ation from the free spin value of $g_e = 2.0023$ is in agreement with the presence of heavy nuclei in both. The similar electron configurations of I and IIb imply that a major factor in the larger deviations of g_I from g_e is the smaller energy gaps to excited states in the larger ring system of I [(A) and (B)]. The magnitudes of the g shifts are inversely proportional to such energies.[10] The major contributors to the Δg_{xy} are probably states in which in-plane nonbonding electrons on chlorine are transferred to the partially vacant π-orbitals.

The metastable triplet state of the parent HCB has $D = 0.154$ cm^{-1}.[11] To a good approximation the spin density should be evenly distributed around the ring ($E = 0.0015$ cm^{-1}).[11] The larger D implies that there is more spin in the ring of the neutral molecule than in I. Thus the molecular orbitals occupied by the unpaired electrons in I include chlorine atomic orbitals and our statement of four π-electrons is only approximate.

There is additional support for this conclusion that the driving force for chlorine π-electrons to enter the ring is delocalization of the positive charge. For the metastable triplet state of benzene, where the net charge is absent, $D = 0.157$ cm^{-1},[12] almost the same as that of the neutral hexachlorobenzene. In the C_5^+ systems, $D_{IIa} = 0.185$ cm^{-1} while $D_{IIb} = 0.144$ cm^{-1}, again indicating movement of spin out of the ring as the positive charge is stabilized by chlorine.

In view of the decrease of D with chlorine substitution in a positively charged system, it is likely that $C_6H_6^{2+}$ will have $D = 0.14$–0.15 cm^{-1}, similar to that of the phosphorescent triplet with little charge and spin delocalization into the C–H bonds.

(10) S. H. Glarum, J. Chem. Phys., 39, 3141 (1963). The spin–orbit contribution to g implies a contribution to D as well.

(11) M. A. El-Sayed, A. A. Gwaiz, and C. T. Lin, Chem. Phys. Lett., 16, 281 (1972).

(12) M. S. de Groot, I. A. M. Hesselman, and J. H. van der Waals, Mol. Phys., 13, 583 (1967).

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Reductive Rearrangement of 5,6:7,8-Bis(dichloromethano)octamethyl-5,6,7,8-tetrahydronaphthalene by Sodium Naphthalene. Evidence of a Carbene Intermediate
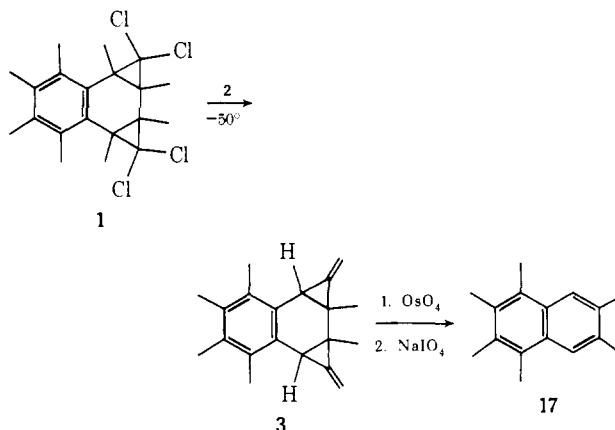
Sir:

The recent report,[1] proposing a carbene intermediate for the reaction of geminate alkyl dihalide with sodium naphthalene, seems to have revealed a new aspect of the reduction of organic halides with naphthalene radical anion.[2] In relation to this finding, the authors herein present the first evidence of substituent shift to a neighboring cyclopropylidene center which is generated from the gem-dichlorocyclopropane function as illustrated by the reduction of compound 1[3] with sodium naph-

(1) G. D. Sargent, C. M. Tarum, Jr., and S. M. Kastner, J. Amer. Chem. Soc., 94, 7174 (1972).

(2) For example, see J. F. Garst, Accounts Chem. Res., 4, 400 (1971).

thalene (2). In this reaction, but at higher temperatures, is also observed a novel skeletal anionic rearrangement of the tricyclo[5.1.0.0^{2,4}] octene system.

