tography. Calibration curves were constructed using the same extraction procedure but omitting the Cr(II) solution.

Analytical Methods. All titrations were carried out potentiometrically with a constant drive buret (E. H. Sargent Co.). The magnetically stirred cell could be thoroughly deaerated by bubbling a stream of nitrogen through the solution. HOAc (10 ml of 4 *M*) was purged of air, and 1 ml of reaction solution added *via* a hypodermic syringe under nitrogen. After 5 min, a thoroughly degassed solution of 0.2 *M* ferric chloride in 2 *M* sulfuric acid (1 ml) was added (the ferric content represented a 100% excess). The solution was then diluted with 50 ml of 2 *M* H_2SO_4 and titrated with standard 0.01 *M* dichromate solution. In the absence of any alkylchromium species, the acetic acid solution was omitted from the procedure.

Gas chromatographic analysis was carried out by the internal standard method. Alkanes containing fewer than four carbon atoms were readily analyzed by sampling the gas phase. All calibrations were performed using standards which matched the reaction conditions as closely as possible. Analyses of liquids were also carried out by the internal standard method on at least two columns loaded with stationary phases of different polarity.

The absorption spectra were measured in 1 cm (~3 ml) cells equipped with standard taper joints using a Beckman DBG spectrometer. The cell was capped with a gas-tight rubber septum and could be thoroughly degassed prior to introduction of various solutions with hypodermic syringes. Inhibitors and dyes were removed by repeatedly boiling the septa in the solvent employed. Small amounts of standard solution were introduced with microliter syringes, and reproducibility was limited to approximately 5%.

Competition Reactions. In all competition experiments, a pair of alkyl halides was used which afforded alkanes separable by gas chromatography. In a typical procedure, 4.5 ml of DMF, 1.75 ml of H_2O, and 2 ml of 1.49 *M* ethylenediamine in DMF were placed in a 50-ml erlenmeyer flask. Solutions (0.8 *M*) of the alkyl halides were added in the proper ratio to maintain a total volume of 6 ml. The flask was sealed with a septum and deaerated with a stream of nitrogen. The reaction was initiated by introduction of 0.75 ml of 1.3 *M* aqueous $Cr(ClO_4)_2$.

Acknowledgment. We wish to thank the National Science Foundation for a generous financial support of this work.

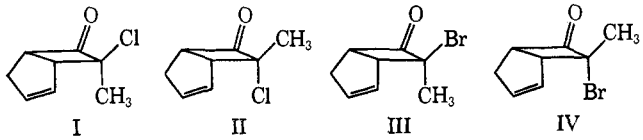
Halogenated Ketenes. X. Further Studies on the Dehydrohalogenation of 2-Halopropanoyl Halides in the Presence of Cyclopentadiene[1]

William T. Brady, Robert Roe, Jr., Edwin F. Hoff, and Fred H. Parry, III[2]

Contribution from the Department of Chemistry, North Texas State University, Denton, Texas. *Received June 5, 1969*

Abstract: The dehydrohalogenation of 2-chloro- and 2-bromopropanoyl halides with triethylamine in the presence of cyclopentene in hexane produced the same distribution of *endo*-methyl and *exo*-methyl 1,2-cycloadducts as cyclopentadiene. Thus, the isomer distribution is not influenced by the residual double bond. However, the isomer distribution of the cycloadducts is strongly dependent upon the polarity of the solvent used in the preparations. The dehydrochlorination of 2-chloropropanoyl chloride in the presence of cyclopentadiene in hexane yielded an *endo*-:*exo*-methyl ratio of 1,2-cycloadducts of 4.3. This became 0.59 when acetonitrile was employed as the solvent. The dehydrochlorination of 2-bromopropanoyl chloride in the presence of cyclopentadiene in hexane produced an *endo*-:*exo*-methyl ratio of 1,2-cycloadducts of 0.71 which became 0.14 in acetonitrile. The dehydrobromination of 2-bromopropanoyl bromide in hexane in the absence or cyclopentadiene produced a solution of methylbromoketene as evidenced by infrared.

