

androstane-3 $\alpha$ -17 $\beta$ -diol, 1.3 g., after recrystallization from methanol. The analytical sample had m.p. 229–231°,  $[\alpha]_D +16^\circ$ . *Anal.* Calcd. for C<sub>20</sub>H<sub>31</sub>NO<sub>2</sub>: C, 75.67; H, 9.84; N, 4.41. Found: C, 75.55; H, 10.00; N, 4.52.

The derived diacetate crystallized from methylene chloride-hexane as prisms, m.p. 215–216°,  $[\alpha]_D +8^\circ$ . *Anal.* Calcd.

for C<sub>24</sub>H<sub>35</sub>NO<sub>4</sub>: C, 71.79; H, 8.79; N, 3.49. Found: C, 71.92; H, 8.82; N, 3.60.

**Acknowledgments.**—Thanks are due to the Universidad Nacional de Mexico for time on the Varian A-60 spectrometer.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

## Conformations. IV. The Conformational Preference of the Phenyl Group in Cyclohexane

BY EDGAR W. GARBISCH, JR., AND DENNIS B. PATTERSON

RECEIVED JUNE 24, 1963

The thermodynamic parameters  $\Delta H = 3.61$  kcal./mole and  $\Delta S = 2.09$  e.u. have been determined for the equilibrium: *trans*-4-*tert*-butyl-1-phenylcyclohexane (III)  $\rightleftharpoons$  *cis*-4-*tert*-butyl-1-phenylcyclohexane (IV). Measurement of the n.m.r. spectrum of IV as a function of temperature demonstrated that an appreciable concentration of the boat form of IV is likely to be present at 25°. The conclusion that the phenyl group has a substantially greater preference for the equatorial position in cyclohexane than do the methyl, ethyl, and isopropyl groups is supported by the n.m.r. spectra of *cis*- and *trans*-4-methyl-1-phenylcyclohexanes.

Several estimations of the free energy difference between equatorial and axial phenyl groups in cyclohexane have been made recently. Eliel and Rerick have estimated this energy difference as roughly 2.6 kcal./mole (35°) by equilibrating *cis*- and *trans*-4-phenylcyclohexanol using a mixed lithium aluminum hydride-aluminum chloride reagent in the presence of the parent ketone.<sup>1</sup> More recently, Allinger and co-workers determined a value of 2.0 kcal./mole (25°) for this free energy difference by dipole moment measurement on 4-methyl-4-phenylcyclohexanone.<sup>2</sup> It appears from this latter result that the phenyl group enjoys about the same preference for the equatorial position in cyclohexane as do the methyl, ethyl, and isopropyl groups (*i.e.*, *ca.* 2 kcal./mole).<sup>3</sup> Since the two approaches used to estimate the conformational preference of the phenyl group in cyclohexane were somewhat indirect, it appeared desirable to determine this quantity by a more direct procedure. Consequently, we have investigated equilibrations between *trans*- and *cis*-4-*tert*-butyl-1-phenylcyclohexane (III and IV, respectively). In this paper, the results of these equilibrations together with results from other related work will be discussed.

### Results

A mixture of stereoisomeric 4-*tert*-butyl-1-phenylcyclohexanols, obtained through reaction between phenylmagnesium bromide and 4-*tert*-butylcyclohexanone, was cleanly separated by chromatography on silica gel to roughly equal amounts of the two stereoisomers. The carbinol eluted first was considered to be *trans*-4-*tert*-butyl-1-phenylcyclohexanol (I) and that eluted last was considered to be the *cis* stereoisomer II.<sup>4</sup> This assignment is substantiated by the n.m.r. spectra of I and II which are shown in Fig. 1 and 2.<sup>5</sup> The higher chemical shift of 8.35  $\tau$  for the hydroxyl proton of I as

