

(3b) in 20 ml of 1:1 anhydrous tetrahydrofuran-ethyl ether cooled to 10° in a water bath. After stirring this mixture at room temperature for 4 hr, the reaction was quenched by slow dropwise addition of water. The mixture was subsequently diluted with 200 ml of water, and the product was isolated by extraction with ether. Recrystallization from benzene, which effected removal of hydrocarbon polymers evidently present in the vinyl lithium reagent, afforded 690 mg (78%) of crystalline diol **4a**: mp 181–183° (lit.⁷ mp 184.5–186°); λ_{\max} (KBr) 3280, 1053, 1028, 917 cm^{-1} ; δ_{TMS} (CD_3COOD) 6.36–5.03 (complex pattern, 4 vinyl H's, peaks at 6.36, 6.19, 6.06, 5.90, 5.43, 5.33, 5.23, 5.06, and 5.03), 1.04 (19- CH_3), 0.94 ppm (18- CH_3).

Pregna-5,17(20)-diene-3 β ,21-diol Diacetate (5b). Treatment of 329 mg (1.04 mmol) of tertiary vinylcarbinol **4a** under the same conditions as described above for the preparation of allylic acetate **9** afforded 376 mg of crude product, which was subsequently chromatographed on 50 ml of silica gel. Elution with hexane–5% ether afforded 84 mg of a viscous oil, homogeneous on silica gel tlc. Recrystallization of this fraction from methanol afforded 60 mg of white crystals: mp 72–78°. The nmr spectrum indicated the presence of at least two unsaturated compounds. In addition to more than one vinyl pattern, peaks were observed at δ_{TMS} (CDCl_3) 2.05 (OCOCH_3), 1.10, 1.07, 1.02, 0.94 ppm.

Elution with hexane–10% ether afforded 254 mg (61%) of crystalline diacetate **5b**: mp 132–133° (lit.⁸ mp 134–135°); δ_{TMS} (CDCl_3) 4.60 (d, $J = 7.0$ Hz, $\text{CH}_2\text{OC}(=\text{O})\text{CH}_3$), 2.06 (6 H's, $\text{OC}(=\text{O})\text{CH}_3$), 1.06 (19- CH_3), 0.81 ppm (18- CH_3).

Acknowledgment. The authors wish to thank Dr. Kurt Rorig of Searle Laboratories, a division of G. D. Searle & Co., for a generous gift of both 3-methoxyestra-1,3,5(10)-trien-17-one and 3 β -acetoxyandrost-5-en-17-one. We also wish to acknowledge Dr. Harvey W. Posvic of Loyola University of Chicago for his helpful suggestions during the course of this project.

Registry No.—**3b**, 853-23-6; **4a**, 10291-86-8; **5b**, 53210-12-1; **7**, 1624-62-0; **8**, 6885-48-9; **9**, 34965-79-2.

Reference and Notes

- For a recent example, see K. A. Parker and W. S. Johnson, *J. Amer. Chem. Soc.*, **96**, 2556 (1974).
- D. F. Morrow, T. P. Culbertson, and R. M. Hofer, *J. Org. Chem.*, **32**, 361 (1967).
- J. H. Babler and D. O. Olsen, *Tetrahedron Lett.*, 351 (1974).
- F. B. Colton, U.S. Patent 2,666,769; *Chem. Abstr.*, **49**, 1827^a (1955). An ir spectrum of 3-methoxy-19-nor-1,3,5(10),17(20)-pregnatetraen-21-ol acetate (**9**), prepared using the route cited in this reference, was sent to us by Dr. Kurt Rorig of G. D. Searle & Co.
- Reactions were carried out under a nitrogen atmosphere. The isolation of reaction products was accomplished by extracting the aqueous layer thoroughly with the specified solvent. Anhydrous magnesium sulfate was used to dry the combined extracts, and the solvent was removed on a rotary evaporator under reduced pressure. Melting points were determined on a Fisher-Johns block and are corrected. The nmr spectra were recorded with a Varian A-60 nmr spectrometer and infrared spectra were obtained using a Beckman Acculab 1 spectrophotometer.
- Available from Ventrion Corporation, Alfa Products, Beverly, Mass. 01915.
- E. B. Hershberg, E. P. Oliveto, C. Gerold, and L. Johnson, *J. Amer. Chem. Soc.*, **73**, 5073 (1951).
- H. Heusser, K. Eichenberger, and Pl. A. Plattner, *Helv. Chim. Acta*, **33**, 1088 (1950).

