (see Table I). When we carried out the reaction of dibromocarbene adduct **1i**[10] with sodium

(1) Baizer, M. M. "Organic Electrochemistry"; Baizer, M. M., Ed.; Marcel Dekker: New York, 1973; pp 256, 683.

(2) For example: (a) Sargent, G. D.; Tatum, C. M., Jr.; Kastner, S. M. *J. Am. Chem. Soc.* **1972**, *94*, 7174. (b) Sargent, G. D.; Tatum, C. M., Jr.; Scott, R. P. *Ibid.* **1974**, *96*, 1602.

(3) (a) Oku, A.; Yagi, K. *J. Am. Chem. Soc.* **1974**, *96*, 1966. (b) Oku, A.; Tsuji, H.; Yoshida, M.; Yoshiura, N. *Ibid.* **1981**, *103*, 1244.

(4) The following reviews do not include the 1,2-migration onto cyclopropylidenes: (a) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971; p 462. (b) Jones, M., Jr.; Moss, R. A. "Carbenes"; Wiley: New York, 1973, 1975; Vol. 1, 2. (c) Noyori, R. "Carbenes, Ylides, Nitrenes, and Benzynes"; Goto, T., Ed.; Hirokawa: Tokyo, 1976; pp 1–186.

(5) (a) Oku, A.; Hino, T.; Matsumoto, K. *J. Org. Chem.* **1975**, *40*, 695. (b) Weyerstahl, P.; Blume, G. *Tetrahedron* **1972**, *28*, 5281. (c) The proof of transoid disposition of two *gem*-dibromocyclopropane rings is important for the establishment of the rearrangement mechanism. Other dichlorocarbene adducts are supposed to have the same geometry as **1i**.

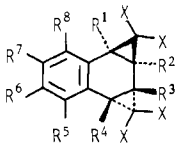
(6) Oku, A.; Yuzen, Y. *J. Org. Chem.* **1975**, *40*, 3850.

(7) (a) Reference 4a, p 103. (b) Köbrich, G. *Angew. Chem.* **1965**, *77*, 75.

(8) (a) Sargent, P. B.; Shechter, H. *Tetrahedron Lett.* **1964**, 3957. (b) Landgrebe, J. A.; Kirk, A. G. *J. Org. Chem.* **1967**, *32*, 3499.

(9) It must be noted that the rearrangement products always had two cyclopropane rings rearranged and half rearranged products were not formed except for **1c**: half rearranged product with a structure corresponding to **14** (X = Cl and H) was isolated in 8% yield; see Experimental Section.

(10) Hart, H.; Oku, A. *J. Org. Chem.* **1972**, *37*, 4269.



1a, R^1-R^8 = Me; X = Cl
b, R^1-R^5, R^8 = Me; X = Cl
c, R^1-R^6 = Me; X = Cl
d, R^1-R^5 = Me; X = Cl
e, R^1-R^4, R^6, R^7 = Me; X = Cl
f, R^1, R^4, R^5-R^8 = Me; X = Cl
g, R^1-R^4 = Me; X = Cl
h, R^1, R^4, R^5, R^8 = Me; X = Cl
i, R^1-R^8 = Me; X = Br

naphthalene in THF (entry 3, Table I), the only product isolated was the rearrangement product **2a**. However, the same reaction in 1,2-dimethoxyethane (DME; entry 4) caused the production of the parent hydrocarbon **6** (X = H) in low yield besides **2a**, but the mixing of a nonpolar solvent such as cumene suppressed the formation of **6** (entries 6 and 7). A remarkable change in product distribution was shown when potassium naphthalene was adopted instead of sodium naphthalene in the reduction of **1i** (X = Br), thus the yield of **6** (X = H) increased while that of **2a** remained unchanged (entry 5). Under the presence of a protic compound such as 2-propanol or *tert*-butyl alcohol in the reaction of **1i** with potassium naphthalene (entry 8), the in situ quenching of α-halocyclopropyl anion intermediates took place to give half-reduced products **6** (X = Br) but not **2a**. The reduction with lithium naphthalene was somewhat different from other reductions: neither **2a** nor **6** (X = H) but a mixture of half-reduced products such as **6** (X = Cl) was produced.[11] In contrast to naphthalenide reductions, the reduction of **1a** with a deficient amount of sodium metal in liquid ammonia did not give **2a** and resulted in the exclusive conversion of the reacted **1** to **6** (X = H)[12] even in the absence of alcohols (entries 10 and 11).

Discussion

How are these rearrangement products formed? Taking **2a** for example, the above-mentioned characteristics of the reaction with regard to the product structure **2** and the stoichiometry tell us that a carbene mechanism is the sole reaction channel, which rationally explains the results (Scheme I). Under electron-transfer conditions, α-halocyclopropyl anion **8** must be the indispensable intermediate formed by a stepwise two-electron reduction of **1a**. This anion, under aprotic conditions, hardly accepts proton from the solvent but generates cyclopropylidene **9** at a low temperature. Carbene **9** immediately undergoes the rearrangement, in which bond a migrates to the carbene center (aryl shift, vide infra) to give a cyclopropene intermediate **10**, which in turn undergoes a base-induced isomerization to yield the *exo*-methylenecyclopropane compound **2**.[13] Under the presence of an olefin (2,3-dimethyl-2-butene or cyclohexene) the formation of neither allene derivatives (**11**)[14] nor cyclopropanation products (**12**) was observed.

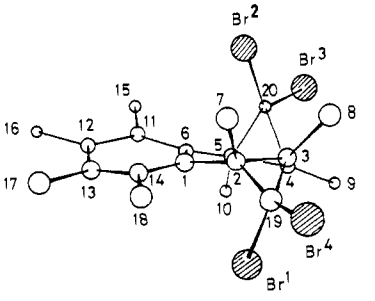
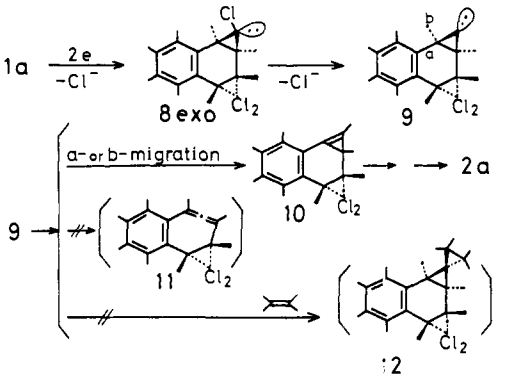


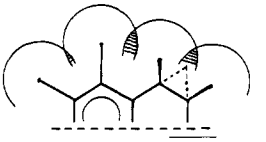
Figure 1. Edge-on view of crystallographic structure of **1i**.

Scheme I



Therefore, it is likely that the generation of **9** and the bond migration take place almost concurrently.

Structural Limitation of the Rearrangement. The requisites of methyl substitution for the rearrangement are two: (1) the existence of two methyl groups at least at paired peri positions (1,8- and/or 4,5-dimethyl groups); (2) the existence of a methyl group at the other side of the cyclopropane ring coupled with the above requirement 1. Additionally, the existence of aromatic methyl group(s) coupled with the peri substitution facilitates the rearrangement. Thus, hexamethyl compounds **1b** and **1c** showed the rearrangement, whereas **1e** and **1f** did not. These observations evidently rule out the F–B–W polar mechanism[8] through which **1f** or **1h** should have rearranged much more easily than **1b** or **1d**, respectively. Therefore, we concluded that the release of a steric strain that is accumulated not only around peri positions and cyclopropane rings, as illustrated by **13**, but also in the nonplanar aromatic ring (see Figure 1) is the driving force of this rearrangement.



