

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE, N. Y.]

## Carbon-Carbon Bond Fission in Cyclopropanes. IV. The Acid-Promoted Opening of the Three-Membered Ring in *exo*-7-Methylbicyclo[4.1.0]heptane and *exo*-6-Methylbicyclo[3.1.0]hexane<sup>1</sup>

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Studies of the position and stereochemistry of the acid-promoted cleavage of strained carbon-carbon bonds in bicyclo[*n*.1.0]alkanes have been extended to *exo*-7-methylbicyclo[4.1.0]heptane and *exo*-6-methylbicyclo[3.1.0]hexane. Acetates afforded by internal bond rupture are predominantly the *trans*-2-methylcycloalkyl acetates. Acetates resulting from external bond rupture are largely the *trans*-2-ethylcycloalkyl acetates. This stereoselectivity in acetate formation is interpreted in terms of nucleophilic solvent participation in ring opening of both internal and external bonds. Since small amounts of *cis*-acetates are produced as well, a carbonium ion process appears to compete to a minor extent. The distribution of products resulting from external and internal cleavage in substituted and unsubstituted substrates are compared. For both bicyclo[*n*.1.0]alkane substrates, alkyl substitution at the one-carbon bridge results in an increase in internal bond opening. This result is in agreement with the result predicted on the basis of a polarized transition state. However, the lack of close agreement between predicted and observed distribution of some specific types of acetates and olefins calls for a refinement of the polarized transition-state explanation in terms of differences in strain energy of substrates or development of nonbonded interactions in the transition state.

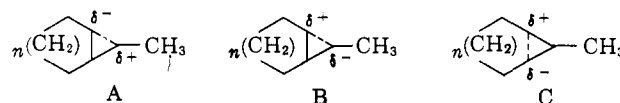
### Introduction

The stereoselective formation of formates<sup>3</sup> and acetates<sup>4,5</sup> which accompanies the acid-promoted fission of the external strained bonds of some bicyclo[*n*.1.0]alkanes has been demonstrated. Stereoselectivity in the addition of acetic acid across internal strained bonds appeared to be an interesting question and led us to consider substrates which carry an alkyl group of known configuration on the one-carbon bridge of a bicyclo[*n*.1.0]-alkane. Such substrates would possess, through the alkyl substituent, the dissymmetry needed to reveal the stereochemistry of nucleophilic attack in internal bond cleavage. Accordingly, the two substrates *exo*-7-methylbicyclo[4.1.0]heptane (I) and *exo*-6-methylbicyclo[3.1.0]hexane (II) were considered well suited to the investigation.



A second reason for our interest in the acid-promoted opening of substrates I and II was to ascertain the effect of alkyl substitution on the extent of internal and external bond opening. Earlier we had proposed<sup>4</sup> that the predominance of external bond opening in bicyclo[*n*.1.0]alkanes (where *n* = 3,4) was determined by the direction of polarization of the three-membered ring by the perturbing electrophilic reagent. A polarized transition state in which a partial negative charge was located on primary carbon and partial positive charge on secondary carbon was considered energetically more favorable than a polarized transition state in which both partial negative and positive charges were located on secondary carbon atoms. Each of the carbon atoms of the three-membered ring in substrates

I and II is alkyl substituted. Polarization of the three-membered ring will result in the development of both negative and positive charges only on secondary carbon atoms as depicted in the structures below. Since there is no electronically preferred polarized transition state, the extent of external and internal bond opening will be



determined ideally by the statistical distribution of the three possible polarized states. Each of the three polarized states (A, B, and C given above) represents one of two possible equivalent ways of polarizing the three-membered ring and accordingly one would expect the distribution of internal to total external opening in product formation to be 1/3 internal opening and 2/3 total external opening. On the basis of this analysis, the anticipated ratio of internal to external opening from substrates I and II would be 0.50 and therefore would exceed the ratio (0.09-0.26) observed<sup>4</sup> for the unsubstituted bicyclo[*n*.1.0]alkanes (where *n* = 3,4).

### Results

Treatment of *exo*-7-methylbicyclo[4.1.0]heptane (I) with 0.09 *N* sulfuric acid in glacial acetic acid at 47° for 36 hr. gave a product mixture containing 47% acetate and 53% olefin as shown by gas chromatography. The gas chromatographic analysis of the olefin component demonstrated the presence of five olefins; these were 3-ethylcyclohexene (49%), 1-ethylcyclohexene (22%), 1-methylcycloheptene (13%), vinylcyclohexene (8%), and 3-methylcycloheptene (8%). These olefins were identified by showing that the retention times of individual peaks were the same as the retention times of authentic olefins. The predominant olefin was isolated and its identity was confirmed by the comparison of its infrared spectrum with the spectrum of 3-ethylcyclohexene. Ethylidenecyclohexane if present is less than 1% of the product.

The mixture of acetates was converted to a mixture of alcohols by treatment with lithium aluminum hy-

(1) Paper III: R. T. LaLonde and J. J. Batelka, *Tetrahedron Letters*, **9**, 445 (1964).

(2) National Science Foundation Cooperative Fellow 1963-1964.

(3) A. C. Cope and G. L. Woo, *J. Am. Chem. Soc.*, **85**, 3601 (1963).

(4) R. T. LaLonde and L. S. Forney, *ibid.*, **85**, 3767 (1963).

(5) R. T. LaLonde and M. A. Tobias, *ibid.*, **85**, 3771 (1963).