compared with that of 8.09  $\tau$  for this proton of II suggests that II is slightly more hydrogen bonded than I.<sup>6</sup> The doublet at 7.48  $\tau$  for II appears to be a low field half of an AB spectrum with each component broadened through further unresolved coupling. The spectrum of the 2,2,6,6-tetradeuterio derivative (Fig. 2) shows that this doublet arises from the 2,6-protons of II and that the high field part of the AB spectrum, also the 2,6-protons, is centered at about 8.3  $\tau$ . The doublet at 7.48  $\tau$  is assigned to the equatorial protons on C<sub>2</sub> and C<sub>6</sub>. The width at half-height of 7.2 c.p.s. for each part of this doublet leads to a value of  $J$  (H<sub>2,6e</sub>, H<sub>3,5a</sub>)  $\cong$  3.6 c.p.s. which is consistent with known couplings of this type.<sup>7</sup> The coupling of approximately 11.5 c.p.s. between H<sub>2,6a</sub> and H<sub>2,6e</sub> is also comparable with known methylene couplings in cyclohexane.<sup>7</sup> The chemical shift difference between H<sub>2,6e</sub> and H<sub>2,6a</sub> of about 0.82 p.p.m. is larger by about 0.2–0.3 p.p.m. than the chemical shift difference between axial and equatorial protons of other cyclohexane derivatives.<sup>8</sup> This is consistent with the phenyl group of II being confined largely to the rotational conformation shown in Fig. 2.<sup>1,2</sup> In this conformation the equatorial and axial protons on C<sub>2</sub> and C<sub>6</sub> are deshielded by the diamagnetic field of the benzene ring, and it can be calculated that the C<sub>2,6</sub> equatorial protons will be deshielded about 0.25 p.p.m. more than the C<sub>2,6</sub> axial protons.<sup>9</sup> From the spectrum of I, nothing can be said about preferred rotational conformations of the phenyl group in this compound, although it is reasonable to expect that the phenyl group is confined for the most part to the conformation shown in Fig. 1.<sup>2</sup>

The hydrogenolysis of the hydroxyl groups of the stereoisomeric 3-phenylcholestanols using Raney nickel is known to proceed with a high degree (>90%) of retention of configuration providing conditions are employed which minimize competing equilibration of the hydrocarbon products.<sup>10</sup> Using these controlled conditions for hydrogenolysis, compound I was converted to *trans*-4-*tert*-butyl-1-phenylcyclohexane (III, m.p. 42°) and II was converted to the *cis* stereoisomer IV (m.p. 24.5°). The n.m.r. spectrum of III shows the benzylic proton absorption at 7.63  $\tau$  (partially masked). The spectrum of 1-phenylcyclohexane has

(6) J. A. Pople, W. G. Schneider, and H. S. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 15.

(7) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 1053 (1962); J. I. Musher, *J. Chem. Phys.*, **34**, 594 (1961); **37**, 2480 (1962).

(8) E. L. Eliel and M. H. Gianni, *Tetrahedron Letters*, 97 (1962).

(9) The method of calculation is that described in paper III, *J. Am. Chem. Soc.*, **85**, 927 (1963).

(10) E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 3363 (1962).

(1) E. L. Eliel and M. Rerick, *J. Am. Chem. Soc.*, **82**, 1367 (1960).

(2) N. L. Allinger, J. Allinger, M. A. DaRooge, and S. Greenberg, *J. Org. Chem.*, **27**, 4603 (1962).

(3) (a) N. L. Allinger and S. Hu, *ibid.*, **27**, 3417 (1962); (b) *J. Am. Chem. Soc.*, **84**, 370 (1962).

(4) Functions in the axial position of cyclohexane derivatives are known to be less strongly absorbed on silica gel or alumina than identical functions occupying the equatorial position. See J. A. Zderic, M. E. C. Rivera, and D. C. Limón, *J. Am. Chem. Soc.*, **82**, 6373 (1960); S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955); and H. E. Zimmerman, *ibid.*, **79**, 6554 (1957).

(5) The n.m.r. spectrum of the acetate of I shows sharp absorptions for the phenyl and acetate protons at 2.79 and 8.07  $\tau$ , respectively. 1-Acetoxy-1-phenylcyclohexane, in which the acetate group probably exists almost exclusively in the axial position, shows identical chemical shifts for these absorptions. The spectrum of the acetate of II, however, shows a broad (28 c.p.s. at 56.4 Mc.) multiplet for the phenyl protons and an acetate proton absorption at 8.24  $\tau$ .