13

The repulsive interaction at the peri position of a naphthalene nucleus has been known in a variety of systems.[15] The crystal structure of octachloronaphthalene[16] informs us that the plane of the nucleus is twisted like a double-bladed propeller structure and that peri methyls are pushed aside toward β-positions increasing the buttress effect of β-methyl groups. Similarly the crystallogram of octamethylnaphthalene–bis(dibromocarbene) adduct (**1i**, Figure 1) shows,[17] in addition to the proof of transoid configuration of the two cyclopropane rings, that (1) the plane of aromatic nucleus is twisted to some extent, (2) the interatomic distances between two methyl carbon atoms at paired peri positions and also between two methyl carbon atoms at a cyclopropane ring are as short as 2.95–3.15 Å, indicating that these methyl groups

(11) The 7-Cl-7-Li-norcarane-type lithium carbenoid seems to be a stable intermediate like vinylidene analogues: (a) Köbrich, G.; Drischel, W. *Angew. Chem.* **1965**, *77*, 95. (b) Köbrich, G. *Tetrahedron* **1966**, *22*, 2621.

(12) Usually, the electron transfer from naphthalenides or solvated electrons in ammonia to halides takes place within the period of reagent mixing: (a) Oku, A.; Yoshiura, N.; Okuda, T. *J. Org. Chem.* **1983**, *48*, 615. (b) Tremelling, M. J.; Bunnett, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 7377. (c) Bard, R. R.; Bunnett, J. F.; Greary, X.; Tremelling, M. J. *Ibid.* **1980**, *102*, 2852. (d) Reference 3b; the exclusive formation of **6** (X = H) was found to be attributable not to the relay effect but to a rapid and consecutive electron transfer that takes place in the vicinity of the added reductant, because the reduction of 1,2-bis(*gem*-dihalocyclopropyl)ethane with sodium in ammonia showed results similar to **1**.

(13) Schroeder, G. *Chem. Ber.* **1963**, *96*, 3178.

(14) (a) Jones, W. M.; Grasley, M. H.; Baarda, D. G. *J. Am. Chem. Soc.* **1964**, *86*, 912. (b) Bond, F. T.; Bradway, D. E. *Ibid.* **1965**, *87*, 4977. In the present study, however, the addition of cyclopropylidene to the central bond would produce a highly strained cyclic seven-membered allene and therefore seems unlikely to occur. Intramolecular C–H insertion, which was the case in a number of studies, was not observed, e.g.: Paquette, L.; Chamot, E.; Browne, A. R. *Ibid.* **1980**, *102*, 637.

(15) For a review, see: Balasubramanian, V. *Chem. Rev.* **1966**, *66*, 567.

(16) (a) Donaldson, D. M.; Robertson, J. M. *J. Chem. Soc.* **1953**, 17. (b) Gafner, G.; Herbstein, F. H. *Nature (London)* **1963**, *200*, 130.

(17) See supplementary materials for the crystallographic data.

Table I. Reduction of 1 with $C_{10}H_8^{-\cdot}$ or Alkali Metal in NH_3[a]

entry	compd	reductant[b] (molar ratio to 1)	solvt[d]	product yield, %[c] 1	2	6 (X = H)	6 (X = Cl)
1	1a	Na naph (4)	THF	0	75	0	0
2	1a	K naph (6)	THF	0	89	0	0
3	1i	Na naph (4)	THF	e	44	0	0
4	1i	Na naph (4)	DME	e	40	5	0
5	1i	K naph (6)	THF	15	45	30	0
6	1i	K naph (6)	DME	24	16	38	0
7	1i	K naph (6)	DME, cumene[f]	50	25	25	0
8	1i	K naph (6)	THF, 2-PrOH[g]	0	0	78	18
9	1i	Na (6)	NH_3/THF, EtOH[h]	32	0	68	0
10	1a	Na (4)	NH_3/THF	57	0	43	0
11	1a	Na (4)	NH_3/THF, EtOH	50	0	50	0
12	1d	Na (4)	NH_3/THF, EtOH	57	0	43	i
13	1g	Na (4)	NH_3/THF, EtOH	62	0	38	i

[a] Temperature: −50 to −78 °C. [b] $C_{10}H_8^{-\cdot}$ was added to a solution of 1 at such a rate that the blue of the reductant was maintained. [c] Isolated yield for $C_{10}H_8^{-\cdot}$ reduction, determined by NMR and VPC for Na/NH_3 reduction. [d] NH_3/THF solvent ratio = 60/40, ROH/1 molar ratio = 20. [e] Not determined. [f] A 50:1 mixture (v/v) of DME and cumene-α-*d* was used. [g] A 100:1 mixture (v/v) of THF and 2-propanol-*O*-*d* was used. [h] See Experimental Section and also ref 12a. [i] A trace amount of 6 (X = Cl, <3%) was formed.

Table II. Selected Interatomic Distances (Å) for 1i[a]

C7–C8	3.154 (81)	Br1–C9	3.367 (142)
C7–C18	3.154 (124)	Br1–C10	3.831 (134)
C9–C10	2.948 (72)	Br2–C7	3.871 (138)
C10–C15	2.979 (118)	Br2–C8	3.590 (156)
C15–C16	2.989 (86)	Br3–C9	3.286 (155)
C16–C17	2.924 (105)	Br3–C10	3.336 (138)
C17–C18	2.933 (86)	Br4–C7	3.389 (139)
C8–C9	3.148 (90)	Br4–C8	3.117 (147)

[a] The values in parentheses are standard deviations in milliangstroms.

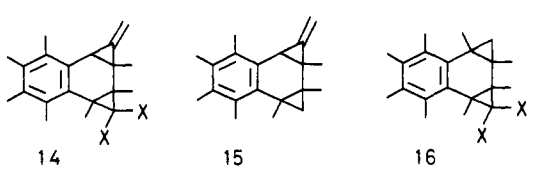
Table III. Selected Distances (Å) to the Plane from Individual Atoms

benzene ring[a] atom	dist	cyclohexane ring[b] atom	dist
C1	−0.104	C1	0.130
C6	0.088	C2	−0.044
C11	0.006	C3	−0.062
C12	−0.070	C4	0.075
C13	0.045	C5	0.021
C14	0.036	C6	−0.119
C15	−0.093		
C16	−0.191		
C17	0.201		
C18	0.253		

[a] Standard deviations of the defined atoms from the plane are 0.073 Å. [b] 0.093 Å.

are considerably compressed; (3) interatomic distances between the exo bromine and methyl carbons on a cyclopropane ring are as short as 3.12–3.39 Å (see Table II and III). Taking into account these steric effects,[18] the strength of strain in a series of **1** can be estimated approximately to be in the decreasing order **1a > 1b > 1c > 1d > 1f > 1h > 1e > 1g**: thus the first four compounds undergo the rearrangement but the rest do not.