TABLE I  
PER CENT DISTRIBUTION OF PRODUCTS FROM THE OPENING OF SOME ALKYL-SUBSTITUTED BICYCLO[*n*.1.0]ALKANES IN ACETIC ACID AS DETERMINED BY V.P.C. ANALYSIS<sup>a</sup>

Substrate	Acetate, %	Alcohol (acetate) component (100%)					Olefin, %	Olefin component (100%)				
		Methylcycloalkylcarbinol	2-Ethylcycloalkanol		2-Methylcycloalkanol			Vinylcycloalkane	3-Ethylcycloalkene	1-Ethylcycloalkene	1-Methylcycloalkene	3-Methylcycloalkene
			<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>						
I <sup>b</sup>	47	44	6	18	0	32	53	8	49	22	13	8
II <sup>c</sup>	80	52	2	7	2	37	20	0	<1*	27	55	18

<sup>a</sup> The estimated maximum errors in the analyses are given in the Experimental. <sup>b</sup> Glacial acetic acid, 0.09 *N* in sulfuric acid, 47°, 36 hr. <sup>c</sup> Glacial acetic acid, 0.09 *N* in sulfuric acid, 47°, 24 hr.

dride. Analysis by gas chromatography indicated the alcohol mixture consisted of *cis*-2-ethylcyclohexanol (6%), *trans*-2-ethylcyclohexanol and/or methylcyclohexylcarbinol (63%), and *trans*-2-methylcycloheptanol (31%). Chromic acid oxidation of the mixture of alcohols produced a mixture of ketones whose gas chromatograms showed a peak (68%) identical in retention time with both methyl cyclohexyl ketone and 2-ethylcyclohexanone and a second peak (32%) identical in retention time with 2-methylcycloheptanone. The ketone present in 32% was isolated by gas chromatography and an infrared spectrum of this material was identical with a spectrum of 2-methylcycloheptanone. Since the distinction between methylcyclohexylcarbinol and *trans*-2-ethylcyclohexanol or their corresponding ketones could not be achieved by chromatographic techniques, an infrared analysis was used. On the basis of both the infrared and chromatographic analyses (see Experimental) it was possible to determine that the mixture of the two inseparable alcohols contained 36% *trans*-2-ethylcyclohexanol and 64% methylcyclohexylcarbinol. Neither *cis*-2-methylcycloheptanol nor tertiary alcohols, if present, account for more than 1% of the product.

The alcohol distribution does not vary substantially with time. The alcohol mixture obtained from *exo*-7-methylbicyclo[4.1.0]heptane after a 1-hr. reaction was shown by gas chromatographic analysis to consist of *cis*-2-ethylcyclohexanol (5%), *trans*-2-ethylcyclohexanol and/or methylcyclohexylcarbinol (64%) and *trans*-2-methylcycloheptanol (31%). Additional evidence pertinent to the question of equilibrium or kinetic control of acetate formation was provided by finding that a mixture of *cis*- and *trans*-2-methylcycloheptyl acetates, when subjected to ring-opening conditions for 24 hr., showed no change in composition. That the acid-promoted addition of acetic acid to olefins is slower than the addition to cyclopropanes has been demonstrated.<sup>1,4,6</sup> On the basis of the slower addition of acetic acid to olefins and the supporting experiments mentioned above, it was concluded that the alcohol mixture represented for the most part the distribution of products originating directly from the acid-promoted ring cleavage of *exo*-7-methylbicyclo[4.1.0]heptane.

That the distribution of olefins is remaining constant also is a reasonable conclusion since the olefins produced by norcarane and bicyclo[3.1.0]hexane,<sup>4</sup> under the same reaction conditions as employed here, did not undergo isomerization in time.

When *exo*-6-methylbicyclo[3.1.0]hexane (II) was treated with 0.09 *N* sulfuric acid in glacial acetic acid for 24 hr., a mixture of acetates (80%) and olefins

(20%) was produced. Gas chromatograms of the olefin component displayed four peaks whose retention times were identical with 1-methylcyclohexene (55%), 1-ethylcyclopentene (27%), 3-methylcyclohexene (18%), and 3-ethylcyclopentene (trace). Neither vinylcyclopentane nor ethylidenecyclopentane could be detected.

The mixture of acetates was converted to a mixture of alcohols and analyzed in the usual manner. The alcohol mixture consisted of *cis*-2-ethylcyclopentanol (2%), *cis*-2-methylcyclohexanol (2%), methylcyclopentylcarbinol (52%), and *trans*-2-methylcyclohexanol and/or *trans*-2-ethylcyclopentanol (44%). By oxidation of the alcohol mixture and subsequent gas chromatographic analysis of the resulting ketone mixture, it was possible to determine that the mixture of alkylcycloalkanols consisted of 7% *trans*-2-ethylcyclopentanol and 37% *trans*-2-methylcyclohexanol. No tertiary alcohols could be detected in the mixture of alcohols. The alcohol distribution was observed to be the same for reactions of 1 and 24 hr. This result indicates that acetate is being formed mainly by the direct addition of acetic acid to II rather than through the addition to olefin. Thus, the olefin mixture consists of olefins which are both disubstituted and trisubstituted. Since the latter predominate and since trisubstituted olefins are generally believed to undergo addition of strong acids more rapidly than disubstituted olefins,<sup>7</sup> one would expect to observe tertiary alcohol developing in time should acetates be formed from olefins. As already noted, tertiary alcohols could not be detected in the mixture of alcohols from the 24-hr. reaction nor could any change in the distribution of alcohols be detected at all.

The product distributions from the acid-promoted opening of the substrates I and II are summarized in Table I.