Ion Cyclotron Resonance Studies of Allene Mercurinium Ions

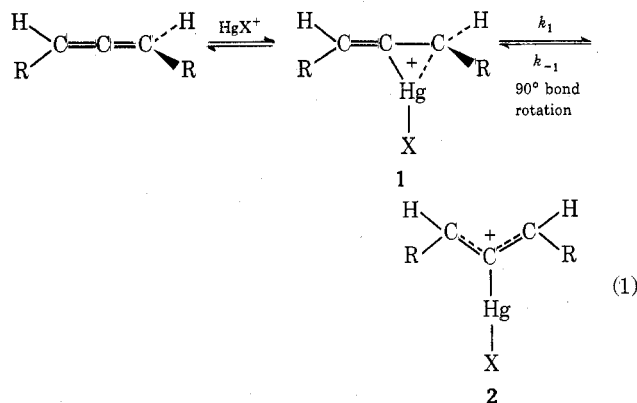
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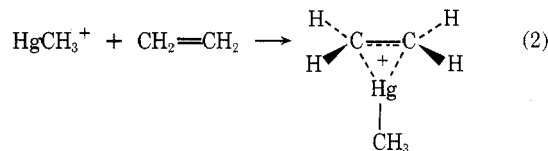
The generally accepted mechanism for the oxymercuration of alkenes in protic solvents involves a bridged or π -complexed mercurinium ion intermediate.¹ Several investi-

gators have also suggested that mercurinium ions are involved in the alkoxymercuration of allenes.² The oxymercuration of optically active allenes² has provided convincing evidence for π bridging since a considerably driving force exists for **1** to form a planar resonance stabilized allylic carbonium ion **2** (eq 1). The formation of optically ac-



tive products in these reactions² precluded exclusive product formation from the planar cation **2** providing evidence for either a mercurinium ion intermediate or a π -bridged transition state. Recently, additional experimental³ and theoretical⁴ evidence has been reported in support of this mechanism. Despite the extensive research on this reaction, unequivocal evidence for mercurinium ions under oxymercuration reaction conditions has not been reported. However, long-lived mercurinium ions derived from alkenes have been observed in solution by nmr spectroscopy.⁵

We have recently provided the first evidence for the existence of π -bridged cyclic mercurinium ions in the gas phase by using ion cyclotron resonance (icr) mass spectrometry.⁶ In this previous study we established that the ion molecule reaction of HgCH_3^+ with ethylene resulted in the formation of a new ion that corresponded to the mass $\text{C}_2\text{H}_4\text{HgCH}_3^+$ as in eq 2. This was a significant finding



since there are few known examples of ion cyclotron resonance (icr) studies on volatile organometallic compounds. Foster and Beauchamp⁷ have reported that ion molecule reactions of $\text{Fe}(\text{CO})_5$ afford ions containing two iron atoms.

We now report the observation of a mercurinium ion derived from the reaction of HgCH_3^+ and allene in the gas phase employing icr mass spectrometry and find that the rate of formation of this ion is the same order of magnitude as the theoretical collision rate constant. We have also examined the relative energies of the various ions formed with extended Hückel molecular orbital calculations to aid in identification of the most probable structures of the product ions.