The mechanistic ambiguity concerning the absence of half-reduced products[9] such as **14–16** seems to be attributable to a rapid

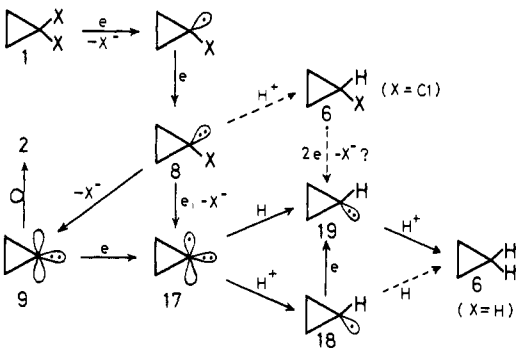


14 15 16

and consecutive electron transfer from naphthalenide to both

(18) The analogous effect of steric strain has been encountered in the acid-catalyzed rearrangement of polymethylnaphthalenes; see ref 6.

Scheme II



gem-dihalocyclopropane rings, occurring exothermically in the region of reagent mixing,[12] and a bis(α-halocyclopropyl anion) may be produced.

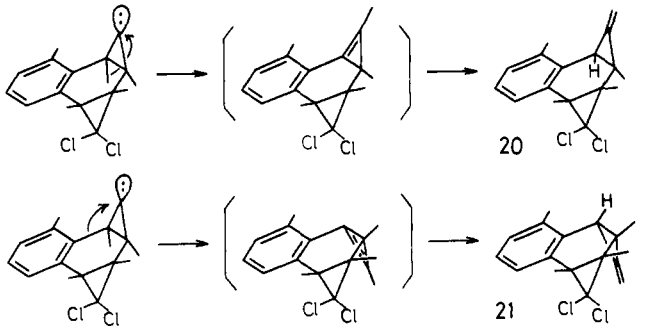
Effect of Solvent, Halogen, and Alkali Metal. The intermediacy of a cyclopropylidene (or its carbenoid) intermediate seems indispensable for the production of **2** (Scheme I), and its generation from **8** is favored over the protonation of **8** in aprotic solvents except for lithium carbenoid, which would be stable at low temperatures. However, when the ion pair of **8** becomes freer in DME than in THF (compare entries 5 and 6 in Table I) and freer with potassium cation than with sodium (entries 3 and 5) and when the halogen is bromine in place of chlorine (entries 2 and 5), the amount of product **6** (X = H) tends to increase relative to that of **2**. Most of these solvent and cation effects are known not only to facilitate the generation of carbenes but also to reinforce the reduction power of naphthalenide[19] and eventually will favor the formation of product **6** (X = H). Thus, an example of the exclusive formation of **6** (X = H) was demonstrated by the Birch-type reductions of **1a** (Table I, entries 9–13), and it can be interpreted in terms of a carbene radical anion mechanism[20] as shown in Scheme II: in ammonia the single electron transfer to **8** or to the vacant p orbital of cyclopropylidene **9** must take place faster than the bond migration.

Shifting Group. It has generally been held that aryl 1,2-migration to a carbene center is facilitated more than the alkyl migration in carbene rearrangements.[4a,b] In the present reaction, however, the rearrangement product **2** can be produced from

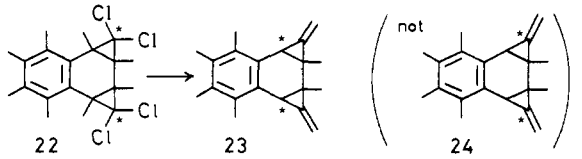
(19) (a) Szwarc, M. *Acc. Chem. Res.* **1972**, *5*, 167. (b) You, F. J.; Dorfman, L. M. *J. Chem. Phys.* **1973**, *58*, 4715.

(20) Carbene radical anion mechanisms have also been proposed in the reduction of *gem*-dihaloalkanes: (a) see ref 2a and 2b. (b) McDonald, R. N.; January, J. R.; Borhani, K. J.; Dale Hawley, M. *J. Am. Chem. Soc.* **1977**, *99*, 1268. (c) McDonald, R. N.; Borhani, K. J.; Dale Hawley, M. *Ibid.* **1978**, *100*, 995. (d) McDonald, R. N.; Lin, K.-W. *Ibid.* **1978**, *100*, 8028.

Scheme III



carbene **9** undergoing either methyl or aryl shift as shown in Scheme I. Here, we must notice that the migration of an aliphatic α-methyl group[21] can take place without reconstructing the initial cis-transoid–cis geometry of the tricyclo[5.1.0.0^{2,4}]octene ring to give **20** (Scheme III) and without reflecting the electronic effect of the aromatic methyl substituent on the transition state of the rearrangement (see eq 5). On the other hand, the aryl migration causes configurational change from a cis–transoid–cis to the highly strained cis–cisoid–cis form **21** and hence does not seem a strongly favored process. To clarify the choice of shifting group, ^{13}C-labeled **1a** (**22**, the content of ^{13}C in the dichloromethylene carbon was



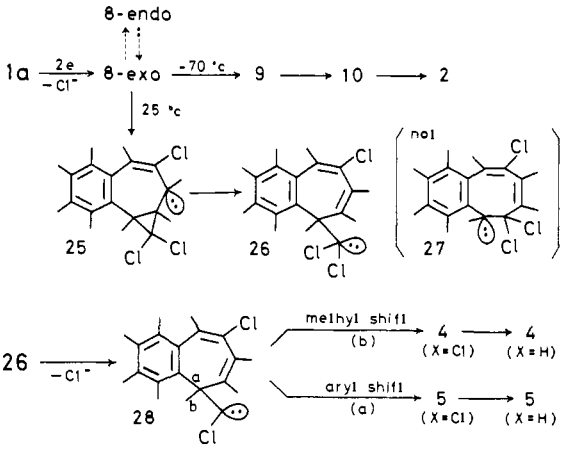
10%) was treated with sodium naphthalene under the rearrangement conditions. The isolated product **2a** was proved to hold the ^{13}C-enriched carbon exclusively at the cyclopropyl methine carbon (δ 26.7) and not at the quaternary olefinic carbon (one of four resonances between δ 128 and 146).[22] This finding evidently proves that the aryl group migration is the sole channel of the rearrangement.

Reaction Control by the Stereochemistry of α-Halocyclopropyl Anion. The stereochemistry of α-halocyclopropyl anion **8** should be discussed with regard to the exo/endo geometry of the anion because it must be playing an important role in controlling the course of the reaction.

The rate of inversion of α-halocyclopropyl radicals has been reported as ranging from 10^6 (X = F) to 10^8 s^{-1} (X = Br, Me) and that of electron transfer in ammonia to a carbon free radical as 10^9–10^{10} M^{-1} s^{-1}.[23] Therefore, the configuration of the α-halocyclopropyl anion may be the same as that of its radical precursor. The inversion of α-halocyclopropyl anions being slow,[24] a relatively fast reaction that follows the anion formation will reflect the stereochemistry of the anion on product structures.

Our hypothesis is that the exo anion is formed under thermodynamically and probably kinetically controlled conditions because, with this hypothesis, we can explain the following key observations.[25]

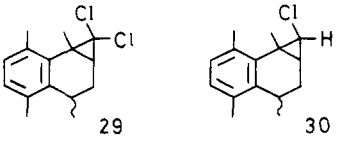
Scheme IV



(1) Isolation of **3** is indicative of the existence of a relatively long-lived exo anion.