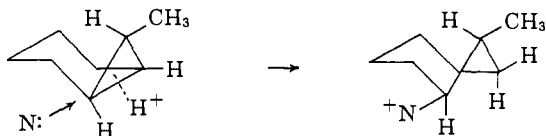
### Discussion

The results reported herein reveal that *trans*-2-methylcycloheptyl acetate is the sole product resulting from the addition of acetic acid across the internal bond of I and that *trans*-2-methylcyclohexyl acetate is the preponderant product resulting from the addition of acetic acid across the internal bond of II. The results also demonstrate that there is a preference for the formation of *trans*-2-ethylcycloalkyl acetates in the addition of acetic acid across the external bonds of I and II. The stereochemical mode of opening can be explained by a mechanistic scheme which involves a nucleophilic solvent attack on a protonated substrate (or substrate being protonated) with inversion of configuration at the carbon atom

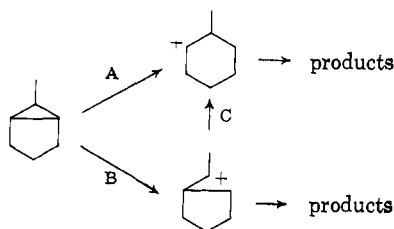
(6) C. D. Lawrence and C. F. H. Tipper, *J. Chem. Soc.*, 713 (1955).

(7) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 226.

undergoing nucleophilic attack. The steric course of nucleophilic attack on a protonated internal bond in *exo*-7-methylbicyclo[4.1.0]heptane is illustrated below. Although solvent attack can be important in acetate formation in some systems, the formation of both 2-bicyclo[2.2.2]octyl acetate and *axial*-2-acetoxycyclo[3.2.1]octane from *exo*-tricyclo[3.2.1.0<sup>2,4</sup>]octane<sup>1</sup> and the relatively low degree of stereoselectivity in the



formation of acetates from bicyclo[5.1.0]octane<sup>3</sup> indicate that in some instances acetate formation may proceed by way of carbonium ions. Recently the predominance of a carbonium ion mechanism in the formation of olefin from 3 $\beta$ -methyl- and 3 $\beta$ -phenyl-2 $\alpha$ ,3 $\alpha$ -methylenecholestane has been pointed out.<sup>9</sup> Formation of small amounts of the *cis*-2-ethylcycloalkyl acetates through external opening and *cis*-2-methylcyclohexyl acetate through internal opening implies that a carbonium ion process may be competing to some minor extent with nucleophilic solvent attack. Possibly the formation of the small amount of *cis*-2-methylcyclohexyl acetate (2%) from II reflects the degree of ring opening which occurs by way of the multiple carbonium ion rearrangement (steps B and C) of the type outlined graphically below. But it should be emphasized that the high degree of stereoselectivity in acetate formation eliminates multiple carbonium ion rearrangements of the type indicated as an important major path in acetate formation.



The second interesting aspect of the results is the influence of alkyl substitution at the one-carbon bridge on the position of ring opening. Summarized in Table II are the distributions of acetates and olefins formed

TABLE II  
PER CENT EXTERNAL AND INTERNAL BOND OPENING.  
DISTRIBUTION OF PRODUCTS AS ACETATES AND OLEFINS

n	R	Acetate component (100%)			Olefin component (100%)		
		Acetate, %	% ext. opening	% int. opening	Olefin, %	% ext. opening	% int. opening
3	H <sup>a,b</sup>	78	78	22	22	60	40
4	H <sup>a,c</sup>	43	86	14	57	91	9
3	<i>exo</i> -CH <sub>3</sub> (II)	80	61	39	20	27	73
4	<i>exo</i> -CH <sub>3</sub> (I)	47	68	32	53	79	21

<sup>a</sup> Carried out in 0.07 N *p*-toluenesulfonic acid in glacial acetic acid at 46.5–48.0°. <sup>b</sup> 41 hr. <sup>c</sup> 24 hr.

(8) R. T. LaLonde and I. S. Forney, *J. Org. Chem.*, in press.

(9) R. C. Cookson, D. P. G. Hamon, and J. Hudec, *J. Chem. Soc.*, 5782 (1963).

through internal and external opening of both substituted and unsubstituted substrates. Distributions are given as percentage of total acetate and percentage of total olefin. Each of the two columns representing acetates and olefins formed through external opening is the sum of products obtained by the two possible modes of external ring opening. Clearly the degree of internal opening is greater for the methyl-substituted substrates than it is for the corresponding unsubstituted substrates. In fact, the relative amount of acetates produced by internal opening agrees closely with the relative amount predicted (33%) on the basis of a statistical distribution of polarized transition states.

While the over-all distribution of products agrees with the distribution predicted on the basis of polarization, there are discrepancies within some groups of acetates and olefins. As Table I illustrates, the acetates produced in external bond cleavage are not evenly distributed between the isomeric 2-ethylcycloalkyl acetates and the methylcycloalkylcarbonyl acetates; the latter type of acetate is produced in excess of the theoretical amount. Likewise, the observed olefin distributions are not in good agreement with the predicted values; the extent of internal opening when olefin is afforded by II is greatly in excess of the predicted amount, while the degree of external opening when olefin is produced by I greatly exceeds the predicted value. The almost total absence of exocyclic olefins as one type of three possible olefinic types is also conspicuous. Apparently other factors besides polarization are influencing the mode of ring opening. These factors seem to be much more important in influencing olefin formation than acetate formation. A difference in ground-state energy may be one such factor. Assuming a resemblance of reactant ground state and transition state, polarization of the three-membered ring in the direction of maximum relief of strain<sup>10</sup> in the ground state, and hence in the transition state, may account for the greater extent of internal cleavage of the bicyclo[3.1.0]hexanes. Alternatively, should the transition state in ring opening not resemble the ground state but begin to resemble the products instead, then the developing nonbonded interactions in the transition state will resemble to some extent the nonbonded interactions in the products. Since staggering of substituents in a cyclopentane derivative is not as complete as in a cyclohexane derivative,<sup>11</sup> one could expect that nonbonded interactions would be more serious in a transition state leading to the formation of cyclopentane derivatives. Consequently, a higher activation energy would be involved than in the formation of cyclohexane derivatives. A similar argument may be invoked to account for the preferential formation of cyclohexane derivatives as opposed to cycloheptane derivatives.

