infrared absorption spectra compared to standard mixtures of VIII and IX. The values obtained by this method were always within 8% of the values obtained by use of the vapor-phase chromatograph. The vapor-phase procedure also was calibrated with several synthetic mixtures of VIII and IX. Values obtained for these synthetic mixtures were always within 4% of the calculated value and usually within 2%.

Acknowledgment.—The authors are indebted for discussions during the course of this work to C. H. De Puy, who has carried out a somewhat related study.

(20) C. H. De Puy, *et al.*, *J. Org. Chem.*, in press.

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Pyrolysis of Esters. XVI. Effect of Ring Size on Formation of Alicyclic Olefins[1]

BY WILLIAM J. BAILEY AND WARREN F. HALE[2]

RECEIVED MAY 15, 1958

Pyrolysis of 1-methylcyclopentyl acetate at 450° produced a mixture of olefins containing 84% of 1-methylcyclopentene and 16% of methylenecyclopentane. Similarly, pyrolysis of 1-methylcycloheptyl acetate at 440° gave a mixture containing 76% of 1-methylcycloheptene and 24% of methylenecycloheptane. Pyrolysis of N-(1-methylcyclohexyl)-acetamide at 570° produced a mixture containing 72% of 1-methylcyclohexene and 28% of methylenecyclohexane. In contrast to the pyrolysis of the corresponding amine oxides, the pyrolysis of esters shows no large effect of ring size on the compositions of the pyrolysates.

In a previous paper[1] it was shown that under usual operating conditions the pyrolysis of 1-methylcyclohexyl acetate gave a mixture of olefins containing 76% of the *endo* isomer, 1-methylcyclohexene, in contrast to work previously reported. In order to determine whether this formation of the *endo* isomer under ordinary pyrolysis conditions was general, the effect of ring size on the direction of elimination of the tertiary esters was investigated. Cope, Bumgardner and Schweizer had carried out a similar study with the corresponding amine oxides, which are thought to decompose by a mechanism similar to that proposed for ester pyrolysis.[3] Their results showed that the five-, six- and seven-membered tertiary cycloalkylamine oxides gave 95.5, 2.8 and 84.8% of the corresponding endocyclic isomers, respectively. The large effect of the size of the ring was quite remarkable. Traynham and Pascual[4,5] have reported that the pyrolyses of 1-methylcyclopentyl and 1-methylcycloheptyl acetates (II and VII) (under the same conditions that 1-methylcyclohexyl acetate was reported to give only methylenecylcohexane) gave only the exocyclic isomers. They did not report any direct evidence to indicate the purity of their product, but the chemical reactions performed on the olefins left little doubt that at least the major component was the *exo* isomer. Thus the photochemical addition of hydrogen bromide to the products of the pyrolyses gave a 60% yield of cyclopentylmethyl bromide and a 61% yield of cycloheptylmethyl bromide, respectively. Similarly, the addition of hypochlorous acid to the pyrolysis product in the five-membered series gave a 58% yield of the 1-chloromethylcyclopentanol and to that from the seven-membered series a 64% yield of 1-chloromethylcycloheptanol. However, since we were not able to duplicate either their results or our previous results in the cyclohexyl series, it was of interest to reinvestigate these reactions.

For our studies 1-methylcyclopentyl acetate (II) was prepared by two different routes. This ester was prepared by the esterification of 1-methylcyclopentanol (I) with pyridine and acetyl chloride as well as with acetic anhydride and magnesium. Pyrolysis of either sample of the tertiary ester II at 450° gave a 63% yield of a mixture of olefins, which was shown by vapor-phase chromatography and infrared analysis to consist of 84% of 1-methylcyclopentene (III) and 16% of methylenecyclopentane (IV). As reference compounds, authentic samples of these two isomeric olefins were prepared independently. Methylenecyclopentane (IV) was prepared in a five-step synthesis starting from 1,1-dicarbethoxycyclopentane in an over-all yield of 34%. Hydrolysis of the diester gave a 96% yield of the corresponding dicarboxylic acid, which was decarboxylated to cyclopentanecarboxylic acid. Reduction with lithium aluminum hydride gave a 76% yield of the corresponding primary alcohol which was, in turn, esterified with acetic anhydride to give cyclopentylmethyl acetate (V) in a 91% yield. Pyrolysis of the primary acetate V at 540° gave a 54% yield of nearly pure methylenecyclopentane (IV), which was identified by infrared analysis and shown by vapor-phase chromatography to contain 2.6% of 1-methylcyclopentene (III). Although Lutz, *et al.*,[6] reported that the dehydration of 1-methylcyclopentanol (I) with iodine gave pure 1-methylcyclopentene (III), from this dehydration we produced a mixture containing approximately 90% of the *endo* isomer III plus 10% of methylenecyclopentane (IV). When this mixture was equilibrated in a hot mixture containing *p*-toluenesulfonic acid and glacial acetic acid, essentially pure 1-methylcyclopentene (III) was obtained.[7] The purity was

(1) Previous paper in this series, THIS JOURNAL, **81**, 647 (1959).

