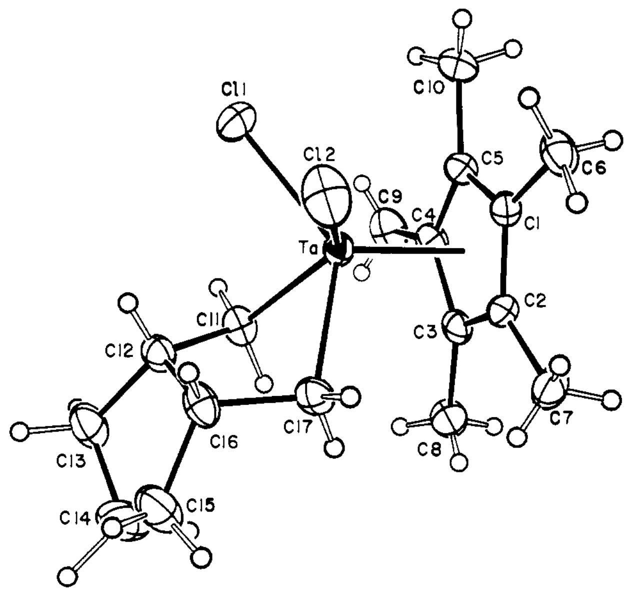

Figure 2. Stereochemistry of the Ta(η^5-C_5Me_5)(C_7H_{12})Cl_2 molecule. Note the "opened envelope" configuration of the TaC_4 ring and the pseudobicyclo[3.3.0]octane system formed by cyclizing the incoming 1,6-heptadiene molecule.

M(en) chelate complexes) and to that found[2] in the PtC_4H_8 ring.] Distances within the five-membered ring follow: Ta-C(1) = Ta-C(1′) = 2.217 (8), C(1)-C(2) = C(1′)-C(2′) = 1.552 (11), and C(2)-C(2′) = 1.553 (12) Å. The C(1)-Ta-C(1′) angle is 72.45 (28)°; other angles are Ta-C(1)-C(2) = Ta-C(1′)-C(2′) = 97.57 (48) and C(1)-C(2)-C(2′) = C(1′)-C(2′)-C(2) = 110.12 (67)°. Distances within other portions of the molecule include tantalum-chlorine = 2.366 (2) and Ta-C(cyclopentadienyl) = 2.371 (10)-2.428 (8) Å.

The high degree of thermal motion in this molecule, taken in conjunction with the crystallographically required C_s symmetry (which could force an unusual conformation on the TaC_4H_8 system) led us to extend our crystallographic investigations to the complex Ta(η^5-C_5Me_5)(C_7H_{12})Cl_2 from eq 2.

This complex crystallizes in the monoclinic space group $P2_1/n$ with a = 9.2051 (13) Å, b = 13.6233 (24) Å, c = 14.1436 (26) Å, β = 96.63 (13)°, V = 1761.8 (5) Å^3, ρ(calcd) = 1.82 g cm^{-3} for mol wt 483.25 and Z = 4. Diffraction data (Mo Kα) were collected as above and the structure was refined to R_F = 4.4% and R_{wF} = 3.4% for 3116 independent reflections with $4° < 2\theta < 50°$ (*none rejected*). All atoms (including all hydrogen atoms) were located; the resulting structure is shown in Figure 2.

The TaC_7H_{12} system defines a bicyclic tantallabicyclo[3.3.0]octane framework, consisting of fused five-membered rings. The bicyclic system has an exo,cis-exo configuration relative to the tantalum atom. Although there is no crystallographically dictated symmetry, the molecule possesses approximate C_s symmetry. The tantallacyclopentane ring again has the "opened envelope" conformation, the angle between the planar C(11)-Ta-C(17) system and the approximately planar (root-mean-square deviation, 0.038 Å) C(11)-C(12)-C(16)-C(17) system being 122.64°.

