

hexylpropionaldehyde over a period of 2 hr. The mixture was stirred for 1 hr. more at 0°, then was allowed to stand at room temperature for 14 hr. It was neutralized (to pH 6) with sodium carbonate and extracted with five 150-ml. portions of ether. The extracts were dried and the ether was distilled, leaving 24.3 g. of crude solid, which showed strong OH absorption and C=O absorption (1710 cm.<sup>-1</sup>) in its infrared spectrum. A sample was sublimed at 114–117° (6 mm.), m.p. 138–150°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>14</sub>O<sub>2</sub>: C, 70.10; H, 9.15. Found: C, 69.80; H, 9.32.

*Bicyclo[3.3.1]nonan-2-ol.* The crude keto alcohol from above, 24.3 g., was treated with 32 g. of *p*-nitrobenzoyl chloride in 70 ml. of dry pyridine. When the initial exothermic reaction had subsided, the mixture was heated on a steam bath for 20 min., then was poured into 800 g. of ice water. The gummy precipitate did not crystallize, and the mixture was extracted with 450 ml. of methylene chloride in three portions. The solution was washed with hydrochloric acid and dried, and the solvent was evaporated. The solid residue was separated by fractional crystallization into 3.4 g. of *p*-nitrobenzoic anhydride, m.p. 186–187°, and 33.2 g. (70%) of *p*-nitrobenzoate ester, m.p. 97–

113°, showing strong infrared absorption at 1720 (C=O) and 1520 (NO<sub>2</sub>), and medium absorption at 1605 cm.<sup>-1</sup>.

A solution of 4.8 g. of the crude ester in 30 ml. of absolute ethanol was boiled with 3.0 g. of *p*-toluenesulfonylhydrazide for 25 min. Then 6 ml. of water was added, and the solution was cooled. Filtration afforded 8.5 g. of solid which was dried to a constant weight of 6.9 g., m.p. 125–147° (92% yield). This solid showed strong infrared absorption at 1720 (C=O), 1520 (NO<sub>2</sub>), and 1170 cm.<sup>-1</sup> (tosyl), as well as weak absorption at 1605 and 1640 cm.<sup>-1</sup> (C=N-).

The crude *p*-tosylhydrazone, 6.9 g., was treated with 4.5 g. of sodium borohydride and 50 ml. of dioxane according to the procedure described above.<sup>13</sup> Gas chromatography of the crude reduction product showed a mixture of ca. 82% *endo*-bicyclo[3.3.1]nonan-2-ol, 4–7% of *exo*-bicyclo[3.3.1]nonan-2-ol (identified by retention time only), and 11% of an unidentified component of longer retention time. Recrystallization of the crude product from pentane gave 1.36 g. of an alcohol, m.p. 168–170°, which was identical (retention time, infrared spectrum, melting point, and mixture melting point of *p*-nitrobenzoate) with bicyclo[3.3.1]nonan-2-ol from the solvolysis of 5.

## Conformations of Seven-Membered Rings. Benzocycloheptenes

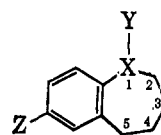
Harold Hart and James L. Corbin

*Contribution of the Chemistry Department, Michigan State University, East Lansing, Michigan. Received February 17, 1965*

In order to study the conformations of the cycloheptene ring, 1,1,4,4-tetramethyl-6,7-benzocycloheptene (VIII) was synthesized. The final step involved cyclization of 2,4,4-trimethyl-6-phenyl-2-hexene (X) which, with aluminum chloride, gave only the tetralin XI, but with boron fluoride etherate gave XI and the desired VIII. The conformations of VIII are discussed, and it is shown by n.m.r. that the enantiomorphic conformations of VIII interconvert rapidly at 35°, but this interconversion can be stopped by lowering the temperature. Both VIII and 1,1,4,4-tetramethyl-6,7-benzocyclohepten-5-one (XIII) had abnormally low extinction coefficients in their electronic spectra.