Treatment of 1 in THF at below $-50°$ with 4 equiv of 2 afforded a product mixture consisting mainly of compound 3, 75%, mp 99°. The mass spectrum of 3 showed its parent ion peak at m/e 264 ($C_{20}H_{24}$), indicative of four chlorine atoms abstructed from 1 without hydrogen substitution. The nmr spectrum indicates a symmetric structure of 3 by the signals appearing at τ 8.59 (6 H, s), 7.85 (2 H, q, $J = 2.0$ and 2.5 Hz), 7.80 (6 H, s), 7.70 (6 H, s), 4.75 (2 H, d, $J = 2.0$ Hz), and 4.58 (2 H, d, $J = 2.5$ Hz). The uv spectrum is similar to that of 1.[4] The oxidation of 3 with osmium tetraoxide in pyridine followed by successive treatment with sodium metaperiodate in methanol yielded 1,2,3,4,6,7-hexamethylnaphthalene (17), 20%. Since the isomeri-

zation of 1,2,3,4,5,8-hexamethylnaphthalene to 17[5] did not take place under the same oxidation condition, product 3 was assigned to 5,6:7,8-bis(ethylideno)-1,2,3,4,6,7-hexamethyl-5,6,7,8-tetrahydronaphthalene.

On the other hand, reduction of 1 at 25° in THF yielded a mixture of complex components different from that at $-50°$. The isolated products were 4, 5, and 6 and their corresponding hydrocarbons 7, 8, and 9, but 3 was not detected.[6] The change of the product composition vs. the amount of the reductant added was analyzed by gc and mass spectral measurements, in which a Cl_3 and two Cl_2 compounds appeared simultaneously as compound 1 was consumed, and these Cl_2 compounds were gradually reduced to hydrocarbons 7 and 8 via some Cl_1 compounds. The structure determination of the products 4–9 was achieved by means of
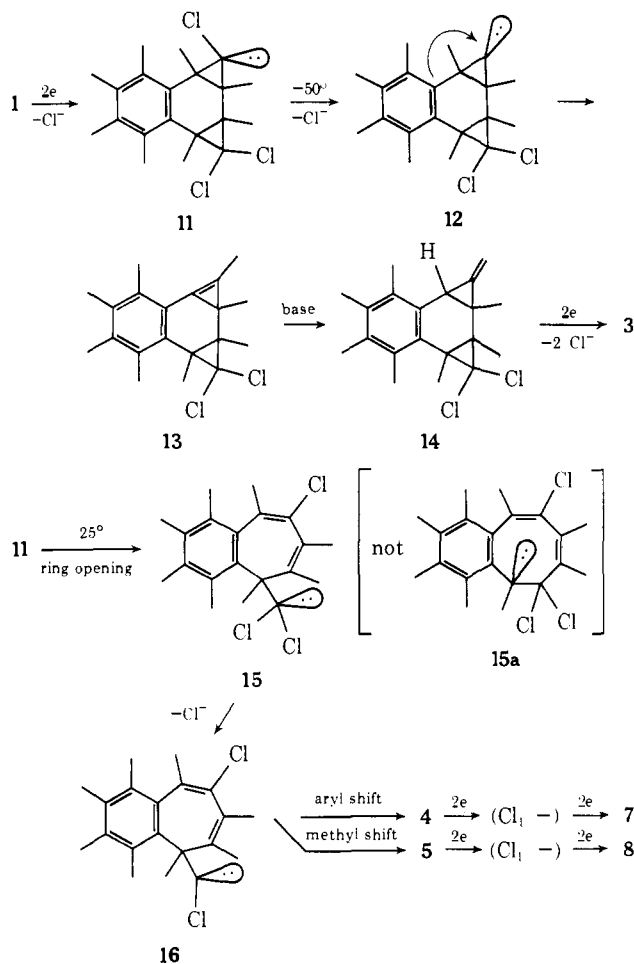

4. X = Cl
7. X = H

5. X = Cl
8. X = H

6. X = Cl
9. X = H
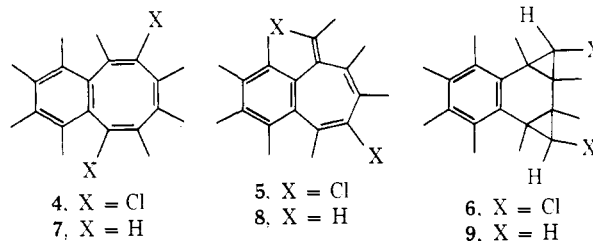
(3) For the addition of CBr$_2$, see H. Hart and A. Oku, J. Org. Chem., 37, 4269 (1972).