Distances within the tantallacyclopentane ring are as follows: Ta-C(11) = 2.191 (6), Ta-C(17) = 2.200 (6), C(11)-C(12) = 1.528 (9), C(17)-C(16) = 1.539 (9), C(12)-C(16) = 1.562 (9) Å. Angles are C(17)-Ta-C(11) = 71.47 (25), Ta-C(11)-C(12) = 101.61 (41), C(11)-C(12)-C(16) = 109.02 (53), C(12)-C(16)-C(17) = 108.89 (53), and C(16)-C(17)-Ta = 104.03 (42)°. Other distances within the molecule include Ta-Cl(1) = 2.375 (2) and Ta-Cl(2) = 2.362 (2) Å, and Ta-C(cyclopentadienyl) = 2.378 (5)-2.469 (6) Å.

The two molecules are characterized by the "opened envelope" conformation for the tantallacyclopentane ring and have their two C(α)-C(β) bonds essentially perpendicular to the η^5-C_5Me_5 ring. It is worth noting that Ta(η^5-C_5Me_5)(C_4H_8)Cl_2 readily dissociates[5] in solution, yielding the olefin complex Ta(η^5-C_5Me_5)(C_2H_4)Cl_2, in which the carbon atoms of the ethylene ligand lie *parallel* to the η^5-C_5Me_5 ring.[7]

Acknowledgments. We thank Professor R. R. Schrock for providing the samples and the National Science Foundation for financial support (through Grant CHE77-04981, to M.R.C.).

References and Notes

(1) Fraser, A. H.; Bird, P. H.; Bezman, S. A.; Shapley, J. R.; White, R.; Osborn, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 597.
(2) Biefeld, C. G.; Eick, H. A.; Grubbs, R. A. *Inorg. Chem.* **1973**, *12*, 2166.
(3) Gillard, R. D.; Keeton, M.; Mason, R; Pielfrow, M. F.; Russell, D. R. *J. Organomet. Chem.* **1971**, *33*, 247.
(4) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1977**, *99*, 3519-3520.
(5) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.*, **1979**, *101*, 4558-4570.
(6) Schrock, R. R., personal communication to M.R.C. (May 11, 1979).
(7) Churchill, M. R.; Youngs, W. J., unpublished work.

Melvyn Rowen Churchill,* Wiley J. Youngs
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

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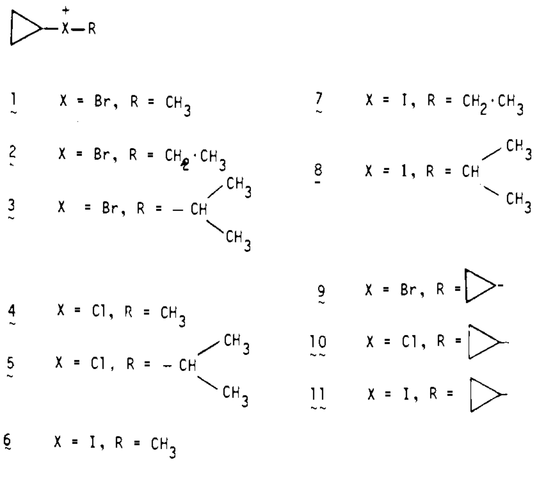
Onium Ions. 21.[1] Cyclopropylhalonium Ions

Sir:

Cyclopropylhalonium ions are one of the major missing class of halonium ions not yet observed despite extensive study on dialkyl-, arylalkyl-, and diarylhalonium ions.[2] Dence and Roberts[3] were the first to attempt the preparation of the cyclopropylphenyliodonium ion from phenyliodo dichloride and cyclopropyllithium. However, they were unable to isolate the corresponding iodonium ion or any product derived from it. We report now the first preparation and NMR spectroscopic observation of a series of cyclopropylhalonium ions.

The series of alkylcyclopropylhalonium ions **1**-**8** were prepared by reacting cyclopropyl halides with ethyl and methyl



fluoride-antimony pentafluoride complexes or isopropyl hexafluoroantimonate in SO_2 or SO_2ClF solutions at −78 °C.