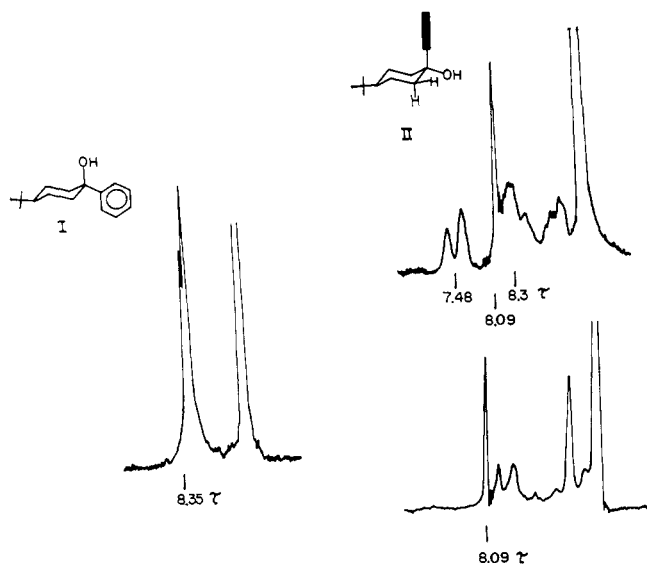


Figure 1.

Figure 2.

Fig. 1.—High field part of the n.m.r. spectrum of I (10% in  $\text{CDCl}_3$  and at 60 Mc.).

Fig. 2.—High field parts of the n.m.r. spectra of II (top) and of 2,2,6,6-tetradeuterio-II (bottom) (10% in  $\text{CDCl}_3$  and at 60 Mc.).

this absorption at  $7.62 \tau$  with  $W_H = 22.5$  c.p.s., and that of IV shows this absorption at  $7.02 \tau$  with  $W_H = 10.5$  c.p.s. 4-*tert*-Butyl-1-phenylcyclohexene was hydrogenated over palladium-on-carbon to a mixture of 45% of III and 55% of IV. This mixture was used for most of the equilibrations which were accomplished by potassium *tert*-butoxide–dimethyl sulfoxide in sealed tubes. Mixtures of III and IV were analyzed by g.l.c. Equilibrations were continued until steady state compositions of III and IV were reached. The results are summarized in Table I.

TABLE I

$T, ^\circ\text{C}^a$	RESULTS OF EQUILIBRATIONS				
	39	56.5	80	118	155.5
% IV <sup>b</sup>	0.86	1.09	1.72 (1.71) <sup>c</sup>	2.63 (2.60) <sup>d</sup>	4.01

<sup>a</sup>  $\pm 1^\circ$ . <sup>b</sup>  $\pm 0.10\%$ . <sup>c</sup> Pure I was used in refluxing ethanol containing Raney nickel (W-2). *trans*-4-*t*-Butyl-1-cyclohexylcyclohexane (1 to 3%) was generated during the equilibration; however, the percentages of IV remained constant. <sup>d</sup> Pure I was used with palladium (100%). 4-*t*-Butyl-1-phenylcyclohexene and *trans*-4-*t*-butyl-1-cyclohexylcyclohexane (*ca.* 3%) in a ratio of *ca.* 3 to 1 were generated during the equilibration. The percentage of IV appeared to decrease significantly (to 2.4%) and that of the by-products appeared to increase upon increasing equilibration time.

Using the data in Table I and the equation  $\ln K = -\Delta H/RT + \Delta S/R$ , values of  $\Delta H = 3.61 \pm 0.16$  kcal./mole and  $\Delta S = 2.09 \pm 0.45$  e.u. are obtained for the equilibrium  $\text{III} \rightleftharpoons \text{IV}$ . Equilibrations using Raney nickel in ethanol and palladium (neat) show that solvent effects are negligible (Table I).