### Introduction

It has long been known that a seven-membered ring fused to a benzene ring is under certain geometric constraints which minimize the overlap of an orbital on atom X with the aromatic π-system, relative to what such overlap would be if X were part of a smaller or larger ring, or no ring at all. Early examples include the slow rate of electrophilic deuteration of I<sup>1</sup>



|     | X  | Y               | Z                  |
|-----|----|-----------------|--------------------|
| I   | N  | CH <sub>3</sub> | H                  |
| II  | C  | =O              | H                  |
| III | O  |                 | H                  |
| IV  | CH | Cl              | H                  |
| V   | O  |                 | CH <sub>2</sub> Cl |
| VI  | CH | H               | H                  |

and the decreased absorption intensities in the electronic spectra of I,<sup>2</sup> II,<sup>3</sup> III,<sup>4</sup> 5,5-dimethyl-III,<sup>5</sup> and 2-carboxy-III,<sup>6</sup> when compared with five- and six-membered analogs. The solvolysis rates of IV<sup>7,8</sup> and V<sup>4</sup> are over two orders of magnitude slower than those of smaller ring analogs, presumably because of decreased charge delocalization in the benzylic car-

(2) W. R. Remington, *ibid.*, 67, 1838 (1945).

(3) G. D. Hedden and W. G. Brown, *ibid.*, 75, 3744 (1953).

(4) G. Baddeley, N. H. P. Smith, and M. A. Vickars, *J. Chem. Soc.*, 2455 (1956).

(5) H. Hart and C. R. Wagner, *Proc. Chem. Soc.*, 284 (1958).

(6) G. Baddeley and J. R. Cooke, *J. Chem. Soc.*, 2797 (1958).

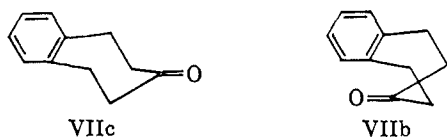
(7) G. Baddeley and J. Chadwick, *ibid.*, 368 (1951).

(8) G. Baddeley, J. Chadwick, and H. T. Taylor, *ibid.*, 451 (1956).

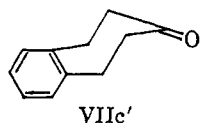
(1) W. G. Brown, A. H. Widiger, and N. J. Letang, *J. Am. Chem. Soc.*, 61, 2597 (1939).

bonium ions. The extinction coefficient of benzocycloalkenes in the region 271–274 m $\mu$  decreased with increasing size, reaching a minimum at benzocycloheptene (VI), then rising slightly for benzocyclooctene,<sup>9</sup> an effect which has been interpreted in terms of specific steric requirements for hyperconjugation. Each of these results implies that I–VI experience difficulty in attaining a conformation in which C-2 is in the same plane as that defined by the aromatic ring and atom X.

Allinger and Szkrybalo concluded from a dipole moment study<sup>10</sup> that 5,6,8,9-tetrahydro-7H-cycloheptabenzen-7-one (VII) exists as an equilibrium mixture of chair (VIIc) and boat (VIIb) forms, the former pre-



dominating to the extent of about 92%.<sup>11</sup> This result implies rapid “flipping” or “wagging” of the carbonyl carbon, but says nothing about the process of interconversion of VIIc or VIIb to their mirror images (for example, VIIc’). If this chair-to-chair inter-



conversion were slow, a suitably substituted benzocycloheptene might be resolved, particularly if substituents were judiciously placed on the aliphatic ring to interfere sterically with the “flipping” process.

The proper placement of substituents required some model for the enantiomorphic interconversion process. Examination of Dreiding models suggested a scheme which, though not entirely correct,<sup>12</sup> is instructive to consider since it dictated our choice of compound for synthesis and study.<sup>13,14</sup> Models indicated that the interconversion of chair (VIIc) and boat (VIIb) forms by “wagging” at C-3 should be facile. Subsequent bond “rotation” in the boat form, similar to that which is well known in the “flexible” form of cyclohexane rings, could lead to the enantiomorphic boat VIIb’ which by another C-3 “wag” would give VIIc’. One intermediate form (VIIIi) seemed from models to be unavoidable in the boat to boat interconversion; this conformation has atoms 1,4,5,6, and 7 in one plane,<sup>15</sup> and requires prohibitively close approach of substituents on C-1 and C-4 if these groups are larger than hydrogen.

