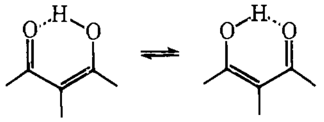
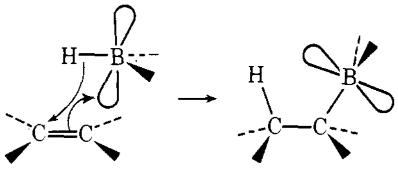
and much less exothermic than the allylic analogue **9** → **10**, the former reaction is far slower ($t_{1/2}^{55^\circ} = 0.5$ h). Rearrangement of **12** was found to be stereospecific, and the exo configuration assigned to **13** was confirmed using Eu(fod)$_3$. Although there is no assurance that *exo*-**1a** and **12** react according to the same mechanism, it is striking that the rearrangement stereochemistry demonstrated for **12** matches that postulated for *exo*-**1a.**[17]

We propose the name *pseudopericyclic* to describe the [1,3]sigmatropic pathway shown in **7.** *A pseudopericyclic reaction is a concerted transformation whose primary changes in bonding compass a cyclic array of atoms, at one (or more) of which nonbonding and bonding atomic orbitals interchange roles.*[18,19] In a crucial sense, the role interchange means a "disconnection" in the cyclic array of overlapping orbitals because the atomic orbitals switching functions are mutually orthogonal. Hence *pseudopericyclic reactions cannot be orbital symmetry forbidden.* The mechanistic idea described here is certainly not new, but we are unaware of a clear and general statement of this concept in the literature. Many apparently pseudopericyclic reactions are known.[20] Prototropy in internally hydrogen bonded enols of β-dicarbonyl compounds (eq 1) is a prosaic example. As the proton tunnels between minima, lone pair and bonding orbitals formally interchange functions at both oxygens in the planar chelate ring.[21-23] In olefin hydroboration (eq 2) the vacant boron orbital presumably switches roles with the orbital employed in bonding to hydrogen. By this device a planar, four-center transition state, normally very high lying, becomes easily accessible.[24]



(1)



(2)

Further studies of sulfoxide rearrangement mechanisms are in progress.

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(1) H. A. Wiebe, S. Braslavsky, and J. Heicklen, *Can. J. Chem.*, **50**, 2721 (1972).

(2) All ^{19}F NMR chemical shifts are expressed in parts per million downfield from external trifluoroacetic acid.

(3) A square pyramidal structure has also been postulated by R. Hoffmann and W. D. Stohrer for (CH)$_5^+$ and its derivatives. See H. Hogeveen and P. W. Kwant, *Acc. Chem. Res.*, **8**, 413 (1975), and references contained therein.

(4) In the ground state of SO there is an orthogonal pair of singly occupied π^* orbitals of the proper symmetry to mix with ψ_2 and ψ_3 of the diene, which are singly occupied in the Huckel approximation. Moreover, the corresponding pair of filled π orbitals in SO could transfer charge to the diene by mixing with ψ_2 and ψ_3, while vacant d orbitals provide for back-donation to sulfur from ψ_1, ψ_2, and ψ_3. R. Hoffmann emphasizes, however, that the sulfur lone pair–ψ_1 interaction would be strongly repulsive.

(5) In local D_{4h} symmetry this transition is rigorously forbidden. While the axial perturbation should confer some intensity on this Raman band, it is expected to be weak. Similarly, the ring breathing mode (ir forbidden in local D_{4h} symmetry) of the tetramethylcyclobutadiene–nickel chloride complex gives rise to a weak band in the infrared (H. P. Fritz in *Adv. Organomet. Chem.*, **1**, 258 (1964).

(6) The Raman spectrum was measured by Dr. Charles W. Gillies at Harvard University.

(7) This band is split slightly (8–9 cm^{-1}) on the low frequency side, perhaps as a consequence of Fermi resonance with the band at 831 cm^{-1}. Incidentally, the vibrational spectra also rule out a rectangularly distorted (C_{2v}) **1b.**

(8) Professor C. Hackett Bushweller of Worcester Polytechnic Institute carried out this experiment.

(9) Y. Kobayashi, I. Kumadaki, A. Ohsawa, and Y. Sekine, *Tetrahedron Lett.*, 2841 (1974).

(10) Though reported as an oil,[9] this diene has been obtained as white crystals, mp 37–38°: ir (vapor) 1724, 1344, 1276, 1218, 1183, 1163, 714 cm^{-1}; ^{19}F NMR (CDCl$_3$) δ 17.40 (m), 15.43 (m); ^{1}H NMR (CDCl$_3$) δ 6.62 (m), 4.88 (m); MS 392 (parent).

