2-Methoxy-4,4,5,5-tetramethyl-2-trifluoromethyl-1,3-dioxolane.—The product of the trifluoroacetylation of pinacol (a mixture of **4** and **5**) was added to a solution of diazomethane in ether and the resultant mixture was separated by glpc on DEGS. The product that had given the only major new glpc peak had a pmr spectrum (CCl_4) consisting of a quartet ($J_{FH} \cong 1.3$ Hz) at τ 6.65 and two singlets, each with an area twice that of the quartet, at 8.63 and 8.70 ppm. The ir showed no absorption band in the carbonyl region.

Trichloroacetate of Pinacol.—The product [bp 75–78° (0.05 mm); ir (CCl_4) 1760 (C=O) and 3590–3000 cm^{-1} (OH)] of the reaction of trichloroacetic acid with tetramethylethylene oxide[11] had a pmr spectrum (CCl_4) consisting of a slightly broadened hydroxy peak at τ 7.50, two methyl peaks, each almost six times as large, at 8.37 and 8.71, and two more methyl peaks, each about 8% as large as the larger methyl peaks, at 8.55 and 8.66 ppm. The pmr spectrum in acetonitrile was quite similar except that the peaks at 8.55 and 8.66 were about 15% as large as those at 8.37 and 8.71 ppm.

2-Methoxy-4,4,5,5-tetramethyl-2-trichloromethyl-1,3-dioxolane.—The trichloroacetate of pinacol was added to a solution of diazomethane in ether and the resultant mixture was separated by glpc on DEGS. The material from the only new glpc peak had no carbonyl band in its ir spectrum and a pmr spectrum consisting of three singlets with a ratio of 1:2:2.

Trifluoroacetates of Isobutylene Glycol.—Reaction of 9.5 g of trifluoroacetic acid and 8 g of isobutylene glycol in 10 g of benzene was allowed to proceed for 20 hr at 25°. Distillation gave 6 g of colorless liquid, bp 65° (20 mm), ir 1780 cm^{-1} (C=O). The pmr spectrum showed singlets at τ 8.68 and 5.80 ppm (areas, 3:2) attributed to the methyl and methylene groups of the primary ester 2-hydroxy-2-methylpropyl trifluoroacetate and two more singlets (τ 8.45 and 6.24 ppm) 3% as large attributed to the methyl and methylene groups of the tertiary ester 1,1-dimethyl-2-hydroxyethyl trifluoroacetate. This mixture reacted with diazomethane in ether to give, after separation by preparative glpc, 2-methoxy-4,4-dimethyl-2-trifluoromethyl-1,3-dioxolane: ir[13] (CCl_4) 2990, 1360, 1240, 1370, 1450, and 2950 cm^{-1}; pmr (CCl_4) τ 6.09 (s, 2, CH_2), 6.62 (s, 3, OCH_3), 8.53 (s, 3, CCH_3), and 8.61 ppm (s, 3, CCH_3).

Trifluoroacetate of Ethylene Glycol.—A mixture of the mono- and diesters, prepared by the literature procedure,[12] was separated by preparative glpc on DEGS to give 2-hydroxyethyl trifluoroacetate, whose pmr spectrum (CCl_4) showed two approximate triplets of equal size at τ 5.34 and 6.02 ppm plus the hydroxyl peak. Methylation by diazomethane gave 2-methoxy-2-trifluoromethyl-1,3-dioxolane: ir[13] (CCl_4) 2910, 2990, 2950, 1430, 1450, 1310, 1360, 1270, 1340, and 2850 cm^{-1}; pmr (CCl_4) τ 5.77 (s, 4, CH_2), 6.60 ppm (s, 3, OCH_3).

Reaction of 2-Hydroxyethyl Trifluoroacetate with Sodium 2-Hydroxyethoxide.—The same results were obtained in this reaction when the diester 1,2-bis(trifluoroacetoxy)ethane was used as when the monoester 2-hydroxyethyl trifluoroacetate was used. Presumably the diester is very rapidly transformed to the monoester under the reaction conditions. Since the diester is more easily obtained in a pure form it was more commonly used. In a typical experiment, 0.2 g of sodium was dissolved in 2.5 ml of anhydrous ethylene glycol under nitrogen. The mixture was cooled to 0° and excess diester was added. After 30 min the pmr of the reaction mixture showed the presence of monoester and ethylene oxide. In other experiments the reaction mixture was evacuated through a trap cooled in liquid nitrogen, which was subsequently found to contain ethylene oxide. The identity of the epoxide was established by glpc on DEGS and SE-30 as well as by pmr. However, in some experiments it was not found, and in no case was its yield greater than about 10%.

Known amounts of the diester were added to standard solutions of sodium 2-hydroxyethoxide in ethylene glycol and absorbance measurements made at the 1680 cm^{-1} absorption maximum for the trifluoroacetate ion. Comparison of standard solutions of sodium trifluoroacetate in ethylene glycol containing the same concentration of sodium 2-hydroxyethoxide as that found by titration to remain in the reaction solution showed that about 1.4 mol of sodium trifluoroacetate had been formed per mole of diester used.

