Further elution with benzene gave a solution shown by infrared analysis of the CN band at 2240 cm^{-1} to contain no more than about 83 mg (20% yield) of $\alpha,\alpha,\alpha',\alpha'$-tetramethyladiponitrile.

Oxidation of 17 with Periodate–Permanganate. A stock oxidant solution was prepared from 20.86 g (97.5 mmol) of sodium periodate and 0.395 g (2.5 mmol) of potassium permanganate in 1 l. of water.[25] A small sample of hydrocarbon **17** was dissolved in 50 ml of *tert*-butyl alcohol and added to 50 ml of the stock oxidant solution (5 mmol of sodium periodate). The reaction mixture was treated with aqueous potassium hydroxide until a pH of 8 was attained and then was stirred at room temperature for 15 hr during which time the original permanganate color was partially discharged. The reaction mixture was then made acidic with a 50% hydrochloric acid solution and treated with aqueous sodium bisulfite until the solution was pale yellow. Aqueous potassium hydroxide was then added until the solution was strongly basic and, after standing for 30 min, the solution was filtered to remove the traces of flocculent brown precipitate which had appeared. The organic solvent was removed and the resulting aqueous solution made strongly acidic with concentrated hydrochloric acid and extracted several times with ether. The ethereal extracts were dried over magnesium sulfate and concentrated. Analysis of the concentrated ether solution by glpc on a Carbowax–terephthalic acid column at 95° with a flow rate of 10 ml/4 sec showed, among other peaks, a peak with retention time 12.6 min, the same as that of acetic acid.

The ether solution containing the oxidation products was then treated with an ethereal solution of diazomethane until the yellow diazomethane color was no longer discharged. The resulting solution was analyzed by glpc using a Ucon column at 71° and showed, among other peaks, a peak with retention time 4 min, the same as that of methyl acetate.

The esterified oxidation products in ether were then analyzed by glpc with a Ucon column at 200° and a flow rate of 46 ml/min. Other than the solvent peak there appeared a peak with retention time of 3.2 min and a peak with retention time 14.4 min, the same as that of dimethyl $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipate. A sample was collected from a similar run using an Apiezon L column and found to have an infrared spectrum identical with that of dimethyl $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipate.

Ozonolysis of Hydrocarbon 17. A solution of 0.226 g (0.83 mmol) of hydrocarbon **17** in 100 ml of methanol was cooled in a Dry Ice–acetone bath and treated with 0.5 mmol of ozone per minute in a stream of oxygen for 7 min. At the end of this time, the solution was clear light blue. The solution was flushed with oxygen and nitrogen and then 0.3 ml (0.25 g, 4.1 mmol) of dimethyl sulfide was added. The solution was left in the bath while it was agitated by nitrogen passing through a bubbler. It was then allowed to stand in the bath for 2 hr and at room temperature for 2 hr. At the end of this period a test for peroxides was negative (potassium iodide–starch solution).

The solvent was taken off on a Rotovap and collected in a Dry Ice trap. The addition of 2% 2,4-dinitrophenylhydrazine in 2 *N* HCl yielded a solid which had an infrared spectrum identical with that of a known sample of formaldehyde 2,4-dinitrophenylhydrazone and melted at 161–164° (lit.[26] mp 166°).

The residue was taken up in water and petroleum ether and the organic phase was washed with water and dried over sodium sulfate. The solvent was taken off on a Rotovap and the residue was purified by column chromatography on silica gel with the chloroform as elutant. The first 20 ml to contain material was concentrated to yield 22 mg of colorless oil, whose spectra are described in the discussion section.

Anal. Calcd for $C_{19}H_{30}O_2$: mol wt, 290.2246. Found: (mass spectrum) mol wt 290.2257. Other possible molecular formulae at parent mass 290 and their calculated precise masses are as follows: $C_{20}H_{34}O$, 290.2610; $C_{18}H_{26}O_3$, 290.1882; $C_{17}H_{22}O_4$, 290.1518; $C_{16}H_{18}O_5$, 290.1154; $C_{16}H_{34}O_4$, 290.2457; $C_{15}H_{30}O_5$, 290.2093.

Acknowledgments. This work was supported in part by National Science Foundation Grants G-7403, GP-166, and GP-4681, and in part by the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the National Science Foundation and to the donors of the Petroleum Research Fund.

(25) E. von Rudloff, *Can. J. Chem.*, **34**, 1413 (1956).

(26) Reference 21, p 283.

Halogenated Ketenes. XXII. Solvolysis of Alkylhaloketene–Cyclopentadiene Adducts to 2-Alkyltropones[1]

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Abstract: The cycloadducts of alkylhaloketenes and cyclopentadiene were solvolyzed in aqueous base to produce 2-alkyltropones. A competing Favorskii-type ring contraction reaction also occurs producing 6-alkyl-6-carboxybicyclo[3.1.0]hex-2-enes. The 2-alkyltropones are produced only from the endo-alkyl isomer of the alkylhaloketene–cyclopentadiene adduct. The relative amounts of 2-alkyltropone and ring contraction product formed are strongly dependent on both the nature of the halogen and the steric size of the alkyl substituent on the alkylhaloketene. The exo-alkyl isomers of the alkylhaloketene–cyclopentadiene adducts undergo only the ring contraction reaction under the conditions used to produce 2-alkyltropone from the endo-alkyl cycloadducts. A mechanistic rationale is provided for these conversions.

There have been several reports on the conversion of the dichloroketene adduct of cyclopentadiene or a cyclopentadiene derivative to tropolone or a substituted tropolone.[2–6] This conversion has been proposed to occur either through a norcaradienone intermediate[4,5] or by substitution on the bridgehead carbon of the adduct through the enol form followed by ring

(1) Paper XXI, W. T. Brady and L. Smith, *J. Org. Chem.*, **36**, 1637 (1971).

(2) H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain, and E. J. Gaughan, *J. Amer. Chem. Soc.*, **87**, 5257 (1965).

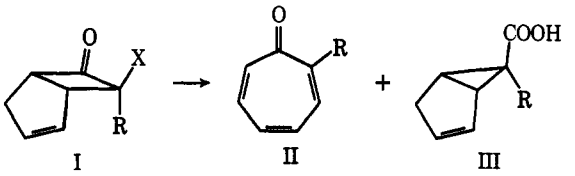
(3) R. Turner and T. Seden, *Chem. Commun.*, 399 (1966).

(4) T. Asao, T. Machiguchi, T. Kitamura, and Y. Kitahara, *ibid.*, 89 (1970).

(5) T. Asao, T. Machiguchi, and Y. Kitahara, *Bull. Chem. Soc. Jap.*, **43**, 2662 (1970).

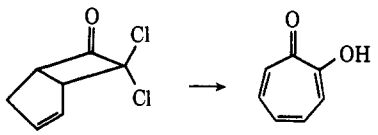
(6) P. Bartlett and T. Ando, *J. Amer. Chem. Soc.*, **92**, 7518 (1970).