### Discussion

The large positive value of 2.09 e.u. for the entropy change for equilibrium 1 was unexpected. It appears likely that this entropy change arises from positive entropy contributions from appreciable concentrations of the boat form IVb of *cis*-4-*tert*-butyl-1-phenylcyclohexane (IV). An unlikely alternative explanation is that the axial phenyl group of the chair form IVa of IV enjoys a greater degree of rotational freedom than does the equatorial phenyl group of III. Unless there exists a large deformation of the cyclohexane ring system of IVa, a higher potential barrier for phenyl ro-

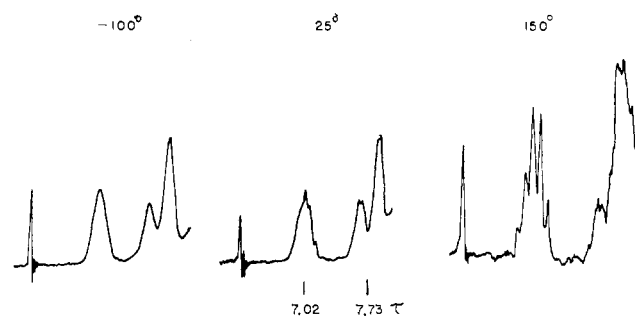
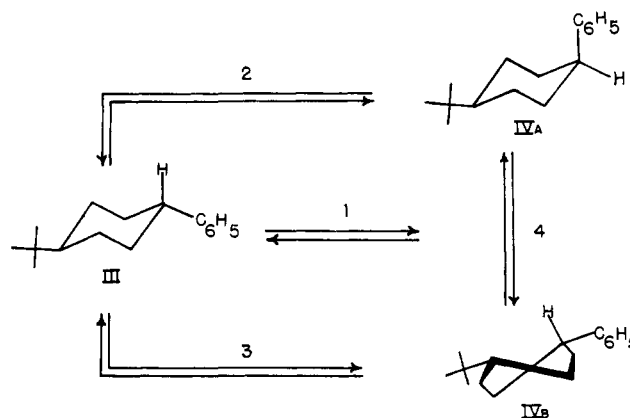


Fig. 3.—N.m.r. spectra (60 Mc.) of the benzylic proton ( $7.02 \tau$ ) and the equatorial protons on  $\text{C}_2$  and  $\text{C}_6$  ( $7.73 \tau$ ) of *cis*-4-*tert*-butyl-1-phenylcyclohexane (IV) at  $-100^\circ$ ,  $25^\circ$ , and  $150^\circ$  (in  $\text{CS}_2$ ). The sharp signal to the left of each spectrum is the TMS side band for  $-100^\circ$  and  $25^\circ$  and the *tert*-butyl side band for  $150^\circ$ .

tation in IVa would be expected than for phenyl rotation in III.



In order to determine whether or not a significant amount of IVb is in equilibrium with IVa, the n.m.r. spectrum of IV was determined over the temperature range of  $-100^\circ$  to  $150^\circ$ . The benzylic proton absorption of IV at  $-100^\circ$ ,  $25^\circ$ , and  $150^\circ$  is shown in Fig. 3. At  $25^\circ$ , this absorption is only partially resolved, and at  $-100^\circ$  a completely structureless absorption band is recorded. However, at  $150^\circ$ , this absorption is nicely resolved into an apparent quintet with spacings of 4.7 c.p.s. It is felt that these results offer positive evidence that there are significant quantities of two forms of IV (IVa and IVb) present over this temperature range. Otherwise, the benzylic proton absorption would not be expected to be affected by temperature change (the appearance of the n.m.r. absorption of the benzylic proton of 1-phenylcyclohexane did not change noticeably with changes in temperature). The gradual collapse of structure of this absorption as the temperature is reduced is indicative of a binary system under equilibration in which the frequency of equilibration is being gradually reduced so that the coupling constants representative of the two forms are becoming deaveraged (with concurrent line broadening) from the weighted average situation observed for the rapidly equilibrating system at  $150^\circ$ . Unfortunately, an estimation of the composition of IVa and IVb at equilibrium at the various temperatures does not seem possible. There should be little question, however, from the spectral changes observed, that an appreciable quantity of the boat form IVb ( $>10\%$ ) is likely to be in equilibrium with the chair form IVa at room temperature.