(11) (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970; (b) J. A. Berson, T. Miyashi, and G. Jones, II, *J. Am. Chem. Soc.*, **96**, 3468 (1974), and references contained therein.

(12) Even though ring opening in *cis*- and *trans*-2,3-diphenylthiirane oxide produces a biradical with benzylic stabilization, these compounds cleave only slowly at room temperature (K. Kondo, M. Matsumoto, and A. Negishi, *Tetrahedron Lett.*, 2131 (1972)).

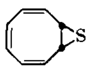
(13) Suitable geometry is a necessary, but not a sufficient criterion for a very low barrier. The Dewar thiophene (**2**) rearranges perceptibly by NMR only above 100 °C. Attempts to oxidize *exo*-**1a** to the sulfone, which of course lacks the lone pair on sulfur, have met with failure.

(14) F. Lautenschlaeger, *J. Org. Chem.*, **34**, 3998 (1969).

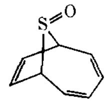
(15) Sufficient "proton sponge" was present in some runs to neutralize the trifluoroacetic acid formed, thus assuring that acid catalysis was not responsible for the rapid rate.

(16) P. Chao and D. M. Lemal, *J. Am. Chem. Soc.*, **95**, 920 (1973), and references contained therein.

(17) Oxidation of i with periodate or *m*-chloroperbenzoic acid (−30 to 0°) gives II. With the reasonable assumption that oxidation occurs on the exo face of i, this stereochemical result parallels those under discussion. Sulfoxide II is capable of further rearrangement on heating, but by a different mechanism. A. G. Anastassiou, J. C. Wetzel, and B. Y.-H. Chao, *J. Amer. Chem. Soc.*, **97**, 1124 (1975).

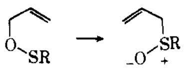


i



ii

(18) A bonding–nonbonding interchange involving *different* atoms does *not* qualify; e.g., III → Iv., a pericyclic reaction:



iii iv

In cheletropic reactions, two atomic orbitals at the same center are intimately involved, but they do not interchange roles.

(19) For the definition of pericyclic reaction, see R. B. Woodward and R. Hoffmann, ref 11a.

(20) Numerous examples will be presented in a full paper.

(21) A bonding p orbital and a "nonbonding" lone pair orbital switch roles at the left-hand oxygen, while a complementary interchange occurs at the oxygen on the right. Although the bonding/nonbonding distinction is obviously not absolute here, the separation of this concerted process into persistently orthogonal σ and π components dramatizes the fact that it is not pericyclic.

(22) The crystal structure of dibenzoylmethane, as its enol, is presented in R. W. G. Wyckoff, "Crystal Structures", 2d ed, Vol. 6, Interscience, New York, N.Y., 1971, pp 125–128.

(23) Many other prototropic processes in conjugated systems are presumably pseudopericyclic, among them the proton tunneling phenomena in DNA which Lowdin has proposed as a basis for mutagenesis (W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, New York, N.Y., 1968, pp 176–178).

(24) K. Fukui, *Bull. Chem. Soc. Jpn.*, **39**, 498 (1966).

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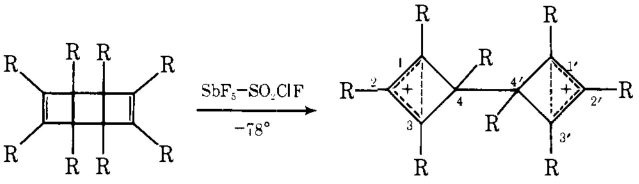
Novel Aromatic Systems. 6.[1] The Bis(tetramethylhomocyclopropenyl) Dication

Sir:

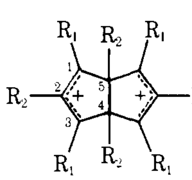
In view of our current interest in the two π electron homoaromatic cyclobutenyl(homocyclopropenyl) cation **1**,[2] we wish to report now the interesting and unexpected finding that the two electron oxidative ring opening reaction of the tetramethylcyclobutadiene dimer **2**[3] in antimony pentafluoride-sulfuryl chloride fluoride solution gives the bis(tetramethylhomocyclopropenyl) dication **3**.