(9) W. R. Moore, E. Marcus, S. E. Fenton, and R. T. Arnold, *Tetrahedron*, **5**, 179 (1959).

(10) N. L. Allinger and W. Szkrybalo, *J. Org. Chem.*, **27**, 722 (1962).

(11) An earlier prediction [R. Pauncz and D. Ginsburg, *Tetrahedron*, **9**, 40 (1960)] that the boat form of cycloheptene will have less energy than the chair form seemed unlikely to Allinger and Szkrybalo (ref. 10, footnote 11) and is inconsistent with the present findings (see accompanying paper<sup>12</sup>).

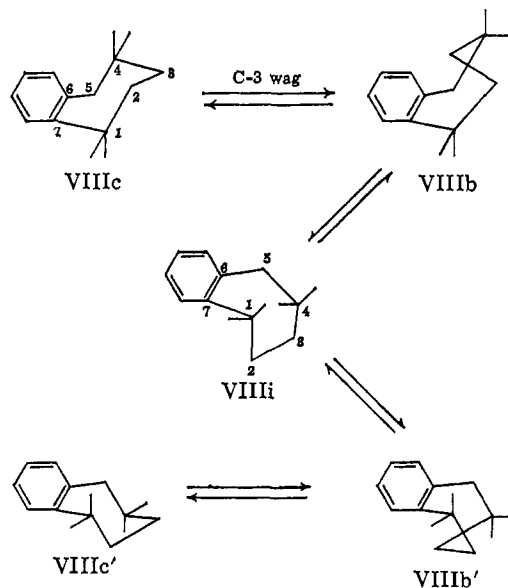
(12) E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **87**, 3139 (1965).

(13) We appreciate helpful discussions with Professor K. Mislow in the early stages of this work.

(14) The numbering of the seven-membered ring is now switched from that used in formulas I–VI to conform with the nomenclature system used for the compounds prepared in the present work.

(15) The relatively high energy of this conformation is perhaps the reason for the various phenomena mentioned in the first paragraph.

Accordingly, 1,1,4,4-tetramethyl-6,7-benzocycloheptene (VIII) was selected for study. It was thought that if the interconversion of conformations VIIIc and

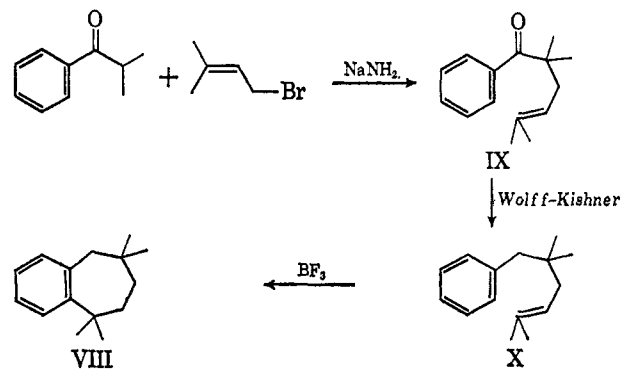


VIIIc’ were slow, this would be evident from different n.m.r. chemical shifts of the two methyls on C-1, the two methyls on C-4, and the two protons on C-5. If “flipping” were rapid, each of these sets of protons should appear as sharp unsplit signals.

## Results and Discussion

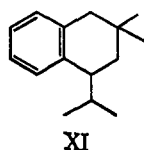
The desired hydrocarbon VIII was best synthesized as shown in Scheme I. Alkylation of isobutyrophenone with 1-bromo-3-methyl-2-butene, using sodamide as the base, gave an 88% yield of ketone IX. Wolff-Kishner reduction of IX gave X; ozonolysis gave a high yield of acetone, showing that the alkaline conditions of the reduction did not cause any double bond isomerizations. Cyclization of X with aluminum chloride at 0° gave a hydrocarbon C<sub>15</sub>H<sub>22</sub> which, however, was not the desired VIII, because its mass spectrum showed the principal fragmentation route to be 202<sup>+</sup> → 159<sup>+</sup> + 43, indicating that the carbon  $\alpha$  to the aromatic