Table I. Ring Contraction *vs.* 2-Alkyltropone Formation from *exo*-Halo-*endo*-alkyl Isomers



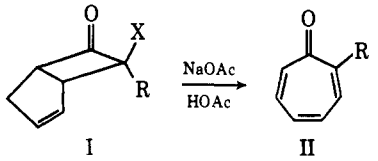
Compd	X	R	Overall yield	Compd	Yield[a]	Compd	Yield	II/III
Ia	Cl	Me	82	IIa	32 (45)	IIIa	50	0.64
Ib	Br	Me	98		5 (22)		93	0.06
Ic	I	Me	29[b]		1		28	0.03
Id	Cl	Et	80	IIb	65	IIIb	15	4.35
Ie	Br	Et	97		27 (45)		70	0.39
If	Br	*n*-Pr	63	IIc	39	IIIc	24	1.60
Ig	Cl	*i*-Pr	88	IId	88		0	
Ih	Br	*i*-Pr	71		71		Trace	20
Ii	Cl	*n*-Bu	71	IIe	66	IIIe	5	13
Ij	Br	*n*-Bu	50		32 (40)		18	1.75
Ik	Br	C_6H_{11}	40	IIf	40		*c*	
Il	Br	C_6H_{11}–CH_2–	35	IIg	35		*c*	
Im	Br	C_6H_{11}–C_2H_5–	30	IIh	30		*c*	
In	Br	*n*-Octyl	40	IIi	40		*c*	

[a] The number in parentheses represents the yield when the solvolysis was conducted in NaOAc–HOAc. [b] Decomposition of starting cycloadduct under reaction conditions. [c] Not measured.



opening and subsequent tautomerism to produce the product.[6] The evidence presented seems to indicate that the latter pathway is followed.

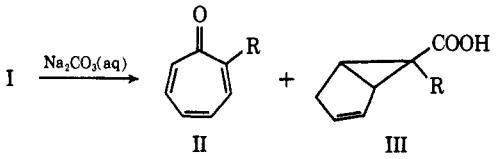
We have recently reported the preparation of 2-alkyltropones (II) by the solvolysis of the *endo*-7-alkyl-*exo*-7-halobicyclo[3.2.0]hept-2-en-6-ones (I) which were



produced by the cycloaddition of alkylhaloketenes to cyclopentadiene.[7] Since this reaction appeared to represent the first general synthesis of 2-alkyltropones from readily available starting materials, it seemed desirable to study this conversion in detail to determine the synthetic utility of this new method and to obtain information relating to the mechanism of 2-alkyltropone formation.

Results

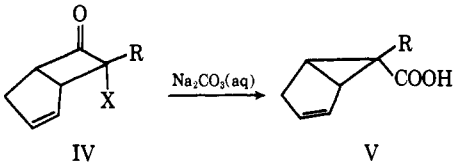
The conversion of I to II is accomplished at a much higher rate if 20% aqueous sodium carbonate is used as the solvolysis media rather than sodium acetate in acetic acid. Stevens and coworkers reported that aqueous carbonate led to cleavage of the cyclobutanone ring in the dichloroketene–cyclopentadiene adduct.[2] We observed no ring cleavage in the alkylhaloketene–cyclopentadiene adducts, but a by-product was observed and identified as *endo*-6-alkyl-*exo*-6-carboxybicyclo[3.1.0]hex-2-ene (III) formed by a stereospecific Favorskii type ring contraction of the starting material.



This ring contraction is analogous to some observed by Brook and coworkers in the treatment of alkylchloroketene–cyclopentadiene adducts with aqueous hydroxide.[8] We have also observed these ring contractions under the influence of sodium methoxide in methanol.[9] The solvolysis of I in sodium acetate–acetic acid also yields III but isolation is difficult.

Table I reveals the effect of varying both the halogen and the alkyl group of the alkylhaloketene on the relative yields of II and III.

The exo-alkyl isomer of the alkylhaloketene–cyclopentadiene adduct, IV, produced no tropone upon solvolysis in aqueous sodium carbonate but produced the ring contraction product, V, in high yield. The



effects of both halogen and alkyl group on the rate of ring contraction are shown in Table II.

Cycloadditions of alkylhaloketenes and 1-methylcyclopentadiene occur smoothly and in good yield. The cycloadducts obtained from methylchloro-, methylbromo-, and isopropylchloroketenes have been treated with base and the results recorded in Table III.

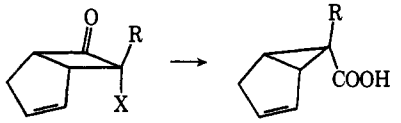
The adduct of methylchloroketene and indene (VI) was solvolyzed in aqueous sodium carbonate and produced VII, the ring contraction product, in 80% yield as the only isolable product.

(7) W. T. Brady and J. P. Hieble, *Tetrahedron Lett.*, 3205 (1970).

(8) P. R. Brook, J. M. Harrison, and A. J. Duke, *Chem. Commun.*, 589 (1970).

(9) W. T. Brady and J. P. Hieble, *J. Org. Chem.*, **36**, 2033 (1971).

Table II. Ring Contractions of exo-Alkyl-endo-halo Isomers



IV V

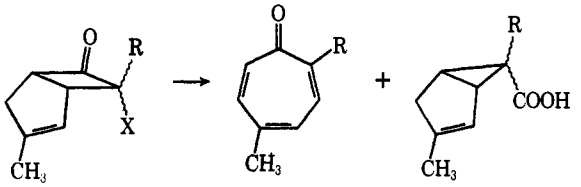
Compd	X	R	Yield, %	Compd	Rel rate[a]
IVa	Cl	Me	75	Va	6.4
IVb	Br	Me	87		25
IVc	I	Me	30		28[b]
IVd	Br	Et	62	Vb	9.5
IVe	Br	*n*-Pr	70	Vc	3.9
IVf	Br	*i*-Pr	75	Vd	1.0
IVg	Cl	H	65	Ve	~50

[a] Average of two determinations, average variance, 10%. [b] Decomposition of starting cycloadduct during reaction.

alkyltropones than the bromo and iodo cycloadducts. Furthermore, as the size of the alkyl group is increased from methyl-, ethyl-, to isopropyl, the yield of II increases from 32, 65, to 88%. These data are consistent with the rate of tropone formation being independent of both halogen and the size of the alkyl group whereas the rate of the ring contraction reaction is dependent on both of these considerations. The results in Table II show that the rate of ring contraction is indeed dependent on both the alkyl group and the halogen.