(2) In the exo anion, the release of steric strain around peri positions can easily be accomplished by shifting an aryl group without reflecting the electronic effect of the aromatic methyl substituents on the transition state (i.e., non-F–B–W-type transition state; cf eq 5), although the first aryl shift causes configurational change from a less-strained cis–transoid–cis (**23**) to a highly strained cis–cisoid–cis form (**24**) as described in the preceding paragraph. This mechanism agrees with the lack of methyl substituent effect described in the section of structural limitation.

(3) Additional evidence for this relatively long-lived exo anion has been obtained: when compound **29**, which does not undergo



the rearrangement, was treated with naphthalenide at −70 °C, it yielded **30**, which has an *exo*-methine hydrogen on the cyclopropyl carbon.[26] The same product was also produced when **29** was reduced by lithium aluminum hydride. Other nonrearrangeable compounds **1f–h** behaved analogously.

Ring-Enlargement Reaction. Scheme IV illustrates the most rational mechanism proposed for the formation of ring-enlarged products **4** and **5** from **1a** at 25 °C. Theoretically, the anion *exo*-**8** can undergo ring opening in a conrotatory fassion to produce either a cis or trans double bond which is built in a benzocycloheptene ring **25** (and so does *endo*-**8** as well). However, the formation of a trans double bond in such a medium-sized ring system as **25** is thermodynamically disfavored. The ring opening of **8** to **25**, which is holding a cis double bond, seems to require a relatively higher activation energy than the cyclopropylidene rearrangement when the molecule possesses the above-mentioned requisites for the rearrangement. When it does not, it will either survive until it is protonated or undergo ring opening, particularly at higher temperatures.

The formation of **26** from **25** seems more favored than the alternative path to anion **27** because **26** is apparently more stable than **27**: this explains the absence of symmetrical benzocyclooctenes in the product mixture. Anion **26** then undergoes the elimination of a chloride ion to generate carbene **28**, which is followed by another carbene rearrangement: the aryl group migration produces an unsymmetrically substituted benzocyclooctene skeleton **5** (X = Cl), and the methyl migration produces a benzocycloheptene skeleton **4** (X = Cl). Since vinylic chloro substituents are labile under electron-transfer conditions, these intermediate products, regardless of being isolated or not isolated,

(21) For alkyl migration competing with aryl migration, see: (a) Ciabattoni, J.; Campbell, R. A.; Renner, C. A.; Concannon, P. W. *J. Am. Chem. Soc.* **1970**, *92*, 3826. (b) Gassman, P. G.; Atkins, T. J. *Ibid.* **1970**, *92*, 5810. (c) Geibel, K. *Chem. Ber.* **1970**, *103*, 1637. (d) Köbrich, G.; Merkel, D. *Angew. Chem.* **1970**, *82*, 257.

(22) ^{13}C NMR spectra of **2a** and **23** are available as supplementary material Figures 3 and 4.

(23) Studies on the inversion of substituted cyclopropyl radicals: (a) Boche, G.; Schneider, D. R. *Tetrahedron Lett.* **1978**, 2327. (b) Boche, G.; Schneider, D. R.; Wintermeyr, H. *J. Am. Chem. Soc.* **1980**, *102*, 5697. (c) See ref 25. (d) Kobayashi, K.; Lambert, J. B. *J. Org. Chem.* **1977**, *42*, 1259.

(24) Walborsky, H. M.; Allen, L. E.; Traenkner, H. J.; Powers, E. J. *J. Org. Chem.* **1971**, *36*, 2937 and references therein.

(25) 1,2-*cis*-Dimethyl substitution on a cyclopropane ring might enhance the kinetically controlled formation of endo radical as reported: Kawamura, T.; Tsumura, M.; Yokomichi, Y.; Yonezawa, T. *J. Am. Chem. Soc.* **1977**, *99*, 8251.

(26) The $LiAlH_4$ reduction of **29** yielded both endo- and exo-Cl isomers of **30**. The assignment of the major isomer is based on the NMR coupling constant of its chloromethano proton, J = 7 Hz.

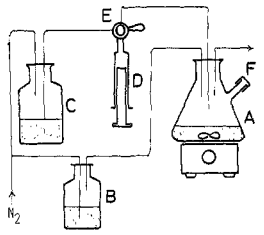


Figure 2. (A) Titrating bottle; (B) nitrogen purifier ($C_{10}H_8^-Na^+$); (C) 1 N AcOH in toluene; (D) syringe buret; (E) rotating valve; (F) septum rubber.

were reduced by naphthalenide to give final hydrocarbon products **4** and **5** (X = H).

Conclusion

The reductive rearrangement reaction of methyl-substituted title compounds by means of naphthalenide revealed the following mechanistic characteristics: (1) Although the reaction seems to occur, in general, in multisubstituted *gem*-dihalocyclopropanes, it requires the release of a steric strain that is accumulated in the substrate. Therefore, compounds with simple structures such as aryl-substituted *gem*-dihalocyclopropanes do not undergo the rearrangement. (2) A moderate reducing power of the reductant seems to be another essential requisite for the rearrangement. A greater reducing power tends to induce the overreduction of reaction intermediates to form carbene radical anions. (3) Being superimposed on the above requisites, other effects such as halogen, solvent polarity, temperature, and the structural stability of carbanion intermediates also control the reaction.

Experimental Section

General Procedures. Temperatures are uncorrected. Mass spectra were taken on a Hitachi Model RMU-6L that was connected to a Hitachi 063-gas chromatograph equipped with a column of Apiezon L, 5%, 4 m. ^1H NMR were recorded on either a Varian T-60 or HA-100 in $CDCl_3$, and chemical shifts are given in δ units. UV spectra were taken on a Hitachi 124 spectrometer. For column chromatography, silica gel (Merck 60-7734) was used as adsorbent.

Analysis of Naphthalenide. Although several methods have been reported for this purpose,[27] their application often involves difficulty in laboratories. We devised a simple and easy-to-operate technique using a few simple equipments (Figure 2).[28] A 1 M solution of AcOH is prepared from dry toluene and dry AcOH. The acid solution is flushed by purified N_2 stream, its normality being determined by acid–base titrimetry, and is stored in bottle C. A THF solution of naphthalenide (approximately 0.2–0.5 M) is prepared by the usual method, and one part of it is used as the N_2 purifying solution in bottle B. A 100-mL two-necked flask A is equipped with a magnetic bar, the side neck is sealed with a rubber septum F, and the top neck is sealed with a silicon stopper equipped with three 1-mm i.d. Teflon inletting tubes: two of them are for the N_2 inlet, and outlet, and the remaining one is connected to the reservoir C via a piston burret D whose head is equipped with a switchable valve E. The valve operates for both sucking the titrant from C and pumping it out into A.

