One surprising aspect of this study is that attempts to add trifluoromethyl hypochlorite to either perfluoro-2-butene or perfluoro-2-butyne were unsuccessful, though in each case the reaction mixture was heated to the decomposition point of the hypochlorite (~150°).

The mechanism for the reactions described here remains uncertain. The direction of addition to unsymmetrical olefins, *i.e.*, $CF_2{=}CH_2$, argues for a "Cl^+" type mechanism rather than a radical process, but the definitive experiments with radical inhibitors and with certain specialized olefins have not been performed.

Registry No.—Pentafluorosulfur hypochlorite, 22675-70-3.

Halogenated Ketenes. XV. Studies on Aldohalo- and Aldoalkylketene Cycloadditions[1]

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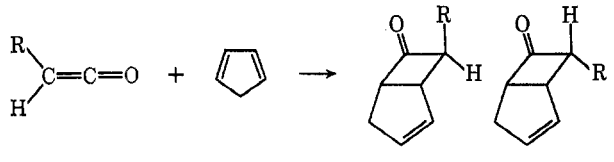
The dehydrohalogenation of haloacetyl halides in the presence of cyclopentadiene produces the corresponding 1,2 cycloadducts of fluoro-, chloro-, and bromoketenes. These unsymmetrical aldohaloketenes undergo cycloaddition stereospecifically to produce only the *endo*-halo isomer. Methyl-, ethyl-, and isopropylketenes were prepared in an analogous manner and the cycloadditions with cyclopentadiene were also stereospecific to yield only the *endo*-alkyl isomers. The results are discussed in terms of the principle of orbital symmetry conservation.

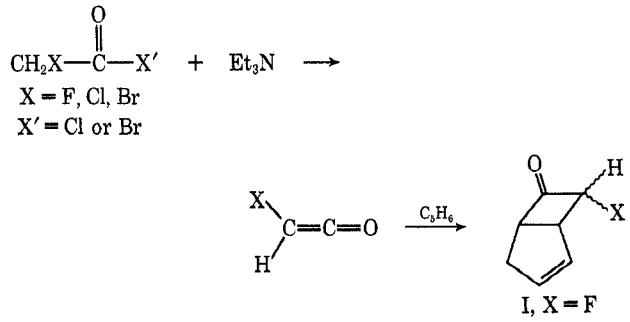
The cycloaddition of ketoketenes and olefins has received a lot of attention in the literature in the past few years. However, there have been essentially no reports on cycloadditions involving aldoketenes, presumably because of the instability of these ketenes and the necessity of performing *in situ* reactions. Since aldoketenes are unsymmetrical, the possibility exists for the formation of two stereomers in the (2 + 2) cycloaddition reaction as illustrated with cyclopentadiene. Unsymmetrical ketoketenes are, of course, also possible but the stereochemistry of these cycloadditions has apparently gone unnoticed. Hasek and Martin have reported the preparation of the cycloadduct of butylethylketene with cyclopentadiene but only mentioned that two isomers were apparently formed as evidenced by vpc.[2] Jaz and Denis have recorded in a communication the preparation of adducts of methyl-, ethyl-, *n*-propyl-, isopropyl- and *n*-butylketenes with cyclopentadiene but no mention was made about the stereochemistry.[3] We have recently reported on the stereochemistry of alkylhaloketene (unsymmetrical ketoketenes) and cyclopentadiene cycloadditions.[4-6]



Continuing our efforts in studies involving the preparation and cycloaddition of halogenated ketenes, we have investigated the aldohaloketenes. There has been only one report on this type of ketene and this was simply the mention of chloroketene by Opitz and coworkers on the cycloaddition with an enamine.[7] Consequently, the purpose of this paper is to describe the preparation of fluoro-, chloro-, and bromoketenes and relate the stereochemistry of the cycloadditions with cyclopentadiene and also the stereochemistry of some aldoalkylketene cycloadditions. Two preliminary reports of this work have appeared.[8,9]

Results

Fluoro-, chloro-, and bromoketenes were prepared by the dehydrohalogenation of the appropriately substituted acetyl halide with triethylamine at −78°. The ketenes could not be isolated but could be trapped by performing the cycloadditions in the presence of cyclopentadiene. The ketenes appeared to be quite stable in the reaction mixture at −78° but upon warming to room temperature polymerized to a black tar. The cycloaddition with cyclopentadiene does not occur at −78° as warming to room temperature is necessary to produce the bicyclo[3.2.0]hept-2-en-6-ones.