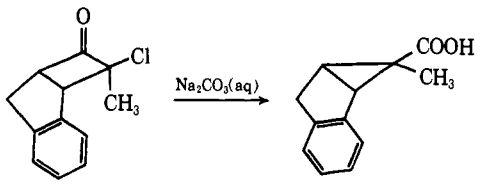
The ring contraction reaction producing III represents a useful method of preparation for this type of compound. It is obvious that the desirable isomer of the cycloadduct for this purpose is the endo-halo isomer since this isomer is not converted to 2-alkyltropone. The data in Table II show the effect of varying the alkyl group and the halogen on the endo-halo-exo-alkyl cy-

Table III. Rearrangements of Alkylhaloketene–1-Methylcyclopentadiene Adducts



VIII IX X

Compd	R	X	Overall yield, %	Compd	Yield, %	Compd	Yield, %	IX/X
VIIIa	*endo*-Me	*exo*-Cl	92	IXa	13	Xa	79	0.17
VIIIb	*endo*-*i*-Pr	*exo*-Cl	92	IXb	92		0	
VIIIc	*exo*-Me	*endo*-Br	88			Xc	88	

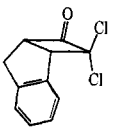
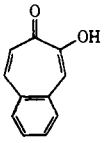


VI VII

The relative rates of formation of tropolone and derivatives from the adducts of dichloroketene and several cyclopentadiene derivatives were measured. In addition, the cycloadducts of cyclopentadiene with dibromo- and bromochloroketenes were solvolyzed to produce tropolone. Triethylammonium acetate in aqueous acetone was used as a solvolysis media in these reactions. The results obtained are recorded in Table IV.

The adducts of alkylhaloketenes and cyclopentadiene were solvolyzed in various other media such as triethylammonium acetate in aqueous acetone, aqueous sodium acetate and trialkylamines in an inert solvent at high temperature. These solvolysis media did not lead to the formation of a significant amount of 2-alkyltropone at a reasonable rate.

Table IV. Solvolysis of Some Dihaloketene Adducts to Tropolones

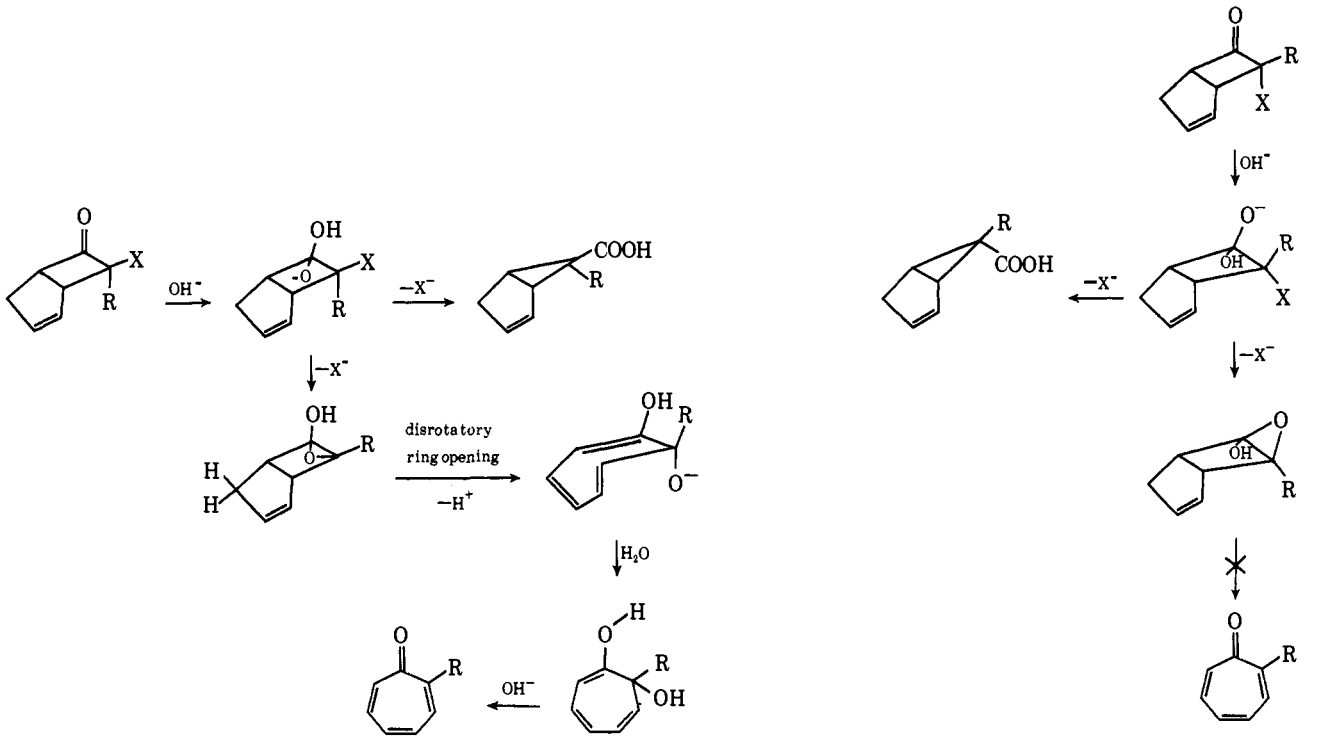
Cycloadduct	Tropolone	Yield, %	Rel rate
7,7-Dichlorobicyclo-[3.2.0]hept-2-en-6-one (XI)	Tropolone (XVI)	60	1
7,7-Dichloro-3-methyl-bicyclo[3.2.0]hept-2-en-6-one (XII)	2-Methyltropotone (XVII)[a]	70	1
7,7-Dibromobicyclo-[3.2.0]hept-2-en-6-one (XIII)	Tropolone (XVI)	45	2
7-Bromo-7-chlorobi-cyclo[3.2.0]hept-2-en-6-one (XIV)	Tropolone (XVI)	55	2
 XV	 XVIII	79	2

[a] The production of 4-methyltropolone is consistent with the observations of Kitahara and Bartlett concerning the position of substituents on the cycloadduct with respect to substituent position on the solvolysis product (ref 4–6).

Discussion

The conversion of the exo-halo isomers of alkylhaloketene–cyclopentadiene cycloadducts, I, into 2-alkyltropones, II, is accompanied by a ring contraction reaction yielding substituted cyclopropanecarboxylic acids, III. The data in Table I reveal that the chlorocycloadducts are converted in higher yields to the 2-cloadducts. It is pertinent to mention that this ring contraction reaction is stereospecific, *i.e.*, the exo-alkyl cycloadduct is converted to the *exo*-alkylcyclopropanecarboxylic acid in agreement with a recent report by Brook.[8]

Scheme I



The results of the reaction of the exo-halo isomers of the cycloadducts of methylchloro- and isopropylchloroketene–1-methylcyclopentadiene adducts are most interesting. The ratio of alkyltropone to ring contraction product is 0.64 for the methylchloroketene–cyclopentadiene adduct (Table I) and 0.17 for the methylchloroketene–1-methylcyclopentadiene adduct (Table III). However, the ring contraction reaction is completely suppressed in the case of the isopropylchloroketene–1-methylcyclopentadiene adduct as only the 2-isopropyltropone is produced in 92% yield (Table III). Yet, the conversion of the isopropylchloroketene–cyclopentadiene adduct to the tropone occurred three times more rapidly than the conversion of the isopropylchloroketene–1-methylcyclopentadiene adduct. It is apparent from these data that the methyl group on the cyclopentadiene ring is influencing the rate of formation of the tropone.