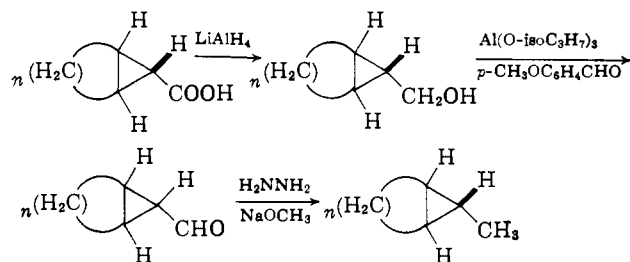
There are other noteworthy facets of the product distribution. Bicyclo[4.1.0]heptanes afford nearly equal amounts of acetates and olefins (Table II) while bicyclo[3.1.0]hexanes give largely acetates. Since the kinetic control of acetates and olefins has been estab-

(10) The strain energy of bicyclo[3.1.0]hexane has been estimated at 30 kcal./mole [C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962, p. 45] which is nearly the sum of the separate strain energies of cyclopentane (6 kcal./mole) and cyclopropane (27 kcal./mole). The strain energy of bicyclo[4.1.0]heptane can be estimated at about 27 kcal./mole, the strain energy of cyclopropane, assuming the strain energy of a half-chair cyclohexane to be nearly zero.

(11) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 250.

lished, the relatively smaller amount of olefins from the bicyclohexanes means a relatively higher activation energy in olefin production from bicyclohexanes. Furthermore, there is a significant difference in the composition of olefin mixtures from bicyclohexanes and bicycloheptanes; the former give largely the more substituted cycloalkenes, while the latter produce largely the least substituted cycloalkene (see Table I and ref. 4). These observations in the light of the frequently observed<sup>12</sup> production of Saytzeff-type product in E<sub>1</sub> eliminations and Hofmann-type product in E<sub>2</sub> eliminations from positively charged substrates strongly suggest that olefin production from the bicyclohexanes occurs largely by a carbonium ion route while olefin production from the bicycloheptanes occurs largely by way of a concerted process.

**Synthesis of Substrates.**—The synthesis of *exo*-7-methylbicyclo[4.1.0]heptane<sup>13</sup> (I) starting from bicyclo[4.1.0]heptane-*exo*-7-carboxylic acid, and *exo*-6-methylbicyclo[3.1.0]hexane (II) starting from bicyclo[3.1.0]hexane-*exo*-6-carboxylic acid is summarized in the general reaction scheme given below. The infra-



red and n.m.r. spectra of both compounds were consistent with the structures of I and II. The homogeneity of both final products was indicated by a single peak in three vapor phase chromatograms. Furthermore, the high degree of stereoselectivity in the acid-promoted conversion of substrate to acetates also demonstrates the isomeric purity of the substrates.

Both methyl-substituted bicyclo[*n*.1.0]alkanes are considered to be the *exo* isomers on the basis of the following evidence and arguments. The starting carboxylic acids were *exo* and consequently the primary alcohols afforded on lithium aluminum hydride reduction would also have the same stereochemistry. Although the subsequent Oppenauer oxidation and Wolff-Kishner reduction involve conditions which might effect the formation of an equilibrium mixture of aldehydes and hydrocarbons, the *exo* isomers would certainly be expected to predominate on the basis that an *exo* substituent would be greatly relieved of steric

crowding relative to an *endo* substituent. The report<sup>14</sup> that *exo*-7-acetylbicyclo[4.1.0]hexane does not undergo isomerization when treated with sodium ethoxide would tend to support this argument.

### Experimental

**Acid-Promoted Opening of *exo*-7-Methylbicyclo[4.1.0]heptane (I).**—A sealed glass tube containing 2.40 g. (21.8 mmoles) of *exo*-7-methylbicyclo[4.1.0]heptane, 133 mg. of 96% sulfuric acid, and 28.5 ml. of glacial acetic acid was maintained at 47° for 36 hr. The tube was opened and the contents dissolved in 100 ml. of water and 100 ml. of ether. The water layer was separated, extracted with ether (3 × 40 ml.) and the combined ether solutions washed with water, 5% sodium bicarbonate, and saturated sodium chloride. After drying over magnesium sulfate the solvent was removed by careful distillation. The remaining 3.89 g. of yellow oil was analyzed<sup>15</sup> on a 4-ft. diethylene glycol adipate on Celite column at 95°. The mixture was shown to consist of 47% acetate and 53% hydrocarbon in addition to a quantity of residual ether. The infrared spectrum of the crude ring-opening mixture showed bands at 5.80, 7.31, 8.06, 8.94, 9.74, 10.21, and 10.58  $\mu$ , with a shoulder at 6.10  $\mu$ .

The ring-opening mixture (3.89 g.) was dissolved in 40 ml. of anhydrous ether and added dropwise to a solution of 0.75 g. of lithium aluminum hydride in 20 ml. of refluxing ether. The contents of the flask were heated to reflux for an additional hour and then hydrolyzed with 10 ml. of saturated sodium sulfate. The resulting salts were dissolved with 6 *N* sulfuric acid, and the water layer extracted with ether (2 × 30 ml.). The combined ether solutions were washed with 5% sodium bicarbonate (30 ml.), saturated sodium chloride (30 ml.), and dried over magnesium sulfate. The solvent was removed by distillation in the usual manner and 3.32 g. of yellow oil remained. The infrared spectrum of this material showed bands at 3.01, 6.08, 7.27, 8.93, 9.65 (broad), and 10.70  $\mu$ .

