

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE 10, N. Y.]

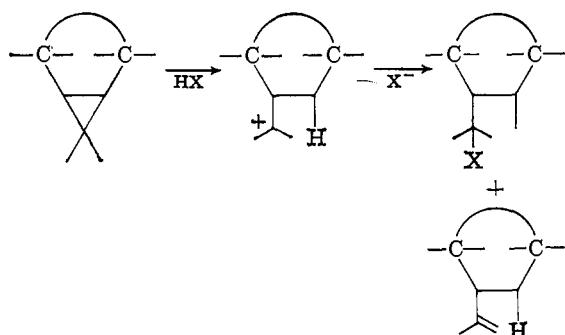
## Carbon-Carbon Bond Fission in Cyclopropanes. I. The Acid-Promoted Opening of the Three-Membered Ring in Bicyclo[4.1.0]heptane, Bicyclo[3.1.0]hexane, and Bicyclo[2.1.0]pentane<sup>1</sup>

BY ROBERT T. LALONDE AND LEROY S. FORNEY<sup>2</sup>

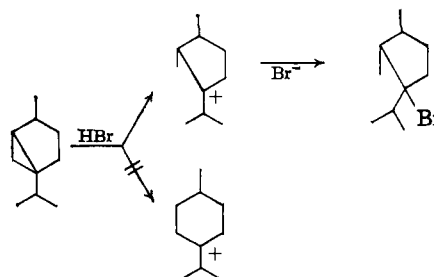
RECEIVED JUNE 13, 1963

Bicyclo[4.1.0]heptane, bicyclo[3.1.0]hexane, and bicyclo[2.1.0]pentane have been treated with sulfuric and *p*-toluenesulfonic acids in acetic acid in order to assess the importance of the various factors which might influence the mode of ring fission. Product analyses demonstrate that the carbon-carbon bond fission in the three-membered ring of bicyclo[4.1.0]heptane and bicyclo[3.1.0]hexane takes place largely externally to the large ring while the only bond cleaved in bicyclo[2.1.0]pentane is the bond common to both rings. These results are interpreted in terms of the polarization and developing nonbonded interactions in the transition state and bond strain in the ground state. The stereoselectivity of the addition of acetic acid which accompanies external bond cleavage is demonstrated by the predominant formation of *trans*-2-methylcyclohexyl acetate from bicyclo[4.1.0]heptane and *trans*-2-methylcyclopentyl acetate from bicyclo[3.1.0]hexane.

**Introduction.**—The fission of carbon-carbon bonds of cyclopropane derivatives by various electrophilic reagents with the resulting addition of the reagent or formation of olefin is well known. Earlier investigations have dealt with the problem of the position of ring fission in terms of the effect of substitution.<sup>3</sup> As a result of these investigations, the mode of ring fission now is generally interpreted in terms of the most stable carbonium ion intermediate produced in the course of the ring opening. Some information pertaining to the mode of cyclopropane ring fission in fused ring systems is inferred from the results taken from the terpene literature. For example, the cleavage of the carbon-carbon bonds external to the six-membered ring of carane<sup>4</sup> and maaliane<sup>5</sup> and external to the seven-membered ring of dihydroaromadendrene<sup>6</sup> occurs, as depicted below, rather than the cleavage of the carbon-carbon bond common to both rings. This mode of cleavage is clearly controlled by the preferred formation of a tertiary carbonium ion.

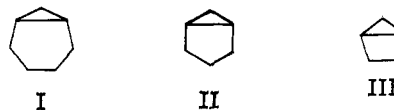


However, a rationalization solely in terms of carbonium ion stability does not suffice. The position of ring opening in the conversion of thujane to 1-bromo-1-[2-propyl]-2,3-dimethylcyclopentane,<sup>7</sup> as shown below, can be explained on the basis of a proton attacking the most negative carbon atom of the three-membered ring which then opens to give the most stable carbonium ion. The numerous examples of ring fission in steroids and



terpenoids which contain unsaturated functional groups located  $\alpha$  or  $\beta$  to a cyclopropane ring are not relevant to this problem since the functional group probably controls the mode of ring fission through conjugative or homoconjugative effects.<sup>8</sup>

We wished to study the ring-opening reactions of fused-ring cyclopropane derivatives unencumbered by functional groups for the purpose of obtaining the background information which ultimately would lead to a mechanistic interpretation of carbon-carbon bond fission in cyclopropanes. Our immediate objective was to obtain information of the ratio of internal bond cleavage to external bond cleavage and the stereochemistry of the addition of the electrophilic reagent. The results disclosed herein deal with the product analyses of mixtures obtained from the action of *p*-toluenesulfonic acid and sulfuric acid in glacial acetic acid on some bicyclo[*n*.1.0]alkanes. These include bicyclo[4.1.0]heptane (norcarane, I), bicyclo[3.1.0]hexane (II), and bicyclo[2.1.0]pentane (III).



