

Conformational Analysis. LXXXIX. Stereochemical Studies of Some Dimethylated Six- and Seven-Membered-Ring Hydrocarbons^{1,2}

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The *cis*- and *trans*-1,2-dimethylcycloheptanes were prepared and equilibrated over palladium in the liquid phase at elevated temperatures. The *trans* isomer was found to be more stable; $\Delta H^\circ = 0.54$, $\Delta G^\circ = 0.59$ kcal/mol, $\Delta S^\circ = 0.15$ eu (25°). The acid-catalyzed equilibria between the 1,2-dimethylcyclohexenes showed that the order of stability was 1,2-dimethylcyclohexene > 1,6-dimethylcyclohexene > 1-methyl-2-methylcyclohexene. Similar experiments with the 1,2-dimethylcycloheptenes led exclusively to ring contraction.

While a great many conformational studies of all kinds have been reported on six-membered hydrocarbon rings,⁴ very much less is known conformationally about the cycloheptane ring. This is in part because of the greater practical importance of six-membered *vs.* seven-membered rings, and also in part due to the fact that while the cyclohexane ring is very simple, containing only two nonequivalent positions, which can become equivalent by ring inversion, the cycloheptane ring contains no less than seven nonequivalent positions, which may become equivalent by ring inversion or by pseudorotation. While a six-membered ring consists of a unique chair form in all but very unusual cases, the seven-membered ring consists of a number of chair forms which are separated by small pseudorotational barriers, plus a boat form which itself consists of several forms separated by small pseudorotational barriers, and the boat form is only somewhat higher in energy than the chair, so that in substituted molecules one cannot assume automatically that the chair form will always predominate.

In an elegant theoretical study of the conformations of cycloheptane, using calculations of the Weissheimer type, Hendrickson⁵ delineated the conformations available to cycloheptane and their relative energies. The data he obtained are still believed to be valid. The important point brought out by his calculations was that substitution of a reasonably small group, say a methyl group, into the cycloheptane ring could take place at any of several points, and lead to a structure that was at an energy minimum, corresponding to an equatorial methyl group in the cyclohexane ring. If two methyls were placed in the ring in positions located 1,3 or 1,4 to each other, and probably also if they were located 1,2 or 1,1, one could always have the methyls in an equatorial-like position, or in the 1,1 case, biaxial, which for purposes of energy calculations is substantially equatorial. Hendrickson therefore concluded that cycloheptane rings with two nonpolar substituents that were not too large would have very similar energies for both the *cis* and *trans* forms, in all cases. Insofar as evidence is available experimentally, this has been

found to be the case. It was already known to Hendrickson that the *cis* and *trans* isomers of 3,5-dimethylcycloheptanone differed in energy by only 0.8 kcal/mol, with the *cis* isomer being the more stable.⁶ Also, equilibration data on the perhydroazulene ring system showed that the *trans* isomer had an enthalpy of 0.3 kcal/mol less than did the *cis* isomer.⁷ Further studies on more complex cycloheptane systems as found in the perhydroazuleneoid sesquiterpenes were carried out by Hendrickson⁸ and similar considerations for A-homo steroids have been reported by Jones, Zander, and Price.⁹

It seemed to us that some more detailed studies on simple cycloheptanes would be desirable, whereupon we chose the dimethylcycloheptanes as suitable simple derivatives on which one could carry out conveniently both thermodynamic studies and force-field calculations. Studies on the 1,2-dimethylcycloheptanes were completed some years back. Subsequently, studies were published by Mann and coworkers¹⁰ on the 1,2, the 1,3, and the 1,4 isomers, which included synthetic and equilibration experiments. Our studies on the 1,2 isomer are in reasonable agreement with those reported by Mann and will be outlined herein. In the course of this work, some studies were also carried out on intermediate olefinic compounds, which are also reported here.

Hendrickson's calculations¹¹ on the 1,2-dimethylcycloheptanes indicated that all dimethylcycloheptanes should have essentially the same energy, the energy difference between any pair of isomers being about 0 kcal/mol. While improvements have been made in force-field calculations since Hendrickson's work in this area, there is no reason to doubt that his conclusions are substantially correct for the case at hand. We therefore did not consider it worthwhile to repeat those calculations, but accept them as they stand.

As analogs we will have occasion to discuss the 1,2-dimethylcyclohexanes. Our synthetic scheme for obtaining both the dimethylcyclohexanes and dimethylcycloheptanes was such as to put a double bond into the ring system at one point. Since mixtures of olefins were obtained, it was of interest to inquire as to where the equilibria between these isomeric olefinic com-

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(3) Correspondence concerning this work should be directed to the University of Georgia.