Elution chromatography of the ring-opening mixture (3.32 g.) using 50 g. of Fisher alumina and pentane as the eluting solvent gave 1.23 g. of colorless oil which was subsequently identified as the olefin fraction. Continued elution with ether followed by methanol produced 1.46 g. of yellow oil later found to be the alcohol fraction.

A sealed glass tube containing 998 mg. of *exo*-7-methylbicyclo[4.1.0]heptane, 54 mg. of 96% sulfuric acid, and 11.9 ml. of glacial acetic acid was maintained at 47° for 1 hr. The tube was opened, and its contents worked up in the same fashion as its 36-hr. counterpart. The residual yellow oil, 1.73 g., was dissolved in 10 ml. of anhydrous ether and added dropwise to a suspension of 500 mg. of lithium aluminum hydride in 20 ml. of ether. The reaction mixture was worked up in the usual fashion, and afforded 1.4 g. of a crude alcohol-hydrocarbon mixture. This material was analyzed directly on an 11-ft. 17% glycerol on Celite column at 102°. The alcoholic fraction displayed peaks at 5.2 (5%), 7.8 (64%), and 10.2 min. (31%).

**Chromatographic Separation of Olefins from I.**—The hydrocarbon fraction was initially analyzed on an 11.5-ft. 4% squalane on Celite column at 82°. The presence of three peaks at 7.8 (7%), 9.8 (57%), and 11.0 min. (36%) was detected. The retention time of the first peak (7%) was identical with that of vinylcyclohexane, whereas the second (57%) was identical with both 3-ethylcyclohexene and 3-methylcycloheptene, and the third (36%) with 1-ethylcyclohexene, 1-methylcycloheptene, and ethylenecyclohexane.

Complete resolution of the hydrocarbon fraction was eventually accomplished on a 12-ft. 30% silver nitrate-triethylene glycol on firebrick column at 53.5°. The composition of the olefinic mixture was: 3-ethylcyclohexene (49%), 1-ethylcyclohexene (22%), 1-methylcycloheptene (13%), vinylcyclohexane (8%), and 3-methylcycloheptene (8%). The infrared spectrum of 3-ethylcyclohexene (independently synthesized) was identical with that of the 49% component as trapped by vapor phase chromatography. On the silver nitrate column at 41° and a helium pressure of 17 p.s.i., the retention times of possible olefins resulting from ring opening are: 1-methylcyclohexene (9.4 min.), ethylenecyclopentane (10.0 min.), 1-ethylcyclopentene (10.9

(14) M. Mousseron, R. Jacquier, and R. Fraisse, *Compt. rend.*, **243**, 1880 (1956).

(15) The estimated maximum error in the v.p.c. analyses for acetate-olefin composition is  $\pm 6\%$ ; the estimated maximum error in the v.p.c. analyses for alcohols and olefins is  $\pm 3\%$ .

(12) (a) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, Inc., New York, N. Y., 1959, pp. 475-477. (b) For a recent review see J. F. Bunnett, *Angew. Chem., Intern. Ed., Engl.*, **1**, 225 (1962). (c) For results and discussion of unimolecular elimination reactions of some 2-alkylcycloalkyl *p*-toluenesulfonates see W. Hükel, *et al.*, *Ann.*, **624**, 142 (1959), especially pp. 178-182, and references therein.

(13) Shortly after we submitted this paper for publication, H. E. Simmons, E. P. Blanchard, and R. D. Smith [*J. Am. Chem. Soc.*, **86**, 1347 (1964)] reported that *exo*-7-methylbicyclo[4.1.0]heptane had been prepared by treating cyclohexene with ethylidene iodide in the presence of zinc-copper couple. By private communication we learned that *exo*-7-methylbicyclo[4.1.0]heptane had also been prepared by the same workers through treatment of 2-ethylidenecyclohexanone with hydrazine and subsequently treating the resulting pyrazoline with base under normal Wolff-Kishner conditions. Dr. Simmons has kindly compared the infrared spectrum of our sample with a spectrum of his *exo*-7-methylbicyclo[4.1.0]heptane and found the spectra to be identical.

min.), 3-methylcyclohexene (16.0 min.), 3-ethylcyclopentene (20.5 min.), and vinylcyclopentane (22.2 min.). No peaks at 10.0 or 22.2 min. could be detected in the chromatogram from the mixture of olefins resulting from ring opening.

**Chromatographic Separation of Alcohols and Ketones from I.**—The alcoholic fraction from the 36-hr. reaction was analyzed on an 11-ft. 17% glycerol on Celite column at 102°, and displayed peaks at 5.2 (6%), 7.8 (63%), and 10.2 min. (31%). These retention times were shown to be identical with retention times of *cis*-2-ethylcyclohexanol (5.2 min.), *trans*-2-ethylcyclohexanol (7.8 min.) or methylcyclohexylcarbinol (7.8 min.), and *trans*-2-methylcycloheptanol (10.2 min.). The retention time of *cis*-2-methylcycloheptanol was 8.9 min. The retention times of 1-ethylcyclohexanol and 1-methylcycloheptanol on a 12-ft. 17% glycerol on Celite column at 105° were 5.0 and 8.2 min., respectively. No peaks at these retention times could be found in the chromatogram of the ring-opening mixture of alcohols.