(2) Office of Naval Research Fellow, 1955–1956; Union Carbide Fellow, 1956–1957.

(3) A. C. Cope, C. L. Bumgardner and E. E. Schweizer, THIS JOURNAL, **79**, 4729 (1957).

(4) J. G. Traynham and O. S. Pascual, *J. Org. Chem.*, **21**, 1362 (1956).

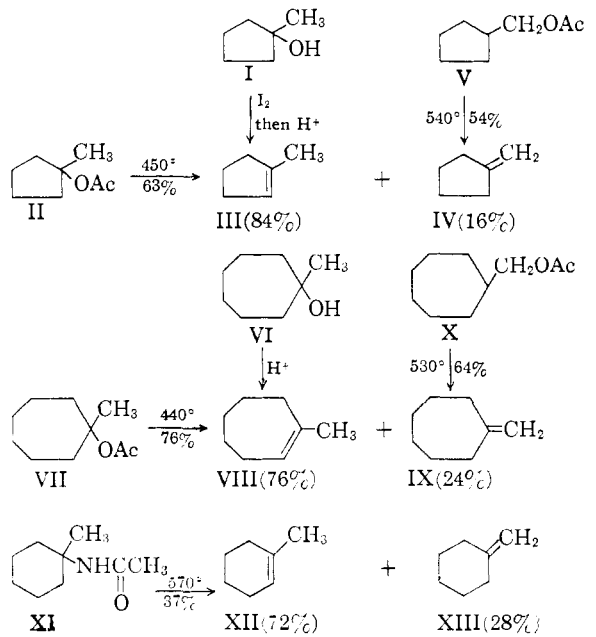
(5) J. G. Traynham and O. S. Pascual, Abstracts of Papers, 131st Meeting of the American Chemical Society, Miami, Fla., April, 1957, p. 45-O.

(6) G. A. Lutz, A. E. Bearse, J. E. Leonard and F. C. Croxton, THIS JOURNAL, **70**, 4139 (1948).

(7) R. B. Turner and R. H. Garner, *ibid.*, **79**, 253 (1957).

confirmed by means of infrared absorption and vapor-phase chromatography.

Similar results were obtained from the pyrolysis of 1-methylcycloheptyl acetate (VII). This tertiary ester VII was prepared from cycloheptanone in an over-all yield of 68% by treatment with methylmagnesium iodide, followed by esterification of the intermediate tertiary alcohol with acetyl chloride and pyridine. Pyrolysis of this tertiary acetate VII at 440° gave a 76% yield of a mixture of olefins. Vapor-phase analysis indicated that the product was composed of 76% of 1-methylcycloheptene (VIII) and 24% of methylenecycloheptane (IX). For reference compounds, authentic samples of both of these olefins were synthesized independently. Thus methylenecycloheptane (IX) was prepared in seven steps from cycloheptanone in an over-all yield of 24%. Lithium aluminum hydride reduction of the ketone gave a 93% yield of cycloheptanol, which was converted to the corresponding bromide with hydrogen bromide in an 83% yield. Carbonation of the resulting Grignard reagent produced a 75% yield of cycloheptanecarboxylic acid, which in turn was reduced with lithium aluminum hydride to the cycloheptylcarbinol in an 88% yield. Treatment of this alcohol with acetic anhydride gave a 76% yield of the corresponding acetate X. Finally, pyrolysis of this primary acetate X at 530° gave a 64% yield of methylenecycloheptane (IX). Vapor-phase chromatography indicated that the pyrolysis product contained 1.7% of the isomeric 1-methylcycloheptene (VIII). Dehydration of 1-methylcycloheptanol (VI) by distillation at 100 mm. of pressure produced a mixture of the two possible isomeric olefins. When this mixture was treated with a hot solution containing *p*-toluenesulfonic acid and glacial acetic acid, a product consisting of 98% of 1-methylcycloheptene (VIII) was obtained. It thus appears that even in the seven-membered series the *endo* olefin is much more stable than the *exo* isomer.



Thus it appears that under usual operating conditions both the five- and seven-membered tertiary esters give the highest proportion of the *endo* isomers, in contrast to the work of Traynham and Pascual. If the evidence is accepted that, under ordinary pyrolysis conditions, 1-methylcyclohexyl acetate gives mostly the *endo* isomer, then (in view of the results obtained with the amine oxides[3]) it would have been indeed surprising if the five- and seven-membered series had yielded the *exo* isomer under the same conditions. One may conclude that there may be conditions for the pyrolysis of tertiary esters that will give mainly the *exo* isomers, but these conditions are not easy to reproduce or define and are not the ordinary conditions used for ester pyrolysis.