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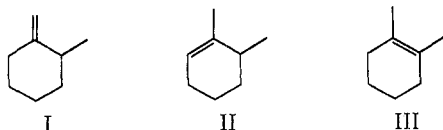
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pounds were to be found. We might consider the six-membered ring first.

The equilibrium between methylcyclohexene and methylenecyclohexane has been exhaustively studied, both experimentally and theoretically, and commented upon in the literature.¹²⁻¹⁴ It is quite clear that the endocyclic isomer strongly predominates over the exocyclic isomer; the most important feature in the energy considerations is that the trisubstituted double bond is more stable than the disubstituted double bond. Also important is the fact that a double bond wants to be eclipsed by a substituent on the sp^3 carbon attached to it; any other alternative corresponds to an increase in torsional energy.

When the second methyl group is placed on the cyclohexane ring, the situation becomes more complicated, because there are now two endocyclic positions and one exocyclic position, which involve one or both of the tertiary centers (structures I-III).



A mixture of I, II, and III was prepared by adding methyl Grignard to 2-methylcyclohexanone to give 1,2-dimethylcyclohexanol. Dehydration of the alcohol with iodine resulted in a mixture of the olefins. Upon vpc analysis there were found three peaks; in order of increasing retention time they corresponded to 3.2, 30.9, and 65.9% of the total olefin. Fractions 2 and 3 were characterized as olefins II and III by isolation and examination of the nmr and ir spectra. Fraction 1 is assumed to be olefin I, but an insufficient amount was obtained for isolation and identification.

This mixture of olefins, which corresponds to a kinetic rather than a thermodynamic composition, was equilibrated in the presence of a trace of sulfuric acid in refluxing pentane. After the olefin composition ceased to change it was assumed that equilibrium was reached, and analysis showed that fraction 2 had decreased to 15.2% of the total, while fraction 3 had increased to 84.8% of the total, and fraction 1 had completely disappeared (less than 0.5%). In terms of free energy, these results indicate that isomer III is the most stable, isomer II having an energy some 1.0 kcal above that of isomer III, while the energy of I must be at least 3.3 kcal higher than that of III.

The synthesis of the seven-membered-ring compounds was carried out beginning with cycloheptanone, which was allowed to react with ethyl oxalate to give a diketo ester, which in turn was decarbonylated to give α -carboethoxycycloheptanone. Alkylation of the latter, followed by hydrolysis and decarboxylation, furnished 2-methylcycloheptanone. Addition of methyl Grignard to the latter gave the corresponding alcohol, which upon dehydration gave dimethylcycloheptane as a mixture of three isomers (by vpc). The three olefins were each isolated by preparative vpc, and identified as (a) the exo methylene compound; (b) the 1,7-

dimethylcycloheptene; and (c) 1,2-dimethylcycloheptene, which could be identified by the absence of vinyl hydrogens. The infrared and nmr spectra of the compounds permitted unequivocal identification. Hydrogenation of the mixture of the olefins gave a mixture of the 1,2-dimethylcycloheptanes, cis and trans.

The equilibration of the seven-membered-ring olefins was carried out in a manner similar to that described for the six-membered-ring analogs. Thus the mixture of a, b, and c was treated with sulfuric acid in pentane at reflux, and the composition of the mixture was analyzed as a function of time. In Table I are summarized the results of the equilibration experiments.

TABLE I
ACID-CATALYZED EQUILIBRATION OF SEVEN-MEMBERED-RING
OLEFINS a, b, AND c IN REFLUXING PENTANE (36°)

Frac- tion no.	Retention time, ^a min	Products, %			
		Initial concn	9 days	28 days	30 days
1 ^b	52.5	9.7	42.1	90.0	90.0
2 ^c	60.0	28.6	4.9	2.3	2.5
3 ^d	62.3	61.7	49.6		
4 ^b	67.5		3.4	7.7	7.5

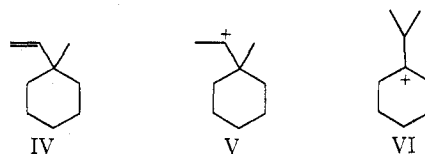
^a Determined at a column temperature of 110°. ^b Structure determined at the end of the equilibration experiment. ^c Structure determined at the start, but not at the end, of the equilibration experiment. ^d Structure determined at the start of the equilibration experiment.

From the information in Table I, obviously events did not pursue the intended course. One certainly would not expect a, the exocyclic olefin, to be the stable one, and yet that is the peak that was the predominant one on vpc after a sufficient time had elapsed. On the other hand, peak 3, which corresponds to the isomer thought to be the most stable, disappeared after a sufficiently long time and, in addition, a new peak (4) appeared.