**Results.**—It was demonstrated earlier that the acid-promoted cleavage of the three-membered ring of norcarane (I) in acetic acid gives a complex mixture of acetates and olefins.<sup>1</sup> Further studies of the reaction with norcarane have been pursued in order to identify conclusively the components of the olefin fraction and to provide information pertaining to the origin of the olefins. Concurrently, information pertaining to the origin of the cycloalkyl acetates has been obtained.

The olefin fraction obtained from norcarane (III) after treatment with 0.07 *N* *p*-toluenesulfonic acid in acetic acid for 86 hr. was separated into its individual

(8) One comparison of several which serves to illustrate the effect of a double bond in conjugation with the three-membered ring on the mode of ring opening is: 3,5-cyclocholest-6-ene on treatment with sulfuric acid gives cholesteryl acetate [B. Reigel, G. B. Hager, and B. L. Zenitz, *J. Am. Chem. Soc.*, **68**, 2562 (1946)] while 3,5-cyclocholestane on treatment with hydrogen chloride in acetic acid gives 3-methyl-A-norcholest-3-ene [H. Schmid and K. Kagi, *Helv. Chim. Acta*, **33**, 1582 (1950)].

(1) For a preliminary account of part of this work see: R. T. LaLonde, *J. Org. Chem.*, **27**, 2275 (1962).

(2) National Science Foundation Cooperative Fellow, 1962-1964.

(3) For leading references see: R. A. Raphael, "Chemistry of Carbon Compounds," IIA, E. H. Rodd, Ed., Elsevier Press, Houston, Texas, 1953, pp. 25-28; R. C. Fuson, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 21-26.

(4) N. M. Kishner and A. Zavadovsky, *J. Russ. Phys. Chem. Soc.*, **43**, 1132 (1911); *Chem. Abstr.*, **6**, 854 (1912).

(5) G. Büchi, M. Schach von Wittenau, and D. M. White, *J. Am. Chem. Soc.*, **81**, 1968 (1959).

(6) G. Büchi, S. W. Chow, T. Matsuura, T. L. Popper, H. H. Rennhard, and M. Schach von Wittenau, *Tetrahedron Letters*, **6**, 14 (1959).

(7) N. M. Kishner, *J. Russ. Phys. Chem. Soc.*, **42**, 1198 (1910); *Chem. Abstr.*, **6**, 84 (1912).

TABLE I  
PER CENT DISTRIBUTION OF PRODUCTS OBTAINED FROM THE ACID-PROMOTED OPENING OF BICYCLO[*n*.1.0]ALKANES IN ACETIC ACID AT 46.5–48.0° AS DETERMINED BY V.P.C. ANALYSIS<sup>a</sup>

Bicyclo- [ <i>n</i> .1.0]- alkane, <i>n</i>	Reacn. time, hr.	Acetate, %	Alcohol (100%)				Olefin (100%)			Internal/ external opening		
			<i>trans</i> -2- Methyl cyclo- alkanol	<i>cis</i> -2- Methyl cyclo- alkanol	1-Methyl cyclo- alkanol <sup>d</sup>	<i>trans</i> -3- and <i>trans</i> -4- methyl cyclo- alkanol	Cyclo- alkanol	Olefin, %	3-Methyl cyclo- alkene		1-Methyl cyclo- alkene	Cyclo- alkene
4 <sup>b</sup>	0.5		77		7	4	12					
	1.0		76		8	3	12					
	24	43	76		8	2	14	57	70	21	9	0.11
	86	47	79		10	2	9	53	71	21	8	.09
4 <sup>c</sup>	1.0	63	68		9	3	20	37	71	17	12	.17
	41	97	66		2	13	20	3	34	15	52	.21
3 <sup>b</sup>	0.5		68	11	1		20					
	1.0		68	6	2		24					
	41	78	68	7	3		22	22	14	46	40	.26
	61	84	66	7	2		24	16	17	57	26	.24
2 <sup>b</sup>	24	100					100					1.00/0.00

<sup>a</sup> The estimated limits of v.p.c. analysis for alcohols and olefins is  $\pm 3\%$ ; the estimated limit of analysis for acetate-olefin composition is  $\pm 6\%$ . The percentage distribution is the average of three v.p.c. analyses of product mixtures. <sup>b</sup> In 0.07 *M* *p*-toluenesulfonic acid in acetic acid. <sup>c</sup> In 2 *N* sulfuric acid in acetic acid. <sup>d</sup> Since complete separation of *cis*-2- and 1-methylcyclohexanols could not be achieved, these figures represent the sum of both alcohols.

components by gas chromatography. The three olefins obtained were conclusively identified as 3-methylcyclohexene, 1-methylcyclohexene, and cycloheptene by the comparison of their infrared spectra with the spectra of authentic materials. The relative amounts of each olefin was determined by analytical gas chromatography and is given in Table I. Analyses of olefin mixtures obtained from reactions of 1 hr. or less could not be achieved because the presence of large amounts of unconverted norcarane made it impossible to determine the very small amount of cycloheptene present. Nevertheless, composition ratios of 1-methylcyclohexene to 3-methylcyclohexene were determined after various reaction times, including reaction times of less than 1 hr., and at the same time the progress of the reaction was followed by determining the amount of unreacted norcarane. The composition ratios of the methylcyclohexenes were found to be constant at 0.30 for reaction times of 0.5–86 hr. Since one-third of the norcarane already had been consumed during the shortest reaction investigated, a further check of the possible isomerization of olefins was carried out by subjecting 1-methylcyclohexene and 3-methylcyclohexene to the conditions of ring opening. No isomerization of olefins could be detected, although both olefins produced small amounts of cycloalkyl acetates. These observations indicate that both 1-methylcyclohexene and 3-methylcyclohexene originate directly from norcarane.