I, X = F
II, X = Cl
III, X = Br

Fluoroketene was also trapped with diisopropylcarbodiimide to form the 1,2 cycloadduct, 3-fluoro-1-isopro-

* To whom correspondence shonld be addressed.

(1) Paper XIV: W. T. Brady and R. Roe, Jr., *J. Amer. Chem. Soc.*, **92**, 4618 (1970).

(2) J. C. Martin, G. P. Gott, V. M. Goodlett, and R. H. Hasek, *J. Org. Chem.*, **30**, 4175 (1965).

(3) E. Jaz and E. Denis, *Bull. Soc. Chim. Belges*, **75**, 845 (1966).

(4) W. T. Brady and B. M. Holifield, *Tetrahedron Lett.*, 5511 (1966).

(5) W. T. Brady and B. M. Holifield, *Tetrahedron*, **23**, 4251 (1967).

(6) W. T. Brady, R. Roe, Jr., E. F. Hoff, Jr., and F. H. Parry, III, *J. Amer. Chem. Soc.*, **92**, 146 (1970).

(7) G. Opitz, M. Kleemann, and F. Zimmermann, *Angew. Chem.*, **74**, 32 (1962).

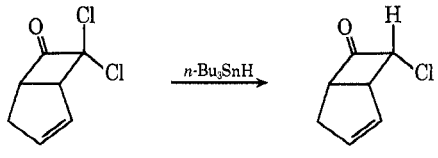
(8) W. T. Brady and E. F. Hoff, Jr., *J. Amer. Chem. Soc.*, **90**, 6256 (1968).

(9) W. T. Brady, E. F. Hoff, Jr., R. Roe, Jr., and F. H. Parry, III, *ibid.*, **91**, 5679 (1969).

pyl-4-isopropyliminoazetidin-2-one which has been reported elsewhere.[10]

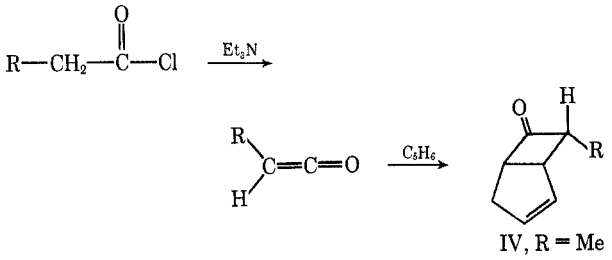
Both the *endo*- and *exo*-halo isomers were expected from each of the systems since the cyclopentadiene adducts from methylchloro- and methylbromoketenes were a mixture of isomers.[4,5] However, distillation of the reaction products yielded only one fraction which contained cycloadduct. An extensive vpc analysis indicated only one isomer was present. A check of the reaction mixture prior to distillation also revealed only one isomer.

In an effort to make a structural assignment of the single isomer produced in each system, the *endo*-chloro adduct (II) was synthesized by an independent method. The cycloadduct of dichloroketene and cyclopentadiene, 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one, was stereoselectively reduced with tri-*n*-butyltin hydride[11] to produce only the *endo*-chloro isomer.[12] The pmr spectrum



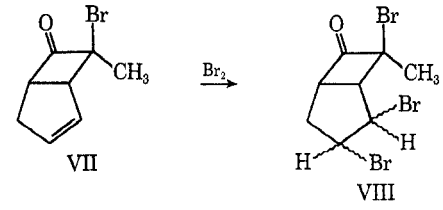
of this compound was compared to the pmr spectrum of the chloroketene–cyclopentadiene adduct and the two were identical.[12] The pmr spectra of the fluoro- and bromoketene cycloadducts with cyclopentadiene were found to be consistent with assignment as the endo isomers.