Solvolysis of the adduct of dichloroketene and indene (XV) occurs smoothly and in good yield to 4,5-benzotropolone (XX) (Table IV). The failure of the methylchloroketene–indene adduct, VI, to produce 2-methyl-4,5-benzotropone suggests that the solvolysis of alkylhaloketene cycloadducts occurs by a different mechanistic pathway than the dihaloketene cycloadducts. Table IV reveals that the dichloroketene adducts of cyclopentadiene (XI), 1-methylcyclopentadiene (XII), and indene (XV) all undergo solvolysis at approximately the same rate as do the adducts of dibromo- and bromochloroketene–cyclopentadiene adducts. These results are consistent with the mechanism proposed by Bartlett and Ando for the formation of tropolone and derivatives from dichloroketene adducts.[6]

Any mechanism proposed for the conversion of alkylhaloketene–cyclopentadiene adducts to 2-alkyltropones must explain the fact that only the endo-alkyl-exo-halo cycloadducts are converted to tropone. This eliminates any mechanism in which the loss of halogen is preceded by ring opening. A loss of halogen concurrent to the sterically required disrotatory ring opening would predict that the exo-alkyl isomer should undergo the ring opening reaction at a faster rate than the endo-alkyl isomer since the loss of the endo halogen during ring opening is analogous to the loss of an endo tosylate in the solvolysis of bicyclic tosylates.[10] In these systems, the endo tosylate solvolyzes five hundred times faster than the exo isomer. The intermediacy of a norcaradienone, as proposed by Kitahara, *et al.*, for tropolone formation, would also predict that the exo-alkyl rather than the endo-alkyl isomer would solvolyze easier.

Bartlett and Ando have proposed a mechanism for the conversion of the dichloroketene–cyclopentadiene adduct to tropolone which initially involves attack by base on C_5 of the adduct. However, substitution at C_5 for the exo-halo isomer, I, or the endo-halo isomer, IV, would be expected to occur with equal ease. In fact, for other alkylhaloketene cycloadducts we have observed this substitution reaction for both isomers.[9] Consequently, this is obviously not the pathway followed by the alkylhaloketene–cyclopentadiene adducts.

A mechanism which seems consistent with all the 2-alkyltropone data as well as explaining the stereospecific ring contraction reaction is shown in Scheme I.

The ring contraction reaction may occur from the oxyanion formed from either endo-alkyl or exo-alkyl isomer stereospecifically as previously proposed by Brook.[8] The key step in the tropone formation is a disrotatory ring opening of the endo epoxide thus effecting the desired trans displacement. The exo epoxide cannot undergo the sterically required disrotatory ring opening with a trans displacement.

In conclusion our results show that the solvolysis of the endo-alkyl-exo-halo isomers of alkylhaloketene–

(10) K. B. Wiberg, V. Z. Williams, Jr., and L. E. Friedrich, *J. Amer. Chem. Soc.*, 92, 564 (1970).

cyclopentadiene adducts is a useful synthesis for 2-alkyltropones. The solvolysis in aqueous sodium carbonate is easily performed and the 2-alkyltropones are produced quickly and in good yield. This synthesis is much superior to the methods previously available for these compounds.[11]

Experimental Section

Proton nmr spectra were recorded on Jeolco Minimar 60-MHz and Jeolco PS-100 nmr spectrometers employing tetramethylsilane as an internal standard and CCl_4 or $CDCl_3$ as solvents. Vpc was performed on an F & M Scientific Model 700 gas chromatograph with a 10 ft × 0.25 in. column packed with 10% SE-30 on acid washed Chromosorb W (80–100 mesh). Hexane and triethylamine were distilled from sodium and stored over Linde type 4-A molecular sieve.

The following alkylhaloketene–cyclopentadiene adducts have been previously reported: methylchloro-,[12] methylbromo-, ethylchloro- and ethylbromo-,[13] methyliodo-,[14] isopropylchloro- and isopropylbromo-,[15] dichloro-,[2] dibromo-,[16] chloro-.[17] Also, the cycloadduct of dichloroketene and indene has been previously reported.[3,18]

The acid chlorides were prepared from commercially available carboxylic acids and thionyl chloride. Bromochloroacetyl chloride was prepared by the method of Crompton.[19,20]

General Procedure for the α-Bromination of Acid Chlorides. The acid chloride (1.0 mol) and bromine (1.1 mol) were heated at 75° until the bromine color had dissipated (usually 12 hr or less). A yield of 90+% of the α-bromoacid chloride was obtained by distillation.

2-Chlorohexanoyl Chloride. This acid halide was prepared by a modification of the procedure of Gleason and Harpp.[21] A mixture of hexanoyl chloride (1.0 mol) and *N*-chlorosuccinimide (1.5 mol) in 300 ml of CCl_4 was refluxed with stirring for 24 hr. The progress of the reaction was followed by periodically withdrawing aliquots, mixing with an equal volume of absolute methanol, and assaying by vpc. After 24 hr refluxing, this assay revealed the conversion to be about 50% complete. Longer reaction times did not increase the amount of chlorinated product. The reaction mixture was filtered, rotary evaporated, and fractionally ditilled to yield 50 g (30%) of 2-chlorohexanoyl chloride, bp 175–157° (lit.[22] 174–156°).

Several attempts to prepare the above acid chloride by direct chlorination of the acid chloride, with or without catalyst, were unsuccessful.

General Procedure for *in Situ* Alkylhaloketene–Cyclopentadiene Cycloadditions. To a solution of 1.1 mol of triethylamine and 2.0 mol of cyclopentadiene in 1 l. of hexane was added 1.0 mol of acid halide in 150 ml of hexane. The addition was made dropwise over a period of 1 hr with vigorous stirring. After the addition was complete, the stirring was continued for 2 hr. The amine salt was removed by filtration and washed with 3 × 150 ml portions of hexane. The filtrate was concentrated on a rotary evaporator and the residue vacuum distilled to yield the alkylhaloketene–cyclopentadiene adduct.

Two isomeric bicyclo[3.2.0]hept-2-en-6-ones were produced in each case. The isomers were separated by fractional distillation at reduced pressure employing either a spinning band column or a 30-plate adiabatic column. Some of the higher boiling cycloadducts could not be fractionated through the above columns without severe decomposition. Consequently, separation was accomplished by repeated vacuum distillation through a short column. This method provided isomeric purity of 75–90%.

7-Bromo-7-*n*-propylbicyclo[3.2.0]hept-2-en-6-one (If). 2-Bromopentanoyl chloride was dehydrochlorinated at room temperature, 70% yield at 73–75° (0.2 mm). An isomer distribution of 1.6 (*endo*-*n*-Pr–*exo*-*n*-Pr) was obtained: ir (both isomers) 1800 cm^{-1}; nmr (*endo*-*n*-Pr) δ 5.90 (m, 2 H), 4.30 (3d, 1 H), 3.82 (m, 1 H), 2.56 (m, 2 H), 1.66 (m, 4 H), 0.96 (m, 3 H); (*exo*-*n*-Pr) δ 5.88 (m, 2 H), 4.01 (3d, 1 H), 3.56 (m, 1 H), 2.53 (m, 2 H), 2.04 (m, 2 H), 1.58 (m, 2 H), 1.00 (t, 3 H).