In order to study the pyrolysis of a compound more closely related to the amine oxides, a tertiary cycloalkyl amide was prepared and pyrolyzed. It was thought that such an amide would be much less prone to undergo an ionic elimination than a tertiary ester. Simple aliphatic amides have been shown to pyrolyze in a manner very similar to esters.[8] For this reason, N-(1-methylcyclohexyl)-acetamide (XI) was prepared in a 92% yield from 1-methylcyclohexanol and acetonitrile by treatment with sulfuric acid, according to the method of Ritter.[9] Pyrolysis of this amide at 570° produced a 37% yield of a mixture of olefins and a 37% yield of acetamide. Vapor-phase chromatography showed that less than 2.5% of acetonitrile was produced in the pyrolysis. Since a 34% recovery of the starting amide was realized, the yield of olefins and acetamide, based on unrecovered material, was 56%. The vapor-phase analysis indicated that the olefin mixture contained 72% of 1-methylcyclohexene (XII) and 28% of methylenecyclohexane (XIII). The close parallel between this result and the composition of the pyrolysate from 1-methylcyclohexyl acetate indicates that the mechanisms and steric requirements of the two reactions are probably very similar. It is also obvious that there is no close parallel with the steric requirements of the amine oxides.

Experimental[10]

1-Methylcyclopentanol (I).—To an ether solution of methylmagnesium iodide [prepared from 73 g. (3.0 moles) of magnesium and 427 g. (3.0 moles) of methyl iodide] was added 168 g. (2.0 moles) of cyclopentanone, b.p. 126–128°. After the reaction mixture had been stirred overnight and cooled in ice, 450 ml. of a saturated ammonium chloride solution was added slowly to decompose the complex. When the salts had coagulated, the ether solution was decanted and concentrated by evaporation to about 800 ml. After this concentrate had been dried over a mixture of anhydrous magnesium sulfate and sodium carbonate, the residual ether was removed by distillation through a 12-inch Vigreux column at atmospheric pressure and the residue was fractionated through the same column to yield 125.7 g. (62.8%)

(8) W. J. Bailey and C. N. Bird, *J. Org. Chem.*, **23**, 996 (1958).

(9) J. J. Ritter and F. X. Murphy, THIS JOURNAL, **74**, 763 (1952).

(10) The authors are indebted to Dr. Mary Aldridge, Kathryn Gerdeman and Jane Swan for the microanalyses. They are further indebted to Dr. E. R. Lippincott, Dr. R. A. Schroeder, Dr. A. Leifer, C. E. White, J. E. Katon and F. E. Welsh for the infrared spectra and aid in their interpretation. The infrared spectra were determined on carbon disulfide solutions in a Beckman IR4 infrared spectrophotometer. All melting points are corrected.

of 1-methylcyclopentanol (I), b.p. 43° (9 mm.), m.p. 36–37° [reported b.p. 82° (100 mm.),[11] m.p. 36°[12])].

1-Methylcyclopentyl Acetate (II). A. Acetic Anhydride–Magnesium Method.—To a mixture of 44.5 g. (0.44 mole) of 1-methylcyclopentanol (I) and 14.0 g. (0.575 mole) of powdered magnesium, heated under reflux with stirring, was added dropwise 90.0 g. (0.88 mole) of acetic anhydride. The heating was continued for 1 hour after the addition of the anhydride was complete. After the solution had been cooled, a saturated sodium carbonate solution was added until no further evolution of carbon dioxide occurred. The organic phase was separated and dried over anhydrous sodium sulfate. Fractional distillation of the dried solution through a 6-inch, helix-packed column produced 20.9 g. (33%) of 1-methylcyclopentyl acetate (II), b.p. 60–61° (25 mm.), $n^{25}D$ 1.4282 (reported[5] b.p. 155–156°, $n^{20}D$ 1.4320).

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.91. Found: C, 67.73; H, 9.61.

B. Acetyl Chloride–Pyridine Method.—The procedure was similar to that reported by Traynham and Pascual.[5] To a 1-liter flask containing a cold mixture of 100 g. (1.0 mole) of 1-methylcyclopentanol (I) and 83.0 g. (1.05 moles) of pyridine was added dropwise 82.4 g. (1.05 moles) of acetyl chloride. Following the addition, the mixture was allowed to come to room temperature and was then heated at 60° for 4 hours. To the cooled reaction slurry, convenient quantities of water and *n*-pentane were added; the pentane layer was separated and washed consecutively with water, with a dilute sodium carbonate solution, and again with water. After the pentane layer was dried over anhydrous sodium carbonate and anhydrous magnesium sulfate, the solution was fractionally distilled through a 6-inch, helix-packed column to yield 95.1 g. (67%) of 1-methylcyclopentyl acetate (II), b.p. 58–58.2° (23 mm.), $n^{25}D$ 1.4281.