In preceding papers, we reported that *endo*- and *exo*-methyl 1,2-cycloaddition isomers are produced from the dehydrohalogenations of 2-haloalkanoyl halides with triethylamine in the presence of cyclopentadiene.[3,4] It was reported that there is a reversal in the *endo*- and *exo*-methyl cycloadduct isomers which appear to be derived from *in situ* reactions of methylchloro- and methylbromoketenes with cyclopentadiene. There was a predominance of the *endo*-methyl isomer I for the 2-chloropropanoyl chloride–triethylamine–cyclopentadiene system and a predominance of the *exo*-methyl IV isomer for the 2-bromopropanoyl bromide–triethylamine–cyclopentadiene system. An examination of molecular models of the ketenes and cyclopentadiene does not reveal an explanation for the observed isomer distributions. We suggested earlier that this could possibly be due to an interaction between the bromine atom and the residual unsaturated system in the adduct. Since the bromine atom is right over this π-electron system, possibly this atom has an orbital far enough out to interact appreciably with this unsaturated system whereas chlorine does not. Also, it was mentioned earlier that two steps may be involved with the isomer distribution being determined by a final ring closing step. However, this seemed unlikely in view of recent reports on the "near-concerted" nature of ketene–olefin cycloadditions.[5-7]



I II III IV

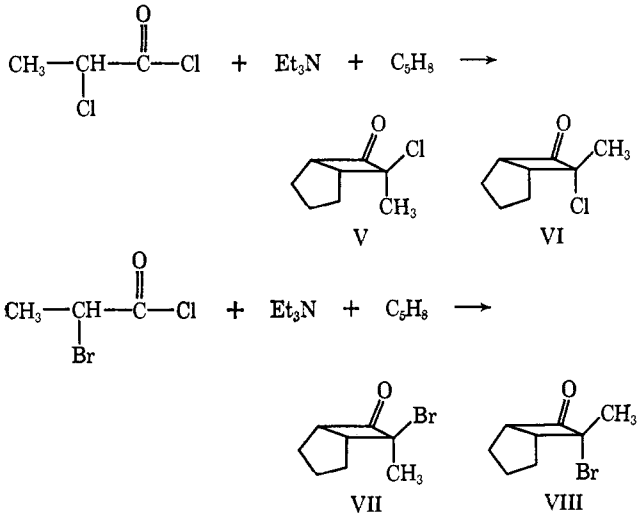
The purpose of this report is to relate some information which indicates that in the dehydrohalogenation of

(1) Paper IX: W. T. Brady, E. D. Dorsey, and F. H. Parry, III, *J. Org. Chem.*, 34, 2846 (1969).
(2) NDEA Title IV Fellow.
(3) W. T. Brady and B. M. Holifield, *Tetrahedron Lett.*, 5511 (1966).
(4) W. T. Brady and B. M. Holifield, *Tetrahedron*, 23, 4251 (1967).
(5) G. Binsch, L. A. Feiler, and R. Huisgen, *Tetrahedron Lett.*, 4497 (1968).
(6) W. T. Brady and H. R. O'Neal, *J. Org. Chem.*, 32, 612 (1967).
(7) W. T. Brady and H. R. O'Neal, *ibid.*, 32, 2704 (1967).

2-halopropanoyl halides, in the presence of cyclopentadiene, the residual double bond does not influence the isomer distribution and, furthermore, this isomer distribution is strongly dependent on solvent polarity.

Results

The dehydrohalogenation of 2-chloro- and 2-bromopropanoyl halides with triethylamine in the presence of cyclopentadiene has been examined in more detail in an effort to understand the reversal in cycloadduct isomer distributions. If this reversal is in any way related to an interaction of one of the halogens with the residual double bond in the diene or adduct, cycloaddition with cyclopentene should lead to a different isomer distribution with at least one of the systems. This cycloaddition was accomplished and is illustrated below.