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Table I. ^{13}C NMR Chemical Shift[a,b] Data of Cyclopropylhalonium Ions in SbF_5/SO_2ClF Solution at −70 °C

ion	α	β	others
1	46.10 (215.0)	9.40	CH_3, 39.00 (161.5)
2[c]	42.40 (211.4)	9.30	CH_2, 67.30; CH_3, 16.40
3	38.80 (200.8)	7.70	CH, 99.20 (163.4) CH_3, 24.10
4	53.80 (214.9)	9.40	CH_3, 50.50
5	46.50 (214.9)	9.30	CH, 108.40 (165.4) CH_3, 23.70 (131.5)
6	13.10 (196.5)	9.30	CH_3, 10.20
7[c]	10.70 (201.7)	8.90	CH_2, 38.30 (161.0) CH_3, 16.30
8	10.20 (201.3)	8.50	CH, 70.60 (173.4) CH_3, 26.40
9	102.60 (186.5)	48.90 (175.1)	

[a] In parts per million from external capillary Me_4Si (J_{CH} in hertz). [b] ^{13}C NMR spectra were recorded on a Varian Associates Model FT-80A spectrometer. [c] In SbF_5/SO_2 solution.

Attempts of preparing cyclopropyl-*tert*-butylhalonium ions were, however, unsuccessful. The ^{13}C NMR chemical shifts of prepared halonium ions are listed in Table I. There is a considerable trend[2] of shielding observed going from chloronium to iodonium ions, consistent with the inductive effect of halogen atoms and also their relative sizes (the smaller the halogen atom, the less positive charge it can accommodate).

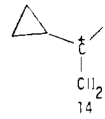
In an effort to prepare the dicyclopropylbromonium ion **9**, cyclopropyl bromide was slowly added to a stirred solution of SbF_5/SO_2ClF at −78 °C. A light brown colored solution was obtained, whose proton decoupled ^{13}C NMR spectrum exhibited two resonances at $\delta(^{13}C)$ 102.60 (J_{CH} = 186.5 Hz) and 48.90 (J_{CH} = 175.0 Hz) ppm, substantially deshielded from those of the parent bromide.[4] The ^{1}H NMR spectrum[5a] showed two multiplets at δ 7.2 and 5.2, respectively (in the ratio of 2:8). No unreacted cyclopropyl bromide was detected. From the observed spectral symmetry, one is tempted to assign the dicyclopropylbromonium ion structure **9** to the observed species **9a**. However, a comparison of the chemical shifts with those of alkylcyclopropylbromonium ions, discussed previously (see Table I), rule out such simple structural representation, as there is obviously very significant deshielding indicating extensive charge delocalization. An opened allylic ion structure **12** with significant 1,3 overlap or an equilibrating nonbonded system including a free cyclopropyl cation **13** is, however, highly unlikely. The significant deshielding of α and β cyclopropyl carbons in the observed ion **9a**[5b-d] is best explained by substantial σ delocalization into the cyclopropyl ring and may involve bromonium ion **9**[5c] with a partially bridged static or rapidly interconverting dynamic structure. Ion **9a** exhibited no temperature-dependent change in the NMR spectrum down to −140 °C and was found stable up to −40 °C, above which it rapidly decomposed.

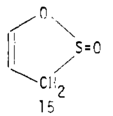

12

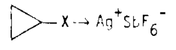
$[C_3H_5]^+$

13

Attempted generation of the dicyclopropylchloronium ion **10** under similar conditions in SO_2ClF/SbF_5 solution was unsuccessful, and resulted instead in rearrangement into the ethyl-α-cyclopropyl-α-chlorocarbinyl cation **14**, whose structure is assigned based on the ^{13}C NMR data.[6] Cyclopropyl chloride in SO_2/SbF_5 solution gave the cyclic sulfinate **15**.[7] The corresponding reactions of cyclopropyl iodide[8] resulted in unidentifiable species. Under milder conditions with $Ag^+SbF_6^-$ in SO_2 solution, all the three halides gave only polarized complexes of type **16.**

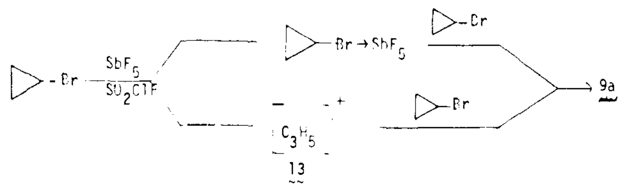

14


15


16 X= Cl, Br, I

The failure to observe dicyclopropylchloronium ion **10** could be attributed to its extreme reactivity. The formation of ion **14** can be rationalized through the intermediacy of **10.** The dicyclopropyliodonium ion **11** may, on the other hand, be unstable under the reaction conditions and be capable of undergoing oxidative side reactions.