Anal. Calcd for $C_{10}H_{13}OBr$: C, 52.50; H, 5.68. Found: C, 52.42; H, 5.87.

7-Chloro-7-*n*-butylbicyclo[3.2.0]hept-2-en-6-one (Ii). 2-Chlorohexanoyl chloride was dehydrochlorinated at 0–5°, 55% yield at 78–80° (0.5 mm). An isomer distribution of 10 (*endo*-*n*-Bu–*exo*-*n*-Bu) was obtained: ir (both isomers) 1800 cm^{-1}; nmr (*endo*-*n*-Bu) δ 5.84 (m, 2 H), 4.22 (3d, 1 H), 3.64 (m, 1 H), 2.56 (m, 2 H), 1.84–1.12 (broad mult, 6 H), 0.92 (t, 3 H). The *exo*-*n*-Bu isomer was not isolated.

Anal. Calcd for $C_{11}H_{15}OCl$: C, 67.80; H, 7.69. Found: C, 67.91; H, 7.82.

7-Bromo-7-*n*-butylbicyclo[3.2.0]hept-2-en-6-one (Ij). 2-Bromohexanoyl chloride was dehydrochlorinated at room temperature, 40% yield at 95–100° (0.3 mm). An isomer distribution of 1.75 (*endo*-*n*-Bu–*exo*-*n*-Bu) was obtained; ir (both isomers) 1800 cm^{-1}; nmr (*endo*-*n*-Bu) δ 5.95 (m, 2 H), 4.33 (3d, 1 H), 3.68 (m, 1 H), 2.56 (m, 2 H), 1.90–1.13 (broad mult, 6 H), 0.93 (t, 3 H); (*exo*-*n*-Bu) δ 5.85 (m, 2 H), 3.97 (3d, 1 H), 3.52 (m, 1 H), 2.53 (m, 2 H), 1.98 (m, 2 H), 1.42 (m, 4 H), 0.92 (t, 3 H).

Anal. Calcd for $C_{11}H_{15}OBr$: C, 54.25; H, 6.15. Found: C, 54.55; H, 5.88.

7-Bromo-7-cyclohexylbicyclo[3.2.0]hept-2-en-6-one (Ik). Bromocyclohexylacetyl chloride was dehydrochlorinated in refluxing hexane, 82% yield at 118–120° (0.3 mm). An isomer distribution of 3 (*endo*-cyclohexyl–*exo*-cyclohexyl) was obtained: ir (both isomers) 1800 cm^{-1}; nmr (*endo*-cyclohexyl) δ 5.90 (m, 2 H), 4.30 (3d, 1 H), 3.89 (m, 1 H), 2.60 (m, 2 H), 2.0–0.95 (broad mult, 11 H). The *exo*-cyclohexyl isomer was not isolated.

Anal. Calcd for $C_{13}H_{17}OBr$: C, 58.01; H, 6.37. Found: C, 58.11; H, 6.33.

7-Bromo-7-cyclohexylmethylbicyclo[3.2.0]hept-2 en-6-one (Il). 2-Bromo-3-cyclohexylpropanoyl chloride was dehydrochlorinated in refluxing hexane, 83% yield at 102–104° (0.1 mm). An isomer distribution of 2.5 (endo-alkyl–exo-alkyl) was obtained: ir (both isomers) 1800 cm^{-1}; nmr (endo-alkyl) δ 5.87 (m, 2 H), 4.36 (3d, 1 H), 3.85 (m, 1 H), 2.58 (m, 2 H), 2.0–1.0 (broad mult, 13 H). The exo-alkyl isomer was not isolated.

Anal. Calcd for $C_{14}H_{19}OBr$: C, 59.37; H, 6.76. Found: C, 59.55; H, 6.94.

7-Bromo-7-(2-cyclohexylethyl)bicyclo[3.2.0]hept-2-en-6-one (Im). 2-Bromo-4-cyclohexylbutanoyl chloride was dehydrochlorinated in refluxing hexane, 92% yield at 135–136° (0.1 mm). An isomer distribution of 2.5 (endo-alkyl–exo-alkyl) was obtained: ir (both isomers) 1800 cm^{-1}; nmr (endo-alkyl) δ 5.96 (m, 2 H), 4.28 (3d, 1 H), 3.87 (m, 1 H), 2.73 (m, 2 H), 2.0–0.90 (broad mult, 15 H). The exo-alkyl isomer was not isolated.

Anal. Calcd for $C_{15}H_{21}OBr$: C, 60.61; H, 7.12. Found: C, 60.32; H, 7.46.

7-Bromo-7-*n*-octylbicyclo[3.2.0]hept-2-en-6-one (In). 2-Bromodecanoyl chloride was dehydrochlorinated at room temperature, 65% yield at 133–135° (0.2 mm). An isomer distribution of 2 (*endo*-*n*-octyl–*exo*-*n*-octyl) was obtained: ir (both isomers) 1800 cm^{-1} nmr (*endo*-*n*-octyl) δ 5.92 (m, 2 H), 4.28 (3d, 1 H), 3.80 (m, 1 H), 2.56 (m, 2 H), 1.72 (m, 2 H), 1.33 (quasi singlet, 12 H), 0.90 (t, 3 H). The *exo*-*n*-octyl isomer was not isolated.

Anal. Calcd for $C_{15}H_{23}OBr$: C, 60.20; H, 7.74. Found: C, 59.91; H, 7.72.

7-Bromo-7-chlorobicyclo[3.2.0]hept-2-en-6-one (XIV). Bromochloroacetyl chloride was dehydrochlorinated in the manner described above at room temperature. A 60% yield of cycloadduct was obtained at 62–63° (0.15 mm). The reaction was apparently stereospecific producing only the endo-bromo isomer. This assignment was made by a comparison of the nmr spectra of the cyclopentadiene adducts of bromochloroketene, dichloroketene, and dibromoketene. This assignment is consistent with the preference of the larger ketene substituent for the endo position in the cycloadduct: ir 1805 cm^{-1}; nmr δ 5.70 (m, 2 H), 4.18 (3d, 1 H), 3.90 (m, 1 H), 2.47 (m, 2 H).

Anal. Calcd for C_7H_6OClBr: C, 37.81; H, 2.71. Found: C, 37.98; H, 2.93.