Peak 4 was separated by preparative vpc, and characterized as isopropylidenecyclohexane by infrared and nmr spectroscopy. Obviously, a skeletal rearrangement had taken place in addition to the hydride migrations which were sought. Peak 1 was therefore isolated and examined, and it proved to be isopropylcyclohexene. No direct evidence for any seven-membered-ring compounds was obtained, although the peak 2 may correspond in part to 1,7-dimethylcycloheptene, but this seems doubtful.

1-Isopropylcyclohexene was then prepared and equilibrated by treatment with sulfuric acid in refluxing pentane and also by sulfuric acid in acetic acid, and the same kind of equilibrium mixture was obtained. Several experiments were carried out, but in no case was it possible to obtain equilibration of the cycloheptene compounds without their conversion to cyclohexene derivatives.

We might note in passing that Mann¹⁰ recently reported upon dehydration of 1,2-dimethylcycloheptanol with *p*-toluenesulfonic acid. It was claimed that 15% of the product consisted of the olefin IV,



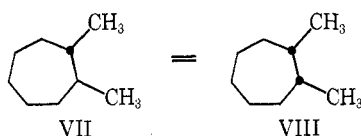
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which is formed *via* cation V. This seems highly unlikely to us, and does not correspond to our observations. The rearrangement of the initially formed cation is more likely to go in stages, through V and on to VI by methyl migration, which then can lose a proton to form a mixture of isopropylidenecyclohexane and isopropylcyclohexene. The product which Mann assigned the structure vinylmethylcyclohexane is probably in fact isopropylidenecyclohexane, but his description of the preparation of the compound and its properties are too sketchy to tell.

The equilibration of the *cis* and *trans* isomers of 1,2-dimethylcycloheptane was carried out in a manner previously described for alkylcyclohexanes,¹⁵ by heating the compounds in sealed tubes with small amounts of palladium at temperatures ranging from 200 to 324°. The tubes were filled sufficiently so that, when the equilibrium temperature was reached, the volume not occupied by the liquid was essentially zero. This avoided the problem of the presence of a gas phase in which the equilibrium constant differs from that in the liquid.¹⁶ After the equilibrium constant ($K = \text{cis}/\text{trans}$) was calculated for each equilibration temperature, enthalpy and entropy values were obtained by a least squares fit of $\ln K$ vs. $1/T$. The thermodynamic quantities for the isomerization of *trans*- to *cis*-1,2-dimethylcyclohexane (VII and VIII) are ΔH°



$= 0.54 \pm 0.02$ kcal/mol; $\Delta S^\circ = 0.15 \pm 0.03$ eu; $\Delta G^\circ_{25^\circ} = 0.59$ kcal/mol.

The data show that the *trans* isomer of 1,2-dimethylcycloheptane is of lower enthalpy than the corresponding *cis* isomer by 0.54 ± 0.02 kcal/mol. This is in accordance to the prediction that the 1,2-*trans* isomer above should be more stable than the 1,2-*cis* isomer and that the difference in energy between the two should be small compared to what is found for similar six-membered-ring isomers.⁴ The entropy difference between *cis*- and *trans*-1,2-dimethylcycloheptane is close to zero. This is reasonable considering that both of the isomers are about equally flexible. The amount of disorder is thus about the same for both isomers.

Experimental Section

1,2-Dimethylcyclohexenes (I, II, and III).—The olefinic mixture was prepared according to the procedure of Signaigo and Cramer.¹⁷ The mixture was separated by preparative vpc (see below), and the compounds II and III were characterized by their nmr and ir spectra.

1,2-Dimethylcycloheptenes.—Methyl iodide, 24.0 g, was added dropwise to 4.1 g of magnesium turnings in 200 ml of anhydrous ether. The mixture was heated under reflux for an additional 1 hr, then 17.2 g of 2-methylcycloheptanone was added dropwise with cooling, and stirring was continued overnight. A saturated solution of ammonium hydroxide was slowly added to the reaction mixture, the ether layer was separated, and the aqueous layer was extracted with ether. The combined ether extracts were washed and dried over magnesium sulfate, the ether was evaporated, and the product was distilled, bp 69° (4 mm), wt

16.5 g (86.6%), ir broad hydroxyl band at 3420, CH_3 bending at 1370 cm^{-1} .