Experimental Section

A Varian V-5900 ion cyclotron resonance mass spectrometer was used for the observations. A flat cell with the drift plates separated by 1.1 cm was used. Some cell modifications and our operating techniques were described previously.^{8,9} Additional modifications are as follows. A Veeco Model RG-830 ionization gauge together with a Model 523H Barocel are now used in place of a cold cathode gauge to monitor cell pressure. The cell was modified for pulsed electron beam modulation by adding a control grid and appropriate pulsing electronics.⁹ A new emission current control amplifier based on a Burr-Brown Model 3013/15 according to a design of J.

L. Beauchamp replaced the unit originally supplied by Varian; this unit allows regulation of emission currents down to 4×10^{-9} A. An oil diffusion pump was added so that the cell can be pumped either with it or with the original ion pump.

Allene was obtained from J. T. Baker Chemical Co. and dimethylmercury was synthesized by T. Weibel of this department. All gases were degassed by freeze-pump-thaw techniques at 77°K before use.

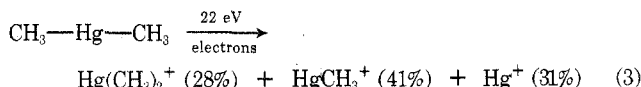
Standard bond angles and distances for allene were used in the extended Hückel calculations.¹⁰ The carbon-mercury bond distances have been given elsewhere.⁴ One-electron wave functions and energies were computed using the following valence orbital ionization potentials (VOIP's) for the diagonal elements of the Hamiltonian matrix (H_{ii} , in eV).

$H(H_{1s}) = -13.60$	$H(C_{2p}) = -10.77$
$H(C_{2s}) = -21.20$	$H(Cl_{3s}) = -25.77$
$H(Cl_{3p}) = -13.69$	$H(Hg_{6s}) = -10.44$
$H(Hg_{6p}) = -5.00$	$H(Hg_{5d}) = -15.66$

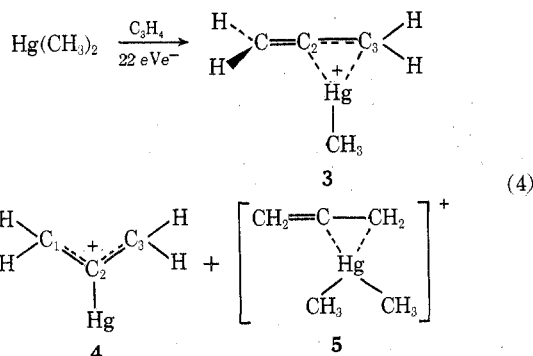
The resonance integrals, H_{ij} , were evaluated using the Wolfsberg-Helmholz expression¹¹ with $K = 1.75$ for both σ and π interactions: $H_{ij} = 1.75S_{ij}(H_{ii} + H_{jj})/2$. The overlap integrals, S_{ij} , were calculated using Clementi's¹² double ζ atomic self-consistent field wave functions. The Herman-Skillman¹³ functions given for the 1^+ metal ion were used for mercury. Charges were iterated to self-consistency using a charge sensitivity factor of 2.00 eV/electron.

Results and Discussion

Dimethylmercury was introduced into the icr mass spectrometer at $2-3 \times 10^{-6}$ Torr with 22 eV ionizing electrons. The mercury-containing ions are given by eq 3. Through a



second inlet $2-18 \times 10^{-6}$ Torr of allene was introduced. Pulsed electron beam modulation in the icr cell at room temperature gave the spectrum shown in Figure 1. Upon adding allene a prominent new peak corresponding to the mass of $\text{C}_3\text{H}_4\text{HgCH}_3^+$ is observed. The mercury-containing ion peaks were broad and consistent with the unresolved mercury isotope distribution from 198 to 204 amu. When special efforts were made to obtain higher resolution the mercury isotopic peaks could be resolved for the primary ions produced from $(\text{CH}_3)_2\text{Hg}$. In addition to the $\text{C}_3\text{H}_4\text{HgCH}_3^+$ product ion, new absorption signals corresponding to $\text{C}_3\text{H}_4\text{Hg}^+$ and probably $\text{C}_3\text{H}_4\text{Hg}(\text{CH}_3)_2^+$ were observed at high sensitivity. The relative intensities of these three new ions are $\text{C}_3\text{H}_4\text{HgCH}_3^+$ (~97%), $\text{C}_3\text{H}_4\text{Hg}^+$ (~3%), and $\text{C}_3\text{H}_4\text{Hg}(\text{CH}_3)_2^+$ (<1%). These observed ion peaks are tentatively assigned to structures 3, 4, and 5 in eq 4.