Registry No.—**4**, 13388-92-6; **4** trichloro analog, 36978-04-8; **5**, 36978-05-9; **5** trichloro analog, 36978-06-0; **6**, 36978-07-1; **7**, 36978-08-2; 2-methoxy-4,4,5,5-tetramethyl-2-trichloromethyl-1,3-dioxolane, 36978-09-3; 2-hydroxy-2-methylpropyl trifluoroacetate, 36978-10-6; 1,1-dimethyl-2-hydroxyethyl trifluoroacetate, 36978-11-7; 2-hydroxyethyl trifluoroacetate, 667-32-3; 2-methoxy-2-trifluoromethyl-1,3-dioxolane 36978-13-9.

Stereochemistry of Medium-Sized-Ring Cyclopropylcarbinyl Radical Rearrangement[1]

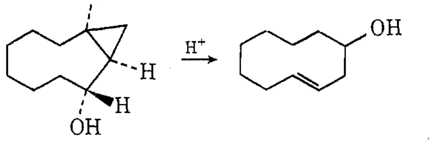
Richard W. Thies* and D. D. McRitchie

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

Received June 8, 1972

tert-Butyl *anti*-bicyclo[7.1.0]decane-2-percarboxylate (**1**) was prepared and assigned stereochemistry by conversion to *anti*-bicyclo[7.1.0]decan-2-ol. Photolytic or thermal decompositions gave complex product mixtures. The formation of both cis and trans cyclodecenes indicates that the cyclopropylcarbinyl radical does not give a stereospecific ring expansion.

Previous work[2] has shown that *anti*-bicyclo[7.1.0]decan-2-ol undergoes an acid-catalyzed, stereospecific ring expansion to *trans*-cyclodec-3-en-1-ol (eq 1) and



(1)

that the syn isomer stereospecifically gives the cis ring expanded product. These results suggest the intermediacy of nonclassical carbonium ions capable of maintaining stereochemistry. However, an argument could be made for classical ions that maintain stereochemistry because of some property of the medium-sized ring system. For example, the stereospecific ring expansions could result from the least motion rearrangements of two classical ions that do not readily undergo conformational interconversion.[3]

The behavior of the corresponding radical is interesting in this regard because radicals do not generally show nonclassical behavior.[4] If the radicals were to

---

(1) We thank the Research Corporation for support of this work.

(2) C. D. Poulter and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4282 (1970).

(3) L. E. Friedrich and F. R. Wight, *ibid.*, **92**, 1807 (1970).

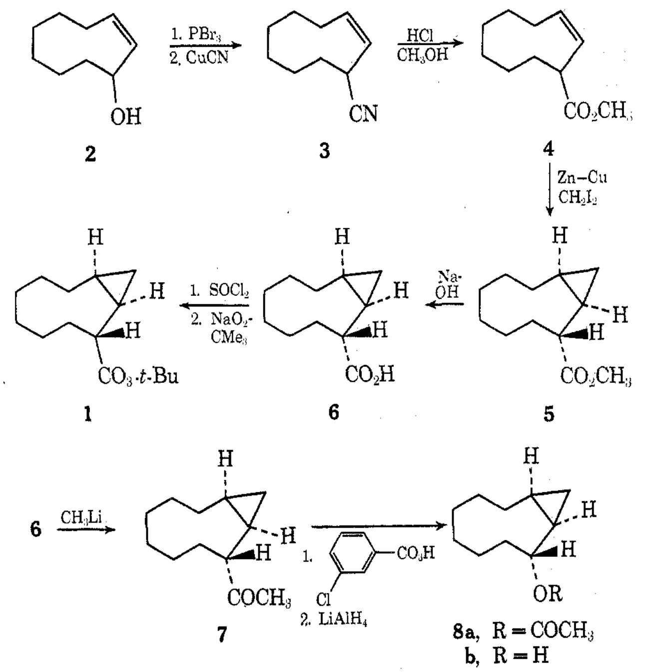
(4) (a) S. J. Cristol and A. L. Noreen, *ibid.*, **91**, 3969 (1969), and references cited therein; (b) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *ibid.*, **91**, 1877 (1969); (c) T. A. Halgren, M. E. H. Howden, M. E. Medorf, and J. D. Roberts, *ibid.*, **89**, 3051 (1967); (d) for a review of earlier work of cyclopropylcarbinyl radicals, see L. K. Montgomery, J. W. Matt, and J. R. Webster, *ibid.*, **89**, 923 (1967).

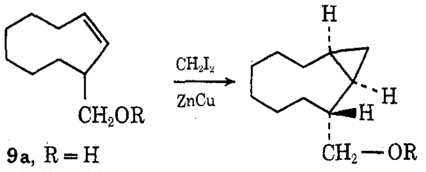
undergo the same type of stereospecific ring expansion as the carbonium ions, there would be little need to invoke nonclassical ions for this case. The present work reports the stereospecific generation of the anti radical and the stereoselectivity of rearrangement.