Molecular models reveal that the endo halogen is right over the residual π system of the diene. Therefore, in an effort to determine if the halogen was causing the endo specificity, the investigation of some aldoalkylketene systems was undertaken. The dehydrochlorination of propionyl chloride, butyryl chloride, and isovaleryl chloride with triethylamine in the presence of cyclopentadiene produced the corresponding 1,2 cycloadducts of methyl-, ethyl-, and isopropylketenes. Only one isomer was produced in each system.

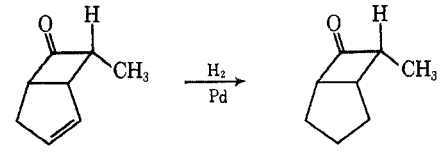


IV, R = Me
V, R = Et
VI, R = *i*-Pr

The pmr spectrum of IV clearly revealed that only the *endo*-methyl isomer had been produced. Also, the pmr spectrum of a brominated IV revealed that the product of bromination was the same as that obtained by the bromination of VII.[5]



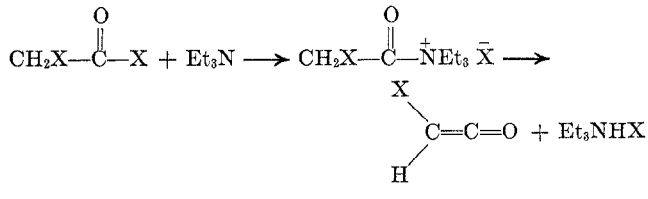
Also, the pmr spectrum of the hydrogenated IV revealed a shift (~2 cps) in the methyl resonance.



Compounds V and VI were also found to be the *endo*-alkyl isomers by pmr analysis of the brominated adducts.

Discussion

In the preparation of the aldohaloketene–cyclopentadiene adducts, the addition of the acid halide to the reaction solution at −78° results in the immediate formation of an insoluble salt. However, the cycloadduct is not produced at this temperature, not even after 48 hr, but upon warming to room temperature the cycloadduct is readily formed. The exothermic nature of the dehydrohalogenation and decreased yields are detrimental to effecting the dehydrohalogenation at room temperature or higher. It is very likely that the salt initially formed is the acyl ammonium salt which upon



warming decomposes to the ketene. Such an acylammonium salt is known and has been characterized.[13]

Integration of the pmr spectrum of I revealed that the area for the vinyl resonance was too large and the area for the proton geminal to fluorine was too small. This was due to the large coupling constant (55 cps) of fluorine which caused half of the resonance for this proton to occur downfield under the vinyl resonance. This was demonstrated by bromination which eliminated the vinyl resonance and revealed a multiplet of equal area, 55 cycles downfield from the resonance assigned to the proton geminal to fluorine. The brominated product could not be distilled nor chromatographed; thus further characterization was not achieved.

A more convincing proof of structure resulted from hydrogenation of I and complete characterization of the product. The pmr spectrum of the hydrogenated product revealed a multiplet (area equivalent to one-half proton) which was 55 cycles downfield from the reso-

(10) W. T. Brady, E. D. Dorsey, and F. H. Parry, III, *J. Org. Chem.*, **34**, 2846 (1969).

(11) H. G. Kuivila, *Accounts Chem. Res.*, 299 (1968).

(12) This same *endo*-chloro isomer was prepared by the zinc–acetic acid stereoselective reduction of the dichloroketene–cyclopentadiene adduct by Professor Andre' Dreiding of the University of Zurich [M. Rey, U. A. Huber, and A. S. Dreiding, *Tetrahedron Lett.*, 3583 (1968)]. The pmr spectrum of this compound was also identical with that of the chloroketene–cyclopentadiene adduct.

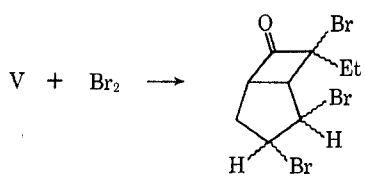
(13) (a) H. Adkins and Q. E. Thompson, *J. Amer. Chem. Soc.*, **71**, 2242 (1949). (b) G. B. Payne, *J. Org. Chem.*, **31**, 718 (1966).

nance assigned to the proton geminal to fluorine (area one-half proton).