Scheme I



ring carried a propyl group (C<sub>3</sub>H<sub>7</sub>).<sup>16</sup> This compound is most likely 1-isopropyl-3,3-dimethyltetralin (XI), ring closure giving the less strained, six-membered ring. Ring closure with boron fluoride etherate in

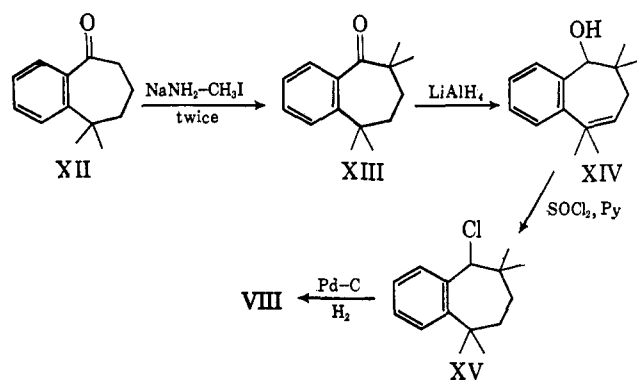
(16) See H. M. Grubb and S. Meyerson in “Mass Spectrometry of Organic Ions,” F. W. Mc Lafferty, Ed., Academic Press Inc., New York N. Y., 1963, Chapter 10.



methylene chloride gave two products in a ratio of 2:1. The former was XI, but the minor product was the desired VIII. The most prominent fragmentation path in the mass spectrum was loss of methyl ( $202^+ \rightarrow 187^+ + 15$ ), indicating an  $\alpha$ -methyl substituent.<sup>16</sup> The ultraviolet spectrum had its major peak at  $262 \text{ m}\mu$  ( $\epsilon$  232), with only a shoulder at the usual<sup>9</sup> position for benzocycloalkenes,  $271 \text{ m}\mu$  ( $\epsilon$  130). The intensity is significantly less than that of benzocycloheptene itself ( $\lambda_{\text{max}}$   $271 \text{ m}\mu$  ( $\epsilon$  292)).<sup>9</sup> The n.m.r. spectrum of VIII, discussed below, was consistent with the assigned structure. The ratio of VIII to XI in the boron fluoride catalyzed ring closure was independent of reaction time; VIII, once formed, was not converted to XI under the reaction conditions.

The structure of VIII was verified by an independent synthesis which, in fact, arose from our first attempt to obtain VIII. This is shown in Scheme II. Ketone XII<sup>17</sup> was dimethylated in two steps using sodamide and methyl iodide to give XIII in 64% yield. XIII had a  $\lambda_{\text{max}}$   $240 \text{ m}\mu$  ( $\epsilon$  5840) and a shoulder at  $272 \text{ m}\mu$  ( $\epsilon$  960). The low extinction coefficient of the main band (cf. acetophenone,  $240 \text{ m}\mu$  ( $\epsilon$  13,000)) is consistent with the carbonyl function being twisted out of coplanarity with the benzene ring. Indeed, the effect is much larger than with 2,3-benzuberone ( $\lambda_{\text{max}}$   $240 \text{ m}\mu$  ( $\epsilon$  9000)),<sup>3</sup> indicating that the four methyl groups were having the desired effect. XIII would not form the usual carbonyl derivatives, and could not be reduced directly to VIII by the Wolff-Kishner or catalytic methods. But reduction to XIV with lithium aluminum hydride was facile (89%). The alcohol, though

Scheme II



benzylic, could not be reduced to VIII by copper chromite and hydrogen, even under severe conditions. XIV was smoothly converted to the chloride XV which was slowly reduced over palladium on charcoal in poor yield to a mixture of several products, the major one of which, separated by gas chromatography, was identical (infrared) with VIII. Since the seven-membered ring was present initially in Scheme II, the structure of VIII seems established.