The formation path of dicyclopropylbromonium type ion **1a** is interesting. Two alternate pathways can be proposed. One occurring through a polarized complex (S_N2 type) and the other through a cyclopropyl cation, more probably a partially ring-opened ion[9,10] (S_N1 type).

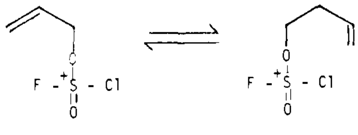


There is considerable interest in the stereochemistry of nucleophilic substitution at cyclopropyl carbons.[11] However, there are only few such bona fide substitution reactions known in the literature. Thus, the present bromonium ion formation reaction may be a suitable probe for the nature of such substitutions. Consequently, we are pursuing such studies.

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

References and Notes

(1) G. A. Olah, B. G. B. Gupta, and S. C. Narang, *J. Am. Chem. Soc.*, **101**, 5317–5322 (1979).
(2) G. A. Olah, "Halonium Ions", Wiley-Interscience, New York, 1975.
(3) J. B. Dence and J. D. Roberts, *J. Org. Chem.*, **33**, 1251–1253 (1968).
(4) The methine and methylene carbons were observed at $\delta(^{13}C)$ 17.20 and 9.10, respectively.
(5) (a) The ^{1}H NMR spectrum was obtained at −80 °C on a Varian Associates Model A-56/60 spectrometer. (b) A donor-acceptor complex with the SbF_5 is ruled out based on related studies with AsF_5. Cyclopropyl bromide, indeed, forms a donor-acceptor complex with AsF_5, which shows characteristic insignificant deshieldings in the ^{13}C NMR spectrum, compared with the parent bromide. For studies on $CH_3F \cdot SbF_5$ and $CH_3F \cdot AsF_5$ complexes, see G. A. Olah and D. J. Donovan, *J. Am. Chem. Soc.*, **100**, 5163–5169 (1978). (c) Ring-opened solvent alkylated ions, such as a or b suggested as possibilities by one of the referees, or some type of diallylbromonium ion are incompatible with the observed ^{13}C NMR data as no olefinic nor allylic carbon resonances were observed. Attempts to prepare diallylbromonium or methylallylbromonium ions by various routes were, so far, unsuccessful. (d) All of our attempts to quench the ion **9a** with CH_3OH/K_2CO_3 at very low temperatures were unsuccessful and resulted only in polymeric mixtures. (e) NOTE ADDED IN PROOF. In work carried out in cooperation with Professor I. Ugi and Dr. D. Lenoir, the deuterated bromonium ion **9** obtained upon ionization of 2,3,3-trideuteriocyclopropyl bromide showed no deuterium at the methine carbon indicative of methine-methylene hydrogen, thus, further excluding the probability of any opened ion. (Details, as well as studies of the stereochemistry of the formation of ion **9** will be reported.)



a

b

(6) The following ^{13}C NMR chemical shifts were observed: 266.90 (s), 60.20 (d), 62.50 (t), 55.60 (t) and 26.1 Hz (q).
(7) The SO_2 adduct showed peaks at $\delta(^{13}C)$ 132.90, 115.70, and 56.00, respectively.
(8) Cyclopropyl iodide was prepared in 37% yield by reacting cyclopropylmagnesium bromide with iodine in tetrahydrofuran solution.
(9) The allylic ion is 39 kcal/mol more favorable than the cyclopropyl cation. See (a) J. D. Roberts and V. Chambers, *J. Am. Chem. Soc.*, **73**, 3176–3179,

5034-5040 (1951); (b) L. Radom, J. A. Pople, P. C. Hariharan, and P. v. R. Schleyer, *ibid.*, **95**, 6531-6544 (1973), and references therein; (c) V. Buss, P. v. R. Schleyer, and L. C. Allen, *Top. Sterochem.*, **7**, 253-293 (1973); (d) L. Radom, J. A. Pople and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8193-8195 (1973); (e) D. H. Aue, W. R. Davidson, and M. T. Bowers, *ibid.*, **98**, 6700-6702 (1976). This reference gives heats of formation of cyclopropyl cations in gas phase.