The cycloalkyl acetate distribution was determined by the gas chromatographic analysis of the alcohols obtained from lithium aluminum hydride reduction of the mixture of acetates. The percentage composition of alcohol mixtures resulting from reactions of various duration is given in Table I. The results show that there is only little if any change in the alcohol distribution for reactions carried out from 0.5 to 86 hr. At the same time, the change in acetate-olefin composition for reactions carried out over the period of 24 and 86 hr. is at most very small. The change in the acetate-olefin composition is undoubtedly a result of the addition of acetic acid to olefins. However, since this secondary reaction is occurring to such a very small extent and the alcohol distribution remains constant, it is reasonable to conclude that *trans*-2-methylcyclohexyl acetate is originating largely from the ring opening of norcarane. The constant alcohol distribution also suggests that at least some of each of the methylcyclohexyl acetates

observed in minor amounts arises directly from norcarane as well. That the formation of *trans*-2-methylcyclohexyl acetate is largely kinetically controlled is also supported by the formation of the thermodynamically unstable 2(a)-acetoxy-3(a)-methyl-*trans*-decalin from 2,3-methano-*trans*-decalin on similar treatment with acetic acid.<sup>9</sup>

A slight increase in the amount of cycloheptane derivatives was noted when norcarane was treated with 2 *N* sulfuric acid in acetic acid. As results summarized in Table I show, relative amounts of cycloheptane derivatives remained the same for 1- and 41-hr. reactions. The large difference in acetate-olefin composition for 1- and 41-hr. reactions can be attributed mainly to the addition of acetic acid to 3-methylcyclohexene. These results demonstrate the changes in the product distribution which can occur in time under more drastic ring-opening conditions and lend additional support to the conclusion that the products obtained from norcarane treated with 0.07 *M* *p*-toluenesulfonic acid are those originating mainly from the ring-opening reaction.

Treatment of bicyclo[3.1.0]hexane (II) with 0.07 *M* *p*-toluenesulfonic acid in acetic acid for various reaction times gave mixtures of olefins and acetates whose compositions are given in Table I. Identification of each of the olefins was made by the comparison of the gas chromatographic retention times and infrared spectra of samples separated by gas chromatography with the reaction times and the spectra of authentic materials. The dependence of the ring opening on the presence of strong acid was shown when only bicyclo[3.1.0]hexane was recovered from a mixture of glacial acetic acid and bicyclo[3.1.0]hexane after 41 hr. at 48°. Gas chromatographic analysis for cyclohexene in a hydrocarbon mixture resulting from a 1-hr. reaction was not achieved since cyclohexene could not be determined in the presence of relatively large amounts of unconverted bicyclo[3.1.0]hexane. However, the composition ratio of 1-methylcyclopentene to 3-methylcyclopentene could be determined after 1 hr. and was found to be 3.5. This composition ratio is essentially the same as those (3.3) of 41- and 61-hr. reactions.

The conspicuous feature of the olefin composition is the change in the relative amount of cyclohexene from the 41-hr. reaction to the 61-hr. reaction. This result

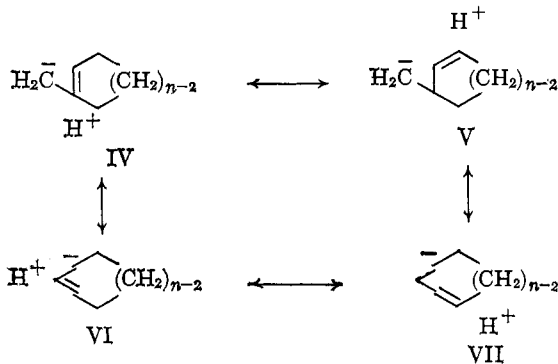
(9) R. T. LaLonde and M. A. Tobias, *J. Am. Chem. Soc.*, **85**, 3771 (1963).

can be attributed to the addition of acetic acid to cyclohexene which when subjected to ring-opening conditions was found to give slowly only cyclohexyl acetate. This explanation would seem to be strengthened by the apparent decrease (6%) in the total composition of olefin. However, the alcohol composition appears to be insensitive to reaction time. Quite likely the additional acetate resulting from cyclohexene is not large enough to be detected, within the limits of the analysis, as an increase in the amount of cyclohexanol. These experimental results indicate that a mixture of olefins resulting directly from bicyclo[3.1.0]hexane would contain all three olefins and would consist of, at the very least, 40% cyclohexene.