If the assumption is made that the phenyl groups of III and IV are rotationally restricted to approximately the same extent<sup>2</sup> and contribute insignificantly to the

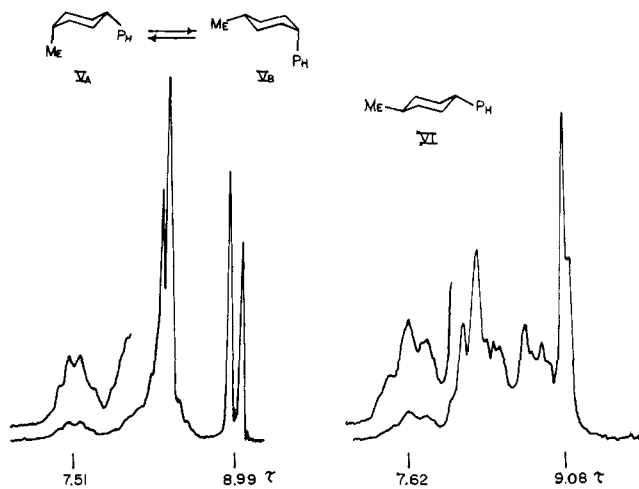


Figure 4.

Figure 5.

Fig. 4.—High field part of the n.m.r. spectrum (60 Mc.) of *cis*-4-methyl-1-phenylcyclohexane (V).

Fig. 5.—High field part of the n.m.r. spectrum (60 Mc.) of *trans*-4-methyl-1-phenylcyclohexane (VI).

entropy change observed for 1, an estimate of the thermodynamic parameters for the chair-chair equilibrium 2 can be made.<sup>11</sup> Using the thermodynamic parameters ( $\Delta G_{25^\circ} = 4.0$  kcal./mole,  $\Delta H = 5.5$  kcal./mole, and  $\Delta S = 4.9$  e.u.)<sup>12</sup> for the chair-boat equilibrium 3, and those found for 1, and taking the percentage of IVb to be 20, the thermodynamic parameters for the chair-chair equilibrium 2 may be calculated to be  $\Delta H = 3.1$  kcal./mole,  $\Delta S = 0.1$  e.u., and  $\Delta G_{25^\circ} = 3.1$  kcal./mole.<sup>13</sup> The calculated  $\Delta G_{25^\circ}$  of 0.9 kcal./mole for 4 (from 2 and 3) compares favorably with the value of 0.8 kcal./mole that is required for 20% of IVb.<sup>14</sup>

The value of 3.0 kcal./mole for  $\Delta G_{25^\circ}$  for equilibrium 1 is in fair agreement with the value of *ca.* 2.6 kcal./mole determined by Eliel and Rerick by a more indirect method; but is in poor agreement with the value of 2.0 kcal./mole reported more recently by Allinger and Hu.<sup>2</sup> These latter workers determined the conformational preference of the phenyl group by balancing it against the methyl group in 4-methyl-4-phenylcyclohexanone and measuring the dipole moment of this molecule, and their results suggest that the methyl and phenyl groups have approximately the same preference for the equatorial position. In order to establish further the difference between the conformational preference of the methyl and phenyl groups for the equatorial position, we have prepared *cis*- and *trans*-4-methyl-1-phenylcyclohexane (V and VI), respectively (by the method used for the preparation of III and IV), and compared the n.m.r. spectra of these stereoisomers, Fig. 4 and 5.<sup>15,16</sup> Two important features of these spectra are:

(11) If there are any shortcomings in this assumption they will stem probably from the not unlikely possibility that the phenyl group in III has a lower potential energy barrier toward rotation than that in IV. This would lead to a negative entropy contribution to the entropy change for 1 and require that a larger percentage of boat form IVb be present.

(12) W. S. Johnson, *et al.*, *J. Am. Chem. Soc.*, **83**, 606 (1961); **85**, 564 (1963); and N. L. Allinger and L. A. Freiberg, *ibid.*, **82**, 2393 (1960).

(13) The entropy of mixing 80% of IVa and 20% of IVb is 1.0 e.u.

(14) It is clear that if the percentage of IVb is appreciable at 25°, the  $\Delta H$  and  $\Delta S$  for 1 will not be constant over the temperature range investigated. The plot of  $\log K_1$  vs.  $1/T$ , however, showed no detectable curvature over 117 degrees. This linearity is predicted because  $\Delta G$  (and  $\log K$ ) measured for 1 matches closely with that calculated for 1 from 2 and 3 after the entropy of mixing IVa and IVb is included.