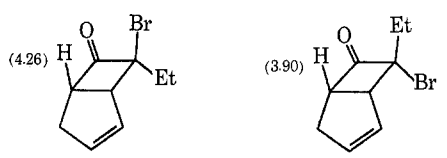
Bromoketene underwent cycloaddition to produce only about a 5% yield of the cycloadduct compared to 40% for the fluoroketene adduct and 60% for the chloroketene adduct. All of the preparations are accompanied by the formation of a black tarry substance which is the result of a competing polymerization reaction of the ketene. Apparently, bromoketene is more susceptible to this undesirable polymerization or less reactive toward cycloaddition.

The methylketene adduct with cyclopentadiene was prepared utilizing the procedure and conditions which were so successful for the chloroketene system. This resulted in a very low yield (~10%), but the reaction conditions and solvents were varied to increase the yield to about 35%. The pmr spectrum of IV revealed a methyl doublet at δ 0.99. Martin and coworkers have reported that the pmr spectrum of the dimethylketene–cyclopentadiene adduct showed the methyl resonance at δ 1.28 and 0.93.[2] We have recently demonstrated in two methylhaloketene–cyclopentadiene systems that the upfield resonance was *endo*-methyl and the downfield resonance the *exo*-methyl. Thus, the methyl resonance at δ 0.99 observed in this system must be due to *endo*-methyl.

The cycloaddition of ethylketene to cyclopentadiene results in the isolation of only one isomer of 7-ethylbicyclo[3.2.0]hept-2-en-6-one as evidenced by vpc. The pmr spectrum did not indicate which isomer was produced. Bromination resulted in the replacement of the proton geminal to the ethyl group by bromine.

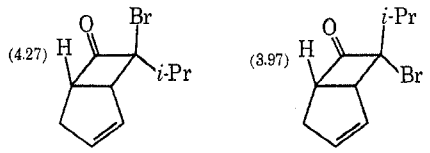


Both endo and exo isomers have been reported for a number of alkylhaloketene–cyclopentadiene cycloadducts. The pmr spectra of these compounds have been thoroughly investigated and a pattern observed for endo and exo isomers. The isomers of the ethylbromoketene cycloadduct are easily distinguished by a consideration of the chemical shift of the proton on carbon atom number five.[1] This resonance occurs at δ 4.26 when the ethyl group is endo and δ 3.90 when exo. Bromination of the ethylketene adduct produced a spectrum like



that of the ethylbromoketene cycloadduct with a resonance at δ 4.3 and no resonance at 3.90.[14]

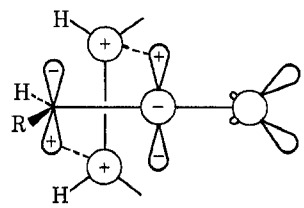
Also, only one isomer was produced in the isopropylketene–cyclopentadiene system and this was the endo isomer as evidenced by bromination and subsequent pmr analysis. The pmr spectrum of the *endo*-isopropyl isomer of the isopropylbromoketene–cyclopentadiene adduct had a resonance at δ 4.27 for the proton on carbon atom number five. The *exo*-isopropyl isomer



showed a resonance at δ 3.97 for this same hydrogen.[1] Bromination of the isopropylketene–cyclopentadiene adduct resulted in the appearance of a characteristic resonance at δ 4.25 and no resonance at δ 3.97.[14]

In summary, all of the aldoketenes investigated in this work were observed to undergo stereospecific cycloaddition with cyclopentadiene under the conditions described.

Woodward and Hoffmann have recently reported that in order for a (2 + 2) cycloaddition to be symmetry allowed as a thermal, concerted process, the reacting molecules must approach one another in an orthogonal manner. Ketenes are considered to play an antarafacial role ($\pi 2_s + \pi 2_a$) in the cycloaddition as illustrated.[15] Steric repulsion prevents the approach of the