The n.m.r. spectrum of VIII, taken in carbon tetra-

(17) S. Julia, M. Julia, and B. Bemont, *Bull. soc. chim. France*, 1449 (1959).

chloride at  $35^\circ$ , showed very quickly that the ring was "flipping" at that temperature. The spectrum had three sharp singlets at  $\tau$  7.34, 8.68, and 9.14 with relative areas 1:3:3, corresponding to the protons  $\alpha$  to the benzene ring and the *gem*-dimethyl groups at carbons 1 and 4, respectively. The compound was sent to Dr. E. Grunwald for a study of its n.m.r. spectrum below room temperature, and his results are reported in the accompanying paper.<sup>12</sup> Two of the predictions made here from a study of models of VIII were verified by his work: that the C-3 "wag" is facile, and that the energy required for interconversion of boat forms VIIIb and VIIIb' is prohibitive. But an alternative chair-chair interconversion route, discussed in detail by Grunwald and Price,<sup>12</sup> proceeds sufficiently rapidly at room temperature to preclude the resolution of VIII.

## Experimental

*1-Phenyl-2,2,5-trimethyl-4-hexen-1-one (IX)*. A solution of 32.8 g. (0.222 mole) of isobutyrophenone in 25 ml. of anhydrous benzene was added dropwise with stirring to a warm ( $50^\circ$ ) suspension of 9.44 g. (0.242 mole) of sodium hydride in 50 ml. of anhydrous benzene, the apparatus being carefully protected from moisture. The dark solution was stirred at reflux for 40 min. A solution of 33.5 g. (0.222 mole) of 1-bromo-3-methyl-2-butene<sup>18</sup> in 25 ml. of dry benzene was added during 30 min. to the refluxing solution, and the mixture was refluxed overnight. Water (100 ml.) was added to the cooled mixture, the layers were separated, and the organic layer was dried over anhydrous sodium sulfate. Work-up gave 42 g. (87.5%) of colorless ketone, b.p.  $81-83^\circ$  (0.07 mm.),  $n_D^{20}$  1.5180, carbonyl stretch at  $1680 \text{ cm}^{-1}$ . Bromate-bromide titration<sup>19</sup> required 100.7% of theory for one double bond. The ketone gave a 2,4-DNP, m.p.  $86.8-87.2^\circ$  (from aqueous ethanol).

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{24}\text{N}_4\text{O}_4$ : C, 63.62; H, 6.10; N, 14.14. Found: C, 63.52; H, 5.95; N, 14.21.

*2,4,4-Trimethyl-6-phenyl-2-hexene (X)*. A mixture of 24.9 g. (0.115 mole) of IX, 30 g. of potassium hydroxide, 30 ml. of 99% hydrazine, and 200 ml. of ethylene glycol was heated for 3 hr., with slow takeoff of distillate, until the pot temperature reached  $195^\circ$ . Reflux was continued for 6 hr. Work-up gave 18.3 g. (79%) of olefin, b.p.  $72-74^\circ$  (0.08 mm.),  $n_D^{20}$  1.5060, with a double bond band at  $1665 \text{ cm}^{-1}$  and no carbonyl band. The molecule absorbed 0.99 mole of bromine (one double bond).<sup>19</sup>

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{22}$ : C, 89.04; H, 10.96. Found: C, 89.13; H, 11.09.

Ozonolysis of 0.108 g. (0.54 mmole) of the ketone in 40 ml. of methanol at  $-50^\circ$  required 45 min. After warming to room temperature, 0.4 g. of potassium iodide was added, followed by 0.9 g. of sodium hydroxide in 8 ml. of water. Then 0.7 g. of iodine in 50 ml. of water containing 1.0 g. of potassium iodide was added. Iodoform, m.p.  $120-122^\circ$ , precipitated immediately (0.160 g.; 76%).

### Reaction of 2,4,4-Trimethyl-6-phenyl-2-hexene (X)

(18) H. Staudinger and K. Schilt, *Helv. Chim. Acta*, 5, 746 (1922).