The alcohols obtained from bicyclo[3.1.0]hexane were identified by their gas chromatographic retention times. In addition, each of the two major components, *trans*-2-methylcyclopentanol and cyclohexanol, was identified by its infrared spectrum. It appears from the nearly constant composition of the four mixtures that the distribution of alcohols must represent products formed directly from bicyclo[3.1.0]hexane.

Cyclopentyl acetate was the only product afforded by the treatment of bicyclo[2.1.0]pentane with acetic acid, 0.07 *M* in *p*-toluenesulfonic acid. This result is in agreement with the direction of the ring opening of bicyclo[2.1.0]pentane as reported by other workers.<sup>10</sup> The addition of acetic acid to bicyclo[2.1.0]pentane also occurred in the absence of *p*-toluenesulfonic acid but, as expected, at a slower rate. Under the same conditions cyclopentene failed to add acetic acid.

**Discussion.**—The predominant formation of methylcycloalkane derivatives from both norcarane and bicyclo[3.1.0]hexane implied that the polarization of the three-membered ring by a perturbing electrophile is the prevailing influence in determining the mode of ring opening for these two cyclopropane derivatives. Representative structures which show the direction of polarization as determined by hyperconjugation are given below. Structures in which the negative charge is located on a secondary carbon atom (structures VI and VII) are the least important contributors to the



polarized state of norcarane and bicyclo[3.1.0]hexane on the well known grounds that a negative charge on secondary carbon is destabilized relative to a negative charge on primary carbon. Consequently, the proton-induced polarized state of norcarane and bicyclo[3.1.0]hexane is largely that represented by structures IV and V.

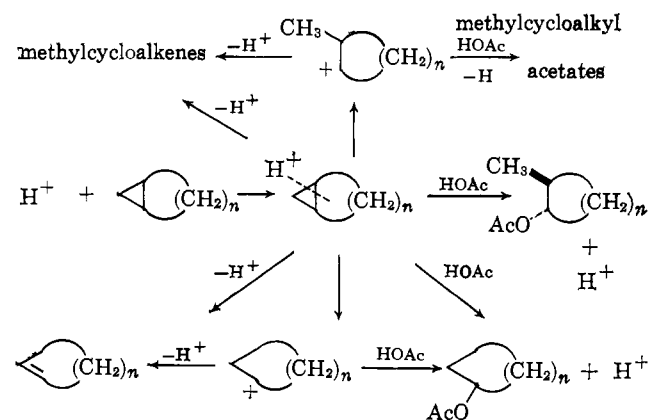
The mode of ring opening for bicyclo[2.1.0]pentane can be explained on the basis of the relief of strain. Since the molecule is highly strained, the transition

(10) See, for example, the conversion of bicyclo[2.1.0]pentane to: (a) cyclopentyl bromide on treatment with aqueous hydrogen bromide [R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957)]; (b) 1,3-diacetoxycyclopentane on treatment with lead tetraacetate [R. Criegee and A. Rimmelin, ref. 10a]; (c) 3-acetoxycyclopentyl mercuric acetate on treatment with mercuric acetate [R. Ya. Levina, V. N. Kostin, and T. K. Ustynyuk, *Zh. Obsch. Khim.*, **30**, 359 (1960)].

state for a concerted ring-opening process would closely resemble the ground state. Polarization of the ground state, and thus the transition state, in the direction of maximum relief of strain would lead to cyclopentane derivatives.

Assuming that all internal cleavage occurs by way of a concerted process, differences in ground-state geometry may also account for the greater amount of internal cleavage observed for bicyclo[3.1.0]hexane than for norcarane. Should internal cleavage in these two systems involve a transition state which does not resemble the ground state, the difference in the extent to which internal cleavage occurs might then be rationalized on the basis of developing nonbonded interactions in the transition state. The difference in the number of nonbonded interactions developing in the transition states leading to the formation of methylcyclopentane and cyclohexane derivatives would appear to be somewhat greater than the difference in the number of nonbonded interactions developing in the transition states leading to the formation of cycloheptanes and axially substituted cyclohexanes.<sup>9</sup> As a consequence the polarization effect would exert a smaller influence in determining the mode of ring opening for bicyclo[3.1.0]hexane than for norcarane.

The high degree of stereoselectivity in the addition of acetic acid to bicyclo[3.1.0]hexane and norcarane is evidenced by the preponderant formation of *trans*-2-methylcyclopentyl acetate and *trans*-2-methylcyclohexyl acetate. Although this result was expected in view of the stereochemical outcome observed in the rupture of epoxides,<sup>11</sup> experimental evidence of cyclopropanes reacting in an analogous manner had been lacking. The stereochemical result strongly implicates a mechanistic scheme involving an attack by nucleophilic solvent on a protonated (or protonating) cyclopropane moiety. Formation of small amounts of *cis*-2- and 1-methylcyclopentyl and *cis*-2- and 1-methylcyclohexyl acetates implies that a carbonium ion process may be operating to some small extent as well. The various modes of nucleophilic attack leading to products are outlined below.