Pyrolysis of 1-Methylcyclopentyl Acetate (II).—By use of the same type pyrolysis apparatus described previously,[1] 48.8 g. (0.343 mole) of 1-methylcyclopentyl acetate was pyrolyzed at 450° at the rate of 0.5 g. per minute. The pyrolysate was washed with water until the organic and water layers were neutral to wet litmus. After the organic phase was dried over anhydrous sodium carbonate and anhydrous magnesium sulfate, it was distilled through a 6-inch, helix-packed column to yield 17.75 g. (63.0%) of a mixture of olefins, b.p. 59.5–59.6° (462 mm.), $n^{25}D$ 1.4287. (Titration of an aliquot of the aqueous washings with standard sodium hydroxide solution indicated that 94.5% of the theoretical amount of acetic acid had been liberated.)

None of the standard chromatographic columns available for use with the Perkin–Elmer vapor fractometer resolved the mixture of 1-methylcyclopentene (III) and methylenecyclopentane (IV). However, the use of a column containing silver nitrate in diethylene glycol absorbed on Johns–Manville Chromosorb (10–30 mesh, acid-washed) in a special vapor-phase chromatograph constructed according to the directions of W. R. Moore and A. C. Cope[13] led to good resolution. At a temperature of 52° and a helium flow of two bubbles per second the retention time of 1-methylcyclopentene (III) was 13 minutes and the isomeric methylenecyclopentane (IV) was 25 minutes. The peaks were identified by comparison of their retention times with those of authentic samples. The composition of the olefin mixture was calculated to be 84% of III and 16% of IV.

Confirmation of this calculation of the composition was obtained from infrared studies. A series of known mixtures of the two olefins III and IV were prepared and their spectra were determined. A graphical interpolation of the spectrum of the mixture gave results in good agreement with the vapor-phase results. Several of the peaks gave values that were very close and the maximum deviation was 10%.

Cyclopentylcarbinol.—By use of the procedure of Haworth and Perkin[14] 1,1-dicarbethoxycyclopentane was hydrolyzed with methanolic potassium hydroxide to give a 96% yield of cyclopentane-1,1-dicarboxylic acid. Decarboxylation of 77.0 g. (0.49 mole) of this diacid produced 52.7 g. (95%) of cyclopentanecarboxylic acid, b.p. 110–115° (20 mm.), $n^{25}D$ 1.4496 (reported[14] b.p. 214–215°, $n^{17.7}D$ 1.4528).

To 25.0 g. (0.63 mole) of lithium aluminum hydride in 150 ml. of dry ether was added dropwise 66.0 g. (0.58 mole) of cyclopentanecarboxylic acid at a rate sufficient to maintain reflux. After the addition of the acid was complete, the reaction mixture was stirred and heated under reflux overnight. After the cooled mixture was decomposed with 800 ml. of 5% hydrochloric acid, the ether layer was separated and the water slurry was washed well with ether. The combined etherates were washed with a saturated sodium carbonate solution, then with water. After the solution was dried over magnesium sulfate, the ether was removed by distillation at atmospheric pressure. The residue was distilled through a Claisen head to yield 43.5 g. (76%) of cyclopentylcarbinol, b.p. 70.5–71.5° (22 mm.), $n^{25}D$ 1.4545 (reported[15] b.p. 160–162°, $n^{20}D$ 1.4554).

Cyclopentylcarbinyl Acetate (V).—To 43.5 g. (0.44 mole) of cyclopentylcarbinol maintained under reflux in a 200-ml. flask was added dropwise 49.3 g. (0.485 mole) of acetic anhydride. After the addition of the anhydride was complete, reflux was continued for an additional 4 hours. The mixture was then cooled and washed consecutively with water, a saturated sodium carbonate solution and again with water. After the organic layer was dried over magnesium sulfate, it was fractionally distilled through a 6-inch, helix-packed column to yield 56.4 g. (91%) of cyclopentylcarbinyl acetate (V), b.p. 70.7–70.8° (14 mm.), $n^{25}D$ 1.4327 [reported[16] b.p. 85–86° (40 mm.), $n^{20}D$ 1.4378].

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.70; H, 9.82.

Methylenecyclopentane (IV).—At the rate of 0.5 g. per minute, 42.7 g. (0.30 mole) of cyclopentylcarbinyl acetate (V) was pyrolyzed at 540° with the apparatus described. No charring was observed on the helix packing of the pyrolysis tube after the reaction. The water-white pyrolysate was washed with water until it was completely neutral to litmus. (Titration of an aliquot of the aqueous washings with a standard sodium hydroxide solution showed that 63% of the theoretical amount of acetic acid had been liberated.) After the organic phase was dried over a mixture of magnesium sulfate and sodium carbonate, the mixture was fractionally distilled through a 6-inch, helix-packed column to yield 10.8 g. (44%) of methylenecyclopentane (IV), b.p. 58.0–58.5° (450 mm.), $n^{25}D$ 1.4323 [reported[16] b.p. 73–73.2° (750 mm.), $n^{20}D$ 1.4342], and 8.2 g. (19% recovery) of cyclopentylcarbinyl acetate (V). The yield of olefin, based on unrecovered starting material, was 54%.