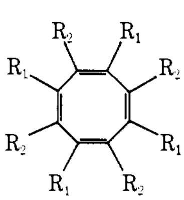
2, R = CH_3
4, R = H

3, R = CH_3
5, R = H

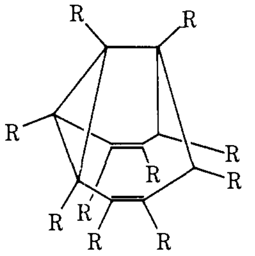
We previously have observed the exclusive formation of the octamethyldihydropentalene dication **6** from isomeric *syn*- and *anti*-octamethyltricyclo[4.2.0.0^{2,5}]octadienes (**2**), octamethylcyclooctatetraene (**7**), and octamethylsemibullvalene (**8**) in fluorosulfuric acid-antimony pentafluoride-sulfur dioxide solution.[4] We recently have also found that antimony pentafluoride oxidizes 1,3,5,7-tetramethylcyclooctatetraene (**10**) to the 8C-6π cyclooctetraene dication **12**, which upon warming immediately rearranged to the tetramethyldihydropentalene dication **9**.[5] No ring opening reaction from ion **12** was observed. In contrast, when *syn*-octamethyltricyclo[4.2.0.0^{2,5}]octadiene (**2**) (as a suspension in SO_2ClF solution) was carefully introduced into a well-stirred SbF_5-SO_2ClF solution at either −78 or −10°, the resulting dark brown solution showed a ^1H NMR spectrum completely different from that of **6**.[5] It consisted of three singlets at δ 2.64, 2.58, and 1.68 in the ratio of 2:1:1 (relative to capillary Me_4Si, −60°). Within the temperature range studied (−125 to 0°) only slight broadening of the two most shielded singlets was observed, while the third at δ 2.64 remained relatively sharp. The FT ^{13}C NMR (proton-coupled) spectrum of the solution showed three singlets at $\delta_{^{13}C}$ 186.2, 179.8, and 81.0 in the ratio of 1:2:1 and three quartets centered at $\delta_{^{13}C}$ 15.1 (1 C), 14.0 (2 C), and 11.4 (1 C). Again, the ^{13}C NMR spectrum obtained from *syn*-**2** in SbF_5-SO_2ClF solution was quite different from that of **6** obtained in FSO_3H-SbF_5-SO_2 solution. The ^1H and ^{13}C NMR spectroscopic data are summarized in Table I for comparison.



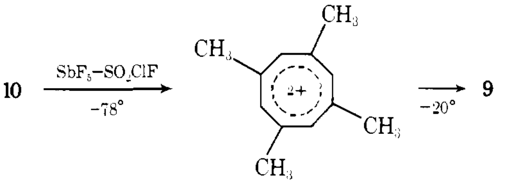
6, $R_1 = R_2 = CH_3$
9, R_1 = H; $R_2 = CH_3$
11, $R_1 = R_2$ = H



7, $R_1 = R_2 = CH_3$
10, R_1 = H; $R_2 = CH_3$



8, R = CH_3



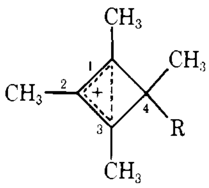
12

Katz and Gold[6] first prepared several polymethylcyclobutenyl cations, and we have recently reported both proton and carbon-13 NMR spectra of a series of these ions. Both the proton and carbon-13 NMR spectra of the species obtained from *syn*-**2** are quite similar to those of the tetramethyl- and tetramethylchlorocyclobutenyl cations, **13** and **14** (Table I), but show more deshielding of C_2 and $C_{2'}$. The NMR data clearly indicate structure **3** for the species obtained from **2** in SbF_5-SO_2ClF solution.

Table I. ^1H and ^{13}C NMR Parameters[a]

Ion		1,3	2	4	C_1-Me	C_2-Me	C_4-Me	$\Delta\delta_{^{13}C}$[b]
		Skeletal position						
1	$\delta_{^1H}$	7.95	9.72	4.53	—	—	—	—
	$\delta_{^{13}C}$	133.5	187.6	54.0	—	—	—	−45.9
3	$\delta_{^1H}$	—	—	—	2.64	2.58	1.68	
	$\delta_{^{13}C}$	179.8	186.2	81.0	14.0	15.1	11.4	−6.4
6	$\delta_{^1H}$	—	—	—	3.29	2.30	2.05	
	$\delta_{^{13}C}$	237.1	158.0	84.2	25.6	21.8	11.4	79.1
9	$\delta_{^1H}$	11.3	—	—	—	3.40	3.02	
	$\delta_{^{13}C}$	230.6	164.5	88.3	—	20.8	14.6	66.1
13	$\delta_{^1H}$	—	—	4.53	2.63	2.37	1.39	
	$\delta_{^{13}C}$	171.3	171.3	57.8	13.5	12.9	11.1	0.0
14	$\delta_{^1H}$	—	—	—	2.91	2.43	2.38	
	$\delta_{^{13}C}$	195.1	174.4	76.0	14.0	9.80	27.3	17.1