The small but significant increase in the amount of cycloheptane derivative produced on increasing the mineral acid concentration might be attributed to the increased ion-solvating ability of the solvent and its favorable effect on carbonium ion formation. Consequently, in a better ion-solvating medium, the formation of cycloheptyl carbonium ion becomes more competitive with routes involving nucleophilic solvent attack.

(11) (a) S. Winstein and R. B. Henderson, *J. Am. Chem. Soc.*, **65**, 2196 (1943); (b) E. L. Eliel, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 130-133 (c) H. B. Henbest, M. Smith, and A. Thomas, *J. Chem. Soc.*, 3293 (1958).

### Experimental

**Reaction of Norcarane with Acetic Acid, 0.07 M in *p*-Toluenesulfonic Acid.**—A sealed glass tube containing 1.96 g. of norcarane and 25 ml. of 0.07 M *p*-toluenesulfonic acid in acetic acid was placed in a constant temperature bath at 47°. After 86 hr. the contents were subjected to work-up in the usual manner.<sup>1</sup> The material obtained (3.44 g.) was subjected immediately to gas chromatographic analysis using a 4-ft. diethylene glycol adipate on Celite column at 80.5°. The chromatogram showed the reaction mixture to consist of 53% olefin and 47% acetate. Gas chromatographic analysis of the product mixture on a 15% Silicon-550 on firebrick column showed the presence of 3-methylcyclohexene (71%), 1-methylcyclohexene (21%), and cycloheptene (8%). The formation of olefin by the elimination of acetic acid from *trans*-2-methylcyclohexyl acetate under conditions of chromatography was not found. Since the separation of 3- and 4-methylcyclohexene could not be achieved conveniently by gas chromatography, it was necessary to determine the absence of the latter olefin in the product mixture by infrared spectral analysis. Each of the three olefins were separated by gas chromatography and its infrared spectrum was found to be identical with the spectrum of authentic olefin purified by gas chromatography. The spectrum of the 3-methylcyclohexene contained no peaks in the regions (9.27, 9.60, 11.14, and 11.32  $\mu$ ) where 4-methylcyclohexene showed strong absorption bands.

Treatment of the crude product mixture with lithium aluminum hydride in ether gave 1.85 g. of an amber-colored oil which on vacuum distillation, b.p. 74–79° (21 mm.), gave 1.53 g. of a mixture of alcohols whose infrared spectrum showed no carbonyl band. The average percentage composition of three gas chromatographic analyses using a 17% glycerol on Celite column at 90° was: 1-methylcyclohexanol and *cis*-2-methylcyclohexanol, 10%; *trans*-2-methylcyclohexanol, 79%; *trans*-4- and/or *trans*-3-methylcyclohexanol, 2%; and cycloheptanol, 9%. Cycloheptanol was separated by gas chromatography and conclusively identified by its infrared spectrum.

In order to follow the change of product mixture with time, 0.07 M *p*-toluenesulfonic acid in glacial acetic acid was added to 3.63 g. of norcarane (37.8 mmoles) in a 50-ml. volumetric flask maintained at 20°. After mixing the contents of the flask, 10-ml. aliquots (7.6 mmoles of norcarane) were rapidly introduced into each of three glass tubes which were maintained at –40°. These tubes were sealed and immersed in a constant temperature bath at 47.5°. A fourth aliquot was withdrawn and immediately subjected to work-up in the usual manner. The ethereal solution of products, reduced in volume by distillation employing a 12-in. Vigreux column, was introduced to a 5-ml. volumetric flask along with an appropriate amount of isooctane used as an internal standard. The flask was made up to the mark with ether and its contents were analyzed by gas chromatography. Analysis of the zero-time aliquot showed the presence of 7.3 mmoles of norcarane. Similar treatment and analyses of the contents of the tubes withdrawn after 0.5, 1.0, and 24.0 hr. showed the presence of 4.8 (66% remaining), 3.8 (55% remaining), and 0.0 moles of norcarane, respectively. Analyses for olefins were made from the same chromatograms. Ratios of 1-methylcyclohexene to 3-methylcyclohexene along with the ratio obtained from the 86-hr. reaction are given in Table II. The crude product mixtures from 0.5-, 1.0-, and 24.0-hr. reactions were then treated with lithium aluminum hydride. The resulting mixture of alcohols was analyzed by gas chromatography in the usual manner. The percentage composition of the three mixtures are given in Table I.