The $\text{C}_3\text{H}_4\text{Hg}^+$ peak is overlapped by much stronger $(\text{CH}_3)_2\text{Hg}^+$ and $\text{C}_3\text{H}_4\text{HgCH}_3^+$ peaks on either side which precludes quantitative pressure studies on this ion. In preliminary investigations with olefins such as 2-butene the log of the $[\text{Hg-olefin}]^+$ intensity increases linearly with olefin pressure to support a bimolecular formation reaction.

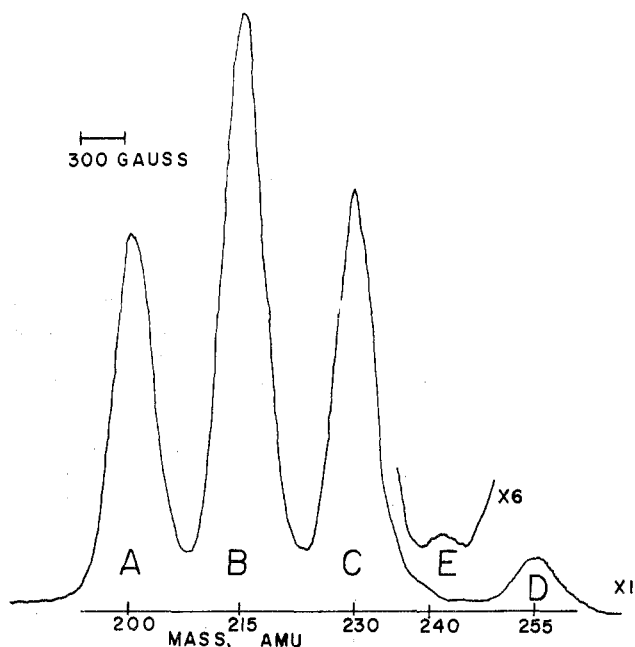
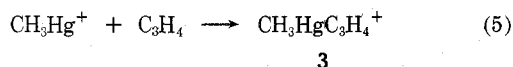


Figure 1. Icr spectrum of a mixture of $\sim 6 \times 10^{-6}$ Torr of allene and $\sim 2 \times 10^{-6}$ Torr of $\text{Hg}(\text{CH}_3)_2$ at 22 eV ionizing electron energy. Peaks A, B, C, D, and E are assigned to Hg^+ , CH_3Hg^+ , $(\text{CH}_3)_2\text{Hg}^+$, $\text{CH}_3\text{HgC}_3\text{H}_4^+$, and HgC_3H_4^+ , respectively.

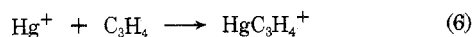
The $\text{C}_3\text{H}_4\text{HgCH}_3^+$ peak could be studied quantitatively with respect to allene pressure. The log of the $\text{C}_3\text{H}_4\text{HgCH}_3^+$ intensity increases linearly with allene pressure and the log of the CH_3Hg^+ intensity decreases linearly with allene pressure to support the bimolecular reaction (reaction 5). The rate constants from these measurements are discussed below.

As additional confirmation of reaction 5, ion ejection experiments, in which a reactant ion is ejected by a strong rf field, were performed on both HgCH_3^+ and C_3H_4^+ . These



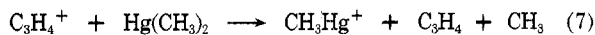
experiments clearly indicate that the formation of 3 occurs by collision of HgCH_3^+ with neutral allene and precludes its formation by collision of C_3H_4^+ with dimethylmercury. It is possible that collision of $(\text{CH}_3)_2\text{Hg}^+$ with allene could also lead to ion 3; this could not be excluded by ion ejection since some 3 is ejected along with $(\text{CH}_3)_2\text{Hg}^+$. We stress that reaction 5 definitely occurs but that this reaction is not necessarily the only pathway to the product 3.