(15) As yet, we have been unable to separate mixtures of V and VI by g.l.c. and consequently have not investigated the equilibration of these stereoisomers. The structural assignments of V and VI were made after it was determined that V was being converted, largely to VI, upon equilibration<sup>10</sup> using Raney nickel.

(1) the differences between the methyl proton absorptions at *ca.* 8.99  $\tau$  for V and at *ca.* 9.08  $\tau$  for VI, and (2) the similarity between the band width at half-height ( $W_H$ ) of the benzylic proton absorption at *ca.* 7.51  $\tau$  for V and at *ca.* 7.62  $\tau$  for VI. The apparent nuclear spin coupling between *equatorial* methyl protons and the adjacent tertiary proton is known to be close to zero for cyclohexane derivatives, whereas that between *axial* methyl protons and the adjacent tertiary proton is generally  $>5$  c.p.s.<sup>17</sup> These splitting trends have been discussed.<sup>18</sup>

The large splitting of the methyl absorption of 6.9 c.p.s. for V as compared with that of about 3.5 c.p.s. for the equatorial methyl of VI suggests that the methyl group of V is confined primarily to the axial position (Va). A rough estimation of the mole fraction of Va in V may be obtained<sup>19</sup> from the  $W_H$  of the benzylic proton absorption of this molecule using the equation:  $N_{Va} = W^\circ - W^{Vb}/W^{Va} - W^{Vb}$ , where  $W^{Vb}$  is equal to the  $W_H$  of the benzylic proton absorption of IV (10.5 c.p.s.),  $W^{Va}$  is equal to the  $W_H$  of this absorption for III and VI (22.5 c.p.s.), and  $W^\circ$  is the  $W_H$  of this absorption for V (20.3 c.p.s.). The value of  $N_{Va}$  is then found to be approximately 0.82 at 25° and this value leads to a difference between the free energy preference of the phenyl and methyl groups for the equatorial position ( $\Delta G_{25^\circ}^{C_6H_5} - \Delta G_{25^\circ}^{Me}$ ) of about -0.9 kcal./mole. This compares favorably with the value of -1.1 kcal./mole predicted using the experimental values of  $\Delta G_{25^\circ}^{Me} = -1.9$  kcal./mole<sup>3a</sup> and  $\Delta G_{25^\circ}^{C_6H_5} = -3.0$  kcal./mole (from equilibrium 1).

## Experimental

*trans*- and *cis*-4-*tert*-Butyl-1-phenylcyclohexanols (I and II).—The Grignard reaction was carried out using 28 g. (0.2 mole) of 4-*tert*-butylcyclohexanol, 36 g. (0.24 mole) of bromobenzene, and 6.0 g. (0.2 mole) of magnesium. Five grams of the crude carbinol product was chromatographed on a 3 × 70 cm. silica gel column slurry packed in hexane. Successive elution with 3 l. of hexane and 2 l. of 2% ether-hexane solutions gave I, 1.91 g., melting at 116–118° after recrystallization from pentane (eluted with 10 to 30% ether-hexane), and II, 4.36 g. melting at 158–159° after digestion with pentane (eluted with 90% ether-hexane).

*trans*-4-*tert*-Butyl-1-phenylcyclohexanol (I) was recrystallized from pentane and melted at 117–118°.

*Anal.* Calcd. for  $C_{16}H_{24}O$ : C, 82.70; H, 10.41. Found: C, 82.78; H, 10.44.

*cis*-4-*tert*-Butyl-1-phenylcyclohexanol (II) was recrystallized from hexane and melted at 158–159°.

*Anal.* Calcd. for  $C_{16}H_{24}O$ : C, 82.70; H, 10.41. Found: C, 82.62; H, 10.45.