TABLE II

RATIO OF 1-METHYLCYCLOHEXENE TO 3-METHYLCYCLOHEXENE PRODUCED FROM NORCARANE AT VARIOUS REACTION TIMES BY 0.07 M *p*-TOLUENESULFONIC ACID-HOAc AT 47.5°

Norcarane consumed, %	Reacn. time, hr.	1-Methylcyclohexene/3-methylcyclohexene
34	0.5	0.31
45	1.0	.32
100	24	.29
100	86	.30

**Reaction of 1- and 3-Methylcyclohexene with Acetic Acid, 0.07 M in *p*-Toluenesulfonic Acid.**—A sealed glass tube containing 91 mg. of 1-methylcyclohexene (0.95 mmole) and 10 ml. of 0.07 M *p*-toluenesulfonic acid (the solution was 0.095 M in substrate) was kept in a constant temperature bath maintained at 47.5° for 68 hr. The contents of the tube after treatment in the usual manner afforded a liquid whose gas chromatogram showed the presence of only 1-methylcyclohexene and residual ether. A sharp symmetrical band at 5.77  $\mu$  in the infrared spectrum indicated that some of the olefin had been converted to 1-methylcyclohexyl acetate.

A sealed glass tube containing 290 mg. of 3-methylcyclohexene (3.02 moles) and 10 ml. of 0.07 M *p*-toluenesulfonic acid in acetic acid (the solution was 0.302 M in substrate) was kept in a constant temperature bath maintained at 47.5° for 68 hr. The contents of the tube, dark in color, were subjected to work-up in the usual manner. Gas chromatographic analysis showed only the presence of 3-methylcyclohexene in addition to residual ether. A broad unsymmetrical band at 5.76  $\mu$  in the infrared spectrum indicated that some of the olefin had undergone addition of acetic acid.

**Reaction of Norcarane with Acetic Acid, 2 N in Sulfuric Acid.**—Norcarane (962 mg., 10.0 mmoles) was treated with 12 ml. of 2 N sulfuric acid in glacial acetic acid in a sealed glass tube for 1 hr. 46.5°. After work-up, the product mixture (1.41 g.) was subjected to gas chromatography. Analysis using a 4-ft. diethylene glycol adipate on Celite column at 82° and a 5% squalane on Celite column at 65° showed the mixture to contain 37% olefin and 63% acetate in addition to residual ether. Analysis using the 5% squalane on Celite column demonstrated the presence of 1-methylcyclohexene, 3-methylcyclohexene, and cycloheptene in 17, 71, and 12%, respectively. Unconverted norcarane was not detected. The crude product mixture was then treated with lithium aluminum hydride. Analysis of the resulting mixture of alcohols showed the presence of 1-methylcyclohexanol and *cis*-2-methylcyclohexanol (9%), *trans*-2-methylcyclohexanol (68%), *trans*-3- and/or *trans*-4-methylcyclohexanol (3%), and cycloheptanol (20%).

Treatment of 827 mg. of norcarane (8.6 mmoles) with 10 ml. of 2 N sulfuric acid in glacial acetic acid for 41 hr. at 48.0° gave a mixture of products which by gas chromatographic analysis was shown to consist of 3% olefin and 97% acetate in addition to residual ether. Components of the olefin fraction were 1-methylcyclohexene, 3-methylcyclohexene, and cycloheptene present in 15, 34, and 52% as shown by gas chromatography. Treatment of the crude product mixture with lithium aluminum hydride in the usual manner gave a mixture of alcohols which consisted of 1-methylcyclohexanol and *cis*-2-methylcyclohexanol (2%), *trans*-2-, *cis*-3-, or *cis*-4-methylcyclohexanol (66%), *trans*-3- or *trans*-4-methylcyclohexanol (13%), and cycloheptanol (20%).

**Reaction of Bicyclo[3.1.0]hexane with Acetic Acid, 0.07 M in *p*-Toluenesulfonic Acid.**—Bicyclo[3.1.0]hexane was prepared by the method of Simmons and Smith.<sup>12</sup> Treatment of 1.72 g. of bicyclo[3.1.0]hexane (21 mmoles) with 25 ml. of 0.07 M *p*-toluenesulfonic acid in glacial acetate and in a sealed glass tube at 48.0° for 41 hr. gave 2.93 g. of a mixture of acetates (78%) and olefins (22%). In the infrared spectrum, this mixture of cycloalkyl acetates and olefins showed the pertinent peaks at 5.77, 6.08, 6.90, 7.30, and 8.08  $\mu$ . Gas chromatographic analysis of the product mixture using an 11-ft. 4% squalane on Celite column at 61°, flow rate 30 ml./min., showed three peaks at 4.04 (14%), 5.91 (46%), and 7.62 min. (40%) in addition to residual ether. Retention times in the order given were identical with retention times of 3-methylcyclopentene, 1-methylcyclopentene, and cyclohexene. The bicyclo[3.1.0]hexane peak at 7.31 min. was absent. Isolation of each of the three olefins was effected by gas chromatography. The infrared spectrum of each was identical with the infrared spectrum of an authentic sample purified by gas chromatography.