(4) λ_{max} (cyclohexane): 1, 223 nm (log ϵ 4.54), 288 (2.48); 3, 220 (4.34), 280 (2.60).

(5) Unpublished results. Acid-catalyzed isomerization of 1,2,3,4,-5,8-hexamethylnaphthalene into 17 via 1,2,3,4,5,7-hexamethyl isomer takes place quantitatively in such strong acidic media as CF$_3$COOH or HCl–ZnCl$_2$.

(6) Yields attained after the addition of 6 equiv mol of 2 were 55, 35, and 7% for 7, 8, and 9, respectively.

$1 \xrightarrow[-Cl^-]{2e}$

11   12

base

$\xrightarrow[-2\,Cl^-]{2e}$ 3

13   14

$11 \xrightarrow[\text{ring opening}]{25°}$ not

15   15a

$-Cl^- \nearrow$

aryl shift $\xrightarrow{2e}$ 4 $\xrightarrow{2e}$ (Cl₁ —) $\xrightarrow{2e}$ 7

methyl shift $\xrightarrow{2e}$ 5 $\xrightarrow{2e}$ (Cl₁ —) $\xrightarrow{2e}$ 8

16

spectroscopic[7] and combustion analysis as well as by the reduction of isolated intermediates.

The exclusive formation of product 3 in the low temperature reduction indicates a mechanistic characteristic of interest, that is, either a carbene (probably not carbenoid) species is involved or a Fritsch–Buttenberg–Wiechell rearrangement may be operating in the rearrangement process. In the former process, carbanion 11, which is formed by the stepwise two-electron reduction[8] of 1, must be the precursor and this undergoes elimination of Cl⁻ to generate cyclopropylidene 12, kinetically favored at lower temperatures. Carbene 12, instead of giving a highly strained allenic structure as the usual behavior of cyclopropylidenes, undergoes aryl shift to give cyclopropene 13, which, in turn, easily isomerizes into methylenecyclopropane derivative 14 by base catalysis.[9] The structure of 3, however, does not exclude the possibility of a methyl shift in 12 although it seems less favorable. Mechanistic possibility of the latter process (F–B–W rearrangement) may

(7) 4: nmr 7.79 (6 H, s), 7.81 (6 H, s), 7.88 (3 H, s), 8.08 (3 H, bs), 8.13 (3 H, s), 8.21 (3 H, bs); P⁺ (m/e) 334; mp 217°. 5: nmr (all singlet) 3 H at 7.80, 7.91, 7.98, and 8.04, 6 H at 7.83 and 8.43; P⁺ 334; mp 187°. 6: nmr (all singlet) 6 H at 7.86, 7.90, 8.44, and 8.79, 2 H at 8.14; P⁺ 336. 7: nmr 3.81 (H, m, J = 1.4 Hz), 4.13 (H, m, J = 1.5 Hz), 7.84 (6 H, s), 7.85 (6 H, s), 8.14 (3 H, d, J = 1.4 Hz), 8.17 (3 H, d, J = 1.5 Hz), 8.43 (6 H, s); P⁺ 266; λmax (cyclohexane) 233 nm (log ε 4.30), 330 (1.46); mp 104°. 8: nmr 3.86 (H, m, J = 1.6 Hz), 4.53 (H, q, J = 7 Hz), 7.73 (3 H, s), 7.76 (6 H, s), 7.78 (3 H, s), 7.91 (3 H, d, J = 1.6 Hz), 8.09 (3 H, bs, J = 2.5 Hz), 8.32 (3 H, bs, J = 2.5 Hz), 8.54 (3 H, d, J = 7 Hz); P⁺ 266; λmax 223 (4.33), 278 (3.67). 9: nmr singlet (6 H) at 7.67, 7.83, 8.74, and 8.84, 2 H at 7.80 and 9.78; P⁺ 268.