(19) W. T. Smith, Jr., and R. L. Shriner, "The Examination of New Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 124.

with Hydrogen Chloride and Aluminum Chloride. Hydrogen chloride was passed for several minutes through a solution of 0.30 g. (2.2 mmoles) of aluminum chloride in 40 ml. of methylene chloride at  $-2^{\circ}$ , after which there was added, during 5 hr., a solution of 1.40 g. (6.94 mmoles) of X in 30 ml. of methylene chloride. The mixture was kept at  $-2^{\circ}$  for 20 hr., then hydrolyzed on ice. The organic layer was washed with dilute hydrochloric acid, then water, and dried over potassium carbonate. Work-up gave 1.13 g. (80.7%) of a pale yellow liquid. It was primarily one component on gas chromatography ( $210^{\circ}$ , 20% silicone column, retention time 28 min.), and was purified this way, giving 1-isopropyl-3,3-dimethyltetralin (XI),  $n_{20}^D$  1.5136. It had bands in the infrared at 1380 and 1365 (*gem*-dimethyl) and  $735\text{ cm}^{-1}$  (1,2-disubstitution), and in the ultraviolet at  $274\text{ m}\mu$  ( $\epsilon$  935), 267 (1030), and 260 (930) in cyclohexane. The n.m.r. spectrum showed no vinyl protons.

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{22}$ : C, 89.04; H, 10.96. Found: C, 89.09; H, 10.93.

*1,1,4,4-Tetramethyl-6,7-benzocycloheptene (VIII).* Boron fluoride was passed into 1 ml. of ether at  $0^{\circ}$  for several minutes. Methylene chloride (25 ml.) was added, and a solution of 1.0 g. (4.9 mmoles) of 2,5,5-trimethyl-6-phenyl-2-hexene (X) in 25 ml. of the same solvent was added dropwise over 2 hr. at  $0^{\circ}$ . After 2 additional hr., the yield and peak ratios of the two products observed on gas chromatography became constant. Water (25 ml.) and concentrated ammonium hydroxide (5 ml.) were added, and the organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. The residue after solvent removal was separated into two components by preparative gas chromatography. The major product (67%) was identical with that formed when aluminum chloride was the catalyst (1-isopropyl-3,3-dimethyltetralin). The minor component (33%) had a slightly longer retention time,  $n_{20}^D$  1.5192, and did not decolorize bromine.

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{22}$ : C, 89.04; H, 10.96. Found: C, 88.87; H, 11.12.

The compound had an intense band at  $752\text{ cm}^{-1}$  (1,2-disubstitution), a weak ultraviolet absorption at  $262\text{ m}\mu$  ( $\epsilon$  232), and an n.m.r. spectrum with singlets at  $\tau$  9.14 and 8.68 (six protons each), a complex multiplet centered at 8.44 (four protons), a sharp singlet at 7.34 (two protons), and a complex multiplet from 2.7 to 3.2 (four protons).

Use of ferric chloride in place of boron fluoride in the cyclization of X gave the same results. Stannic chloride gave recovered olefin, even after 12 hr.

*1,1,4,4-Tetramethyl-6,7-benzocyclohepten-5-one (XIII).* A solution of 10.0 g. (0.053 mole) of 1,1-dimethyl-6,7-benzocyclohepten-5-one (XII) in 10 ml. of toluene was added, during 20 min., to a warm, stirred suspension of 2.26 g. (0.058 mole) of sodium amide in 10 ml. of the same solvent. The deep red solution was refluxed for 25 min., then 8 ml. of methyl iodide was added slowly. After 2 hr. of reflux, the cooled mixture was washed twice with 10 ml. of water, dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The dark residue was distilled, yielding 8.7 g. of a pale yellow liquid boiling at  $78-90^{\circ}$  (0.08 mm.). The alkylation

reaction was repeated on this crude product using the same procedure but only 1.7 g. of sodium amide. Distillation through a Vigreux column gave 7.3 g. (64%) of the ketone XIII, b.p.  $79-83^{\circ}$  (0.075 mm.),  $n_{25}^D$  1.5280, as a pale yellow liquid with a carbonyl band at  $1690\text{ cm}^{-1}$  (see text for ultraviolet spectrum).

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{20}\text{O}$ : C, 83.28; H, 9.32. Found: C, 83.36; H, 9.24.