A portion of the alcohol mixture (755 mg.) resulting from hydrogenolysis of acetate was dissolved in 50 ml. of acetone. A solution consisting of 427 mg. of chromic anhydride and 635 mg. of 96% sulfuric acid in 5 ml. of water was added dropwise to the acetone solution. After 3 hr., 100 ml. of water was added and the aqueous layer separated and extracted with ether. The combined extracts were washed with water, 5% sodium bicarbonate, saturated sodium chloride, and dried over magnesium sulfate. Removal of the solvent left 632 mg. of yellow oil which was analyzed on an 11.5-ft. Carbowax 20M column at 160.5°. The crude ketone mixture showed two apparent products with retention times of 16.3 (68%) and 19.2 min. (32%). Methyl cyclohexyl ketone, 2-ethylcyclohexanone, and 2-methylcycloheptanone were independently synthesized and displayed retention times of 16.3, 16.3, and 19.2 min., respectively. 2-Methylcycloheptanone was separated from the mixture of ketones by vapor phase chromatography. Its infrared spectrum was identical with that of an authentic sample. The material composing 68% of the ketone mixture was analyzed further by trapping it from the Carbowax column and subjecting it to quantitative infrared analysis. The analysis was accomplished by the utilization of a strong band at 8.6  $\mu$  present in the methyl cyclohexyl ketone but absent in 2-ethylcyclohexanone. The results showed that in fact this isolated material consisted of methyl cyclohexyl ketone (64%) and 2-ethylcyclohexanone (36%). The spectrum of this mixture contained no peaks other than those found in the two pure ketones and was superimposable on a spectrum of a synthetic mixture consisting of 36% 2-ethylcyclohexanone and 64% methyl cyclohexyl ketone. Accordingly, the original ketone mixture consisted of 44% methyl cyclohexyl ketone, 24% 2-ethylcyclohexanone, and 32% 2-methylcycloheptanone. Since 6% of the 2-ethylcyclohexanone was obtained from the oxidation of *cis*-2-ethylcyclohexanol, the relative amount of *trans*-2-ethylcyclohexanol in the mixture of alcohols from ring opening must be 18%.

**Acid Treatment of *cis*- and *trans*-Methylcycloheptyl Acetate.**—A mixture of *cis*- (62%) and *trans*-2-methylcycloheptanol (38%) was converted to a mixture of acetates with acetic anhydride and pyridine; 605 mg. of this mixture of acetates was dissolved in 9.8 ml. of glacial acetic acid containing 46 mg. of 96% sulfuric acid. This solution was divided into four equal portions and placed into sealed tubes which were placed in a constant temperature bath at 47°. Tubes were withdrawn at 2, 6, 10, and 24 hr. The contents of each tube was worked up in a manner identical with that employed in the ring opening of 7-methylbicyclo[4.1.0]heptane and then subjected to lithium aluminum hydride hydrogenolysis. Analysis on a 17% glycerol column gave the results

Time, hr.	<i>cis</i> -Alcohol, %	<i>trans</i> -Alcohol, %
2	61	39
6	62	38
10	60	40
24	61	39

**Acid-Promoted Opening of *exo*-6-Methylbicyclo[3.1.0]hexane (II).**—A sealed glass tube containing 1.50 g. (15.6 mmoles) of *exo*-6-methylbicyclo[3.1.0]hexane, 95 mg. of 96% sulfuric acid, and 20.4 ml. of glacial acetic acid was maintained at 47° for 24 hr. The resulting product (3.01 g.) was analyzed on a 4-ft. diethylene glycol adipate on Celite column at 83°. The mixture was shown to be composed of 80% acetate and 20% hydrocarbon in addition to residual ether. Its infrared spectrum displayed

bands at 5.85, 7.28, 8.06, 8.90, and 9.68  $\mu$ , with a shoulder at 6.10  $\mu$ .

The ring-opening mixture (3.0 g.) was dissolved in 40 ml. of anhydrous ether and added dropwise to a solution of 0.75 g. of lithium aluminum hydride in 20 ml. of refluxing ether. The resulting product mixture showed infrared bands at 3.01, 6.15, 7.27, 9.0 (broad), 9.35, 9.6 (broad), and 10.80  $\mu$ .

Elution chromatography of the ring-opening mixture produced a hydrocarbon fraction (310 mg.) and an alcohol fraction consisting of 1.70 g.

A sealed glass tube containing 500 mg. of *exo*-6-methylbicyclo[3.1.0]hexane, 39 mg. of 96% sulfuric acid, and 6.8 ml. of glacial acetic acid was maintained at 47° for 1 hr. The tube was opened and the contents subjected to hydrogenolysis by lithium aluminum hydride, yielding 924 mg. of light yellow oil. Vapor phase chromatography on a 12-ft. 17% glycerol on Celite column at 103° showed peaks at 5.7 (2%), 6.5 (2%), 7.2 (51%), and 8.5 min. (45%).

**Chromatographic Separation of Olefins from II.**—The hydrocarbon fraction was initially analyzed on an 11.5-ft. 4% squalane on Celite column at 67.5°. Retention times and percentile distribution of the five peaks were: 4.2 min. (3%), 4.8 min. (6%), 5.4 min. (19%), 6.3 min. (20%), and 7.5 min. (52%). These retention times were shown to correspond with those of 3-ethylcyclopentene (4.8 min.), 3-methylcyclohexene (5.4 min.), 1-ethylcyclopentene (6.3 min.), and 1-methylcyclohexene (7.5 min.). The olefin mixture was further analyzed on a 10-ft. 30% silver nitrate-triethylene glycol on firebrick column at 42°, and showed the presence of 55% 1-methylcyclohexene, 27% 1-ethylcyclopentene, 18% 3-methylcyclohexene, and a trace amount of 3-ethylcyclopentene.