Both the *endo*- and *exo*-methyl isomers were produced as evidenced by vpc. The adducts with cyclopentadiene were separated by preparative vpc and differentiated by nmr. Hydrogenation of I and II produced V and VI, respectively, as evidenced by corresponding identical infrared and nmr spectra and vpc retention times. Isomers VII and VIII were similarly related to the hydrogenated isomers of III and IV, respectively. The isomer distributions are shown in Table I. The cyclo-

Table I. Cycloadduct Isomer Distribution with Cyclopentene and Cyclopentadiene in Hexane[a]

X	Olefin	Temp, °C	% yield	*endo*-:*exo*-methyl ratio
Cl	Cyclopentadiene	0–5	75	4.3
Cl	Cyclopentadiene	40	61	4.5
Cl	Cyclopentene	0–5	35	4.2
Cl	Cyclopentene	40	48	4.2
Br	Cyclopentadiene	40[b]	69	1.3
Br	Cyclopentene	40	37	1.2

[a] All of the isomer distributions reported were determined by vpc and further verified by nmr. [b] The dehydrochlorination of 2-bromopropanoyl chloride in the presence of cyclopentene produced such a low yield at 0–5° it was necessary to raise the reaction temperature to 40° to compare with the cyclopentadiene adduct.

addition reactions were accomplished in solvents of varying polarity and the results are shown in Table II.

Cycloadditions were conducted with both acid chlorides and acid bromides as well as by employing the

Table II. Cyclopentadiene Adduct Isomer Distributions in Various Solvents at 0–5°

X	Solvent	% yield	*endo*-:*exo*-Methyl Ratio
Cl	Hexane	75	4.3
Cl	Triethylamine	32	2.2
Cl	Chloroform	40	1.6
Cl	Acetonitrile	62	0.59
Br	Hexane	63	0.71
Br	Triethylamine	53	0.28
Br	Acetonitrile	60	0.14

tertiary amines, diisopropylethylamine and 1,4-diazabicyclo[2.2.2]octane. The isomer distributions of the cycloadducts were unaffected. However, better yields of cycloadducts were obtained from the acid chlorides.

Methylbromoketene was generated in hexane by the dehydrobromination of 2-bromopropanoyl bromide with triethylamine in the absence of cyclopentadiene as evidenced by infrared. The reaction mixture was filtered under a nitrogen atmosphere to yield a hexane solution of methylbromoketene which was treated with cyclopentadiene. The cycloadducts obtained from this system had an *endo*-:*exo*-methyl ratio of 0.84 which closely corresponds to the respective *in situ* reaction ratio of 0.79 at this temperature.

Discussion

The nmr spectra of the cycloadducts obtained from 2-halopropanoyl halides, triethylamine, and cyclopentadiene are very interesting (I, II, III, and IV). The chemical shift of the *endo*-methyl is upfield from the *exo*-methyl.[8] We have demonstrated that it is the *endo*-methyl isomer which has the chemical shift of the methyl group upfield by bromination of the residual double bond, which results in the *endo*-methyl resonance shifting downfield to the *exo*-methyl resonance.[3,4] We previously stated that the *endo*-methyl singlet is shifted upfield because of shielding by the double bond. It is now obvious this is not the case since the saturated *endo*-methyl isomers reveal the methyl-singlet resonances still considerably upfield from the methyl-singlet resonances of the *exo*-methyl isomers. It is coincidental that bromination of the *endo*-methyl isomer results in a downfield shift at or very near the *exo*-methyl resonance.

Since cyclopentene underwent cycloaddition in the two systems under investigation and produced essentially the same *endo*-:*exo*-methyl ratios as cyclopentadiene (Table I), the isomer distribution must not be influenced by the residual double bond. The yields with cyclopentene were considerably lower but this is as expected since cyclopentene is an unactivated olefin, unlike cyclopentadiene.