Results

The title compound, **1**, was prepared from cyclonon-2-en-1-ol (**2**) as shown in Scheme I. The stereochemistry was assigned by converting **6** to the ketone **7**, which was degraded by Baeyer-Villiger oxidation to the known alcohol,[2] *anti*-bicyclo[7.1.0]decan-2-ol (**8b** >99% anti). The Baeyer-Villiger reaction is known[5] to proceed with retention of stereochemistry, which means that the Simmons-Smith reaction gives highly stereoselective formation of the anti isomer **5**. This suggests the same sort of directive effect[6] as seen with compound **2**, which gives the anti isomer, **8b**, under Simmons-Smith conditions. On the other hand, the stereospecificity could be due to steric effects, since the trimethylsilyl derivative **9b** also gives only the anti isomer. Efforts to epimerize the ester **5** were unsuccessful, as were the other attempts to generate the epimer by alternative synthetic routes.

Scheme I





9a, R = H
b, R = SiMe$_3$

Photolytic or thermal decomposition of **1** in pentane[7] gave a complex set of products that could be separated into four groups by gas chromatography (Table I).

Table I
Variation of Product Composition[a] with Time of Photolysis of *anti*-Bicyclo[7.1.0]decane-2-percarboxylate (1) in Pentane Solvent

Compd type[b]	Separable components	Time, min 2	10	20	40	80
$C_{10}H_{18}$ and $C_{10}H_{16}$[c]	6	3	6	11	17	19
$C_{10}H_{17}$–O-*t*-Bu[d]	4	2	10	8	9	10
$C_{10}H_{17}$–C_5H_{11}	4	5	13	17	21	25
$C_{10}H_{17}$–$C_{10}H_{17}$	6	1	15	23	44	46
1	1	90	57	42	9	

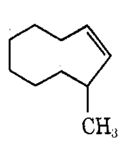
[a] The composition is presented as moles of "$C_{10}H_{17}$" in that product group, normalized to 100; *i.e.*, the numbers represent the relative peak areas on gc divided by the molecular weight (or the molecular weight/2 for the C_{20} dimer). Corrections were not made for relative response to the flame ionization detector but it was determined that the corrections are small for these compounds. Internal gc standard indicated that the material balances based on the ten carbon radical were 80–90%. [b] A 2% unknown component is not shown. [c] The cyclodecenes represent 56% of this group. [d] Part of this group is either a contaminent in 1 or is formed during LiAlH$_4$ reduction of 1. The 2-min sample was a different batch of starting peresters.

Further separation of the components within each group required capillary gas chromatography, which precluded collecting each component, so that detailed structures for most of the products could not be readily assigned. A gas chromatograph–mass spectrometer combination was used to obtain mass spectra for most of the individual components. The compound types shown in Table I were assigned from these mass spectra and infrared and nmr spectra of each group.

The *trans*- and *cis*-cyclodecenes, **10** and **11**, were intermingled with four compounds that contained two less hydrogens. The gas chromatographic peak for each cyclodecene was enhanced by coinjection of an authentic sample. The mass spectrum for the cis isomer was superimposable with that of authentic *cis*-cyclodecene. The mass spectrum for the trans isomer was similar to that for the authentic sample but showed additional peaks throughout the spectrum that indicated a contaminant with two less hydrogens. The mass spectra for the trans isomer obtained by photolysis of **1** in cyclohexene (see below) was superimposable with that of an authentic sample.

A search was made for two other likely C$_{10}$ products, *cis*-bicyclo[7.1.0]decane (**12**) and 3-methylcyclononene (**13**). Coinjection of authentic **12** enhanced the gas chromatographic peak assigned to the trans isomer but the mass spectra is quite different at high mass; *viz.*, **12** gives a much weaker molecular ion peak and a much stronger M − 15 peak than the cyclodecenes. A small amount of **12** could be hidden in the **10** peak but it could not be a major component. The methyl compound, **13**, has a much shorter retention time than

12



13

---

[5] J. A. Berson and S. Suzuki, *J. Amer. Chem. Soc.*, **81**, 4088 (1959), and references cited therein.

[6] C. D. Poulter, E. C. Friedrich, and S. Winstein, *ibid.*, **91**, 6892 (1969).

[7] Photolysis in cyclohexane gave similar products except that no $C_{10}H_{17}$–solvent products were observed and solvent dimer (bicyclohexyl) was formed.

any of the C_{10} group and would be easily seen if it were formed. No **13** was detected.[8]

The photolytic decomposition in cyclohexene (Table II) gives a similar set of products but the cyclodecenes are slightly enhanced, certain decadienes nearly disappear, and $C_{10}H_{17}$–C_6H_9 products supplant the dimeric products almost completely.

TABLE II

VARIATION IN PRODUCT COMPOSITION[a] WITH TIME OF PHOTOLYSIS OF *anti*-BICYCLO[7.1.0]DECANE-2-PERCARBOXYLATE (1) IN CYCLOHEXENE SOLVENT[a]

Compd type[b]	Separable components	Time, min 7	40	90
$C_{10}H_{18}$ and $C_{10}H_{16}$[c]	6	2	20	22
$C_{10}H_{17}$–*O*-*t*-Bu	4	1	9	15
$C_{10}H_{17}$–C_6H_9[d]	4	<1	20	53
$C_{10}H_{17}$–$C_{10}H_{17}$	6		2	10
1		97	49	

[a] See footnote *a*, Table I. [b] Solvent dimers are also formed. [c] The cyclodecenes make up 68% of this group. [d] This group contains components with mass 220, presumably $C_{10}H_{17}$–C_6H_{11} resulting from addition of radicals from **1** to solvent.