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General Procedure for *in Situ* Ketene Cycloadditions to 1-Methylcyclopentadiene. The cycloadditions were conducted as described above for cyclopentadiene except that a mixture of 1-methyl- and 2-methylcyclopentadiene in approximately equal amounts was used instead of cyclopentadiene. This mixture was obtained by thermally cracking commercially available methylcyclopentadiene dimer at 180° and collecting the monomeric product by fractional distillation at 70–71°. A fourfold excess of methylcyclopentadiene to acid chloride was employed. The reaction mixture was worked up as soon as the addition of acid halide was complete since in this manner the unreacted methylcyclopentadiene could be removed before dimerization had occurred (the dimer was very difficult to separate from the cycloadduct). In all cases the major product obtained was identified as the adduct of the ketene with 1-methylcyclopentadiene; a small amount (<10%) of the 2-methylcyclopentadiene adduct was observed in some cases. These results correspond to those obtained by Dreiding and Huber in the cycloaddition of dimethylketene to mixed methylcyclopentadienes.[23]

7,7-Dichloro-3-methylbicyclo[3.2.0]hept-2-en-6-one (XII). Dichloroacetyl chloride was dehydrochlorinated at 0–5°, 55% yield at 75–77° (0.3 mm). Vpc revealed the adduct to be a mixture of two components in a ratio of about 10. The major component was identified as the adduct of dichloroketene and 1-methylcyclopentadiene by subsequent solvolysis to the known 4-methyltropolone: ir 1805 cm^{-1}; nmr δ 5.34 (m, 1 H), 4.00 (m, 2 H), 2.57 (m, 2 H), 1.70 (s, 3 H).

Anal. Calcd for $C_8H_8OCl_2$: C, 50.26; H, 4.17. Found: C, 50.11; H, 4.34.

7-Chloro-3,7-dimethylbicyclo[3.2.0]hept-2-en-6-one (VIIIa). The reaction was conducted at room temperature, 75% yield at 52–53° (0.1 mm). An isomer distribution of 4 (*endo*-methyl–*exo*-methyl) was obtained. No significant amount of the 2-methylcyclopentadiene adduct was produced: ir (both isomers) 1800 cm^{-1}; nmr (*endo*-methyl) δ 5.44 (m, 1 H), 4.20 (3 d, 1 H), 3.64 (m, 1 H), 2.49 (m, 2 H), 1.75 (s, 3 H), 1.45 (s, 3 H).

Anal. Calcd for $C_9H_{11}OCl$: C, 63.53; H, 6.47. Found: C, 63.92; H, 6.41.

7-Chloro-7-(2-propyl)-3-methylbicyclo[3.2.0]hept-2-en-6-one (VIIIb). 2-Chloro-3-methylbutanoyl chloride was dehydrochlorinated at room temperature, 60% yield at 71–72° (0.1 mm). An isomer distribution of 10 (*endo-i*-Pr–*exo-i*-Pr) was obtained: ir 1800 cm^{-1}; nmr (*endo-i*-Pr) δ 5.43 (m, 1 H), 4.18 (3d, 1 H), 3.58 (m, 1 H), 2.44 (m, 2 H), 2.16 (h, 1 H), 1.80 (s, 3 H), 1.04 (2d, J = 8 cps, 6 H). The *exo-i*-Pr isomer was not isolated.

Anal. Calcd for $C_{11}H_{15}OCl$: C, 67.85; H, 7.56. Found: C, 68.05; H, 7.84.

7-Bromo-3,7-dimethylbicyclo[3.2.0]hept-2-en-6-one (VIIIc). 2-Bromopropanoyl chloride was dehydrochlorinated at 0–5° in acetonitrile instead of hexane, 50% yield at 75–77° (0.2 mm) (*exo*-7-methyl–*endo*-7-methyl >20); ir 1800 cm^{-1}; nmr δ 5.36 (m, 1 H), 4.04 (3d, 1 H), 3.46 (m, 1 H), 2.49 (m, 2 H), 1.92 (s, 3 H), 1.82 (s, 3 H).

Anal. Calcd for $C_9H_{11}OBr$: C, 50.23; H, 5.12. Found: C, 50.44; H, 5.32.

11-Chloro-11-methyltricyclo[7.2.0.0^{2,7}]undeca-2,4,6-trien-10-one (VI). A solution of 1.0 mol of indene and 0.75 mol of triethylamine in dry hexane was refluxed with stirring while 0.5 mol of 2-chloropropanoyl chloride was added dropwise over a period of 1 hr. Work-up in the usual manner yielded 80 g (78%) of the cycloadduct at 105–108° (0.1 mm) which solidified on standing, mp 45–46°. An isomer distribution of 5 (*endo*-methyl–*exo*-methyl) was obtained: ir 1800 cm^{-1}; nmr (*endo*-methyl) δ 7.21 (s, 4 H), 4.42 (3d, 1 H), 4.04 (m, 1 H), 3.15 (m, 2 H), 1.28 (s, 3 H). The *exo*-methyl isomer was not isolated.

Anal. Calcd for $C_{12}H_{11}OCl$: C, 69.74; H, 5.36. Found: C, 69.79; H, 5.52.

General Procedure for the Sodium Carbonate Solvolysis of *endo*-Alkyl-*exo*-haloketene–Cyclopentadiene Adducts. The endo-alkyl isomer of the alkylhaloketene–cyclopentadiene adduct (0.15 mol) and 250 ml of 20% aqueous Na_2CO_3 solution were refluxed with vigorous stirring. Periodically 1-ml aliquots were withdrawn by syringe and mixed with an equal volume of $CHCl_3$. The organic layer was assayed by vpc to determine the extent of reaction. It was necessary to assay the solvolysis mixtures of the alkylbromoketene adducts by ir analysis of the $CHCl_3$ extracts, observing the disappearance of the cyclobutanone carbonyl absorption at 1800 cm^{-1} and the appearance of the strong tropone carbonyl absorption at 1575 cm^{-1}. When all the cycloadduct had been consumed, the reaction mixture was extracted with $CHCl_3$. The combined $CHCl_3$ extracts were dried over $CaCl_2$, rotary evaporated, and distilled to yield the 2-alkyltropone. The aqueous layer was acidified with 6 N HCl solution. The 6-alkyl-6-carboxybicyclo[3.1.0]hex-2-ene would separate as either a solid precipitate or an oil. The solid was collected by filtration and purified by vacuum sublimation at 0.1 mm. If the product was an oil, the acidified reaction mixture was extracted with $CHCl_3$. This extract was dried over $CaCl_2$, rotary evaporated, and distilled. The distillate generally solidified on standing and no further purification was necessary. For the yields of 2-alkyltropone and 6-alkyl-6-carboxybicyclo[3.1.0]hex-2-ene, see Table I.

2-Methyltropone (IIa): bp 70–72° (1.0 mm); ir (cm^{-1}) 1630 (s), 1575 (vs), and 1525 (s); nmr δ 6.95 (m, 5 H), 2.19 (s, 3 H). (The ir spectrum was identical with that reported in the literature for this compound.)[24]

2-Ethyltropone (IIb): bp 78° (1.5 mm) (lit.[11] 63–64° (0.05 mm); ir (cm^{-1}) 1630 (s), 1575 (vs), and 1525 (s); nmr δ 7.04 (m, 5 H), 2.80 (q, 2 H), 1.27 (t, 3 H).