After flushing A with N_2, purified THF is added into A as a diluent (ca. 10 mL) through F followed by successive injection of such an amount of naphthalenide solution as will turn the solution in A green. The solution is preliminarily titrated with AcOH solution by operating D until the color disappears. After this operation the solution in A, completely free of moisture and oxygen, is ready for use as the solvent base of titration. A measured volume of naphthalenide (usually 2.00 mL of ca. 0.3 M solution) is injected into A through F and is titrated carefully by the operation of D until the blue of the solution disappears. This operation (injection and titration) can be repeated successively at least five times in the same flask without washing off the titrated solution. The arithmetic mean of several titers is calculated. Other titrants such as di-*tert*-butyl peroxide and dibenzoyl peroxide can also be used. However, AcOH has been proved the best because it gives a clearly distinguishable titration endpoint within the error of 0.8%. For comparison, gasmetric analysis of naphthalenide with O_2 or CO_2 using an automatic gas burret was performed, and it gave an excellent agreement with the above-mentioned titration.

Polymethylnaphthalene–Dihalocarbene Adducts (1a–e and 1g–j). The CX_2 adducts (**1a–e** and **1g–j**) were prepared by the reported method.[5a] Some adducts (**1a**, **1c**, **1d**, **1h**) were also prepared (60%, 32%, 57%, and 98% respectively) by using phase-transfer catalysts (cetyltrimethylammonium bromide). The ^{13}C-labeled **1a** (**22**, isotope concentration 10%) was prepared from octamethylnaphthalene by the reaction with $^{13}CHCl_3$ (supplied by MSD Isotopes Inc.).

Preparation of 1f. Dichlorocarbene adduct **1h** (15 mmol) was chloromethylated by $ClCH_2OCH_3$ (180 mmol) and $SnCl_4$ (2 mmol) in CS_2 (11 mL) to give 6-chloromethylated **1h** (I, 93%): mp 155–158 °C; ^1H NMR (singlets) δ 1.48, 1.51 (3 H each), 1.91 (2 H), 2.43 (6 H), 4.53 (2 H), 7.08 (1 H). Compound I (13.6 mmol) was treated with $LiAlH_4$ (27 mmol) in ether to give 6-methylated **1h** (II, 46%): mp 172–4 °C; ^1H NMR (singlets) δ 1.46, 1.49 (3 H each), 1.86 (2 H), 2.22 (6 H), 2.35 (3 H), 6.86 (1 H). Compound II was again chloromethylated analogously to give 7-chloromethylated II (III, 98%): mp 211–212.5 °C; ^1H NMR (singlets) δ 1.45 (6 H), 1.88 (2 H), 2.32 (6 H), 2.44 (3 H), 4.64 (2 H). The $LiAlH_4$ reduction of III gave **1f** in 87% yield: mp 220–223 °C; mass spectrum, *m/e* 376 (M^+); ^1H NMR (singlets) δ 1.43 (6 H), 1.83 (2 H), 2.20 (6 H), 2.27 (6 H). Anal. Calcd for $C_{18}H_{20}Cl_4$: C, 57.17; H, 5.33. Found: C, 57.26; H, 5.26.

Spectral data of unsymmetrical adducts **1c**, **1d**, and **29**, whose preparations were not reported in the literature,[5a] are listed here. **1c**: mp 106–108.5 °C; NMR δ 1.40, 1.43 (3 H each, s), 1.60 (6 H, s), 2.21, 2.24 (3 H each, s), 6.93, 7.13 (1 H each, d, J = 8 Hz). **1d**: mp 115–116.5 °C; ^1H NMR δ 1.43, 1.49 (3 H each, s), 1.59 (6 H, s), 2.36 (3 H, s), 7.1–7.3 (3 H, m). **29**: liquid, bp 103 °C (0.25 torr); ^1H NMR δ 0.9 (1 H, m), 1.22 (3 H, d, J = 7 Hz), 1.5–2.0 (2 H, m), 1.66 (3 H), 2.20, 2.33 (3 H each, s), 2.9 (1 H, m), 6.84 (2 H, s). Compound **29** was prepared from 1,2-dihydro-1,4,5,8-tetramethylnaphthalene in 58%.

Reduction of 1a at −70 °C. 1a (4.06 g, 10 mmol) was dissolved in dry THF (110 mL), and the solution was flushed with an N_2 stream that was preliminarily dried by being bubbled through Na naphthalene/THF solution. The solution was cooled to −70 °C, and a THF solution of Na naphthalene (40 mmol) was added over 30 min. After the solution stirred for 1 h at −72 °C, 20 mL of a mixture of THF and water (10:1 v/v) was added, and the temperature was raised to 20 °C. After the solvents were removed, the residue was worked up with benzene and water and dried ($MgSO_4$), and the benzene was removed. Naphthalene was sublimed off (50 °C), and the residue was chromatographed (petroleum ether) to give 1,2:3,4-diethylideno-1,2,3,4-tetrahydro-2,3,5,6,7,8-hexamethylnaphthalene (**2a**, 75%): mp 99 °C; mass spectrum, *m/e* 264 (M^+), (**1a** − 4Cl); ^1H NMR δ 1.41 (6 H, s), 2.15 (2 H, dd, J = 2.0, 2.5 Hz), 2.20 (6 H, s), 2.30 (6 H, s), 5.25 (2 H, d, J = 2.0 Hz), 5.42 (2 H, d, J = 2.5 Hz); ^{13}C NMR ($CDCl_3$) δ 16.4, 16.6, 21.5, 25.6, 26.7, 99.8, 127.8, 131.7, 132.5, 145.9; UV (cyclohexane) λ_{max} 220 nm (log ϵ 4.34), 280 (2.60). Anal. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 91.12; H, 9.01. Two minor products were isolated. **4a** (X = Cl, 12%): mp 216.5–217.5 °C; ^1H NMR (singlets) δ 1.79, 1.87, 1.92, and 2.12 (3 H each), 2.19, 2.21 (6 H each); mass spectrum, *m/e* 334 (M^+). Anal. Calcd for $C_{20}H_{24}Cl_2$: C, 71.64; H, 7.21; Cl, 21.15. Found: C, 71.72; H, 7.38. **5a** (X = Cl, 8%): mp 186–188 °C; ^1H NMR (singlets) δ 1.57 and 2.17 (6 H each), 1.96, 2.02, 2.09, 2.20 (3 H each). Anal. Calcd for $C_{20}H_{24}Cl_2$: C, 71.64; H, 7.21. Found: C, 71.90; H, 7.35. Mass spectrum, *m/e* 334 (M^+); UV (cyclohexane) λ_{max} 290 nm (log ϵ 2.70), 220 (4.50).

The reduction of ^{13}C-labeled **1a** (**22**) was carried out under the same conditions as described here, and the ^{13}C NMR spectrum of the isolated **2a** showed an enhanced resonance at δ 26.7 approximately 11 times stronger than the unlabeled.

Oxidation of 2a by $OsO_4/NaIO_4$. A pyridine solution of **2a** (0.5 mmol) was treated with OsO_4 (1.1 mmol) at 0 °C for 29 h.[29] After successive workup with $NaHSO_3$, CH_2Cl_2, dilute HCl, and $NaHCO_3$, the organic residue was treated with $NaIO_4$ (0.5 g) in MeOH/water at 5 °C for 42 h. The reaction mixture was chromatographed (benzene) to give 1,2,3,4,6,7-hexamethylnaphthalene (35%), which was identical with the authentic sample.[30] A mixture of 1,2,3,4,5,8-hexamethylnaphthalene (100 mg), $NaIO_4$ (460 mg), MeOH (20 mL) and water (2 mL) was stirred at 0–20 °C for 51 h. No trace of 1,2,3,4,6,7-hexamethylnaphthalene was detected by NMR and VPC, only the starting naphthalene.