[a] Proton and carbon-13 chemical shifts are given in parts per million from external Me_4Si (capillary). [b] $\Delta\delta_{^{13}C} = \delta C_{1,3} - \delta C_2$.



13, R = H
14, R = Cl

Our previous studies showed a continuum of increasing homoaromatic contributions in going from fully substituted to the parent cyclobutenyl cation and clearly established the puckered conformation of the latter, i.e., the homocyclopropenyl cation **1**.[2] Substantial 1,3-orbital interaction, intermediate between σ and π, drastically reverses the order of deshielding between the terminal (C_1 and C_3) and central (C_2) allylic carbons.[2,7] The terminal carbons in the allylic fragment of ion **3** are found to be 6.4 ppm *less* deshielded than is the central carbon. The difference in carbon shifts ($\Delta\delta_{^{13}C}$) for ions **13** and **14** are 0.0 and 17.1 ppm, respectively. Positive charge is found to be shared predominantly by the terminal allylic carbons in dihydropentalene dications **6** ($\Delta\delta_{^{13}C}$ = 79.1) and **9** ($\Delta\delta_{^{13}C}$ = 66.1). Steric constraint might be the reason of better 1,3-overlap in ion **3** as indicated by the higher deshielding at the central allylic carbon over the terminal ones, thus causing **3** to be a truly homoaromatic dication.

The bis(tetramethylhomocyclopropenyl) dication **3** apparently is quite stable and shows no tendency to become transformed into the dihydropentalene dication **6**. Attempts to generate the parent bishomocyclopropenyl dication **5** from the cyclobutadiene dimers **4** (syn and anti)[8] have, however, failed. This observation is also in accord with the apparent thermal instability of the parent cyclooctatetraene dication **15**, the preparation of which has to date remained elusive.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

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A Trans Cyclohexene

Sir:

We wish to report experimental evidence for a twisted form of 1-phenylcyclohexene presenting a double bond past orthogonality and commonly called *trans*-1-phenylcyclohexene.

Laser photolysis[1] of 1-phenylcyclohexene (I) in methanol solution at room temperature forms a transient species which absorbs in the range 300–430 nm with a maximum near 380 nm. The lifetime of this transient, $\tau = 1/k_1$, is 9 μs and it is unaffected by the presence of dissolved oxygen. A transient species with absorption characteristics similar to those obtained in methanol solution is also observed in the laser photolysis of I in acetonitrile and cyclohexane solution (lifetimes: 14 and 9 μs, respectively).

In methanol solution, the 1-phenylcyclohexene transient is quenched by hydrogen ion with a rate constant $k_Q = 7.6 \times 10^6$ $M^{-1}\ s^{-1}$, as found by plotting the reciprocal of the decay-time of the transient as a function of added acid concentration. This sensitivity of the transient species to proton concentration is an indication that it may be identical with the intermediate postulated by Kropp[2] on purely photochemical grounds. We now proceed to demonstrate this identity.

Let us consider the classical mechanism of acid-catalyzed photodddition of methanol, where X is the reactive intermediate and II the methyl 1-phenylcyclohexyl ether:

$$\mathrm{I} \xrightarrow{h\nu} \mathrm{X} \qquad \varphi \text{ (quantum yield)}$$
$$\mathrm{X} \rightarrow \mathrm{I} \qquad k_0$$
$$\mathrm{X} + \mathrm{H}^+ \rightarrow \text{carbocation} \qquad k_Q|\mathrm{H}^+|$$
$$\text{carbocation} \xrightarrow{\mathrm{MeOH}} \mathrm{II} \qquad \alpha \text{ (chemical yield)}$$

completed by reactions accounting for photochemical disappearance of I in neat methanol.

$$\mathrm{X} + \mathrm{MeOH} \rightarrow \text{carbocation} + \mathrm{MeO}^- \quad k'|\mathrm{MeOH}| = k'_r$$
$$\mathrm{X} \xrightarrow{\mathrm{MeOH,I}} \text{products} \qquad k_r''\,^3$$