Ion ejection experiments also indicate that Hg^+ reacts with allene to form 4. Again, the reaction of HgCH_3^+ with allene to produce ion 4 could not be definitely tested by ion ejection. However, ion 4 is also produced by ionization of elemental mercury at 40 eV and $8-9 \times 10^{-6}$ Torr of allene. Thus reaction 6 definitely occurs.



It was not possible to clearly test whether $\text{Hg}(\text{CH}_3)_2^+$ leads to 5 or not because of the low intensity of 5. The intensity of ion 5 was always weak but it appears to be reproducibly formed. It seems probable that 5 is a loosely bound radical ion complex and its structural assignment is tentative.

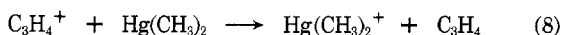
The net loss of CH_3Hg^+ corresponds to a rate constant of $1.5 \pm 0.5 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \text{ mol}^{-1}$ and the formation rate constant of $\text{CH}_3\text{HgC}_3\text{H}_4^+$ (see eq 5) is $1.4 \pm 0.5 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \text{ mol}^{-1}$. These rates appear comparable but HgCH_3^+ may also be produced by reaction 7. This reaction



was demonstrated by ion ejection of C_3H_4^+ which reduces the intensity of CH_3Hg^+ . Thus, the net rate constant for loss of CH_3Hg^+ is a result of its loss and formation in reactions 5 and 7. The rate constant for loss of CH_3Hg^+ from reaction 5 is expected to be comparable to the theoretical collision rate constant calculated from $K = 2\pi e(\alpha_{\parallel}/\mu)^{1/2}$ where μ is the reduced mass of the ion-neutral system and α_{\parallel} is the parallel component of the polarizability of allene ($29.6 \times 10^{-25} \text{ cm}^3$) which is perpendicular to the nodal plane of the double bond and hence in the direction of probable attack by the positive ion.¹⁴ We find $K(\text{theory}) = 6.9 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \text{ mol}^{-1}$. If the isotopic polarizability of allene ($55.5 \times 10^{-25} \text{ cm}^3$) is used the theoretical rate constant becomes $9.5 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \text{ mol}^{-1}$. It is seen that the net rate constant for loss of CH_3Hg^+ is 5–6 times smaller than the theoretical maximum expected from reaction 5 alone. Thus, we may reasonably conclude that the rate constant for loss of CH_3Hg^+ from reaction 5 is somewhat larger than the measured net rate constant and that product 3 is formed with less than 20% efficiency.

The suggested product ions in reactions 5 and 6 are adducts in which the unknown reaction exothermicity must be distributed among internal vibrational and rotational modes such that dissociation is not complete. Although our mass resolution cannot exclude product ions with one less hydrogen atom, it seems that stabilization of some adduct ions will be facilitated by the heavy Hg and the large number of other atoms. The efficiency of vibrational to translational relaxation is unknown in such heavy atom systems. In these experiments the reactant ions have only thermal kinetic energies and the adduct ions are undoubtedly the primary products. The dissociation of these adduct ions could best be studied quantitatively by varying the kinetic energy of the reactant ions.