(8) (a) D. B. Ledrie, R. L. Thorne, and G. Weiss, J. Org. Chem., 36, 2186 (1971); (b) J. Jacobus and D. Pensak, Chem. Commun., 401 (1969).

(9) G. Schroeder, Chem. Ber., 96, 3178 (1963).

also exist. For example, sodium naphthalene reduction of the adduct obtained by the addition of dichlorocarbene to 1,2,3,4-tetramethylnaphthalene did not give a similar product as 3 but ring opened products even at −78°. However, referring to the less covalent character of the sodium–carbon bond and the configuration of the anionic center,[10] this process seems less plausible. More evidence for carbene intermediate was offered by the sodium naphthalene reduction of 7,7-dichloro-1,6-dimethylnorcarane,[11] in which the formation of hydrocarbons C_9H_{14} and $C_{18}H_{28}$ was confirmed.

The ring-opening process[12] predominating at 25° apparently requires higher activation energy than ring retention. Actually, however, the energy can be lowered by the release of strain of the tricyclic system 11. Formation of a stable carbanion, 15, which is more stable than the alternative, 15a, may also be another cause of lowering energy if the opening of two rings is concerted. Carbanion 15, thus formed, behaves as a precursor of carbene 16, which undergoes β-bond migration of either aryl or methyl to give 4 or 5, respectively.

(10) In F–B–W-type rearrangement, the leaving halide group should be oriented trans to the migrating aryl moiety (see Kirmse "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971, p 103), that is, anion 11 should have syn configuration which seems less likely; see also footnote 12.

(11) Unpublished results.

(12) According to the Woodward–Hoffmann rule, only anti anion 11 can give rise to ring opened products having cis olefinic bonds. Syn anion, which may be a minor portion, if any, may therefore operate in the proton abstraction to give 6 and 9. The predominant population of the anti anion would be due to charge repulsion between the electron-rich aryl ring and carbanion orbital.

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Thermal Rearrangement of 3,4-Bis(trimethylsiloxy)-endo-tricyclo[4.2.1.0²·⁵]nona-3,7-diene and the C_9H_{10} Rearrangements Controversy

Sir:

At temperatures between 350 and 450° (<2 sec contact time) in a conventional Vycor flow system, the title compound (1)[1] is quantitatively isomerized to 4,5-bis(trimethylsiloxy)-cis-8,9-dihydroindene (2). At 325°, the rearrangement proceeds to approximately half completion and no other intermediates or products are detected by pmr examination of the crude pyrolysate. Compound 2 is characterized by its uv spectrum[2] ($\lambda_{max}^{cyclohexane}$ 281 nm (ε 4400)), ir spectrum ($\nu_{C=C}^{neat}$ 1590, 1660 cm⁻¹), mass spectrum (M⁺ 294), and pmr spectrum (see Figure 1).

Owing to the complexity of the pmr spectrum, de-

(1) H. Bode, Chem. Ber., 70, 1167 (1937), describes the diester which can be converted by the method of J. J. Bloomfield, Tetrahedron Lett., 587 (1968), to 1: 66% yield; bp 94–95° (0.5 mm); M⁺ 294; nmr spectrum (CCl₄, 60 MHz) δ 0.16 (s, two OSiMe₃), 1.44 and 1.87 (broadened AB, CH₂ bridge, Jab = 8.0 Hz), 2.38 to 2.70 (m, four bridgehead H's), 5.68 (t, two olefinic H's, J ≃ 1 Hz). Dr. R. D. Miller in a private communication has confirmed the endo configuration by spectral comparison with both isomers; cf. R. D. Miller and D. Dolce, Tetrahedron Lett. 4541 (1972). All new compounds had satisfactory microanalyses.

(2) T. J. Katz and P. J. Garratt, J. Amer. Chem. Soc., 85, 2852 (1963), report λ_{max}^{EtOH} at 262 (ε 3710) and 271 nm (ε 3240) for cis-8,9-dihydroindene and Jab = 12 Hz for the bridgehead protons (whereas Jab = 20 Hz for the trans isomer).