(10) G. A. Olah, G. Liang, D. B. Ledlie, and M. G. Costapoulos, *J. Am. Chem. Soc.*, **99**, 4196-4199 (1977).

(11) T. ElGomati, D. Lenoir, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **14**, 59-61 (1975); R. W. Gray, C. B. Chapleo, T. Vergnani, A. S. Dreiding, M. Liesner, and D. Seebach, *Helv. Chim. Acta*, 1547-1552 (1976); J. Schaffler and J. Retey, *Angew. Chem., Int. Ed. Engl.*, *17*, 845-846 (1978); H. Dauner and D. Lenoir, *Angew. Chem.*, in press.

George A. Olah,* G. K. Surya Prakash, Mark R. Bruce

Hydrocarbon Research Institute
and Department of Chemistry
University of Southern California
Los Angeles, California 90007

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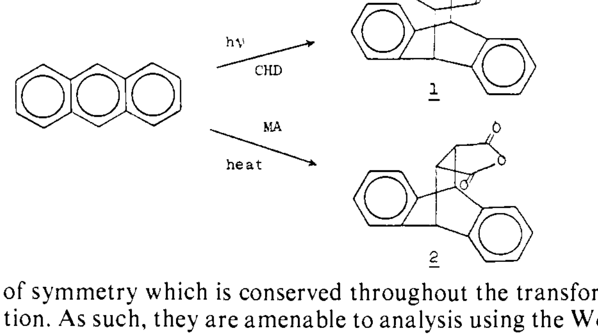
Chemistry of Exciplexes. 8. The Role of Conservation of Orbital Symmetry in Cycloadditions of Olefins to Aromatic Hydrocarbons

Sir:

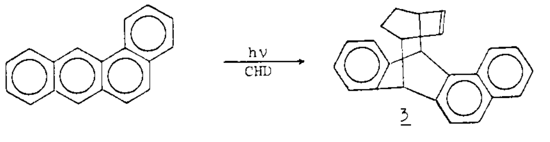
Cycloaddition reactions may proceed via a concerted or a stepwise reaction pathway.[1-6] The rule of conservation of orbital symmetry, commonly known as the Woodward-Hoffmann rule,[1] plays on important role in determining the pathway of cycloadditions. The Diels-Alder reaction in which an aromatic hydrocarbon functions as the diene component is well known.[7-10] More recently, the photocycloaddition of conjugated polyenes to aromatic hydrocarbons and their derivatives has been described.[11-14] These reactions are believed to involve concerted pericyclic bond formation and follow the precepts of the Woodward-Hoffmann rule.[15,16] In this communication, we report on the photocycloadditions favored by the higher cata-condensed polynuclear aromatic hydrocarbons with 1,3-cyclohexadiene (CHD). In these reactions, the symmetry of the relevant reactive orbitals in the arene may supersede the symmetry (when present) of the entire system conserved in the transformation. Our findings suggest that the local symmetry in the frontier orbitals about the reactive positions implicitly determines the favorable pathway of cycloaddition of unsaturated compounds to aromatic hydrocarbons.