1-Methylcyclopentene (III).—Dehydration of 1-methylcyclopentanol (I) was carried out according to the procedure of Lutz, *et al.*[6] In a 100-ml. flask fitted with a Claisen distilling head and a condenser were placed 24.1 g. (0.24 mole) of 1-methylcyclopentanol and 0.1 g. of iodine. The flask was heated at 120° and the olefin–water distillate was collected in a receiver cooled in ice. The crude olefin, 16.0 g. (81%), was separated and dried over sodium sulfate. Fractionation of the crude product through a 12-inch, helix-packed column yielded slightly impure 1-methylcyclopentene (III), b.p. 74.0–74.2° (754 mm.), $n^{25}D$ 1.4281 (reported[6] b.p. 75°, $n^{20}D$ 1.4325). An examination of the infrared spectrum of a sample of this material indicated that it was contaminated with at least 10% of methylenecyclopentane (IV).

The equilibration of the above olefin mixture was carried out by use of the procedure of Turner and Garner.[7] For 17 hours, 11.6 g. (0.14 mole) of 1-methylcyclopentene (contaminated with methylenecyclopentane), 15 ml. of glacial acetic acid and 0.3 g. of *p*-toluenesulfonic acid were heated under reflux. The mixture was then cooled and poured into 100 ml. of cold water. After the organic phase had been washed with ten 50-ml. portions of water, it was dried over a mixture of anhydrous sodium carbonate and magnesium sulfate. The dried solution was distilled through an 8-inch Vigreux column to yield 4.6 g. (40%) of essentially pure 1-methylcyclopentene (III), b.p. 73–74° (764 mm.), $n^{25}D$ 1.4280. Examination of the infrared spectrum of this olefin showed it to be nearly pure III. A vapor-phase chromato-

(11) N. Zelinsky and S. Namjetkin, *Ber.*, **35**, 2683 (1902).

(12) C. R. McLellan and W. R. Edwards, Jr., THIS JOURNAL, **66**, 409 (1944).

(13) The authors are indebted to Dr. W. R. Moore and Dr. A. C. Cope, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass., for their help in constructing this versatile high temperature vapor-phase chromatograph.

(14) E. Haworth and W. H. Perkin, *J. Chem. Soc.*, **65**, 86 (1894).

(15) E. E. Royals and A. H. Neal, *J. Org. Chem.*, **21**, 1454 (1956).

(16) R. Y. Levina, N. N. Mezentsova and P. A. Akishin, *Zhur. Obschei. Khim.*, **23**, 562 (1953) [*C. A.*, **48**, 6970 (1954)].

graph also indicated that no methylenecyclopentane (IV) was present in this sample of III.

1-Methylcycloheptanol (VI).—In a 2-liter, three-necked flask, equipped with a condenser, a dropping funnel and a mechanical stirrer, were placed 16.3 g. (0.670 mole) of magnesium powder and 250 ml. of dry ether. At a rate sufficient to maintain reflux, 94.8 g. (0.668 mole) of methyl iodide in 250 ml. of dry ether was added dropwise. After all the methyl iodide solution had been added, the mixture was heated under reflux for 30 minutes and then cooled in ice. To the cooled mixture, 50.0 g. (0.446 mole) of freshly distilled cycloheptanone (Aldrich Chemical Co.) in 250 ml. of dry ether was added over a 90-minute period. The mixture was then stirred for an additional 12 hours while it was immersed in an ice–water-bath. With continued cooling of the mixture, 85 ml. of cold, saturated ammonium chloride solution was added to decompose the Grignard complex. The ether layer was decanted and concentrated by evaporation on the steam-bath to about 400 ml., and the concentrate was dried over a mixture of anhydrous sodium carbonate and magnesium sulfate. After the remaining ether had been removed through a 12-inch Vigreux column, the residue was fractionally distilled through the same column to yield 44.9 g. (79%) of 1-methylcycloheptanol (VI), b.p. 45.0–45.2° (2.0–2.1 mm.), $n^{25}D$ 1.4693 [reported[17] b.p. 82–83.5° (20 mm.), $n^{20}D$ 1.4690].

Anal. Calcd. for $C_8H_{16}O$: C, 75.11; H, 12.58. Found: C, 75.35; H, 12.65.

1-Methylcycloheptyl Acetate (VII).—The method described by Traynham and Pascual[4] using acetyl chloride and pyridine was employed to convert 1-methylcycloheptanol (VI) to the corresponding acetate VII. Fractional distillation through a 12-inch, helix-packed column gave an 86% yield of 1-methylcycloheptyl acetate (VII), b.p. 99.5–100.5° (30 mm.), $n^{25}D$ 1.4479 [reported[4] b.p. 110–111° (40 mm.), $n^{20}D$ 1.4528].

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.84; H, 10.73.