2-*n*-Propyltropone (IIc): bp 78–80° (0.5 mm); ir (cm^{-1}) 1640 (s), 1580 (vs), and 1530 (s); nmr δ 7.04 (m, 5 H), 2.63 (t, 2 H), 1.58 (sextet, 2 H), 0.93 (t, 3 H).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.08; H, 8.10. Found: C, 81.48; H, 8.20.

2-(2-Propyl)tropone (IId): bp 75–76° (0.1 mm) (lit.[11] 59–60° (0.01 mm)); ir (cm^{-1}) 1630 (s), 1575 (vs), 1525 (s); nmr 7.13 (m, 5 H), 3.44 (h, 1 H), 1.13 (d, J = 7 cps, 6 H).

2-*n*-Butyltropone (IIe): bp 115–117° (2.0 mm); ir (cm^{-1}) 1640 (s), 1580 (vs), 1525 (s); nmr δ 6.94 (m, 5 H), 2.50 (t, 2 H), 1.37 (m, 4 H), and 0.90 (t, 3 H); mass spectrum, *m/e* 162 (theory 162).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.49; H, 8.64. Found: C, 81.47; H, 8.82.

2-Cyclohexyltropone (IIf). An isomeric mixture containing 80% of the *endo*-cyclohexyl isomer was used as starting material, bp 120–125° (1.0 mm); ir (cm^{-1}) 1640 (s), 1575 (vs), 1530 (s); nmr δ 7.16 (m, 5 H), 2.57 (m, 1 H), 2.05–0.95 (broad mult, 10 H); mass spectrum, *m/e* 188 (theory 188). An acceptable elemental analysis could not be obtained due to residual starting material (*exo*-cyclohexyl isomer) which could not be removed.

2-Cyclohexylmethyltropone (IIg). An isomeric mixture containing 85% of the *endo*-cyclohexylmethyl isomer was used as starting material, bp 112–115° (0.3 mm); ir (cm^{-1}) 1640 (s), 1580 (vs), 1530 (s); nmr δ 6.84 (m, 5 H), 2.48 (d, J = 5 cps, 2 H), 1.95–0.80 (broad mult, 11 H); mass spectrum, *m/e* 202 (theory 202). An acceptable elemental analysis could not be obtained due to residual starting material (*exo*-cyclohexylmethyl isomer) which could not be removed from the tropone.

2-(2-Cyclohexylethyl)tropone (IIh). An isomeric mixture containing 85% of the *endo*-2-cyclohexylethyl isomer was used as starting material, bp 140–145° (0.4); ir (cm^{-1}) 1635 (s), 1575 (vs), 1520 (s); nmr δ 6.90 (m, 5 H), 2.36 (t, 2 H), 1.88–0.76 (broad mult, 13 H); mass spectrum, *m/e* 216 (theory 216). An acceptable elemental analysis could not be obtained due to residual starting material (*exo*-2-cyclohexylethyl isomer) which could not be removed from the tropone.

2-*n*-Octyltropone (IIi). An isomer mixture containing 90% of the *endo-n*-octyl isomer was used as starting material, bp 125–127° (0.1 mm); ir (cm^{-1}) 1640 (s), 1580 (vs), 1520 (s); nmr δ 7.00 (m, 5 H), 2.62 (t, 2 H), 1.32 (m, 12 H), 0.95 (t, 3 H); mass spectrum, *m/e* 218 (theory 218). An acceptable elemental analysis could not be obtained due to residual starting material (*exo-n*-octyl isomer) in the tropone.

2,5-Dimethyltropone (IXa). This tropone was obtained from the cycloadduct of methylchloroketene and 1-methylcyclopentadiene by the procedure described above, bp 72–74° (0.5 mm); ir (cm^{-1}) 1640 (s), 1570 (vs), 1540 (s); nmr δ 7.27 (m, 4 H), 2.22 (s, 3 H), 2.15 (s, 3 H).

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.53; H, 7.68.

2-(2-Propyl)-5-methyltropone (IXb). This tropone was obtained from the cycloadduct of isopropylchloroketene and 1-methylcyclopentadiene by the procedure described above, bp 89–90° (0.1 mm); ir (cm^{-1}) 1640 (s), 1575 (vs), 1540 (s); nmr δ 7.00 (m, 4 H), 3.40 (h, 1 H), 2.23 (s, 3 H), 1.17 (d, J = 7 cps, 6 H).

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Anal. Calcd for $C_{11}H_{15}O$: C, 81.41; H, 8.64. Found: C, 81.07; H, 8.93.

exo-**6-Carboxy-*endo*-6-methylbicyclo[3.1.0]hex-2-ene (IIIa):** mp 82–84°; nmr δ 11.96 (s, 1 H), 5.76 (s, 2 H), 2.68 (m, 2 H), 2.26 (m, 2 H), 1.00 (s, 3 H).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.61; H, 7.25. Found: C, 69.81; H, 7.50.

exo-**6-Carboxy-*endo*-6-ethylbicyclo[3.1.0]hex-2-ene (IIIb):** mp 55–60°; nmr δ 12.12 (s, 1 H), 5.58 (s, 2 H), 2.56 (m, 2 H), 2.18 (m, 2 H), 1.68 (m, 1 H), 0.96 (m, 4 H).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.0; H, 7.89. Found: C, 71.19; H, 8.02.

exo-**6-Carboxy-*endo*-6-*n*-propylbicyclo[3.1.0]hex-2-ene (IIIc):** bp 110–112° (0.1 mm); mp 48–50°; nmr δ 12.70 (s, 1 H), 5.70 (s, 2 H), 2.60 (m, 2 H), 2.20 (m, 2 H), 1.28 (m, 4 H), 0.84 (t, 3 H).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.31; H, 8.43. Found: C, 71.93; H, 8.40.

exo-**6-Carboxy-*endo*-6-*n*-butylbicyclo[3.1.0]hex-2-ene (IIId):** bp 125–127° (0.1 mm) (this acid did not solidify after distillation); nmr δ 12.23 (s, 1 H), 5.74 (s, 2 H), 2.61 (m, 2 H), 2.20 (m, 2 H), 1.33 (m, 6 H), 0.92 (t, 3 H).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.35; H, 8.88. Found: C, 73.21; H, 8.85.

exo-**6-Carboxy-*endo*-6-methyl-3-methylbicyclo[3.1.0]hex-2-ene (Xa):** mp 106–108°; nmr δ 11.53 (s, 1 H), 5.54 (m, 1 H), 2.44 (m, 2 H), 2.12 (m, 1 H), 1.90 (m, 1 H), 1.64 (s, 3 H), 0.93 (s, 3 H).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.0; H, 7.89. Found: C, 69.93; H, 7.63.

exo-**10-Carboxy-*endo*-10-methyltricyclo[7.1.0.0^{2,7}]deca-2,4,6-triene (VII).** A mixture of 10 g (0.1 mol) of the *endo*-methyl isomer of the cycloadduct of methylchloroketene and indene in 200 ml of 20% aqueous Na_2CO_3 solution was refluxed with stirring until solution was accomplished (~5 hr). The reaction solution was neutralized while still hot with 6 *N* HCl solution and the precipitated produce (5 g, 60%) was collected by filtration, mp 118–120°; nmr δ 9.36 (s, 1 H), 6.96 (m, 4 H), 3.16 (m, 2 H), 2.72 (d, J = 9 cps, 1 H), 2.40 (m, 1 H), 0.76 (s, 3H).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.26; H, 6.42.