As noted above, reactions 5 and 6 do not involve C_3H_4^+ . At least two pathways involving C_3H_4^+ are given in eq 7 and 8. The evidence for reaction 8 is an observed decrease



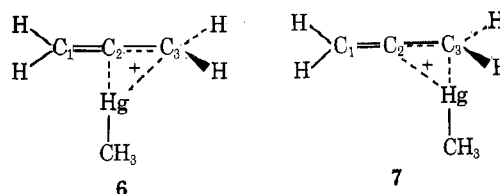
in $(\text{CH}_3)_2\text{Hg}^+$ upon ejection of C_3H_4^+ . The mechanism for reaction 7 could either involve dissociative charge exchange or formation of 5 followed by dissociation. The relevant appearance potentials are C_3H_4^+ ($10.2 \pm 0.2 \text{ eV}$), $(\text{CH}_3)_2\text{Hg}^+$ ($9.0 \pm 0.2 \text{ eV}$), and CH_3Hg^+ ($10.4 \pm 0.2 \text{ eV}$)¹⁵; so dissociative charge exchange is just possible and neither mechanism can be clearly excluded. The appearance potentials are favorable for a charge exchange mechanism for eq 8.

An ion residence time in the icr cell of about $3 \times 10^{-3} \text{ sec}$ establishes ions 3 and 4 as truly stable gas-phase species. The relative intensities of ions 3–5 did not change much with electron energy over a range of 20–70 eV. Thus, although these adduct ions are internally excited, they do not seem to be on the verge of dissociation.

We also wish to suggest the probable structure for ions 3 and 4 based upon extended Hückel (EH) molecular orbital calculations.¹⁶ We first examined the geometry of 3 to establish whether any deviation of the $180^\circ \text{ C}_1\text{--C}_2\text{--C}_3$ bond angle of the allene due to partial σ bonding occurs.¹⁷ However, our calculations indicate that any deviation of the linear allene in the π complexes with Ag^+ , Hg^+ , Hg^{2+} , HgCH_3^+ , and HgCl^+ results in an increase in the total energy of the ion. Previous calculations^{4,6} have suggested that silver ion and mercury ion complexes with ethylene are also essentially planar ions that are more adequately described as π complexes rather than as σ -bonded cyclic intermediates with rehybridization at carbon.

We next examined the potential energy required to move

the HgCH_3^+ moiety over at a fixed distance (2.347 Å) from the $\text{C}_2\text{--C}_3$ double bond to afford ions 6 and 7. The unsym-



metrically bonded ions 6 and 7 are 13.0 and 19.0 kcal/mol higher in energy than ion 3 where the mercury atom is equidistant between the $\text{C}_2\text{--C}_3$ carbons. Our calculations also suggest that the highly reactive allene complex ion derived from interaction with Hg^{2+} , where considerably greater perturbation of the π bond results in a substantial charge on carbon, would also be more stable in the gas phase when symmetrically bonded to $\text{C}_2\text{--C}_3$.

A potential driving force exists for alkyl substituted ions such as 1 to form a planar resonance stabilized allylic carbonium ion 2 (eq 1). The possibility that the resonance stabilized cation may also be formed in the gas phase in the absence of solvent prompted us to calculate the total energy difference between the mercurinium ions of HgCH_3^+ and Hg^+ and their open cation structures 2 and 4. The mercurinium ions 3 derived from allene and Hg^{2+} , HgCH_3^+ , and HgCl^+ are all considerably lower in energy than their corresponding planar allylic cations 2. Our calculations suggest that a $90^\circ \text{ C}_2\text{--C}_3$ bond rotation for 3 with concomitant rehybridization at C_2 in the gas phase would be endothermic by 142 kcal/mol (see eq 1). In contrast, the open acyclic cation 4 is calculated to be 27 kcal/mol more stable than the allene π complex of Hg^+ . However, it should be noted that conversion of the cyclic π complex to 4 would have a calculated activation energy of at least 53 kcal/mol. This estimate is based upon the increase in total energy observed upon a $90^\circ \text{ C}_2\text{--C}_3$ bond rotation of the π complex of allene and Hg^+ without rehybridization at C_2 . In contrast, the π complexes, 3, of Hg^{2+} , HgCH_3^+ , and HgCl^+ do not exhibit a higher total energy on 90° bond rotation than their corresponding rehybridized allylic planar cations 2.²¹ These data suggest that the exothermic conversions of the allylic planar cations 2 of Hg^{2+} , HgCH_3^+ , and HgCl^+ to the cyclic π -complex cations 3 could occur without substantial activation energy. Thus, we wish to suggest that the ion derived from HgCH_3^+ and allene is a π -bridged cyclic mercurinium ion, (3) while the ion derived from Hg^+ (4) is an acyclic planar allylic cation if the cyclic π -complex 3 has sufficient internal energy to achieve bond rotation to form resonance stabilized planar ion 4.