**Chromatographic Separation of Alcohols and Ketones from II.**—The mixture of alcohols obtained from the 24-hr. reaction was analyzed on a 12-ft. 17% glycerol on Celite column at 103°. The chromatogram showed peaks at 5.7 (2%), 6.5 (2%), 7.2 (52%), and 8.5 min. (44%). These retention times were shown to be identical with authentic samples of *cis*-2-ethylcyclopentanol (5.7 min.); *cis*-2-methylcyclohexanol (6.5 min.), methylcyclopentylcarbinol (7.2 min.), and *trans*-2-methylcyclohexanol (8.5 min.) or *trans*-2-ethylcyclopentanol (8.5 min.). The retention times of 1-ethylcyclopentanol and 1-methylcyclohexanol on a 12-ft. 17% glycerol on Celite column at 105° were 3.6 and 4.6 min., respectively. No peaks at these retention times could be found in the chromatograms of the ring-opening mixture of alcohols.

A portion of the alcohol mixture (750 mg.) was dissolved in 50 ml. of acetone to which 5 ml. of water containing 450 mg. of chromic anhydride and 675 mg. of 96% sulfuric acid was added dropwise. The crude ketone mixture was analyzed on an 11.5-ft. Carbowax 20M column at 141°. The chromatogram showed a peak at 16.2 min. accompanied by an irresolvable shoulder at 17.5 min. Together, peak and shoulder made up 61% of the reaction mixture. A second peak was found at 18.8 min. (39%). Under identical conditions, methyl cyclopentyl ketone, 2-ethylcyclopentanone, and 2-methylcyclohexanone showed retention times of 16.2, 17.5, and 18.8 min., respectively. Both 2-methylcyclohexanone and methyl cyclopentyl ketone were separated from the mixture of ketones by vapor phase chromatography. Each infrared spectrum was identical with that of an authentic sample.

The observations that the ketone mixture contains 39% 2-methylcyclohexanone and that the alcohol mixture contains 2% *cis*-methylcyclohexanol indicate that the 44% (8.5 min.) cycloalkanol peak, as analyzed on 17% glycerol, must contain 37% *trans*-2-methylcyclohexanol and 7% *trans*-2-ethylcyclopentanol.

**Bicyclo[4.1.0]heptane-*exo*-7-carboxylic Acid.**—Ethyl bicyclo[4.1.0]heptane-7-carboxylate was prepared by treating cyclohexene with ethyl diazoacetate in the presence of copper powder according to a synthetic scheme reported.<sup>16</sup> The method was slightly modified by treating commercially available, purified copper powder with 10% hydrochloric acid (4  $\times$  25 ml.), water (4  $\times$  30 ml.), absolute ethanol (4  $\times$  30 ml.), anhydrous ether (4  $\times$  30 ml.), and drying for 30 min. at 110°. The use of copper powder treated in this manner resulted in the greater conversion of reactants to ethyl bicyclo[4.1.0]heptane-7-carboxylate. Saponification of ethyl bicyclo[4.1.0]heptane-7-carboxylate gave bicyclo[4.1.0]heptane-*exo*-7-carboxylic acid, m.p. 97–99°. The acid prepared in this manner was identical with a saturated

(16) P. Besinet, R. Fraisse, R. Jacquier, and P. Vaillfont, *Bull. soc. chim. France*, 1377 (1960).

carboxylic acid (m.p. 97–99°) obtained by hydrogenating the one (m.p. 91–93°) of two isomeric bicyclo[4.1.0]hept-3-en-7-carboxylic acids which did not undergo iodolactonization. A similar test of the configuration of the carboxylic acid function has been reported.<sup>16</sup>

**exo-7-Hydroxymethylbicyclo[4.1.0]heptane.**—Eleven grams (78.6 mmoles) of bicyclo[4.1.0]heptane-*exo*-7-carboxylic acid, m.p. 97–99°, was dissolved in 50 ml. of anhydrous ether and added dropwise to 3.0 g. (79 mmoles) of lithium aluminum hydride suspended in 250 ml. of ether heated to reflux. Refluxing was continued for 1 hr. and the reaction mixture hydrolyzed with saturated sodium sulfate and 6 *N* sulfuric acid. The ether layer was separated, washed with 50 ml. of saturated sodium chloride, and dried over magnesium sulfate. Removal of the solvent followed by distillation yielded 8.3 g. (83.5%) of homogeneous alcohol, b.p. 106–107° (17 mm.),  $n_D^{25.5}$  1.4832, reported<sup>14</sup> b.p. 105° (18 mm.). The presence of only one alcohol was indicated by vapor phase chromatography on an 11-ft. 17% glycerol on Celite column at 102°.

*exo*-7-Hydroxymethylbicyclo[4.1.0]heptane was converted to its 3,5-dinitrobenzoate, m.p. 102–103°.

*Anal.*<sup>17</sup> Calcd. for C<sub>8</sub>H<sub>14</sub>O<sub>6</sub>N<sub>2</sub>: C, 56.25; H, 5.04; N, 8.75. Found: C, 56.50; H, 5.10; N, 8.72.

**Bicyclo[4.1.0]heptane-7-carboxaldehyde.**—According to the method of Lauchenaure and Schinz,<sup>18</sup> 8.0 g. (63.5 mmoles) of 7-hydroxymethylbicyclo[4.1.0]heptane, b.p. 106–107° (17 mm.), was heated between 90 and 95° at 17 mm. with 4.4 g. of aluminum isopropoxide until all of the isopropyl alcohol had been displaced by the higher boiling alcohol. At this point, 13.0 g. (150%) of freshly distilled anisaldehyde was added and the reaction mixture heated to 150° over a period of 12 min. at 17 mm. The distillate, b.p. 96–103°, was placed in ether, washed with water and saturated sodium chloride, and dried over magnesium sulfate. Removal of the solvent and subsequent distillation yielded 4.3 g. (54.5%) of colorless oil, b.p. 92–94° (17 mm.),  $n_D^{26}$  1.4883 (reported<sup>14</sup> b.p. 98° (20 mm.)).