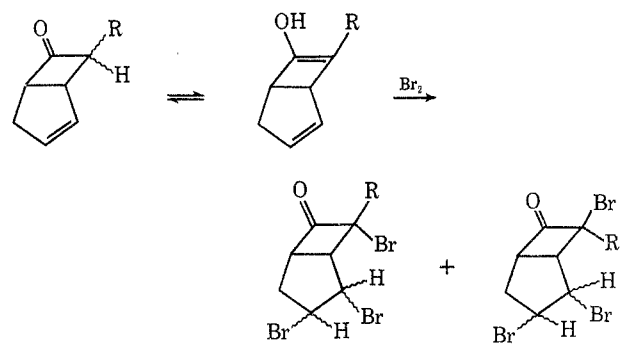


olefin on the side of the much larger R group. Also, in the sterically preferred approach, the bulky substituent on the olefin is away from the ketene hydrogen. These steric considerations in the orthogonal transition state lead to the prediction of a strong preference for the endo isomer. Since this is exactly what we have observed, this represents an excellent correlation with the recent theoretical developments in this area.

Experimental Section

Vpc separations were accomplished with an Aerograph AP-49 or Varian Model 1525-B instrument, using thermal conductivity detectors. Separations were achieved employing a 10 ft × 1/4 in. column packed with 15% Ucon 50 HB 2000 Polar and 2% Oronite NIW on Chromosorb W (DNSC) 60–80 mesh, or a 10 ft × 1/4 in. column packed with 10% QF-1 on Chromosorb W (acid washed) 60–80 mesh.

(14) It was expected that the bromination of IV, V, and VI would proceed through the enol form of the cycloadduct and produce both *endo*- and *exo*-bromo isomers. Since both isomers were not produced, another pathway



was indicated whereby a retention of configuration occurred at C_7. This is supported by the fact that IV was established to be *endo*-methyl isomer by pmr; yet bromination afforded only the *endo*-methyl isomr.

(15) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

Pmr spectra were obtained with a Varian A-60 nuclear magnetic resonance spectrometer, employing tetramethylsilane as the internal standard at 25°.

All solvents were dried and purified by distillation from calcium hydride or lithium aluminum hydride and subsequently stored over calcium hydride or molecular sieves 4A.

Fluoroacetyl chloride was prepared from sodium fluoroacetate and phosphorous pentachloride according to the procedure of Truce.[16] All of the other acid halides were prepared from commercially available acids by standard procedures. Cyclopentadiene was obtained by thermally cracking commercially available dicyclopentadiene at about 140°. Tri-*n*-butyltin hydride was prepared from commercially available tri-*n*-butyltin chloride and lithium aluminum hydride.[17] The dichloroketene–cyclopentadiene adduct was prepared by the dehydrochlorination of dichloroacetyl chloride in the presence of cyclopentadiene.[18]

7-Fluorobicyclo[3.2.0]hept-2-en-6-one (I).—A solution containing 40 g (0.395 mol) of triethylamine and 120 g (1.87 mol) of cyclopentadiene in 125 ml of ether was cooled to −78°. A 34.5-g (0.35 mol) portion of fluoroacetyl chloride was added to the cold solution dropwise and with stirring over a period of about 30 min. After the addition was complete, the cold bath was removed and the reaction mixture was allowed to warm to room temperature overnight. The originally white colored salt turned brown as the temperature rose. The salt was removed by filtration and the filtrate concentrated on a rotatory evaporator. The concentrate was distilled at 73.5° (4.5 mm) to yield 17.5 g (40%) of the adduct: ir 1800 (C=O) and 1605 cm^{-1} (C=C); pmr (CCl_4) δ 2.6 (m, 2 H), 3.45 (m, 1 H), 3.85 (m, 1 H), 5.52 (m, 1 H), and 5.87 (m, 2 H); the pmr employing a fluorine decoupler demonstrated the presence of fluorine.

Anal. Calcd for C_7H_7FO: C, 66.65; H, 5.59. Found: C, 66.50; H, 5.55.

Bromination of 7-Fluorobicyclo[3.2.0]hept-2-en-6-one.—A 0.16-g (1.3 mmol) portion of I in 0.25 ml of CCl_4 in an nmr tube was treated with a solution of 0.20 g (1.27 mmol) of bromine in 0.25 ml of CCl_4 with intermittent agitation. The pmr spectrum revealed that saturation of the vinyl region had occurred because the vinyl resonance disappeared and upfield resonances were more complicated. However, elimination of the vinyl resonance revealed the other half of the resonance for the proton geminal to fluorine.