Acknowledgment is made to the National Institutes of Health (ES 00761-03) for support of this work. We thank J. Beauchamp for a schematic of his emission control circuit and T. Weibel for the synthetic work.

Registry No.—3, 53198-73-5; 4, 53198-74-6; 5, 53198-75-7; dimethylmercury, 593-74-8; allene, 463-49-0.

References and Notes

- (1) W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968).
- (2) W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Amer. Chem. Soc.*, **90**, 6741 (1968); (b) R. D. Bach, *Tetrahedron Lett.*, 5841 (1968); (c) R. D. Bach, *J. Amer. Chem. Soc.*, **91**, 1771 (1969); (d) W. S. Linn, W. L. Waters, and M. C. Caserio, *ibid.*, **92**, 4018 (1970).
- (3) D. J. Pasto and J. A. Gontarz, *J. Amer. Chem. Soc.*, **93**, 6902 (1971); R. D. Bach and R. F. Richter, *ibid.*, **94**, 4747 (1972).
- (4) R. D. Bach and H. F. Henneke, *J. Amer. Chem. Soc.*, **92**, 5589 (1970); R. D. Bach and P. A. Scheer, *ibid.*, **94**, 220 (1972).

- (5) G. A. Olah and P. R. Clifford, *J. Amer. Chem. Soc.*, **93**, 1261, 2320 (1971).
- (6) R. D. Bach, J. Gaughofer, and L. Kevan, *J. Amer. Chem. Soc.*, **94**, 6860 (1972).
- (7) M. S. Foster and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **93**, 4924 (1971).
- (8) T. Su and L. Kevan, *J. Phys. Chem.*, **77**, 148 (1973).
- (9) J. Gaughofer, Ph.D. Thesis, Wayne State University, 1972.
- (10) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 11 (1958).
- (11) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).
- (12) E. Clementi, *IBM J. Res. Develop., Suppl.*, **9**, 2 (1965).
- (13) F. Herman and S. Skillman, "Atomic Structure Calculations," Prentice Hall, Englewood Cliffs, N.J., 1963.
- (14) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).
- (15) *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 26 (1969).
- (16) R. Hoffman, *J. Chem. Phys.*, **39**, 1397 (1963).
- (17) The allene skeleton has been shown to be distorted in platinum (142° C₁-C₂-C₃ bond angle)¹⁸ and rhodium (153° ¹⁹ and 158° ²⁰) complexes.
- (18) M. Kadonaga, N. Yasouka, and N. Kasai, *Chem. Comm.*, 1597 (1971).
- (19) P. Racanelli, G. Pantini, A. Immirizi, G. Allegra, and L. Porri, *Chem. Commun.*, 361 (1969).
- (20) T. Kashiwagi, N. Yasouka, N. Kasai, and M. Kukudo, *Chem. Commun.*, 317 (1969).
- (21) The calculated charge distributions on carbon and mercury are also consistent with the above results. With the ions derived from Hg²⁺, HgCH₃⁺, and HgCl⁺, conversion from the π complex to the allylic cation resulted in a significant increase in charge at C₁ and C₂ and a concomitant decrease in charge on mercury. The opposite trend was noted with Hg⁺ ions thus rendering the cation 2 more stable since mercury can more readily accommodate a positive charge than carbon.