In pentane, the *cis*- to *trans*-cyclodecene ratio is 75:25 ± 1 from 10% to 58% conversion. The latter two times in Table I give a slightly increased ratio (78:22 and 79:21, respectively), indicating a possible slow interconversion of trans to cis. Control experiments showed that, when *trans*-4-trimethylsiloxycyclodecene (**14**) (a model for **10**) is added to the perester solution, it isomerizes slowly to the cis form under the reaction conditions (7% isomerization after 15 min of reaction). Similar results were observed when *tert*-butyl peracetate was decomposed in the presence of **14** (8% isomerization after 10 min, 33% isomerization after 40 min). *cis*-Cyclodecene did not isomerize measurably to the trans isomer under these conditions.

In cyclohexene the *cis*- to *trans*-cyclodecene ratio was 76:24 ± 1 and did not change even at longer times.

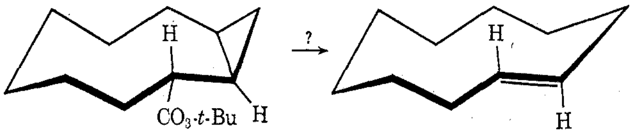
Discussion

The products from photolytic decomposition of **1** are similar to those previously reported for other stabilized radicals.[10,11] Peresters lose carbon dioxide to give the alkyl radical and *tert*-butoxy radical. The alkyl radicals can abstract hydrogen ($C_{10}H_{18}$), undergo hydrogen abstraction by another radical ($C_{10}H_{16}$), dimerize ($C_{10}H_{17}$–$C_{10}H_{17}$), or combine either with *tert*-butoxy radical ($C_{10}H_{17}$–O-*t*-Bu) or solvent radicals ($C_{10}H_{17}$–C_5H_{11}). The latter type of product is less common than the others but has been reported in cumene solvent.[11]

If the radical were to behave in the same way as the carbonium ion, the anti perester should lead to a trans double bond in the ring-expanded products. Models suggest that the best conformation for the system is a crown form (Chart I) which would initially generate a radical that is favorably aligned for internal cyclopropane bond cleavage leading to a trans double bond. There are no reasonable conformations that would favor the cis isomer.

CHART I

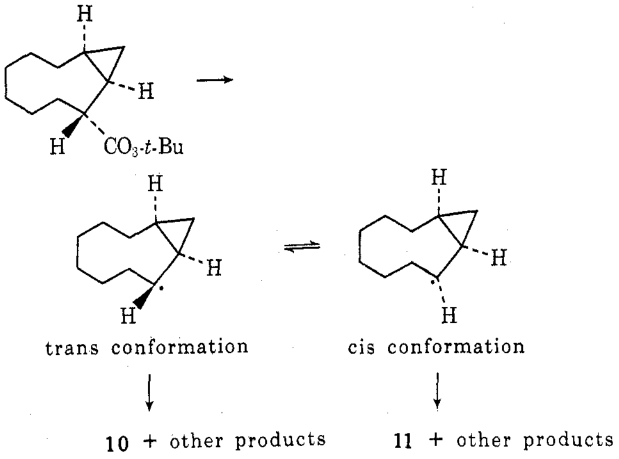
CONFORMATIONAL PREFERENCE FOR TRANS ISOMER



1 **10**

In pentane and cyclohexene, both *trans*- and *cis*-cyclodecene (**10** and **11**) are formed, the cis isomer predominating 3:1. The other products could not be examined individually, but the trans double bond infrared absorption (a relatively strong band) was not appreciable in any of the other groups of products. Since **10** and **11** only interconvert slowly under the experimental conditions, both must be formed directly from the radical. Thus the radical must interconvert readily between conformations leading to cis and trans ring expanded products (Scheme II). The observed ratio of *cis*- to *trans*-cyclodecene presumably reflects the transition state energy differences leading to the products,[12] although little significance should be placed on the exact ratio because the cyclodecenes represent only 10–15% of the products.

SCHEME II



In summary, the present work provides a striking contrast to the medium-sized-ring cyclopropylcarbinyl carbonium ion rearrangements that give stereospecific ring expansion. The corresponding radical reported here gives nonstereospecific rearrangement.