The thermal reaction of maleic anhydride (MA) with anthracene[7] and the photocycloaddition of CHD to anthracene[13] can be examined as characteristic concerted cycloadditions (eq 1). In these reactions, reactants and products possess a plane of symmetry which is conserved throughout the transformation. As such, they are amenable to analysis using the Woodward-Hoffmann orbital symmetry approach,[1] or using Fukui's simplification of analyzing interacting fragments.[6] Consequently, the thermal reaction is interpreted as an "allowed" $[_{4}\pi_{s} + {}_{2}\pi_{s}]$ concerted process and the photochemical reaction as an "allowed" $[_{4}\pi_{s} + {}_{4}\pi_{s}]$ process. Furthermore, naphthalene and benzene react photochemically with CHD and(or) its derivatives to give the corresponding $[_{4}\pi_{s} + {}_{4}\pi_{s}]$ adducts,[11-13] in accordance with the postulate of Woodward and Hoffmann and that of Fukui.



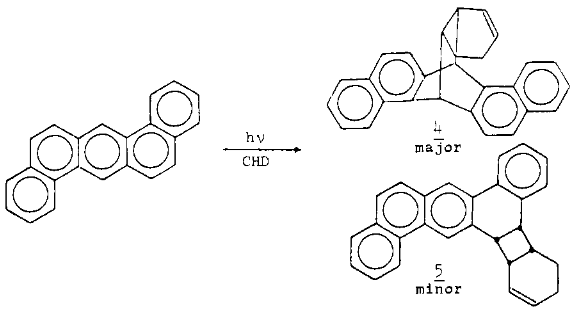
(1)

Benz[*a*]anthracene, formally lacking an element of symmetry maintained throughout the transformations, nevertheless undergoes cycloadditions which are analogous to those of anthracene. The Diels-Alder reactions have been described previously.[9,17] The major product from the photocycloaddition of benz[*a*]anthracene with CHD was assigned the structure **3** (69%, mp 152-153 °C) (eq 2) on the basis of high resolution NMR spectroscopy with spin decoupling and its conversion into a dihydro derivative.[18] This adduct has the stereochemistry predicted by the consideration of maximum secondary orbital overlap and bond order calculations. As with anthracene, the photocycloaddition of benz[*a*]anthracene with CHD affords a $[_{4}\pi_{s} + {}_{2}\pi_{s}]$ adduct (8%, mp 141-143 °C) as a minor product.[14,19,20]



(2)

Although the reaction of dibenz[*a,h*]anthracene with MA was found to occur under forceful conditions, i.e., in boiling xylene with a large excess of the dienophile,[9,21] we found that the concerted photocycloaddition of dibenz[*a,h*]anthracene with CHD was effectively foiled. Unlike anthracene and benz[*a*]anthracene, the fluorescence of dibenz[*a,h*]anthracene was not quenched by CHD,[22] and prolonged irradiation afforded a $[_{4}\pi_{s} + {}_{2}\pi_{s}]$ adduct, **4** (82%, mp 162-164 °C), as the major product together with a small amount of **5** (7%) (eq 3).[23]



(3)

No $[_{4}\pi_{s} + {}_{4}\pi_{s}]$ adduct was detected in the reaction mixture.

The photochemical behavior of dibenz[*a,h*]anthracene with CHD cannot be rationalized by the simplified Woodward-Hoffmann rule, which predicts a $[_{4}\pi_{s} + {}_{4}\pi_{s}]$ process, nor can it be explained by the method of Fukui as the result of a LUMO-LUMO interaction.[6] However, consideration of the local symmetry of the relevant orbitals involved in nascent bond formation (boxed in Figure 1) provides an insight into the observed behavior of aromatic hydrocarbons toward cycloadditions. Clearly, the local symmetry of the relevant reactive orbitals in arenes is similar to that for a typical diene (e.g., CHD) in all cases depicted, with the exception of dibenz[*a,h*]anthracene. Hence, the recognition of the local symmetry would seem to be a requisite for concerted cycloaddition(s) to be allowed at the meso positions of higher benzenoid aromatic hydrocarbons. It should be noted that, in the reaction of dibenz[*a,h*]anthracene with tetracyanoethylene, an axis of symmetry of conserved; nevertheless, no reaction is observed between these reagents under ordinary laboratory conditions.[24] Consequently, the local symmetry may be more important than the orbital symmetry of the entire system in determining an energy barrier in a concerted reaction. Fukui's method[6] of examining only the interaction of those atomic

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