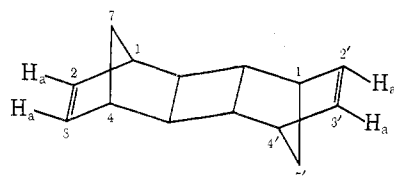
Trimeric Structure and Mixed Cycloaddition from the Nickel-Catalyzed Reaction of Norbornadiene

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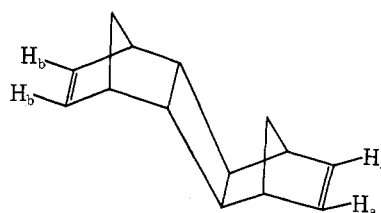
Contribution from the Department of Chemistry, Montana State University, Bozeman, Montana 59715

Received August 2, 1974

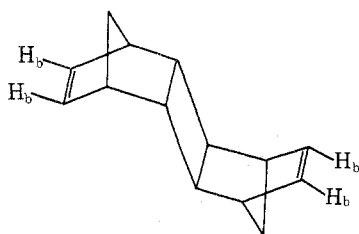
Since Cookson² reported on the cycloaddition of norbornadiene using Fe(CO)₅ as a promotor, several investigators have studied the reaction which yields a myriad of norbornyl dimers, ketones, and trimers.³ Efforts to catalyze a mixed [2 + 2] cycloaddition of norbornadiene and other olefins have been few.⁴ In fact, to the best of our knowledge, no one has been successful in coupling norbornadiene and norbornene. In this paper, we wish to present a structure proof for one of the trimeric compounds of norbornadiene



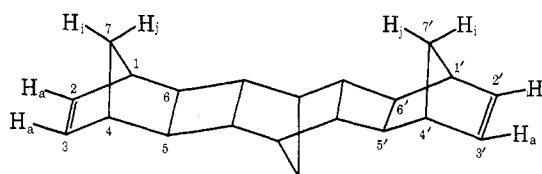
I
exo,trans,exo



II
endo,trans,exo



III
endo,trans,endo



IV
exo,trans,exo,trans,exo

Table I

Position (see Figure I)	Trimer, δ , ppm	exo,trans,exo Dimer
2,2',3,3'-Olefinic protons	5.93	6.01
1,1',4,4'-Bridgehead protons	2.61	2.61
7,7'-Bridge methylenes	1.90 and 1.82 AX 1.20 and 1.12 quartet	1.88 1.79 1.32 1.23

and to present evidence that (Ph₃P)₂Ni(CO)₂ catalyzes the mixed cycloaddition of norbornadiene to the dimer which is a pseudo norbornene.

Chemical shift data garnered from the nmr spectrum of trimer IV are listed in Table I.

By comparing the nmr spectra of IV with well-characterized spectra of analogous dimers, several conclusions could be made. A single olefinic resonance at 5.77^{3a,5} accounting for four protons indicated that compound IV had two carbon-carbon double bonds and the protons on them were in identical environments. Mass spectral analysis of IV confirmed the molecular weight as 276 and a m/e of 280 for the hydrogenated product of IV confirmed the presence of two carbon-carbon double bonds. Dimers which have an *exo*-cyclobutane ring across the norbornyl unit from the olefin moiety, as in I, have single olefin resonances between 5.65 and 5.97.^{3a} In structures having both *endo*- and *exo*-bonded cyclobutane rings, as in II, two olefinic resonances are found. Finally, in compounds such as III where both rings have *endo*-bonded cyclobutanes, a single olefin resonance is observed around 6.15 to 6.25.³ Thus, from the close agreement between dimer I and trimer IV nmr spectra (Table I),⁹ it was reasonable to conclude that each outer norbornyl unit of IV had an *exo*-bonded cyclobutane ring across from the olefin.

The bridge proton resonances provided additional proof for the identical character of the two exterior norbornyl units. Again, based on the nmr spectra of dimer structures, the two bridge protons (at 7 or 7') will appear in the spectra as a 4-line AB or AX quartet. Their resonance positions are also a function of the position of the cyclobutane ring. In the spectrum of IV, there appears to be only one AX quartet which indicates again that the outer norbornyl units are identical.