**exo-7-Methylbicyclo[4.1.0]heptane.**—According to the method of Whitmore,<sup>19</sup> 8.9 g. (71.2 mmoles) of bicyclo[4.1.0]heptane-7-carboxaldehyde, 8.5 g. of 85% hydrazine hydrate, and 0.3 ml. of glacial acetic acid were heated together until the temperature reached 155°, at which point 5.4 ml. of hydrazine and water had distilled from the reaction vessel. Two grams of sodium methoxide suspended in 25 ml. of triethylene glycol was then added and the temperature slowly raised to 205°. When the evolution of nitrogen was complete, the distillate was placed in 25 ml. of water, and the organic layer separated. The water layer was extracted with ether and the combined extracts washed with 1:1 hydrochloric acid, 5% sodium bicarbonate, and 10 ml. of saturated sodium chloride. After drying over magnesium sulfate and sodium carbonate, the solvent was removed and the crude hydrocarbon was distilled yielding 4.9 g. (62.5%) of colorless oil, b.p. 123–125° (750 mm.),  $n_D^{26}$  1.4496. The homogeneity of this material was demonstrated by v.p.c. on a 4% squalane on Celite column, a 15% Silicone 550 on firebrick column, and a 30%

silver nitrate-triethylene glycol on firebrick column. The infrared spectrum displayed pertinent bands at 7.29 and 9.82  $\mu$ . The n.m.r. spectrum showed a single methyl doublet ( $J = 5.0$  c.p.s.) at 9.03  $\tau$  imposed on an unresolved multiplet and a methine peak (three protons) at 9.56  $\tau$ .

*Anal.* Calcd. for C<sub>8</sub>H<sub>14</sub>: C, 87.19; H, 12.81. Found: C, 87.45; H, 12.99.

**Bicyclo[3.1.0]hexane-*exo*-6-carboxylic Acid.**—The synthesis of ethyl bicyclo[3.1.0]hexane-6-carboxylate was essentially the same as that reported.<sup>16</sup> Saponification and repeated crystallization from nitromethane gave bicyclo[3.1.0]hexane-*exo*-6-carboxylic acid, m.p. 59–61°. The acid prepared in this manner was identical with a saturated carboxylic acid (m.p. 59–61°) obtained by hydrogenating the one (m.p. 80–82°) of two isomeric bicyclo[3.1.0]hept-3-ene-6-carboxylic acids which did not undergo iodolactonization. The same test of the stereochemistry of the carboxylic acid function has been reported.<sup>16</sup>

**exo-6-Hydroxymethylbicyclo[3.1.0]hexane.**—Bicyclo[3.1.0]hexane-*exo*-6-carboxylic acid (10.5 g., 83.4 mmoles, m.p. 58–61°) was dissolved in 50 ml. of anhydrous ether and added dropwise to 3.8 g. (0.1 mole) of lithium aluminum hydride suspended in 250 ml. of refluxing ether. After heating to reflux for 4 hr., the reaction yielded 7.8 g. (83.5%) of colorless oil, b.p. 82–83° (11 mm.),  $n_D^{26}$  1.4752. The presence of only one alcohol was indicated by vapor phase chromatography on an 11-ft. 17% glycerol on Celite column at 102°.

6-Hydroxymethylbicyclo[3.1.0]hexane was converted to its 3,5-dinitrobenzoate, m.p. 116–117°.

*Anal.* Calcd. for C<sub>14</sub>H<sub>14</sub>O<sub>6</sub>N<sub>2</sub>: C, 54.90; H, 4.61; N, 9.15. Found: C, 55.04; H, 4.78; N, 9.31.

**Bicyclo[3.1.0]hexane-6-carboxaldehyde.**—Eleven grams (99 mmoles) of 6-hydroxymethylbicyclo[3.1.0]hexane was treated with 6.8 g. of aluminum isopropoxide followed by 20.4 g. (150%) of freshly distilled anisaldehyde. Isolation of the crude product and distillation yielded 6.5 g. (59.1%) of colorless oil, b.p. 63–65° (11 mm.),  $n_D^{26}$  1.4792.

Bicyclo[3.1.0]hexane-6-carboxaldehyde was converted to its semicarbazone, m.p. 161–163°.

**exo-6-Methylbicyclo[3.1.0]hexane.**—Treatment of 6.4 g. (57.6 mmole) of bicyclo[3.1.0]hexane-6-carboxaldehyde with 6.8 g. of 85% hydrazine hydrate and 0.2 ml. of glacial acetic acid gave 3.3 g. (60%) of colorless hydrocarbon, b.p. 100–102° (750 mm.),  $n_D^{26}$  1.4358. This material was shown to contain less than 1% impurity by v.p.c. on a 4% squalane on Celite column and a 30% silver nitrate-triethylene glycol on firebrick column. Its infrared spectrum displayed pertinent bands at 7.27 and 10.07  $\mu$ . The n.m.r. spectrum showed a single methyl doublet ( $J = 5.5$  c.p.s.) centered at 9.05  $\tau$  and a methine multiplet (one proton) centered at 9.52  $\tau$ .

*Anal.* Calcd. for C<sub>7</sub>H<sub>12</sub>: C, 87.42; H, 12.58. Found: C, 87.14; H, 12.66.

**Infrared and N.m.r. Spectra.**—All infrared spectra were determined in carbon tetrachloride solution using a Baird infrared spectrophotometer. The n.m.r. spectra were obtained from a Varian Model A-60 employing carbon tetrachloride as a solvent and tetramethylsilane as an internal standard.

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(17) All elemental analyses by H. Gailbraith, Knoxville, Tenn.

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