Experimental Section

The infrared spectra were measured on a Beckman IR-8 or Perkin-Elmer Model 621. Nmr spectra were measured on a Varian Associates HA-100 instrument. Mass spectra were obtained on a Varian MAT CH7 mass spectrometer. Elemental analyses were done by Alfred Bernhardt Analytical Laboratory. Analytical gas–liquid chromatography (gc) utilized a Varian

---

[8] Although **13** was not found, related products arising from external cyclopropane bond cleavage cannot be ruled out in the other types of products. Such external cleavage has been observed in certain other systems.[9]

[9] (a) P. K. Freeman, F. A. Raymond, J. C. Sutton, and W. R. Kindley, *J. Org. Chem.*, **33**, 1448 (1968); (b) A. L. J. Beckwith and G. Phillipou, *Chem. Commun.*, 658 (1971); (c) E. C. Friedrich and R. L. Holmstead, *J. Org. Chem.*, **36**, 971 (1971); (d) J. K. Crandell, J. P. Arrington, and C. F. Mazer, *ibid.*, **36**, 1428 (1971).

[10] R. A. Sheldon and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 5175, 4395 (1970).

[11] J. P. Engstrom and F. D. Greene, *J. Org. Chem.*, **37**, 968 (1972).

[12] Acid-catalyzed equilibration of the cyclodecenes give a 94:6 ratio of *cis*- to *trans*-cyclodecenes at 79.9°; A. C. Cope, and P. T. Moore, *J. Amer. Chem. Soc.*, **82**, 1744 (1960).

Model 1200 with flame ionization detector. The following columns were used: column A, 0.01 in. × 125 ft, UCON Polar LB550X capillary; column B, 0.01 in. × 75 ft, DEGS (diethylene glycol succinate) capillary; column C, 0.01 in. × 100 ft, Apiezon N capillary; column D, 0.125 in. × 15 ft, 5% SF-96 on 110/120 Anachrom. The flow through the capillaries was approximately 2 ml/min and the temperature range was 100–140°. The flow through the 0.125-in. column was normally 25 ml/min and the temperature was usually 140°. Gas chromatographic separation with collection was accomplished on a Varian A-90 instrument equipped with column E, $^1/_4$ in. × 6 ft, 33% SF-96 on 80/90 Chromasorb A. Photolysis was done in a Rayonet Srinivasan-Griffin photochemical reactor RPR-100 (The Southern New England Ultraviolet Co.).

***cis*-Cyclonon-2-en-1-ol (2)** was prepared by the method of Santelli, *et al.*,[13] bp 72° (0.5 mm) (lit.[13] bp 62° (0.5 mm)].

***cis*-3-Bromocyclononene.**—A solution containing 16.8 g of *cis*-8-cyclononenol, 60 ml of dry ether, and 1.0 g of dry pyridine was cooled in an ice bath under a nitrogen atmosphere. To the cooled solution was added, with magnetic stirring, a solution of 10.4 g of phosphorus tribromide in 50 ml of dry ether. The addition required 30 min, after which the ice bath was removed and the solution was stirred further at room temperature for 4 hr and then poured into 100 ml of ice water. The ether layer was separated and washed successively with 3 × 50 ml of cold 5% sodium carbonate and 3 × 50 ml of cold water, dried ($MgSO_4$), concentrated, and distilled, which gave 22.7 g (93%) of the bromide: bp 54° (0.4 mm); ir (neat) 3350 (OH), 740 (cis C=C), 690 cm^{-1} (CBr); nmr (CCl_4) δ 5.5 (m, 2), 4.9 (m, 1), 2.1 (m, 4), 1.7 (m, 2), 1.4 (m, 6).

Anal. Calcd for $C_9H_{15}Br$: C, 53.21; H, 7.42. Found: C, 53.05; H, 7.61.

***cis*-3-Cyanocyclononene (3).**—In a typical preparation, 10 g of *cis*-3-bromocyclononene was mixed well with 4.7 g of cuprous cyanide and 20 ml of cyclohexane in a 250-ml flask equipped with an efficient reflux condenser and mechanical stirrer. The mixture was refluxed and moderated when the reaction became vigorous. Refluxing was maintained for an additional 1 hr. The reaction was diluted with 50 ml of cyclohexane and allowed to stir overnight at room temperature. The insoluble portion was separated by filtration, ground with additional cyclohexane, and filtered. The combined organic phase was diluted with an equal volume of cyclohexane and decanted from an ether-insoluble yellow polymer precipitate. The solvent was removed and the resulting yellow oil was vacuum distilled, bp 69–70° (0.5 mm), giving 5.6 g (75%) of **3**: ir (neat) 735 (cis C=C), 2240 cm^{-1} (CN); nmr (CCl_4) δ 5.72 (d of t, J = 11, 6 Hz, 1), 5.38 (t, J = 11 Hz, 1), 3.50 (t of d, J = 11, 4 Hz, 1), 2.10 (m, 2), 1.2–1.9 (m, 10).

3-Carbomethoxycyclononene (4).—Dry AR methanol (400 ml) was chilled in an ice bath and anhydrous hydrogen chloride was passed in until the solution was saturated. To this was added 29 g of **3** and the reaction was refluxed. The solution was cooled, poured into 500 ml of saturated ammonium chloride solution, and extracted with 3 × 100 ml of ether. The ether extracts were combined and washed successively with 3 × 50 ml of sodium bicarbonate and 3 × 50 ml of water, and dried over anhydrous sodium sulfate. Solvent was removed and the colorless liquid was distilled, bp 80° (1 mm), which gave 32 g (90%) of **4**: ir (neat) 730 (cis C=C), 1725 cm^{-} (C=O); nmr (CCl_4) δ 5.5 (m, 2), 3.57 (s, 3), 3.4 (m, 1), 2.1 (m, 2), 1.3–1.8 (m, 10).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.40; H, 9.95. Found: C, 72.19; H, 9.99.