Reduction of 1a. Isolation of Intermediate 3. 1a was treated analogously with Na naphthalene (5 equiv). After the addition of every mole

(27) (a) Stevenson, G. R.; Valentin, J.; Meverden, C. *J. Am. Chem. Soc.* **1978**, *100*, 353. (b) Hayano, S.; Fujihira, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1496.

(28) We are indebted to Professor S. Kato at the Junior College of Kyoto Institute of Technology for his technical advice.

(29) Criegee, R.; Marchand, B.; Wannowius, H. *Justus Liebigs Ann. Chem.* **1942**, *550*, 99.

(30) (a) Oku, A.; Ohnishi, Y.; Mashio, F. *J. Org. Chem.* **1972**, *37*, 4264. (b) Oku, A.; Kakihana, T.; Hart, H. *J. Am. Chem. Soc.* **1967**, *89*, 4554. (c) Reference 6.

equivalent of the reductant, an aliquot of the reaction mixture was quenched and analyzed by VPC. After the addition of 1 mol, intermediate **3** appeared besides **1a**; after 2 mol, **2a** began to appear together with **1a** and **3** and small amounts of other products; after 3 mol, the amount of **2a** increased while those of **1a** and **3** decreased; after 5 mol, **1a** and **3** disappeared while **2a** remained the major component. **3**: mp 219–220 °C; mass spectrum, *m/e* 370 (M^+; **1a** − Cl + H); ^1H NMR (singlets) δ 1.23, 1.28, 1.47, 1.50 (3 H each), 2.17, 2.22 (6 H each), 3.03 (1 H). This was assigned to 1,2-(dichloromethano)-3,4-(*endo*-chloromethano)-1,2,3,4-tetrahydrooctamethylnaphthalene by comparison with authentic compound which was prepared by the $LiAlH_4$ reduction of **1a** (vide infra).

Reduction of 1a at 25 °C. Reduction of **1a** (3.0 g, 7 mmol) with Na naphthalene (60 mmol) was carried out in a way analogous to that described above except at 25 °C. Three products were separated by a column chromatography (petroleum ether). The product with the shortest VPC retention time (t_r) was determined to be **5a** (X = H, 55%): mp 103.5–104 °C; mass spectrum, *m/e* 266 (M^+); ^1H NMR δ 1.57 (6 H, s), 1.83 (3 H, d, *J* = 1.5 Hz), 1.86 (3 H, d, *J* = 1.4 Hz), 2.15 (6 H, br s), 2.18 (6 H, s), 5.87 (1 H, m, *J* = 1.5 Hz), 6.19 (1 H, m, *J* = 1.4 Hz); UV (cyclohexane) λ_{max} 233 nm (log ε 4.30), 330 (1.46). Anal. Calcd for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 89.97; H, 9.97. The product (half-solid) with the second shortest t_r was determined to be **4a** (X = H, 35%): mass spectrum, *m/e* 266 (M^+); ^1H NMR δ 1.46 (3 H, d, *J* = 7 Hz), 1.68 (3 H, br q, *J* = 2 Hz), 1.91 (3 H, br q, *J* = 2 Hz), 2.09 (3 H, d, *J* = 1.6 Hz), 2.22 (3 H, s), 2.24 (6 H, s), 2.27 (3 H, s), 5.47 (1 H, q, *J* = 7 Hz), 6.14 (1 H, m, *J* = 1.6 Hz); UV (cyclohexane) λ_{max} 213 nm (log ε 4.34), 223 (4.32), 278 (3.67). Anal. Calcd for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.12; H, 9.82. The third product (>3%) was not determined.

Reduction of 4a (X = Cl) with Na Naphthalene.[31] To a THF solution (5 mL) of the intermediate product **4a** (X = Cl; 170 mg, 0.5 mmol), which was isolated from the reduction of **1a** at −70 °C, was added dropwise a THF solution (0.40 M) of Na naphthalene (6.5 mL, 2.5 mmol) at −70 °C under a N_2 atmosphere. After workup analogous to that reported,[30] **4a** (X = H, 85%) was obtained.

Reduction of 1i. CBr_2 adduct **1i** (3.8 mmol)[10] was treated with K naphthalene (23 mmol) in a mixed solvent of THF (60 mL) and 2,3-dimethyl-2-butene (1.4 g) at −78 °C in a way analogous to that used for **1a**. Two major products, **2a** and **6a** (X = H), were isolated by column chromatography (cyclohexane) besides unreacted **1i** (15%); **2a**, 44%, vide supra. 1,2:3,4-Dimethano-1,2,3,4-tetrahydrooctamethylnaphthalene (**6a**, X = H, 33%): mp 107–109 °C; mass spectrum, *m/e* 268 (M^+); ^1H NMR δ 0.69, 0.79 (2 H each, 2 d, *J* = 4 Hz), 1.13, 1.24, 2.08, 2.24 (6 H each, s). Anal. Calcd for $C_{20}H_{28}$: C, 89.49; H, 10.51. Found: C, 89.36; H, 10.58.

Reduction of 1a with Sodium in Ammonia. In a mixture of **1a** (0.40 g, 1 mmol), ethanol (1 mL, 20 mmol), and THF (40 mL), ammonia was condensed at −60 °C to a total volume of 100 mL. To this solution was added a block of sodium metal (0.10 g, 4.4 mg atom), and the total mixture was stirred at −60 °C under a nitrogen atmosphere for 1 h. The mixture was warmed to an ambient temperature to remove ammonia and was extracted with pentane to give a mixture of unreacted **1a** (50%) and **6a** (X = H, 50%) almost quantitatively.

Reduction of 1a with $LiAlH_4$. Independent Synthesis of 3. **1a** (5 mmol) was treated with $LiAlH_4$ (5 mmol) for 5 h in THF under solvent reflux. After workup, the product mixture was chromatographed (cyclohexane) into two fractions. The first fraction (two components) was again chromatographed and recrystallized to give two products, A and B. The second fraction (two components) was chromatographed to give two isomeric products, C and D, contaminated by each other. A was identical with **3** (vide supra). B: *exo*-chloromethano isomer of **3**: mp 153–155 °C; ^1H NMR (singlets) δ 1.13, 1.25, 1.42, 1.44 (3 H each), 2.18, 2.22 (6 H each, br s), 2.91 (1 H); mass spectrum, *m/e* 370 (M^+). C: 1,2:3,4-bis(*endo*-chloromethano) derivative of **6a** (X = Cl); ^1H NMR (singlets) δ 1.22, 1.39, 2.16, 2.22 (6 H each), 3.00 (2 H); mass spectrum, *m/e* 336 (M^+). D: 1,2-(*endo*-chloromethano)-3,4-(*exo*-chloromethano) derivative of **6a** (X = Cl): ^1H NMR (singlets) δ 1.13, 1.19 (3 H each), 1.34, 2.16, 2.22 (6 H each), 2.95, 3.09 (1 H each); mass spectrum, *m/e* 336 (M^+).