Attempts to prepare an oxime, dinitrophenylhydrazone, or semicarbazone of XIII were unsuccessful. Attempted catalytic reductions of XIII (copper chromite,  $200^{\circ}$ , 2200 p.s.i. of hydrogen, ethanol solvent; 5% palladium on charcoal,  $50^{\circ}$ , 58 p.s.i. of hydrogen, ethanol solvent) were unsuccessful (no hydrogen uptake).

*1,1,4,4-Tetramethyl-6,7-benzocyclohepten-5-ol (XIV).* A solution of 5.8 g. (0.0268 mole) of XIII in 10 ml. of tetrahydrofuran was added slowly to a stirred suspension of 1.0 g. (0.0264 mole) of lithium aluminum hydride in 15 ml. of the same solvent. The reaction was exothermic enough to reflux the solvent. The mixture was refluxed for 2 additional hr. Sodium hydroxide (10%) was added until no more precipitate formed, and the mixture was allowed to stand overnight. The clear organic layer was decanted, and the residue was washed twice with 20 ml. of solvent. Combined organic layers were stripped of solvent (steam bath) and the colorless residue was distilled (Vigreux) to give 5.2 g. (89%) of viscous alcohol XIV, b.p.  $108-110^{\circ}$  (0.09 mm.),  $n_{20}^D$  1.5338. The infrared spectrum showed no carbonyl band and a sharp hydroxyl band at  $3450\text{ cm}^{-1}$ .

A solution of 0.4 g. of XIV, 0.5 g. of 3,5-dinitrobenzoyl chloride, and 1.5 ml. of pyridine was heated on a steam bath for 8 hr. The dark solution was poured onto ice and extracted three times with 7 ml. of ether, and the combined extracts were washed successively with dilute sodium carbonate, dilute hydrochloric acid, and water. After drying (sodium sulfate) and evaporation of the solvent, a viscous yellow oil was obtained which could not be induced to crystallize. A solid  $\alpha$ -naphthylamine adduct<sup>20</sup> was obtained by adding a solution of 0.3 g. of the amine in 2 ml. of ether to 0.3 g. of the ester in 2 ml. of the same solvent. An oil separated which crystallized to red-orange needles after 3 days. Recrystallization from ethanol gave 0.3 g. of adduct, m.p.  $94.5-95.5^{\circ}$ .

*Anal.* Calcd. for  $\text{C}_{32}\text{H}_{33}\text{N}_3\text{O}_6$ : C, 69.17; H, 5.99; N, 7.56. Found: C, 69.21; H, 5.99; N, 7.56.

An attempt to reduce 4.0 g. of XIV in 20 ml. of ethanol, using 1.0 g. of copper chromite catalyst,  $220^{\circ}$ , and 2350 p.s.i. of hydrogen, gave no uptake of hydrogen during 10 hr. The alcohol was recovered.

*5-Chloro-1,1,4,4-tetramethyl-6,7-benzocycloheptene (XV).* A mixture of 5.0 g. (0.023 mole) of XIV, 3.0 ml. of pyridine, 2.5 ml. of thionyl chloride, and 20 ml. of carbon tetrachloride was stirred for 12 hr. at room temperature, then refluxed for 2 hr. The cooled mixture was poured onto ice and the organic layer washed once with water, then dried over anhydrous sodium sulfate. After removal of the solvent at atmospheric pressure, the residual oil was distilled through a small Vigreux column, yielding 4.4 g. of a pale yellow

(20) O. T. Benfey, J. R. Stanmeyer, B. Milligan, and E. M. Westhead, *J. Org. Chem.*, 20, 1777 (1955).

liquid boiling at 85–94° (0.3 mm.). Redistillation afforded 3.9 g. (71%) of XV, b.p. 89–91.50° (0.2 mm.),  $n^{24}_D$  1.5380.

*Anal.* Calcd. for  $C_{15}H_{21}Cl$ : C, 76.09; H, 8.94; Cl, 14.97. Found: C, 75.94; H, 8.85; Cl, 14.82.