Hydrogenation of 7-Fluorobicyclo[3.2.0]hept-2-en-6-one.—A mixture of 0.1 g of palladium black and 50 ml of absolute ethanol was stirred at 27° under a hydrogen atmosphere. A 1.4 g (0.01 mol) portion of I was injected into the system and hydrogen absorbed continuously for 1.5 hr and more slowly for another 3 hr. A total of 252 ml (0.01 mol) of hydrogen was absorbed. The alcohol was removed by distillation and the hydrogenated product purified by vpc at 150° on a 10 ft × 1/4 in. XF-1150 column: ir 1795 cm^{-1} (C=O) and no C=C; pmr (CCl_4) δ 1.86 (m, 6 H), 3.38 (m, 2 H), and a pair of multiplets separated by 55 cps centered at 5.52 (1 H).

7-Chlorobicyclo[3.2.0]hept-2-en-6-one (II). Method A.—To a solution containing 11.6 g (0.115 mol) of triethylamine and 84.4 g (1.3 mol) of cyclopentadiene in 250 ml of hexane was added, dropwise at −78°, 17 g (0.108 m) of chloroacetyl bromide with stirring. Upon warming overnight, the salt was removed and the filtrate yielded 9.2 g (60%) of II at 64° (0.6 mm): ir 1795 (C=O) and 1605 cm^{-1} (C=C); pmr (CCl_4) δ 2.6 (m, 2 H), 3.84 (m, 2 H), 5.08 (m, 1 H), and 5.81 (m, 2 H).

Anal. Calcd for C_7H_7ClO: C, 58.8; H, 4.91. Found. C, 58.55; H, 4.93.

Method B.—A solution of 8.85 g (0.05 mol) of 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one in 15 ml of toluene was rapidly added to 16.3 g (0.056 mol) of tri-*n*-butyltin hydride in 5 ml of toluene. The resulting solution is allowed to stand for 1 hr and distilled to yield 6 g (84%) of II at 40–45° (0.2–0.3 mm). The ir and pmr spectra were identical with those recorded above.

7-Bromobicyclo[3.2.0]hept-2-en-6-one (III).—A 60-ml portion of ether, 50 g (0.5 mmol) of triethylamine, and 80 g (1.41 mol) of cyclopentadiene were stirred at −78° while 50.5 g (0.25 mol) of bromoacetyl bromide was added dropwise. After warming to room temperature, the amine salt was removed and the solvent evaporated on a rotorary evaporator. Such a small amount of liquid remained that distillation was not attempted. Purification was accomplished by vpc and estimations indicated the yield was approximately 5%: ir 1795 (C=O) and 1617 cm^{-1} (C=C); pmr (CCl_4) δ 2.6 (m, 2 H), 3.87 (m, 2 H), 5.14 (m, 1 H), and 5.8 (m, 2 H).

Anal. Calcd for C_7H_7BrO: C, 44.8; H, 3.74. Found: C, 45.1; H, 3.96.

7-Methylbicyclo[3.2.0]hept-2-en-6-one (IV).—To a refluxing solution of 50 g (0.5 mol) of triethylamine, 165 g (2.5 mol) of cyclopentadiene, and 100 ml of hexane was added dropwise 46 g (0.5 mol) of propionyl chloride. After the addition was complete, refluxing was continued 1.5 hr and then the reaction mixture was allowed to cool to room temperature overnight. The amine salt was removed by filtration, the solvent evaporated, and the residue distilled at 60–65° (4.7 mm) to yield 57 g of a mixture of IV and dicyclopentadiene. Vpc was necessary to accomplish a separation and revealed that approximately 20 g (33%) was produced. The ir and pmr data were consistent with those already in the literature.[3]

Hydrogenation of 7-Methylbicyclo[3.2.0]hept-2-en-6-one.—A mixture of 0.1 g of palladium black and 50 ml of absolute ethanol was stirred for about 1 hr at 27° under a hydrogen atmosphere and then 1.6 g (0.013 mol) of IV was injected into the system. When hydrogen was no longer absorbed, the solution was concentrated by distillation of the alcohol and the product purified by vpc at 125° using the Ucon–Oronite column: ir 1744 cm^{-1} (C=O), no C=C; pmr (CCl_4) δ 0.95 (d, 3 H), 1.72 (m, 6 H), 2.95 (m, 2 H), and 3.5 (m, 1 H).