The 1,2-dimethylcycloheptanol obtained above, 16.5 g, was heated with a few iodine crystals and distilled to yield a fraction boiling at 90–155°. The water was separated from the distillate, and the hydrocarbon layer was dried with magnesium sulfate. Distillation gave the product, bp 150–152°, wt 11.2 g (77.9%).

Anal. Calcd for C_9H_{16} : C, 87.02; H, 12.98. Found: C, 87.11; H, 12.96.

Vpc Separation of Isomeric Olefins.—The Varian Autoprep (Model 700) was used for separation purposes throughout this work. A 20 ft \times 0.375 in. aluminum column containing 30% SE-30 on Chromosorb W (45/60 mesh) was used. The flow rate 200 ml/min, with helium carrier gas. Analyses were by the height \times half band width technique.

The 1,2-dimethylcyclohexene isomers were separated at a temperature of 110°, as were the 1,2-dimethylcycloheptene isomers. The nmr and ir spectra of each fraction was consistent with the assignment made.

1-Isopropylcyclohexene and Isopropylidenecyclohexane.—Isopropyl bromide, 61.5 g, was added slowly to 15.2 g of magnesium turnings in 200 ml of dry ether. Cyclohexanone, 39.2 g, was then slowly added to the reaction flask, and the reaction mixture was stirred overnight. A saturated solution of ammonium chloride was added, and the ether layer was collected, washed with water, and dried over magnesium sulfate. The solution was filtered and the ether was evaporated. The ir of the residue showed a strong hydroxyl band.

A crystal of iodine was added to the above product and the mixture was refluxed in toluene overnight. A Dean-Stark trap was used to remove the water formed. The solvent was then removed and the product was distilled, bp 142°. The distillate was injected into the vpc at 110°. Two peaks were detected and were collected as fractions 1 and 2 with retention times of 52.5 and 67.5 min, respectively. Fraction 1 was the largest of the two by 9:1.

The data on the vpc fractions are as follows. Fraction 1 had nmr (neat with TMS) multiplet at δ 5.38 (1 H), multiplet between 1.40 and 2.32 (9 H), and a doublet at 0.95 (6 H) separated by 7.0 Hz.

Anal. Calcd for C_9H_{16} : C, 87.02; H, 12.98. Found: C, 87.17; H, 12.86.

Fraction 2 had nmr (neat with TMS) broad singlet at δ 2.14 (4 H) and a broad region between 1.30 and 1.80 (12 H).

Anal. Calcd for C_9H_{16} : C, 87.02; H, 12.98. Found: C, 87.09; H, 12.99.

1,2-Dimethylcycloheptane.—A mixture of 1,2-dimethylcycloheptenes was hydrogenated using platinum oxide in acetic acid. The product was worked up as usual and it showed a negative tetranitromethane test. Vpc analysis at 110° showed two peaks with retention times of 47.5 (19% of total area) and 53.5 min (81% of total area). When the hydrogenation was carried out in ethanol with palladium catalyst, the composition of the mixture varied slightly, 31.7 and 68.3% of the two fractions being obtained. The *cis* structure is assigned to the predominant isomer (fraction 2).

The data on the two vpc fractions are as follows. Fraction 1 had nmr (neat with TMS) broad region between δ 1.12 and 1.80, converging to a singlet at 1.52 (10 H), sharp singlet at 0.96 (8 H). The latter is attributed to the sum of the methyl protons and the methine protons, and is similar to what is found with *trans*-1,2-dimethylcyclohexane.¹⁸

Anal. Calcd for C_9H_{18} : C, 85.63; H, 14.37. Found: C, 85.38; H, 14.16.

Fraction 2 had nmr (neat with TMS) broad region between δ 1.10 and 2.00, converging to a singlet at 1.52 (12 H), and a doublet at 0.85 (6 H), with a separation of 6.5 Hz.

Anal. Calcd for C_9H_{18} : C, 85.63; H, 14.37. Found: C, 85.41; H, 14.18.

Equilibration of 1,2-Dimethylcycloheptane Isomers.—In a capillary ampoule 1,2-dimethylcycloheptane (mixture of *cis* and *trans*) was inserted along with about 10% by weight of 10% palladium on carbon. The total amount of hydrocarbon was about 25 μl , which occupied approximately 70–80% of the capillary's volume. The ampoule was sealed and immersed in a furnace for the desired length of time at the proper temperature. Immediately upon removal from the furnace, the ampoule was

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

cooled in ice water. The contents of the ampoule were then analyzed by vpc. Each sample was analyzed at least twice and an average value was taken. The average deviation was about 0.1–0.2%. In Table II the results of the analysis are given.