For reductions described hereafter, the procedures are analogous to that adopted for **1a**, and, therefore, the descriptions are abbreviated.

Reduction of 1b. Product **2b** was separated by VPC: 65%; mp 91–92 °C; mass spectrum, *m/e* 236 (M^+); ^1H NMR δ 1.39 (6 H, s), 2.18 (2 H, q, *J* = 2.0, 2.5 Hz), 2.23 (6 H, s), 5.23 (2 H, d, *J* = 2.0 Hz), 5.43 (2 H, *J* = 2.5 Hz), 6.72 (2 H, s).

Reduction of 1c. Four products were separated. The major product was assigned to 1,2,5,7,8,9-hexamethylbenzocyclooctene (**5c**, 60%): mass spectrum, *m/e* 238 (M^+); ^1H NMR δ 1.63 (3 H, d, *J* = 1.5 Hz), 1.70 (3 H, br s), 1.90 (3 H, d, *J* = 1 Hz), 1.92 (3 H, s), 2.05 (3 H, s), 2.20 (3 H, s), 5.40 (1 H, m, *J* = 1.5 Hz), 6.10 (1 H, m, *J* = 1 Hz), 6.6–6.95 (2 H, m). The second product was tentatively assigned to 1,2-(chloromethano)-3,4-ethylideno-1,2,3,4-tetrahydro-1,2,3,5,6-pentamethylnaphthalene (**14c**, 8%): mass spectrum, *m/e* 272 (M^+); ^1H NMR δ 1.70 (6 H, s), 1.96 (1 H, m, coupled with δ 5.00 and 5.13), 2.10, 2.16, 2.24 (3 H each, s), 3.57 (1 H, s), 5.00, 5.13 (1 H each, 2 q, each coupled with δ 1.96), 6.90 (2 H, m). The third product was assigned to 1,2:3,4-diethylideno-1,2,3,4-tetrahydro-2,3,5,6-tetramethylnaphthalene (**2c**, 4%): mass spectrum, *m/e* 236 (M^+); ^1H NMR δ 1.40 (6 H, s), 2.05 (2 H, q, *J* = 2.5, 2.0 Hz), 2.20 (6 H, s), 5.15 (2 H, br d, *J* = 2.0 Hz), 5.35 (2 H, d, *J* = 2.5 Hz), 6.75 (2 H, s).

Reduction of 1d. After chromatographic separation by column chromatography (petroleum ether) and VPC, a small amount of rearranged product **2d** (5%) was obtained as a half solid: mass spectrum, *m/e* 222 (M^+); ^1H NMR δ 1.42 (6 H, s), 2.13 (2 H, q, *J* = 2.0, 2.5 Hz, coupled with δ 5.20 and 5.42), 2.32 (3 H, s), 5.20 (2 H, br d, *J* = 2.0 Hz), 5.42 (2 H, d, *J* = 2.5 Hz), 6.95 (3 H, s). The major product was the dichloromethano–monochloromethano derivative of **1d** (50%): mass spectrum, *m/e* 328 (M^+); ^1H NMR (singlets) δ 1.34 (3 H), 1.47 (6 H), 1.53, 2.04 (3 H each), 2.90 (1 H), 7.0 (3 H, m).

Reduction of 1e. No evidence for exo-methylene protons in the product mixture was found by NMR. Four products were formed, and their structures were estimated by VPC–MS analysis. Product A (20%): mass spectrum, *m/e* 272 (M^+), (**1e** − 3Cl + H), ring-enlarged monochloro derivative of either **4** or **5**. Product B: mass spectrum, *m/e* 274 (M^+), (**1e** − 3Cl + 3H), ring retaining monochloro product. Products C and D (17% each): mass spectrum, *m/e* 238 (M^+), (**1e** − 4Cl + 2H), ring-enlarged hydrocarbon products corresponding to **4** and **5**.

Reduction of 1f. Column chromatography gave two products besides unreacted **1f** (20%). The first eluting product was 1,2:3,4-bis(*endo*-chloromethano)-1,2,3,4-tetrahydro-1,4,5,6,7,8-hexamethylnaphthalene (**6f**, 28%): mp 174.5–176.5 °C; ^1H NMR δ 1.25 (2 H, *J* = 7 Hz), 1.20, 2.18, 2.25 (6 H each, s), 3.48 (2 H, d, *J* = 7 Hz). The second eluting product was the 1,2-(*endo*-chloromethano)-3,4-(dichloromethano) derivative (29%): mp 188–189.5 °C; ^1H NMR δ 1.35–160 (2 H, m), 1.21, 1.42 (3 H each, s), 2.19, 2.27 (6 H each, s), 3.50 (1 H, d, *J* = 7 Hz).

Reduction of 1g. After addition of every mole equivalent of the reductant, an aliquot of the reaction mixture was analyzed by VPC. When 4 equiv of the reductant was added, **1g** almost disappeared. After 5 equiv, the whole reaction mixture was worked up. Three major VPC fractions were separated. The fraction with the longest t_r consisted of inseparable two components, endo–endo and endo–exo isomers of 1,2:3,4-bis(chloromethano)-1,2,3,4-tetrahydro-1,2,3,4-tetramethylnaphthalene (**6g**, 25%): mass spectrum, *m/e* 280 (M^+), (**1g** − 2Cl + 2H); ^1H NMR δ 1.38–1.48 (12 H, 4 s), 2.78, 2.86 (2 s, ratio of 1:5, total 2 H), 6.89–7.45 (4 H, m). This fraction was again chromatographed by VPC into two portions whose NMR spectra showed different integration ratios at δ 2.78 and 2.86. On the basis of the assumption that the exo-H of the endo–exo-Cl isomer appears at the same position as that of the endo–endo-Cl isomer, the endo–endo/endo–exo isomer ratio was calculated to be 2:1. The second fraction consisted of three inseparable components: mass spectrum, *m/e* 244 (M^+); ^1H NMR δ 1.45 (6 H, s), 1.60 (3 H, br s), 1.98 (3 H, br s, *J* = 1 Hz), 2.83 (1 H, m, *J* = 5 Hz), 5.68 (1 H, m, *J* = 1 Hz), 7.04 (4 H, br s). Their structures were not determined.

Reduction of 1h. The reaction gave 1,2:3,4-bis(*endo*-chloromethano)-1,2,3,4-tetrahydro-1,4,5,8-tetramethylnaphthalene (**6h**, 25%) as the major product, small amount each (<0.3%) of the bis(*exo*-chloromethano) isomer of **6h** (*m/e* 280, M^+), chloromethano–methano derivative (*m/e* 246, M^+) of **6h**, and a ring-enlarged product (*m/e* 212). **6h**: mp 118.5–120.5 °C; mass spectrum, *m/e* 280 (M^+); ^1H NMR δ 1.26 (6 H, s), 1.24 (2 H, br d, *J* = 7 Hz), 2.33 (6 H, s), 3.43 (2 H, d, *J* = 7 Hz), 6.86 (2 H, s).