Bromination of 7-Methylbicyclo[3.2.0]hept-2-en-6-one.—Bromine was slowly and cautiously added dropwise to a 30% solution of IV in CCl_4 in an nmr tube. The addition was done intermittently and continuously until the pmr spectrum revealed no resonance for vinyl protons. However, this spectrum also showed the proton geminal to the methyl group had been displaced by bromine; this was obvious because the methyl doublet (δ 0.99) disappeared and a singlet appeared downfield at δ 1.9. Attempts to purify the brominated product resulted in decomposition.

7-Ethylbicyclo[3.2.0]hept-2-en-6-one (V).—A gently refluxing solution of 34 g (0.336 mol) of triethylamine, 66 g (1 mol) of cyclopentadiene, and 100 ml of CCl_4 was treated with a 32-g (0.30 mol) portion of butyryl chloride dropwise over a 15-min period. Refluxing was continued for 1.5 hr and the solution was allowed to cool overnight. Removal of salt, concentration of the filtrate, and distillation resulted in 14 g (34%) of V at 70–71.5° (4.7 mm): ir 1773 (C=O) and 1613 cm^{-1} (C=C); pmr (CCl_4) δ 1.02 (m, 3 H), 1.90 (m, 2 H), 2.45 (m, 2 H), 3.2–4.1 (m, 3 H), and 5.8 (m, 2 H).

The 2,4-dinitrophenylhydrazone derivative was prepared by a standard procedure.

Anal. Calcd for $C_{15}H_{16}N_4O_4$: C, 56.96; H, 5.06; N, 17.72. Found: C, 57.22; H, 5.14; H, 17.96.

Partial bromination of the cycloadduct with a 10% solution of bromine in CCl_4 resulted in displacement of the proton geminal to the ethyl group by bromine. This was evident from the pmr spectrum because part of the multiplet at δ 3.2–4.1 was eliminated and a pattern appeared at δ 4.3 which was easily recognized as part of the *endo*-ethyl isomer of ethylbromoketene–cyclopentadiene cycloadduct.

7-(2-Propyl)bicyclo[3.2.0]hept-2-en-6-one (VI).—To a refluxing solution of 66 g (1 mol) of cyclopentadiene and 25 g (0.25 mol) of triethylamine in 120 ml of $CHCl_3$ was added 24 g (0.2 mol) of isovaleryl chloride dropwise over a 15-min period. Refluxing was continued 1.5 hr and the solution cooled while standing overnight. Filtration, concentration, and distillation afforded 11 g (37%) of VI at 79–80° (4.7 mm): ir 1770 (C=O) and 1607 cm^{-1} (C=C); pmr (CCl_4) δ 0.94 (m, 6 H), 1.6 (m, 1 H), 2.4 (m, 2 H), 3.0–3.9 (m, 3 H), and 5.8 (m, 2 H).

Anal. Calcd for $C_{10}H_{14}O$: C, 80.0; H, 9.34. Found: C, 80.3; H 9.59.

Partial bromination of VI with a 10% solution of bromine in CCl_4 resulted in displacement of the proton geminal to the isopropyl group by bromine. This was apparent from the pmr spectrum because part of the resonance at δ 3.0–3.9 was eliminated and a new resonance appeared at δ 4.25 which was recognized as part of the *endo*-isopropyl isomer of the isopropylbromoketene–cyclopentadiene cycloadduct.

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Registry No.—I, 25975-83-1; II, 25169-61-3; III, 25975-85-3; IV, 25169-69-1; V, 25975-87-5; VI, 25975-88-6.