Some recent evidence has been found which suggests the dehydrohalogenation of certain 2-halo-acid halides is a stepwise process (ElcB) with the initial formation of an oxyanion.[9–11] This has been demonstrated by trap-

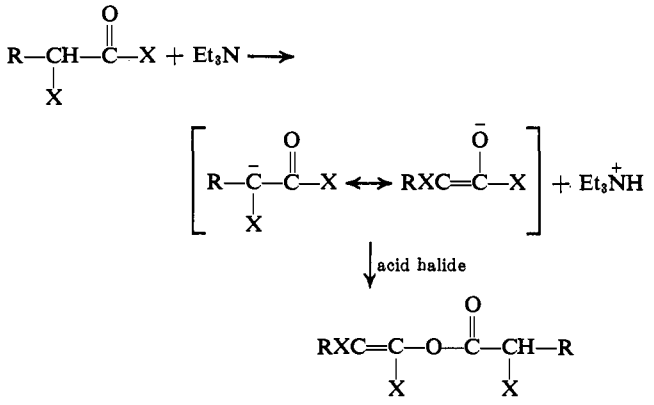
(8) The nmr spectrum of the dimethylketene–cyclopentadiene adduct reveals a singlet at 1.28 ppm and another upfield at 0.93 ppm (J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *J. Org. Chem.*, **30**, 4175 (1965)).

(9) von R. Giger, M. Rey, and A. S. Dreiding, *Helv. Chim. Acta*, **51**, 1466 (1968).

(10) J. M. Lavanish, *Tetrahedron Lett.*, 6003 (1968).

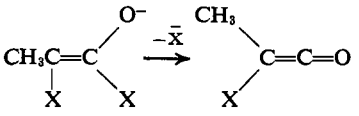
(11) W. T. Brady, F. H. Parry, III, R. Roe, E. F. Hoff, and L. Smith, *J. Org. Chem.*, in press.

ping the intermediate by acylation to produce an α-halovinyl ester. The 2-halopropanoyl halides studied in



this investigation yield the *cis* and *trans* α-halovinyl esters in the absence of cyclopentadiene under the appropriate conditions.[11]

Apparently the oxyanion loses a halide ion in a second step to produce the methylhaloketenes. This is dem-



onstrated by the direct observation by infrared of methylbromoketene. When the methylhaloketenes are generated in the presence of cyclopentadiene, the 1,2-cycloadducts are readily formed and no ketene can be detected.

The solvent in which the dehydrohalogenation–cycloaddition reactions are conducted exerts a strong influence on the isomer distribution as illustrated in Table II. Additional study in this area is in progress in an effort to more fully understand this isomer distribution dependence on solvent polarity.

Experimental Section

Proton nmr spectra were taken with a Varian A-60 nmr spectrometer employing tetramethylsilane as an internal standard. Vapor phase chromatography was done on an F & M Scientific Model 700 with a 10 ft by 1/4 in. column packed with 2% Silicone Fluid FS-1265-GF-1 on Chromosorb G. Hexane was dried over "Linde" type 4-A Molecular Sieve.

7-Chloro-7-methylbicyclo[3.2.0]heptan-6-one (V and VI). To a solution of 25 g (0.25 mol) of triethylamine, 68 g (1.0 mol) of cyclopentene, and 150 ml of hexane at reflux was added dropwise over a 1-hr period a solution of 25 g (0.20 mol) of 2-chloropropanoyl chloride in 25 ml of hexane. After the addition was complete, the mixture was stirred an additional hour and allowed to cool to room temperature. Filtration removed the amine salt and the solvent was removed by a rotatory evaporator. Vacuum distillation through a 24-in. Vigreux column yielded 15.2 g (48%) of the cycloadduct at 48–58° (1.0 mm): ir absorption of both isomers 1796 cm^{-1} (C=O); nmr (CCl_4) *endo*-methyl isomer, δ 1.43 (singlet), 1.7 (multiplet), 3.03 (multiplet), and 4.03 (multiplet); *exo*-methyl isomer, δ 1.70 (singlet), 1.7 (multiplet), 2.89 (multiplet), and 3.76 (multiplet). The isomer distribution was determined by vpc and nmr prior to distillation and is recorded in Table I.