Methyl Bicyclo[7.1.0]decane-2-carboxylate (5).—A mixture of 31 g of zinc–copper couple,[14,15] 100 ml of anhydrous ether, and 40 g of methylene iodide was refluxed under nitrogen for 30 min. To this was added 30 g of methyl cyclononene-3-carboxylate in 125 ml of ether. The mixture was refluxed for 1 hr and then an additional 40 g of methylene iodide in 40 ml of ether was added dropwise over a 2-hr period while maintaining reflux. The reaction was monitored by gc (column A) and found to be about 85% complete at the end of the addition. An additional 2-hr reflux gave complete reaction. The reaction was quenched at room temperature with 150 ml of saturated ammonium chloride solution. The ether layer was separated and washed successively with 1 × 50 ml of saturated ammonium chloride, 3 × 50 ml of 10% sodium carbonate solution, and 3 × 50 ml of water, dried (Na_2SO_4), concentrated, and distilled to yield 29 g (90%) of ester, bp 78° (0.7 mm). The ester eluted as a single peak on columns A, B, and D, indicating that only one isomer had been obtained. The ester was reduced with lithium aluminum hydride in ether solution and the TMS ether **9b** was prepared from the resulting alcohol **9a** and TriSil Concentrate. The ether eluted as a single peak on columns A, B, C, and D. Compound **5** showed the following characteristics: ir (neat) 3060 (cyclopropyl H), 1725 cm^{-1} (C=O); nmr (CCl_4) δ 3.36 (s, 3), 2.2–0.9 (m, 12), 0.9–0.2 (m, 4), −0.38 (q, J = 4 Hz, 1).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.42; H, 10.23. Found: C, 73.26; H, 10.32.

Bicyclo[7.1.0]decane-2-carboxylic Acid (6).—The methyl ester **5** was hydrolyzed by refluxing for 1 hr in 50 ml of methanol and 50 ml of 5% sodium hydroxide. Recrystallization of the acid from ethanol–water gave 12.3 g (97%) of acid **6**: mp 77–78°; ir (KBr) 2700 (broad CO_2H), 1700 cm^{-1} (C=O); nmr (CCl_4) δ 11.4 (s, OH), 2.2–1.1 (m, 12), 1.1–0.5 (m, 4), −0.14 (q, J = 4 Hz, 1).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.40; H, 9.95. Found: C, 72.29; H, 9.97.

The acid was reduced with an ether solution of lithium aluminum hydride and the resulting alcohol, **9a**, was treated with TriSil Concentrate. The resulting TMS ether **9b** eluted as a single peak on columns A, B, C, and D. Coinjection of this ether with the ether obtained from ester **5** still produced only a single peak on column A. Conditions for the saponification do not cause observable epimerization.

Bicyclo[7.1.0]decane-2-carboxylic Acid Chloride.—A solution of 5 g of **6** in 5 ml of thionyl chloride was carefully heated to reflux in an oil bath. When the evolution of acid gases had stopped, usually 1 hr or less, the excess thionyl chloride was removed with the aid of a water aspirator, and the residual yellow oil was distilled, bp 66° (0.2 mm), which gave 5.0 g (90%) of the acid chloride: ir (neat) 3060 (cyclopropyl H), 1780 cm^{-1} (C=O); nmr (CCl_4) δ 2.3–2.6 (m, 1), 2.3–1.1 (m, 11), 0.7–1.1 (m, 4), −0.02 (m, 1).

***tert*-Butyl *exo*-bicyclo[7.1.0]decane-2-percarboxylate (1)** was prepared from the acid chloride and sodium *tert*-butyl peroxide as described by Bartlett, *et al.*[16] Chromatography on Florisil gave **1**: ir (neat) 3060 (cyclopropyl H), 1770 (C=O), 1194, 1365, 1390 cm^{-1} (*tert*-butyl); nmr (CCl_4) δ 2.4–1.1 (m, 12), 1.1 (s, 9), 0.5–1.0 (m, 4), −0.15 (m, 1). Lithium aluminum hydride reduction of **1** gave **9a** contaminated with *ca.* 8% of a material that is probably *tert*-butyl bicyclo[7.1.0]decan-2-yl ether: ir (neat) 3060 (cyclopropyl H), 1052 (COC), 1197 1363, 1386 cm^{-1} (*tert*-butyl). The retention time of this contaminent corresponds to the major component of the $C_{10}H_{17}$-O-*t*-Bu group of products.