Pyrolysis of 1-Methylcycloheptyl Acetate (VII).—The apparatus described was used to pyrolyze 46.3 g. (0.27 mole) of 1-methylcycloheptyl acetate (VII). With the Vycor tube heated at 440°, the acetate was added dropwise at the rate of 0.5 g. per minute. The water-white pyrolysate was washed and dried in the usual manner. Examination of the pyrolysis tube indicated that no charring had occurred during the pyrolysis. (Titration of an aliquot of the water washings indicated that 97% of the theoretical amount of acetic acid had been liberated.) After the crude olefin had been dried, it was distilled through a 6-inch, helix-packed column to yield 22.2 g. (76%) of a mixture of olefins, b.p. 135–135.4° (766 mm.), $n^{25}D$ 1.4560. A gas chromatogram in a column containing silver nitrate and diethylene glycol absorbed on Chromosorb, as described above, indicated that this mixture was composed of 76% of 1-methylcycloheptene (VIII) and 24% of methylenecycloheptane (IX). With the temperature of the column at 99° and the helium flow at 1.5 bubbles per second the *endo* isomer VIII was eluted in 9 minutes and the *exo* isomer IX in 13 minutes.

Cycloheptanecarboxylic Acid was prepared by a modification of the method of Royals and Neal.[15] Reduction of 100 g. (0.89 mole) of cycloheptanone with an excess of lithium aluminum hydride gave, after fractional distillation through a 12-inch Vigreux column, 94.2 g. (93%) of cycloheptanol, b.p. 70–73° (5–7 mm.), $n^{25}D$ 1.4740 [reported[15] b.p. 79.5–80.5° (9–11 mm.), $n^{20}D$ 1.4760]. Addition of 93.7 g. (0.82 mole) of cycloheptanol to a large excess of 48% hydrobromic acid in concentrated sulfuric acid was carried out according to the procedure of Grummitt.[18] Distillation of the crude product through a 12-inch Vigreux column yielded 120.5 g. (83%) of cycloheptyl bromide, b.p. 65–66° (6–8 mm.), $n^{25}D$ 1.5014 [reported[15] b.p. 79–80° (12 mm.), $n^{24}D$ 1.5025].

In a 1-liter, three-necked flask were placed 17.0 g. (0.70 mole) of magnesium powder and 100 ml. of dry ether. Dropwise addition of 120.5 g. (0.68 mole) of cycloheptyl bromide in 400 ml. of dry ether was carried out at a rate sufficient to maintain steady reflux. After the bromide had been added, the mixture was heated under reflux for 2 hours and then stirred at room temperature overnight. With the flask cooled in an ice–salt-bath, carbon dioxide, which had previously been passed through a calcium chloride drying tube and a concentrated sulfuric acid trap, was led into the reaction flask through an inlet tube placed about 50 mm. above the vigorously stirred solution. Addition of the carbon dioxide was continued for 30 minutes after the reaction temperature had dropped from −5 to −12°. After the complex had been hydrolyzed by the dropwise addition of 300 ml. of 6 *N* hydrochloric acid, the ether layer was separated and the aqueous slurry was washed with three portions of ether. The combined etherates were washed with three portions of water, and the combined aqueous extracts were saturated with sodium chloride. The saturated solution was washed with three portions of ether, which were then washed with saturated sodium chloride solution. The ether layers were combined, dried over sodium sulfate and fractionated through a 12-inch Vigreux column to yield 72.4 g. (75%) of cycloheptanecarboxylic acid, b.p. 93–95° (0.8–0.9 mm.), $n^{25}D$ 1.4708 [reported[15] b.p. 133–135° (9 mm.), $n^{25}D$ 1.4730].

Cycloheptylcarbinol.—To a stirred slurry of 24.0 g. (0.63 mole) of lithium aluminum hydride in 150 ml. of dry ether, 72.4 g. (0.51 mole) of cycloheptanecarboxylic acid in 150 ml. of dry ether was added at a rate sufficient to maintain reflux. After the mixture was stirred and heated under reflux overnight, it was decomposed with 800 ml. of 5% hydrochloric acid. The ether layer was separated, the water slurry was washed well with ether and the combined etherates were washed with a saturated sodium carbonate solution and then with water. After the ether layer had been dried over magnesium sulfate, the ether was removed at atmsopheric pressure. The residue was distilled through a 12-inch Vigreux column to yield 57.5 g. (88%) of cycloheptylcarbinol, b.p. 73–75° (2.5–3 0 mm.), $n^{25}D$ 1.4730 (reported[15] 79–82° (4 mm.), $n^{28}D$ 1.4748).