Anal. Calcd for $C_8H_{11}ClO$: C, 60.57; H, 6.94. Found: C, 60.30; H, 7.01.

7-Bromo-7-Methylbicyclo[3.2.0]Heptan-6-one (VII and VIII). The same procedure was followed as described above: bp 60–68° (1.0 mm); ir absorption of both isomers 1799 cm^{-1} (C=O); nmr (CCl_4) *endo*-methyl isomer, δ 1.58 (singlet), 1.6 (multiplet), 2.87 (multiplet), and 3.89 (multiplet); *exo*-methyl isomer, δ 1.6 (multiplet) and 1.87 (singlet), 2.83 (multiplet) and 3.86 (multiplet). The isomer distribution was determined by vpc and nmr prior to distillation and is recorded in Table I.

Other Cycloadditions. All other cycloadditions were accomplished as previously described except for changing the solvent and/or temperature.[3,4]

Hydrogenation of 7-Chloro-7-methylbicyclo[3.2.0]hept-2-en-6-one (I and II). To 50 ml of ethanol and 0.5 g of palladium black was added 5 g (0.03 mol) of 7-chloro-7-methylbicyclo[3.2.0]hept-2-en-6-one (both isomers in a ratio of 0.59 *endo*-:*exo*-methyl). Hydrogenation was effected at room temperature until a theoretical amount of hydrogen was consumed. The catalyst was removed by filtration and the solvent evaporated on a rotatory evaporator. Vacuum distillation afforded 3.5 g (70%) of V and VI at 47–58° (1.0 mm) with an isomer distribution of 0.5 *endo*-:*exo*-methyl; ir absorption of both isomers 1796 cm^{-1} (C=O).

Approximately 0.25 ml of the *endo*-methyl isomer of 7-chloro-7-methylbicyclo[3.2.0]hept-2-en-6-one (I) separated from the *exo*-methyl isomer II by preparative vpc was hydrogenated as described above and purified by preparative vpc.

The vpc retention times and nmr spectra of hydrogenated I and II corresponded to V and VI, respectively.

The methylbromo adducts were hydrogenated, isolated, and characterized in the same manner.

Methylbromoketene. A solution of 8.1 g (0.08 mol) of triethylamine in 25 ml of hexane was added dropwise to a solution of 21.6 g (0.1 mol) of 2-bromopropanoyl bromide in 150 ml of hexane at −78°. Upon warming to room temperature with stirring, a yellow color developed. An aliquot was removed and using a fixed thickness cell an infrared scan made which revealed the asymmetric bond stretching at 2125 cm^{-1} and the symmetric bond stretching at 1120 cm^{-1}. Stirring was continued at room temperature and ir samples were run periodically until the ketene concentration reached a maximum. The mixture was cooled in a Dry Ice–acetone bath and the amine salt removed by filtration under a nitrogen atmosphere to yield a hexane solution of methylbromoketene.

Methylbromoketene Cycloaddition with Cyclopentadiene. The above described hexane solution of methylbromoketene was slowly added to a solution of 30 ml of cyclopentadiene in 150 ml of hexane at room temperature. After 1 hr of efficient stirring, the solution was concentrated by evaporation and the isomer distribution determined by vpc and nmr and found to be 0.84 *endo*-:*exo*-methyl. A corresponding *in situ* dehydrohalogenation–cycloaddition at about the same temperature produced an *endo*-:*exo*-methyl ratio of 0.79.

Acknowledgment. Support of this investigation by the Robert A. Welch Foundation and National Science Foundation Grant GP-7386 is gratefully acknowledged.