Methyl Bicyclo[7.1.0]decane 2-Ketone (7).—A solution of 2.7 g of the acid **6** in 5 ml of dry ether was stirred under a nitrogen atmosphere while 21 ml of a 1.8 *M* methyllithium solution was added at a rate to maintain gentle reflux. When addition was complete, the reaction mixture was quenched with ammonium chloride, extracted into ether, washed with water, dried ($MgSO_4$), concentrated, and distilled, bp 75° (0.4 mm), which gave 2.2 g (80%) of **7**. Chromatographic analysis on column A indicated that the compound was contaminated with about 20% of the alcohol resulting from addition of a second molecule of methyllithium. Preparative gas chromatography on column E at 150° gave pure **7**, ir (neat) 1700 (C=O), 3060 cm^{-1} (cyclopropyl H).

Anal. Calcd for $C_{12}H_{20}O$: C, 80.00; H, 11.18. Found. C, 80.20; H, 10.98.

Bicyclo[7.1.0]decane-2-acetate (8a).—A solution containing 0.5 g of ketone **7** in 5 ml of chloroform was mixed with 0.5 g of *m*-chloroperbenzoic acid dissolved in 10 ml of chloroform. The solution was left in the dark for 1 week at room temperature. The reaction mixture was concentrated and extracted into ether solution which was washed successively with 2 × 30 ml of cold 1 *N* sodium hydroxide, 3 × 30 ml of cold water, and 1 × 30 ml of brine, and dried over magnesium sulfate. Purification by gas chromatography on column E at 180° gave **8a**: ir (neat) 3060 (cyclopropyl H), 1725 (C=O), and 1245 cm^{-1} (COAc).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.42; H, 10.23. Found: C, 73.30; H, 10.11.

---

[13] M. Santelli, M. Bertrand, and M. Ronco, *Bull. Soc. Chim. Fr.*, 3273 (1964).

[14] E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

[15] H. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Amer. Chem. Soc.*, **86**, 1347 (1964).

[16] P. D. Bartlett and R. E. Pincock, *ibid.*, **87**, 2590 (1965).

Simmons–Smith[15] Reaction of the Trimethylsilyl Derivative of *cis*-Cyclonon-2-enylmethanol (**9**).—Ester **4** was reduced ($LiAlH_4$) and silylated (TriSil, Pierce Chemical Co) to give **9**. The Simmons–Smith reaction, conducted in the same way as for compound **6**, gave two products: *anti*-bicyclo[7.1.0]decyl-2-methanol (**9a**) and its trimethylsilyl derivative **9b** (approximately 50:50). The alcohol **9a** was identical with that obtained by reduction ($LiAlH_4$) of **5**. Silylation of the mixture of **9a** and **9b** gave only **9b**: ir 3060 (cyclopropyl H), 1253 cm^{-1} [$Si(CH_3)_3$].

Anal. Calcd for $C_{13}H_{26}SiO$: C, 69.93; H, 11.73. Found: C, 70.04; H, 11.57.

***cis*-Cyclodecene** (**11**).—An authentic sample (95% pure) of **11** was prepared by azeotroping water from a solution of cyclodecanol in benzene with *p*-toluenesulfonate catalyst. The spectrum agrees with that reported previously.[17]

***trans*-Cyclodecene** (**10**).—A mixture of 4 g of *cis,anti*-bicyclo[7.1.0]decan-2-ol and 7.1 g of triphenylphosphine in 25 ml of dry dimethylformamide was treated with bromine in dimethylformamide until the orange color persisted. The reaction mixture was distilled under reduced pressure, yielding an oil that was dissolved in ether, washed (5 × 50 ml of water), and dried. The infrared showed that *trans*-3-bromocyclodecene had been produced: no 3060-cm^{-1} band (cyclopropyl H) and a strong absorption at 980 cm^{-1} (trans C=C). Reduction of the bromide by refluxing for 24 hr with excess ethereal lithium aluminum hydride followed by purification on column E gave **10**, whose properties coincide with those reported previously.[17]

Bicyclo[7.1.0]decane (**12**) was obtained by hydrogenation over Adams catalyst of bicyclo[7.1.0]deca-3,6-diene.[18] The spectral properties agree with those previously reported.[19] The mass spectrum gave the following data (70 eV): *m/e* (rel intensity) 138 (not measurable), 123 (1), 110 (4), 109 (6), 96 (16), 95 (28), 82 (36), 81 (56), 68 (48), 67 (100).

***cis*-3-Methylcyclononene** (**13**) was prepared by reducing ($LiAlH_4$) **4** to the corresponding alcohol, which was then converted to the *p*-toluenesulfonate derivative: mp 77.6–79.0; nmr (CCl_4) δ 7.72 (d, J = 8 Hz, 2), 7.28 (d, J = 8 Hz, 2), 5.57 (q, J = 9 Hz, 1), 5.10 (t, J = 9 Hz, 1), 3.85 (d, J = 6 Hz, 2), 2.83 (m, 1), 2.50 (s, 3), 2.12 (m, 2), 1.55 (m, 10). The *p*-toluenesulfonate was reduced ($LiAlH_4$) to give **13**: ir (CS_2) 742 cm^{-1} (cis C=C); nmr (CCl_4) δ 5.0–5.6 (m, 2), 2.4–2.8 (m, 1), 2.4–2.0 (m, 2), 1.1–1.9 (m, 10), 1.0 (d, J = 6 Hz, 3); mass spectrum (70 eV) *m/e* (rel intensity) 138 (4), 123 (5), 110 (9), 109 (10), 96 (19), 95 (25), 82 (25), 81 (54), 68 (64), 67 (100). *Anal.* Calcd for $C_{10}H_{18}$: *m/e* 138.141. Found: *m/e* 138.144.[20]