Cycloheptylcarbinyl Acetate (X).—In a 200-ml., three-necked flask equipped with a condenser and a dropping funnel was placed 57.5 g. (0.45 mole) of cycloheptylcarbinol. With the alcohol heated under reflux, 49.3 g. (0.48 mole) of acetic anhydride was added dropwise over a 45-minute period. After the addition of the anhydride was complete, the mixture was heated under reflux for 4 hours. The cooled mixture was then washed consecutively with water, a saturated sodium carbonate solution and again with water. The crude ester was dried over magnesium sulfate and fractionated through a 12-inch Vigreux column to yield 58.0 g. (76%) of cycloheptylcarbinyl acetate (X), b.p. 77° (3.5 mm.), $n^{25}D$ 1.4517.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.56; H, 10.66. Found: C, 70.85; H, 10.94.

Methylenecycloheptane (IX).—Dropwise addition of 40.7 g. (0.24 mole) of cycloheptylcarbinyl acetate (X) to the Vycor tube, as described above, was carried out at a temperature of 530° and a drop rate of 0.5 g. per minute. No charring on the helix packing was observed and the pyrolysate was water-white. After the pyrolysate had been washed with water until it was neutral to litmus, the organic layer was diluted with ether. The ether solution was washed first with a saturated sodium bicarbonate solution and then with a saturated sodium chloride solution. (Titration of an aliquot of the water washings indicated that 69% of the theoretical amount of acetic acid had been liberated.) The ether layer, dried over a mixture of anhydrous sodium carbonate and magnesium sulfate, was distilled through a 6-inch, helix-packed column to yield 14.0 g. (53%) of methylenecycloheptane (IX), b.p. 134.5–134.8° (758 mm.), $n^{24}D$ 1.4600 (reported[4] b.p. 138–140°, $n^{20}D$ 1.4611), and 7.0 g. (17% recovery) of cycloheptylcarbinyl acetate (X). The yield of olefin, based on the amount of unrecovered acetate, was 64%. A gas chromatograph indicated that this olefin was contaminated with 1.7% of 1-methylcycloheptene (VIII).

1-Methylcycloheptene (VIII).—A mixture of 1-methylcycloheptene and methylenecycloheptane was prepared by the thermal dehydration of 1-methylcycloheptanol by distillation at 100 mm. pressure. The infrared spectrum of this olefin mixture indicated the presence of a considerable amount of methylenecycloheptane. In a 50-ml. flask were placed 11.4 g. (0.10 mole) of this olefin mixture, 15 ml. of glacial acetic acid and 0.1 g. of *p*-toluenesulfonic acid. After this mixture was heated under reflux for 16 hours, 100 ml. of cold water was added to the cooled mixture. The organic layer was separated and washed with ten portions of cold water and dried over sodium carbonate and magnesium

(17) H. C. Brown and M. Borkowski, THIS JOURNAL, 74, 1000 (1952).

(18) O. Grummitt, *Org. Syntheses*, 19, 94 (1939).

sulfate. Fractional distillation of the crude product through an 8-inch Widmer column at atmospheric pressure yielded 3.94 g. (35%) of an olefin mixture, b.p. 136–137°, $n^{25}D$ 1.4552. An examination of the infrared spectrum of this material showed considerably less methylenecycloheptane than was present in the sample from thermal dehydration of 1-methylcycloheptanol. However, a small amount of the *exo* double bond absorptions was still apparent in the spectrum. A vapor-phase chromatograph indicated that the amount of methylenecycloheptane (IX) did not exceed 2%.

N-(1-Methylcyclohexyl)-acetamide (XI).—In a 200-ml. flask were placed 22.8 g. (0.20 mole) of 1-methylcyclohexanol, 8.2 g. (0.20 mole) of acetonitrile and 43.5 ml. of glacial acetic acid. To this rapidly stirred mixture was added dropwise 13.5 ml. of concentrated sulfuric acid and the mixture was allowed to stand at room temperature for 8 hours. The contents were poured onto crushed ice and the resulting mixture was neutralized with sodium bicarbonate. After the solid had been removed by filtration, it was washed with three portions of cold water and then dried over calcium chloride in an evacuated desiccator to yield 28.6 g. (92%) of crude N-(1-methylcyclohexyl)-acetamide (XI), b.p. 76–80°. Two recrystallizations of this crude material from *n*-hexane gave analytically pure material, m.p. 85–86°.

Anal. Calcd. for $C_9H_{17}NO$: C, 69.63; H, 11.04, N, 9.02. Found: C, 69.87; H, 10.97; N, 9.16.