TABLE II
EQUILIBRATION OF *cis*- AND *trans*-1,2-DIMETHYLCYCLOHEPTANE

Temp, °C	Length of run, hr	Fraction 1, % trans	Fraction 2, % cis
200	336	65.72	34.27
225	144	64.98	35.02
250	72	64.60	35.40
274	24	63.94	36.06
300	24	63.38	36.62
324	24	62.99	37.01

Acid-Catalyzed Equilibration Procedure.—1,2-Dimethylcycloheptene (mixture of isomers), 0.5 g, was heated under reflux in

TABLE III
ACID-CATALYZED EQUILIBRATION OF 1-ISOPROPYLCYCLOHEXENE IN REFLUXING PENTANE (36°)




Frac-tion no.	Structure assigned	Reten-tion time, ^b min	Products, %				
			Initial concn	5 days	21 days	42 days	50 days
1		52.5	100.0	90.0	90.6	90.4	90.4
2	^a	60.0				2.3	2.2
3		67.5		9.6	9.3	7.3	7.4

^a Not isolated. ^b Determined at a column temperature of 110°.

25 ml of olefin-free pentane containing 2 drops of concentrated sulfuric acid. Samples were occasionally withdrawn and checked by vpc. At suitable intervals, larger samples were run through the preparative vpc and fractions were isolated. The fractions were identified by infrared and nmr spectra.

Other equilibration experiments starting with 1-isopropylcyclohexene and the 1,2-dimethylcyclohexenes were carried out in a similar manner. The results are summarized in Tables III and IV.

TABLE IV
ACID-CATALYZED EQUILIBRATION OF SIX-MEMBERED OLEFINS I, II, AND III IN REFLUXING PENTANE (36°)

Frac-tion no.	Structure assigned	Retention time, ^a min	Products, %		
			Initial concn	6 days	9 days
1		31.2	3.2		
2		35.2	30.9	15.2	15.1
3		42.5	65.9	84.8	84.9

^a Determined at a column temperature of 110°.

Registry No.—1,2-Dimethylcycloheptanol, 37102-80-0; 1,2-dimethylcycloheptene, 20053-89-8; 1-isopropylcyclohexene, 4292-04-0; isopropylidenecyclohexane, 5749-72-4; *trans*-1,2-dimethylcyclohexane, 6876-23-9; *cis*-1,2-dimethylcyclohexane, 2207-01-4; 1-methyl-2-methylenecyclohexane, 2808-75-5; 1,6-dimethylcyclohexene, 1759-64-4; 1,2-dimethylcyclohexene, 1674-10-8.

Steric and Polar Effects in the Decarboxylation of Mercuric Salts of Unsymmetrical Aromatic 1,2-Dicarboxylic Acids (the Pesci Reaction). An Improved Procedure^{1a}

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The conversion of mercury(II) salts of unsymmetrical aromatic 1,2-dicarboxylic acids to monocarboxylic acids through the intermediate anhydrohydroxymercuric acids (Pesci reaction) is discussed in terms of polar and steric effects. An improved procedure which involves heating of the mercury(II) salts in hexamethylphosphoramide containing powdered glass yields anhydrohydroxymercuric acids in higher yield and in shorter time than does the previously described procedure. The anhydrohydroxymercuric acids are rapidly and almost quantitatively converted into aromatic monocarboxylic acids by treatment with sodium borohydride.

The reaction of phthalic acid with mercury(II) acetate produces a salt (1) which on heating in boiling water yields anhydro-2-hydroxymercuribenzoic acid² (2) (eq 1). When the latter is refluxed for several days with aqueous hydrochloric acid benzoic acid is produced (eq 2).² If the mercury(II) salt of a 3-substituted phthalic acid is used, two anhydro-2-hydroxymercuric acids (2, 3) and from them two substituted benzoic acids (4, 5) may be formed. The object of the work herein reported was to study the effect of hydrocarbon moieties in the 3 position on the course of the Pesci reaction. During this work

marked improvements in the method of decomposition of the mercury(II) phthalates, as well as replacement of mercury in the anhydro-2-hydroxymercuribenzoic acids, were made.

In earlier work, 3-chlorophthalic acid³ (6), 3-bromophthalic acid³ (7), 3-nitrophthalic acid³ (8), and hemimellitic acid⁴ (9) were subjected to the Pesci reaction. Each was reported to yield exclusively the corresponding meta-substituted benzoic acid (4). The conversion of 1,2-anthraquinonedicarboxylic acid to 2-carboxyanthraquinone was also noted.⁵ Because all of

(1) (a) This work was supported by Grant 12445 of the National Science Foundation. (b) Predoctoral Research Associate.

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