Photolyses.—Solutions, 1% of **1** in dry pentane or cyclohexene, were photolyzed in a quartz tube for various times, removed, reduced with ethereal lithium aluminum hydride, and analyzed by gc on column A using a 100 to 180° temperature program. For the cyclohexene case, it was necessary to treat the mixture with TriSil (Pierce Chemical) to prevent serious overlap between the reduced perester and the $C_{10}H_7$–C_6H_9 group. This column was connected to the mass spectrometer inlet, which allowed mass spectral analysis of the individual components of the mixture. Control studies used 1% of **11** or **14** and 1% of *tert*-butyl peracetate or 0.5% of **14** in the reaction mixture with **1**.

Pyrolyses used 1% solutions in dry pentene that were warmed at 100° and analyzed as above. The product mixture was similar to photolysis but less $C_{10}H_{18}$–$C_{10}H_{16}$ products were formed.

Product Data (Analyzed on Column A). $C_{10}H_{18}$–$C_{10}H_{16}$ Group.—In pentane there are six separable components in a ratio of 11:11:11:45:7:15. The second and fourth components were the *trans*- and *cis*-cyclodecenes; mass spectrum (cis) (70 eV) *m/e* (rel intensity) 138 (17), 110 (17), 109 (14), 96 (27), 95 (44), 82 (53), 83 (75), 68 (50), 67 (100); (trans) 138 (11), 110 (11), 109 (10), 96 (17), 95 (34), 82 (43), 83 (71), 68 (57), 67 (100). The other components all gave 136 molecular ion peaks. The infrared spectrum of the group showed a weak band at 980 (*trans* C=C) and a strong band at 708 cm^{-1} (cis C=C). The nmr spectrum showed vinyl protons but no appreciable high-field cyclopropyl protons.

In cyclohexene, there are six separable components in a ratio of 2:16:52:6:17:6. The second and third components were *trans*- and *cis*-cyclodecenes.

$C_{10}H_{17}$–O-*t*-Bu Group.—The gc analysis showed two poorly resolved doublets in an approximate ratio of 12:8:50:30. The major peak gave a parent ion at *m/e* 210. The group showed the following absorbances: ir 1052 (COC), 1197, 1363, 1386 (*tert*-butyl), 980 cm^{-1} (weak, trans C=C); nmr (CCl_4) δ 5.38 (vinyl H), 3.0–3.5 (OCH), 1.15 (O-*t*-Bu), 0.8 and −0.15 (cyclopropyl H). The nmr indicates a 2:1 ratio of cyclopropyl to olefinic compounds.

$C_{10}H_{17}$–C_5H_{11} Group.—The gc analysis gave two poorly resolved doublets in an approximate ratio of 50:30:12:8. The mass spectra of each component gave a molecular ion at *m/e* 208 and a fragmentation pattern similar to that below for the major isomer (70 eV): *m/e* (rel intensity) (fragment lost) 207 (69) (–H), 193 (6) (–CH_3), 179 (25) (–Et), 165 (44) (–Pr), 137 (100) (–C_5H_{11}). The group showed characteristic absorbances: nmr (CCl_4) δ 5.3 (m, vinyl H), 1.4 (m, –CH_2–), 0.86 (m, CH_3).

$C_{10}H_{17}$–C_6H_9 Group.—The gc analysis gave five peaks in a ratio of 5:59:19:5:12. The mass spectra gave molecular ion peaks at *m/e* 218 and strong peaks at *m/e* 137, 95, and 81. Part of this group gave molecular ion peaks at *m/e* 220 and strong peaks at *m/e* 137, 95, and 81 (see Table II, footnote *d*).

$C_{10}H_{17}$–$C_{10}H_{17}$ Group.—The mass spectra was characteristic for dimers, *i.e.*, molecular ions at *m/e* 274 with the next prominent mass at *m/e* 137.

Registry No.—**1**, 36976-79-1; **3**, 36976-80-4; **4**, 36976-81-5; **5**, 36976-82-6; **6**, 36976-83-7; **7**, 36976-84-8; **8a**, 36982-08-8; **9b**, 36982-09-9; **13**, 36982-10-2; *cis*-3-bromocyclononene, 33332-75-1; bicyclo[7.1.0]-decane-2-carboxylic acid chloride, 36982-12-4.

Acknowledgment. We thank the Research Corporation for partial support of this work. We also thank M. A. Battiste for generously allowing D. D. M. to complete this work in his laboratories.

---

[17] A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, *J. Amer. Chem. Soc.*, **74**, 3636 (1952).

[18] We thank the late Saul Winstein for this sample.

[19] J. G. Traynham and J. S. Dehn, *J. Amer. Chem. Soc.*, **89**, 2139 (1967).

[20] We thank the University of Oregon for the use of their CEC 110B instrument.