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Stereochemistry of Solvolytic Cyclization of the 5-Hexenyl System. Acetolysis of Methyl-5-hexenyl *p*-Bromobenzenesulfonates[1a]

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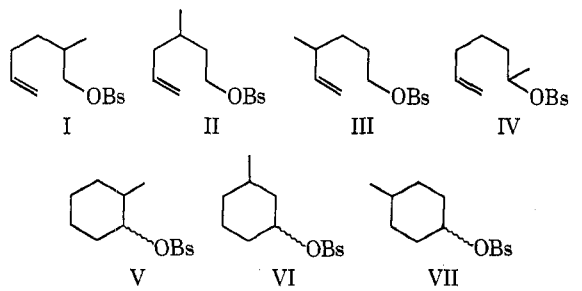
The rates and products of acetolysis of 2-, 3-, and 4-methyl-5-hexenyl *p*-bromobenzenesulfonates are reported, as well as the products of acetolysis of *cis*- and *trans*-2-, 3-, and 4-methylcyclohexyl and 6-hepten-2-yl *p*-bromobenzenesulfonates, thus furnishing data for comparison of π- and σ-route products for the three secondary methylcyclohexyl cations. As found in most previous instances for secondary carbonium ions, the π route yields less than half as much elimination product as the σ route. The stereochemistry of the substitution products from the π-route reactions strongly implies cyclization through a chairlike conformation and very rapid reaction of the resulting chair cyclohexyl cation with solvent.

Solvolytic cyclization of 5-hexenyl systems to cyclohexyl cations, the so-called π route[2] to these cations, has received considerable study,[3,4] and even synthetic use.[5] It is usually assumed that the cyclohexyl cation produced in these cyclizations is in a chair conformation, and Johnson and Harding have presented rather compelling evidence that this is the case for the mechanistically similar acid-catalyzed cyclization of 4-(3-butenyl)-3-cyclohexenol systems.[6] However, it was not at all clear that simpler, more flexible, 5-hexenyl systems should necessarily yield only the chair form of the cation in reactions involving intramolecular displacement of the leaving group by the π bond. It was therefore felt important to examine a simple system, employing a relatively innocuous marker, a methyl group, for detection of the preferred conformation of cyclization. At the same time it was hoped that presence of such a marker might help show other differences in product formation from π- and σ-route cyclohexyl cations. To this end, the rates and products of acetolysis of 2-, 3-, and 4-methyl-5-hexenyl *p*-bromobenzenesulfonates (I, II, and III) were determined, as well as the acetolysis products of 6-hepten-2-yl *p*-bromobenzenesulfonate (IV) and cis and trans isomers of 2-, 3-, and 4-methylcyclohexyl *p*-bromobenzenesulfonates (V, VI, and VII).



I II III IV

V VI VII

a, cis

b, trans

Results and Discussion

The products of acetolysis of all the brosylates are given in Table I. Because of the many components present in the product mixtures a rather elaborate method of analysis was necessary. Three separate analyses were performed on each product mixture. First, the initial pentane extract (see Experimental Section) was subject to gc analysis using a silver nitrate–ethylene glycol column which effectively separated 1-methylcyclohexene from 3- and 4-methylcyclohexene as well as "baseline" separating all the other hydrocarbons. (The separation of 3- and 4-methylcyclohexene could not be completely achieved and their yields are lumped together in Table I.) Secondly, a suitable internal standard was added to the pentane extract and the solution analyzed on a "UC-W98" (silicone rubber) column. This column separated all acetates (except certain of the cyclic ones from each other) and acyclic olefins (dienes) from cyclic ones. Finally, the product mixtures were subjected to lithium aluminum hydride reduction to convert acetates to alcohols and the resulting product mixture analyzed either with a glycerol column or a combination column composed of a forecolumn of THEED (tetrahydroxyethylethylenediamine) preceding a diglycerol column. Certain pairs of alcohols could not be separated on any columns tried. These were *trans*-3- and *cis*-4-methylcyclohexanol and *cis*-3- and *trans*-4-methylcyclohexanol. This is unfortunate, but in several instances the peak in question was collected, its ir spectrum being measured, and shown to be at least predominantly the expected isomer and not that resulting from hydride shift. All results shown in Table I are the average of at least two separate experiments. As mentioned previously,[7] the reproducibility in measurement of peak areas was no worse than $\pm 10\%$ for small peaks

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