General Procedure for the Acetic Acid–Sodium Acetate Solvolysis of *endo*-Alkyl-*exo*-haloketene–Cyclopentadiene Adducts. The solvolysis media was prepared by dissolving 200 g of $NaOAc \cdot 3H_2O$ in a mixture of 800 ml of glacial acetic acid and 300 ml of water. To 300 ml of this solution was added 0.15 mol of cycloadduct (endo-alkyl isomer) and the mixture refluxed. The cycloadduct was soluble in the solvolysis media and no stirring was required. The progress of the reaction was followed by withdrawing aliquots periodically, neutralizing with 30% aqueous NaOH, extracting with an equal volume of $CHCl_3$, and assaying by vpc or ir as described for the sodium carbonate solvolysis. Upon completion of the reaction, neutralization was effected with a 30% aqueous NaOH solution to a pH of about 10 and the mixture extracted with 2 × 500 ml portions of $CHCl_3$. The combined $CHCl_3$ extracts were dried over $CaCl_2$, rotary evaporated, and distilled to yield the 2-alkyltropone. This procedure was used to prepare 2-methyl-, 2-ethyl-, and 2-*n*-butyltropones. The yields are recorded in Table I.

General Procedure for Determining the Relative Rates of Ring Contraction of *exo*-Alkyl-*endo*-haloketene–Cyclopentadiene Adducts. A mixture of 0.03 mol of the *exo*-alkyl-*endo*-haloketene–cyclopentadiene cycloadduct and 100 ml of 20% aqueous Na_2CO_3 was refluxed with stirring. Periodically, 2-ml aliquots were withdrawn from the aqueous layer, diluted with 50 ml of water, and titrated with 0.1 *N* standard HCl solution using Thymol blue as an indicator. The relative rates of reaction were obtained by comparing the amounts of acid required to neutralize the reaction mixture *vs.* time. These plots were essentially linear until about 50% of the cycloadduct had been consumed. The reactions were allowed to go to completion and then worked up in the usual manner. The yield of product and the relative rate of ring contraction for different alkyl groups and halogens are shown in Table II.

endo-**6-Carboxy-*exo*-6-methylbicyclo[3.1.0]hex-2-ene (Va):** mp 93–95° (lit.[8] 95.5°); nmr δ 10.84 (s, 1 H), 5.68 (m, 2 H), 2.68 (m, 2 H), 2.14 (m, 1 H), 1.72 (m, 1 H), 1.38 (s, 3 H).

endo-**6-Carboxy-*exo*-6-ethylbicyclo[3.1.0]hex-2-ene (Vb):** mp 52–54° (lit.[8] 55°); nmr δ 11.64 (s, 1 H), 5.48 (m, 2 H), 2.56 (m, 2 H), 1.96 (m, 2 H), 1.56 (m, 1 H), 1.16 (m, 1 H), 1.00 (t, 3 H).

endo-**6-Carboxy-*exo*-6-*n*-propylbicyclo[3.1.0]hex-2-ene (Vc):** bp 105–106° (0.1 mm); mp 37–40°; nmr δ 11.80 (s, 1 H), 5.68 (m, 2 H), 2.68 (m, 2 H), 2.20–1.08 (complex mult, 6 H), 0.94 (t, 3 H).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.31; H, 8.43; Found: C, 71.93; H, 8.40.

endo-**6-Carboxy-*exo*-6-(2-propyl)bicyclo[3.1.0]hex-2-ene (Va):** bp 103–105° (0.1 mm); mp 66–69° (lit.[8] 70°); nmr δ 9.38 (s, 1 H), 5.64 (m, 2 H), 2.64 (m, 2 H), 2.12 (m, 1 H), 1.48 (m, 1 H), 1.28 (h, 1 H), overlapping 1.08 (2d, J = 7 cps, 6 H).

endo-**6-Carboxy-*exo*-6-methyl-3-methylbicyclo[3.1.0]hex-2-ene (Xc).** This compound was obtained from VIIIc employing the procedure described above, mp 46–48°; nmr δ 10.68 (s, 1 H), 5.32 (m, 1 H), 2.60 (m, 2 H), 2.04 (m, 1 H), 1.72 (m, 1 H), overlapping 1.65 (s, 3 H), 1.32 (s, 3 H).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.0; H, 1.89. Found: C, 69.93; H, 7.63.

6-Carboxybicyclo[3.1.0]hex-2-ene (Vc). This compound was obtained from the *endo*-chloro isomer of IVg. A mixture of *endo*-carboxy and *exo*-carboxy isomers was produced. This was probably the result of isomerization of the chloroketene–cyclopentadiene adduct by base before the ring contraction occurs, bp 94–96° (0.4 mm); mp 75–80°; nmr δ 10.64 (s, 1 H), 5.72 (m, 2 H), 2.56 (m, 3 H), 1.88 (m, 2 H).

Anal. Calcd for $C_7H_8O_2$: C, 67.60; H, 6.45. Found: C, 67.67; H, 6.59.

General Procedure for the Triethylammonium Acetate Solvolysis of Dihaloketene–Olefin Cycloadducts. The solvolysis media was prepared by mixing 50 g of glacial acetic acid, 60 g water, and 100 g of triethylamine and adding acetone (~300 ml) to form a homogeneous solution. To 300 ml of this solution, 0.08 mol of cycloadduct was added and the solution refluxed. The progress of the reaction was followed by periodically withdrawing samples and assaying by vpc. Indene was added to provide a reference peak. The area of the cycloadduct peak was measured as a function of time. After the cycloadduct had been consumed, the reaction mixture was extracted with 2 × 500 ml portions of ether. The combined ether extracts were rotary evaporated and the residue added to 300 ml of benzene. The residual water was removed by azeotropic distillation. The benzene was evaporated on a rotatory evaporator and the product vacuum distilled. The yields of product and relative rates of formation are shown in Table IV.

Tropolone (XVI): bp 80–84° (0.1 mm); mp 49–50 (lit.[25] 51°).

4-Methyltropolone (XVI): bp 95–100° (0.1 mm); mp 74–75° after vacuum sublimation (lit.[26] mp 75°); nmr δ 8.95 (s, 1 H), 7.10 (m, 4 H), 2.43 (s, 3 H).

4,5-Benzotropolone (XVIII). The tropolone precipitated from the residue of the initial ether extraction of the reaction mixture after rotary evaporation, mp 157–159° (lit.[27] 159–160°); nmr δ 7.95–7.05 (complex mult).

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