If ϕ and ϕ' are respectively the quantum yields of disappearance of I and of formation of II, then:

$$\phi = \varphi \frac{k_r + k_Q|\mathrm{H}^+|}{k_1 + k_Q|\mathrm{H}^+|} \tag{1}$$

and

$$\phi' = \varphi' \frac{k_r' + k_Q|\mathrm{H}^+|}{k_1 + k_Q|\mathrm{H}^+|} \tag{1'}$$

with $k_1 = k_0 + k_r' + k_r''$, $k_r = k_r' + k_r''$ and $\varphi' = \alpha\varphi$. The value of ϕ for any H^+ concentration is given by the relation:

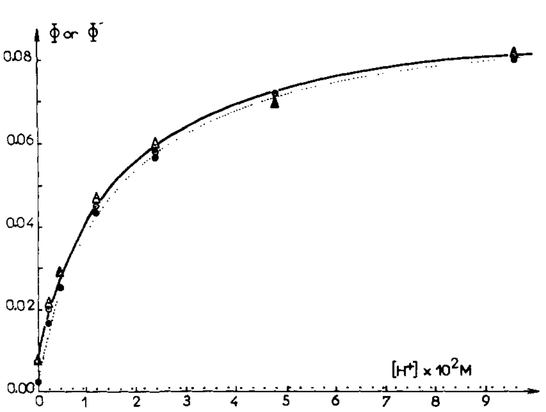

Figure 1. Dependence of the quantum yields ϕ and ϕ' on the hydrogen ion concentration, $|\mathrm{H}^+|$. The curves are the theoretical variations of ϕ (solid line) and ϕ' (dotted line) calculated using the expression (eq 2) given in the text. Plots are experimental values of ϕ measured by uv spectroscopy (⊙) and GC (△) and of ϕ' measured by gc (●).

$$\phi = \frac{\phi_0 + \varphi|\mathrm{H}^+|k_Q/k_1}{1 + |\mathrm{H}^+|k_Q/k_1} \tag{2}$$

From two particular values of ϕ, measured in neat methanol and in an acid solution ($\mathrm{H}^+ = 0.096$ N) and respectively denoted ϕ_0 and ϕ_1, combined with the values of k_1 and k_Q measured in the laser-photolysis experiments reported above, we calculate: first, the value of $\varphi = 0.082$ obtained from

$$\varphi = \phi_1 + \frac{k_1(\phi_1 - \phi_0)}{0.096 k_Q}$$

derived from relation 2 then the function

$$\frac{\phi_0 + \varphi|\mathrm{H}^+|k_Q/k_1}{1 + |\mathrm{H}^+|k_Q/k_1} = f(\mathrm{H}^+)$$

represented in Figure 1 (solid line).

Relations 1 and 1′ having identical functional dependence, the same treatment applies to quantum yields ϕ', ϕ_0', ϕ_1', and φ'. Measurements of ϕ and ϕ' [4] for other H^+ concentrations give the experimental values also plotted in Figure 1. The good agreement of the experimental plots with the calculated curves indicates that relation 2 is verified within experimental errors. Therefore the ratio k_Q/k_1 is the same for the reactive intermediate involved in the above mechanism and for the transient observed in laser-photolysis experiments. Such a coincidence would be highly improbable if there were two different species; this leads us to conclude that the transient observed in laser photolysis is the reactive intermediate involved in Markovnikov addition reactions.

The observed intermediate can be potentially identified with (a) orthogonal triplet phenylcyclohexene A, (b) an orthogonal zwitterionic phenylcyclohexene B, or (c) the trans phenylcyclohexene C (with partial singlet diradical character if the twist is not fully completed to 180°).

Rosenberg and Serve[5] identified the reactive intermediate with the triplet state. In fact their experiments, as well as many other works[6] on sensitization of the photosolvatation of cycloalkenes by triplet donors, demonstrate only that the triplet state is either the reactive intermediate or a precursor of this intermediate. The intermediate is not quenched by dissolved oxygen and its lifetime would be surprisingly long for an orthogonal alkene triplet;[7] hence intermediate A is highly improbable but our work is consistent with the possibility that the triplet, like the singlet, is a precursor of the intermediate, without being the intermediate itself.

The chemistry of the intermediate is consistent with both B and C. Although our initial purpose was to trap a zwitterionic intermediate such as B, the relative insensitivity of lifetime to the polar nature of the solvent appears to rule out the sol-