Reduction of 29. Compound **29** (5 mmol) was treated with Na naphthalene (10 mmol) at −72 °C. Two products were detected by VPC, and the major product was separated and assigned to 1,2-(*endo*-chloromethano)-1,2,3,4-tetrahydro-1,4,5,8-tetramethylnaphthalene (**30**, 17%): mass spectrum, *m/e* 234 (M^+); ^1H NMR δ 1.1–1.5 (1 H, m), 1.28 (3 H, d, *J* = 7 Hz), 1.45 (3 H, s), 1.6–2.2 (2 H, m), 2.25, 2.32 (3 H each, s), 2.65–3.1 (1 H, m), 3.32 (1 H, d, *J* = 7 Hz), 6.85 (2 H, s). The minor product, which was not isolated, was assigned to the *exo*-chloromethano isomer of **30** by only a VPC–mass spectrum analysis, *m/e* (234 (M^+), 0.8%.

The reduction of **29** with $LiAlH_4$ also gave an isomeric mixture that was analogous to that obtained in the above naphthalenide reduction. The exo-Cl/endo-Cl isomer ratio was 1/8.

(31) The procedure was analogous to that reported for 2-chloro-1-methylene-1*H*-benzocycloheptene: Oku, A.; Matsumoto, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 524.

Collection of X-ray Data and Structure Determination. Data were collected on a Rigaku AFC-6A diffractometer using Cu Kα (1.5418 Å) radiation from a graphite-crystal monochromator. Least-squares refinement of the setting angles gave the following values for the cell parameters: $a = 9.147 \pm 0.006$ Å, $b = 20.925 \pm 0.01$ Å, $c = 11.276 \pm 0.013$ Å, $\beta = 109.33 \pm 0.06°$, $V = 2036.6$ Å^3, M_r 584.08, calculated density 1.90 g/cm^3, space group Cc, $Z = 4$. For the data collection, a monoclinic single crystal of approximate dimensions 0.5 × 0.5 × 0.5 mm was mounted on the diffractometer. Measurements were made at ambient temperature (ca. 293 K) with scan technique $2\theta/\omega$, scan rate 8 deg/min, and $2\theta_{max}$ 135°. A total of 3980 independent reflections were collected, and 1500 reflections were used. The structure was solved by using the direct (MULTAN) method. The agreement factor was $R = 0.080$. Selected values of interatomic distances and of the distances to the best plane from the individual atoms are listed in Tables II and III. Complete listings of these parameters (Tables IV and V), positional and thermal parameters (Table VI), and F_o–F_c Table (Table VII) are available as supplementary materials.

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Registry No. **1a**, 78184-63-1; **1b**, 85848-84-6; **1c**, 85781-56-2; **1d**, 85848-83-5; **1d** (dichloromethano–monochloromethano derivative), 85781-73-3; **1e**, 85848-85-7; **1f**, 85781-57-3; *endo*-**1f** (chloromethano–dichloromethano derivative), 85781-70-0; **1g**, 78184-64-2; **1h**, 85849-45-2; **1i**, 36807-30-4; **2a**, 85848-89-1; **2b**, 85781-63-1; **2c**, 85781-66-4; **2d**, 85781-67-5; *endo*-**3**, 85781-62-0; *exo*-**3**, 85848-86-8; **4a** (X = Cl), 52126-70-2; **4a** (X = H), 52033-58-6; **5a** (X = Cl), 52033-55-3; **5a** (X = H), 52033-57-5; **5c** (X = H), 85781-64-2; **6a** (X = *endo*-Cl), 85848-87-9; **6a** (X = H), 78184-65-3; **6f** (X = *endo*-Cl), 85781-69-7; **6g** (X = *endo*-Cl), 85781-71-1; **6g** (X = *endo,exo*-Cl), 85848-88-0; **6h** (X = *endo*-Cl), 85781-72-2; **14c**, 85781-65-3; **29**, 85781-61-9; **30**, 85781-68-6; I, 85781-58-4; II, 85781-59-5; III, 85781-60-8; Na, 7440-23-5; Na naph, 3481-12-7; K naph, 4216-48-2; 1,2-dihydro-1,4,5,8-tetramethylnaphthalene, 4422-10-0.

Supplementary Material Available: Listings of interatomic distances, distances to the best plane from atoms, positional and thermal parameters, and observed and calculated structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

Acid-Catalyzed and Photochemical Isomerization of Steroidal Cyclopropenes

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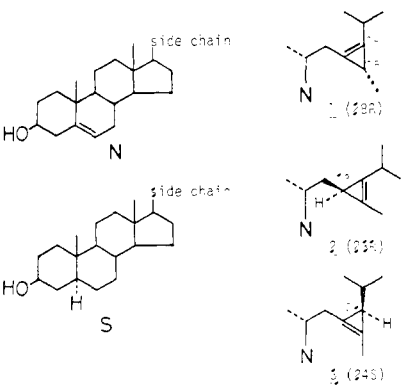
Abstract: The acid-catalyzed and photochemical isomerization of two naturally occurring steroidal cyclopropenes, (28*R*)-calysterol (**1**) and (23*R*)-23*H*-isocalysterol (**2**), is described. Cyclopropene **1** on treatment with methanolic sulfuric acid afforded 23-ethylated cholesterol derivatives containing conjugated diene systems or methoxylated side chains. The sole production of C-23 ethylated sterols demonstrates that this cyclopropene undergoes acid-promoted bond cleavage only between C-24 and C-28. By contrast, methanolic sulfuric acid treatment of the isomeric cyclopropene **2** generated conjugated dienes with 24-methyl-24-homocholestane and 24-ethylcholestane side chains, together with their methoxylated derivatives. This implies that bond fission between C-23 and C-24, as well as C-23 and C-28, is operating in this instance, which is of mechanistic significance. Photolysis by direct irradiation of cyclopropenes **1** and **2** afforded isomerized cyclopropenes, which suggests that the reaction proceeded through an electronically excited singlet state via vinylcarbene intermediates. Among the fragmentation products from the photolysis were isolated the acetylenes 26,27-dinorcholestan-5-en-23-yn-3β-ol (**34**) and cholest-5-en-23-yn-3β-ol (**35**), which had been encountered earlier as the only naturally occurring steroidal acetylenes. Their generation can be rationalized by carbene elimination from the corresponding cyclopropenes.

Introduction

Calysterol [23,28-cyclostigmasta-5,23(24)-dien-3β-ol, **1**, Chart I],[1,2] the principal sterol component of the marine sponge *Calyx niceaensis*, possesses one of the most intriguing functionalities—a cyclopropane ring—among the great variety of unusual side-chain substituents found in marine sterols.[3] Recently we determined the absolute configuration (28*R*) of calysterol[2] and isolated two novel steroidal cyclopropenes, (23*R*)-23*H*-isocalysterol [(23*R*)-23,28-cyclostigmasta-5,24(28)-dien-3β-ol, **2**][2] and (24*S*)-24*H*-isocalysterol [(24*S*)-23,28-cyclostigmasta-5,23(28)-dien-3β-ol, **3**][4] from *C. niceaensis*. The natural occurrence of cyclopropenes is extremely rare: sterculic and related acids[5] and the polyandrocarpidines[6] are the only heretofore known natural cyclopropenes aside from the calysterols **1–3**.

Chart I



Because of the strain associated with the unsaturated three-membered ring, the chemistry of cyclopropenes has attracted considerable interest.[7-10] Although some isomerization reactions

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