Pyrolysis of N-(Methylcyclohexyl)-acetamide (XI).—The dropping funnel of the pyrolysis apparatus was heated with resistance wire to liquefy the amide and the ground-glass stopcock of the funnel was heated with an infrared lamp to prevent solidification. At a temperature of 570°, 4.5 g. (0.029 mole) of N-(1-methylcyclohexyl)-acetamide (XI) was pyrolyzed at the rate of 1 g. per minute. The receiver for the collection of the pyrolysate was connected directly to the exit end of the pyrolysis tube and was cooled in a Dry Ice–methyl Cellosolve-bath. (After the pyrolysis, there was a small carbonaceous deposit at the top of the helix packing.) The pyrolysate was immediately heated at 100° and 120 mm. and 1.0 g. (37%) of crude olefin was collected in a receiver immersed in a Dry Ice cooling bath. (A vapor-phase chromatograph of this crude olefin indicated the presence of 72% of 1-methylcyclohexene (XII) and 28% of methylenecyclohexane (XIII)). After the solid residue from the distillation had been broken up and mixed with 20 ml. of water, it was heated on the steam-bath for 10 minutes. The mixture was then cooled in ice and filtered to yield, after it was dried, 1.5 g. (34% recovery) of N-(1-methylcyclohexyl)-acetamide (XI), m.p. 84–85°. The filtrate was heated under reduced pressure to remove the water and then dried to yield 0.6 g. (37%) of impure acetamide, m.p. 67–72.5° (reported[19] m.p. 82–83°). After two recrystallizations from a 10:1 mixture of ether and methanol, a melting point of 79.5–81° was obtained for this sample of acetamide. A mixed melting point determination with an authentic sample of acetamide showed no depression. However, when the acetamide from the pyrolysis was mixed with a sample of N-(1-methylcyclohexyl)-acetamide (XI), there was an 11° depression of the melting point of XI. Acetonitrile was found in the volatile portion of the pyrolysate in a 2.5% over-all yield, calculated from the vapor-phase chromatograph.

(19) E. C. Wagner, *J. Chem. Ed.*, **7**, 1135 (1950).

COLLEGE PARK, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

1,2-Dihydro-*endo*-dicyclopentadiene[1]

BY PELHAM WILDER, JR., CHICITA F. CULBERSON AND GEORGE T. YOUNGBLOOD[2]

RECEIVED JULY 21, 1958

1,2-Dihydro-*endo*-dicyclopentadiene (I), prepared by an unequivocal reaction sequence, is shown to be identical with the dihydrodicyclopentadiene of Bruson and Riener,[3] synthesized by the Diels–Alder addition of cyclopentene and cyclopentadiene. The chemistry of this compound and the stereochemical problem are discussed.

In a study of the acid-catalyzed hydration and rearrangement of *endo*-dicyclopentadiene, Bruson and Riener reported a dihydrodicyclopentadiene prepared by the reaction of cyclopentene and cyclopentadiene at elevated temperature and pressure.[3,4]

The synthetic method used by Bruson and Riener suggests that the adduct has a norbornylene ring, and by application of Alder's empirical rules concerning the stereochemical course of the diene synthesis it may be inferred that the adduct has the *endo*-configuration. However, no statement concerning the stereochemistry of the cyclopentyl ring was made. In the present paper the stereochemical problem is solved by identifying Bruson and Riener's olefin with an authentic sample of 1,2 - dihydro - *endo* - dicyclopentadiene (I). The chemistry of the olefin is described.

The synthesis of 1,2-dihydro-*endo*-dicyclopentadiene (I) described here is shown schematically in Fig. 1. From *endo*-dicyclopentadiene the dimeric nitroso chloride II is prepared with nitrosyl chloride by the method of Kraemer and Spilker.[5] On reduction with zinc and acetic acid in isoamyl alcohol, the dimeric nitroso chloride gives two products, the unsaturated monomeric oxime III and derived ketone which is then reconverted to the ketoxime with hydroxylamine. The saturated ketoxime IV, obtained by the catalytic hydrogenation of III, is then converted into 9-aminotetrahydro-*endo*-dicyclopentadiene (V) by a sodium–alcohol reduction. The tertiary amine, 9-dimethylaminotetrahydro - *endo* - dicyclopentadiene (VI), prepared by treating the primary amine with formalin in a formic acid medium, is converted with methyl iodide into the quaternary salt, trimethyl-9-tetrahydro-*endo*-dicyclopentadienyl ammonium iodide (VII). Treatment of the methiodide with silver oxide and decomposition at elevated temperature yield the olefin, 1,2-dihydro-*endo*-dicyclopentadiene (I). This olefin is identical with the adduct of Bruson and Riener.

The formation of an addition product with phenyl azide,[6,7] and the method of synthesis show

(1) Taken in part from a dissertation submitted by G. T. Youngblood to the Graduate School of Duke University in partial fulfillment of the requirements for the Ph.D. degree, October, 1956. For the previous paper in this series, see G. T. Youngblood and P. Wilder, Jr., *J. Org. Chem.*, **21**, 1436 (1956).

(2) American Cyanamid Pre-doctoral Fellow, 1955–1956.

(3) H. A. Bruson and T. W. Riener, THIS JOURNAL, **67**, 723 (1945).

(4) P. D. Bartlett and A. Schneider, *ibid.*, **68**, 6 (1946).

(5) G. Kraemer and A. Spilker, *Ber.*, **29**, 552 (1896).

(6) K. Alder and G. Stein, *Ann.*, **485**, 211 (1931).

(7) K. Alder, G. Stein and H. Finzerhagen, *ibid.*, **485**, 223 (1931).