Treatment of the crude product mixture (2.93 g.) with lithium aluminum hydride gave a mixture of alcohols (2.11 g.). Pertinent bands in the infrared spectrum were found at 2.79, 2.94, 6.11, 6.87, and 7.28  $\mu$ . Gas chromatographic analysis using an 11-ft. 17% glycerol on Celite column at 100°, flow rate 35.7 ml./min., showed four peaks, at 8.05 (3%), 9.27 (7%), 13.3 (68%), and 23.2 min. (22%); the retention times in the order given were identical with retention times of 1-methylcyclopentanol, *cis*-2-methylcyclopentanol, *trans*-2-methylcyclopentanol, and cyclohexanol. Cyclohexanol and *trans*-2-methylcyclopentanol were isolated from the mixture of alcohols by preparative scale gas chromatography. The infrared spectra of the two alcohols were identical with the spectra of authentic cyclohexanol and *trans*-2-methylcyclopentanol.

A sealed tube containing 4.11 g. of bicyclo[3.1.0]hexane (50 mmoles) and 50 ml. of acetic acid was kept in a constant temperature bath at 48° for 41 hr. Work-up in the usual manner furnished an oil which by gas chromatographic analysis on an 11-ft. 4% squalane on Celite column showed only the presence of bicyclo[3.1.0]hexane.

A sealed tube containing 1.72 g. of bicyclo[3.1.0]hexane (21 mmoles) and 25 ml. of 0.07 M *p*-toluenesulfonic acid in acetic acid was kept at 48° for 61 hr. Analyses of olefin, acetates, and alcohols were obtained by employing gas chromatography in the manner described above. The crude mixture (2.87 g.) contained 16% olefin and 84% acetate and some residual ether. The olefin fraction consisted of 1-methylcyclohexene (57%), 3-methylcyclohexene (17%), and cyclohexene (26%). The mixture of cycloalkanol (1.84 g.) obtained from lithium aluminum hydride treatment of crude product mixture consisted of 1-methylcyclo-

pentanol (3%), *cis*-2-methylcyclopentanol (7%), *trans*-2-methylcyclopentanol (68%), and cyclohexanol (22%).

A sealed tube containing 1.72 g. of bicyclo[3.1.0]hexane (21 mmoles) and 25 ml. of 0.07 *M* *p*-toluenesulfonic acid in acetic acid was kept at 48° for 1 hr. Analysis of the crude product mixture (1.56 g.) by gas chromatography showed the presence of 82% hydrocarbon and 18% acetate. The hydrocarbon fraction contained 80% bicyclo[3.1.0]hexane and cyclohexene, 16% 1-methylcyclopentene, and 4% 3-methylcyclopentene. The mixture of alcohols (0.76 g.) obtained from the lithium aluminum hydride treatment of the crude product mixture consisted of 2% 1-methylcyclopentanol, 6% *cis*-2-methylcyclopentanol, 68% *trans*-2-methylcyclopentanol, and 24% cyclohexanol.

A sealed tube containing 1.72 g. of bicyclo[3.1.0]hexane (21 mmoles) and 25 ml. of 0.07 *M* *p*-toluenesulfonic acid in acetic acid was kept at 48° for 0.5 hr. The mixture of alcohols obtained in the usual way from the crude product mixture consisted of 1% 1-methylcyclopentanol, 11% *cis*-2-methylcyclopentanol, 68% *trans*-2-methylcyclopentanol, and 20% cyclohexanol.

**Reaction of Cyclohexene with Acetic Acid, 0.07 *M* in *p*-Toluenesulfonic Acid.**—Treatment of 501 mg. of cyclohexene (6.1 mmoles) with 25 ml. of 0.07 *M* *p*-toluenesulfonic acid in acetic acid for 8 hr. in a sealed glass tube gave a product mixture consisting of cyclohexene and only a trace of cyclohexyl acetate. Similar treatment of 500 mg. of cyclohexene for 44.5 hr. gave a product mixture consisting of 78% unconverted cyclohexene and 22% acetate. Treatment of this mixture with lithium aluminum hydride gave only cyclohexanol in addition to olefin.

**Reaction of Bicyclo[2.1.0]pentane with Acetic Acid, 0.07 *M* in *p*-Toluenesulfonic Acid.**—Bicyclo[2.1.0]pentane was prepared according to the method of Criegee and Rimmelin.<sup>10a</sup> A sealed glass tube containing 2.00 g. of bicyclopentane (25 mmoles) and 40 ml. of 0.07 *M* *p*-toluenesulfonic acid in glacial acetic acid was placed in a constant temperature bath at 47°. After 24 hr. the contents of the tube were subjected to the work-up procedure. Gas chromatographic analysis of the product (2.28 g.) employing

a 5% squalene on Celite column showed only the presence of residual ether in the short retention time region of the chromatogram. Distillation of 2.0 g. of the crude ring-opening product gave 962 mg. of material, b.p. 85° at 87 mm., whose infrared spectrum was identical with the spectrum of cyclopentyl acetate. Treatment of 921 mg. of the acetate with lithium aluminum hydride gave 609 mg. of material, b.p. 82–85° at 90 mm., whose infrared spectrum was identical with the spectrum of cyclopentanol. The gas chromatogram, obtained by employing a 17% glycerol on Celite column, showed only a single peak whose retention time was identical with the retention time of cyclopentanol.