A solution of 7.3 g. (0.031 mole) of XV in 30 ml. of ethanol was hydrogenated over 5% palladium on charcoal at room temperature and several atmospheres of pressure. Hydrogen was slowly absorbed for 20 hr. The solution was filtered, the solvent was distilled at

atmospheric pressure, and the residue (5.74 g.) was subjected to preparative gas chromatography (205°, 20% silicone on Chromosorb W, Perkin-Elmer Model 154 vapor fractometer). The major component (of six) was collected; it had an infrared spectrum identical with that of VIII obtained from cyclization of X.

*Acknowledgment.* We are indebted to the Petroleum Research Fund of the American Chemical Society and to the National Science Foundation for financial support of this work.

## Mechanism of Conformational Changes in Medium-Sized Rings. Nuclear Magnetic Resonance Studies of 1,1,4,4-Tetramethyl-6,7-benzocycloheptene

Ernest Grunwald<sup>1</sup> and Elton Price

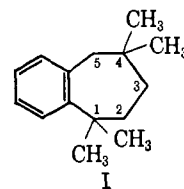
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The n.m.r. spectrum of racemic 1,1,4,4-tetramethyl-6,7-benzocycloheptene at low temperatures is that of a mixture of two racemic conformational isomers called *d,l-B* and *d,l-C*. Evidence is presented that the seven-membered ring is in the boat conformation in the *B*-isomer, and in the chair conformation in the *C*-isomer. The equilibrium constant,  $K = [C]/[B]$ , was obtained from the n.m.r. data and is represented by the equation,  $\log K = -0.026 + 69.2/T$ ;  $\Delta H^\circ = -317$  cal.;  $\Delta S^\circ = -0.12$  e.u. From observations of proton exchange, two separate conformational changes could be characterized. The first is isomerization without racemization,  $d-C \rightleftharpoons d-B$  and  $l-C \rightleftharpoons l-B$ . Kinetic results are:  $\log k_{C \rightarrow B} = 10.919 - 2134/T$ ;  $\Delta H^* = 9.3$  kcal.; and  $\Delta S^* = -10$  e.u. The second is racemization of the *C*-isomer,  $d-C \rightleftharpoons l-C$ . Kinetic results are:  $\log k_{d-C \rightarrow l-C} = 12.847 - 2870/T$ ;  $\Delta H^* = 12.6$  kcal.; and  $\Delta S^* = -1$  e.u. To rationalize these results, a notation has been developed that introduces appropriate plus or minus signs into the chemical structural formula. With this notation it becomes easy to represent all stable and metastable ring conformations and to characterize the conformational changes as simple wagging motions that invert specific carbon atoms of the ring.

Substances consisting of molecules with medium-sized rings often produce highly temperature-dependent n.m.r. spectra.<sup>2-4</sup> The spectra indicate that there is exchange of nuclei between different resonance frequencies, the rate of which increases with the temperature. In most such cases it is reasonable to assume that the exchange results from the interconversion of specific conformational isomers of the ring. This

theory has been applied successfully to relatively simple and symmetrical rings, such as cyclohexane<sup>2,5,6</sup> or cyclohexyl fluoride,<sup>4</sup> where the exchange is a simple, first-order process.

In this paper we discuss conformational changes in more complex rings of lower symmetry, where the exchange can involve several first-order processes in parallel. Our specific example is the hydrocarbon 1,1,4,4-tetramethyl-6,7-benzocycloheptene (I).<sup>7a</sup> Hart and co-workers<sup>7b</sup> had noted, as early as 1960, that the



proton magnetic resonance (p.m.r.) spectrum of I becomes strongly temperature dependent below 0°, showing the characteristics that are usually associated with exchange between different conformational species. When Hart described these observations to us, we decided to undertake a quantitative study. He helped us by supplying, first a purified, then a doubly purified, sample of I, and by thoughtful comment. Our p.m.r. measurements were made on 5–10 wt. % solutions of I in carbon disulfide.

Compound I is well suited for the study of intramolecular motions by the p.m.r. method because there are several nonequivalent kinds of protons to provide diagnostic chemical shifts, yet the spin-spin interactions are relatively simple. In particular, the four methyl groups in each molecule have character-

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