Bicyclo[2.1.0]pentane, 544 mg., was treated with glacial acetic acid in a sealed glass tube at 47°. After 24 hr. the contents of the tube were subjected to the work-up procedure. Distillation of the ether from the ethereal solution of products using a 20-in. spinning band column gave an oil which by gas chromatographic analysis at 30° was shown to contain residual ether, unconverted bicyclopentane, but no cyclopentene. An infrared spectrum showed the presence of acetate ester bands at 5.78 and 8.08  $\mu$  and the bands (7.88, 9.55, 9.76, 10.30-doublet, 10.97  $\mu$ ) characteristic of bicyclopentane.

Cyclopentene, 944 mg., was treated with glacial acetic acid in a glass tube at 47°. After 42 hr. the contents were subjected to the same work-up procedure as given immediately above. The material obtained was shown by gas chromatographic and infrared analyses to contain only residual ether and unconverted cyclopentene.

**Infrared Spectra.**—The infrared spectra of all the olefins were determined neat in microcavity cells using a Baird-Atomic infrared spectrophotometer. The spectra of the cycloalkenols were determined as solutions in carbon tetrachloride.

**Acknowledgment.**—The authors gratefully acknowledge the support of this research by the Research Corporation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE 10, N. Y.]

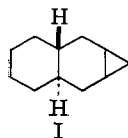
## Carbon-Carbon Bond Fission in Cyclopropanes. II. The Acid-Promoted Opening of the Three-Membered Ring in 2,3-Methano-*trans*-decalin<sup>1</sup>

BY ROBERT T. LALONDE AND MICHAEL A. TOBIAS<sup>2</sup>

RECEIVED JUNE 13, 1963

2,3-Methano-*trans*-decalin was synthesized and subjected to treatment with sulfuric acid in glacial acetic acid in order to determine the steric course of carbon-carbon bond fission in a cyclopropane ring fused to a rigid ring system. The predominant acetate was found to be 2(a)-acetoxy-3(a)-methyl-*trans*-decalin, while the olefin fraction consisted of the isomeric 3-methyl-*trans*- $\Delta^1$ -octalins, 2-methyl-*trans*- $\Delta^1$ -octalin, and 2-methyl-*trans*- $\Delta^2$ -octalin. The results are interpreted in terms of solvent attack on carbon or hydrogen.

The stereoselectivity in the formation of 2-methylcycloalkyl acetates by the acid-promoted addition of acetic acid to norcarane and bicyclo[3.1.0]hexane has been demonstrated.<sup>1</sup> The work reported herein is concerned with the acid-promoted opening of the three-membered ring in 2,3-methano-*trans*-decalin (I), a compound bearing a cyclopropane ring fused to a conformationally rigid ring system. Our primary purpose in



undertaking this work was to obtain additional information pertaining to the steric disposition of the fission of carbon-carbon bonds in cyclopropanes.

2,3-Methano-*trans*-decalin was prepared directly in 34% yield by the action of methylene iodide on *trans*- $\Delta^2$ -octalin according to the method of Simmons and Smith.<sup>3</sup> The preparation of I was also realized in 27% over-all yield by the two-step process involving the

treatment of *trans*- $\Delta^2$ -octalin with bromoform and potassium *t*-butoxide and subsequent hydrogenolysis of the resulting 2,3-(dibromomethano)-*trans*-decalin with sodium in methanol. The infrared spectrum of I showed bands characteristic of cyclopropane derivatives<sup>4</sup> and the n.m.r. spectrum displayed cyclopropyl proton resonance characteristics similar to those observed in the n.m.r. spectrum of norcarane.

The treatment of I with 0.09 *N* sulfuric acid in glacial acetic acid at 47° gave a product mixture containing acetates, alcohols, and olefins which were present in 40, 2, and 58%, respectively, of the total product mixture as shown by gas chromatography.

Product analysis of the acetates was not carried out directly; the acetates were converted by lithium aluminum hydride hydrogenolyses to a mixture of alcohols whose gas chromatograms indicated the presence of eight alcohols. The major alcohol was present in 59% as shown by gas chromatographic analysis and was the only pure alcohol which could be isolated by elution chromatography. This alcohol was found to be 3(a)-methyl-*trans*-2(a)-decalol<sup>5</sup> (II, R = H). A second al-

(1) Previous paper in this series: R. T. LaLonde and L. S. Forney, *J. Am. Chem. Soc.*, **85**, 3767 (1963).

(2) National Science Foundation Cooperative Fellow, 1963–1964.

(3) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

(4) A. D. Cross, "Introduction to Practical Infrared Spectroscopy," Butterworths Publications Ltd., London, 1960, p. 57.

(5) The nomenclature employed here is: (a) for axial and (e) for equatorial substituents. This system of nomenclature has been used previously