*trans*- and *cis*-4-*tert*-Butyl-1-phenyl-2,2,6,6-tetradeuteriocyclohexanols.—A mixture of 9.0 ml. of deuterium oxide (99.5%), 1.0 g. of 4-*tert*-butylcyclohexanone, and 150 mg. of anhydrous sodium carbonate was refluxed for 4.5 hr. Approximately 90% of the mixture was then distilled. The deuterated ketone was extracted with pentane, the extract dried with sodium sulfate, and the pentane then evaporated. The resulting 4-*tert*-butyl-2,2,6,6-tetradeuteriocyclohexanone was treated with phenylmagnesium bromide. The resulting mixture of stereoisomeric carbinols was separated by chromatography as described above.

*trans*- and *cis*-4-*tert*-Butyl-1-phenylcyclohexanes (III and IV).—A mixture of 100 mg. of I, 3.0 g. of wet Raney nickel (W-2),<sup>20</sup> and 4.0 ml. of ethanol was refluxed for 15 min. The ethanol

(16) These stereoisomers were prepared and their n.m.r. spectra measured after considering a suggestion to this effect by a referee.

(17) J. I. Musher, *Spectrochim. Acta*, **16**, 835 (1960).

(18) F. A. L. Anet, *Can. J. Chem.*, **39**, 2262 (1961). The larger splitting for an axial methyl group as compared with that for an equatorial methyl group in cyclohexane probably arises because in the former the chemical shift difference between the tertiary proton and the adjacent secondary protons is greater than this difference in the latter. When this chemical shift difference becomes close to or less than the methyl proton-tertiary proton coupling, virtual coupling between the methyl and secondary protons leads to a complex or structureless methyl proton absorption.

(19) E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 4249 (1962).

(20) R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 181.

was then decanted into a mixture of pentane and water and the nickel rinsed twice with pentane. The rinses and the aqueous mixture were combined and the pentane phase washed with water and dried over calcium chloride. The pentane was then evaporated and the residue crystallized from ethanol to give 70 mg. of *trans*-4-*tert*-butyl-1-phenylcyclohexane (III), m.p. 42°.

A more convenient route to III was achieved by shaking 6.0 g. of 4-*tert*-butyl-1-phenylcyclohexene,<sup>21</sup> 200 mg. of 10% palladium-on-carbon, and 25 ml. of acetic acid under 40 p.s.i. of hydrogen at room temperature until the reaction was complete. The resulting mixture of stereoisomeric 4-*tert*-butyl-1-phenylcyclohexanes consisted of 45% of III and 55% of IV (by g.l.c.). The hydrogenation mixture was transferred to a boiling flask and refluxed for 1.5 hr. The mixture was then filtered into 30 ml. of water and the solid collected by filtration. Recrystallization from ethanol gave 3.9 g. of III, m.p. 41–42°. Further recrystallization raised the melting point to 42°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>24</sub>: C, 88.82; H, 11.18. Found: C, 88.70; H, 10.94.

The preparation of IV was effected<sup>10</sup> by refluxing a mixture of 1.64 g. of II, 5.0 g. of Raney nickel,<sup>20</sup> 70 mg. of sodium methoxide, and 25 ml. of ethanol for 30 min. The mixture was filtered and the filtrate was cooled in methanol–Dry Ice. The material which crystallized was collected by filtration and recrystallized twice from methanol to give 0.75 g. of IV, m.p. 24.5°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>24</sub>: C, 88.82; H, 11.18. Found: 89.03; H, 11.18.

**General Equilibration Procedure** (Table I).—Equilibrations of III and IV were carried out by sealing in Pyrex tubes under nitrogen mixtures of 100 mg. of a mixture of 45% of III and 55% of IV, 40–50 mg. of potassium *tert*-butoxide,<sup>22</sup> and 1.0 g. dry dimethyl sulfoxide. The tubes were then placed in refluxing reagent grade acetone (for 56.5°), benzene (for 80°), acetic acid (for 118°), or bromobenzene (for 155.5°); or in a thermostated water bath at 39°. Tubes were withdrawn periodically and the contents poured into water. The hydrocarbon mixture was extracted with pentane and the pentane extract washed and dried over calcium chloride. The pentane was evaporated and the residue analyzed at 200° by g.l.c. using a 14-ft. column packed with QF-1 on firebrick. Equilibrations were continued until steady state compositions of III and IV were reached. The equilibrium data in Table I represent averages of a total of at least ten analyses (planimeter integration) of at least two mixtures at equilibrium at each temperature. At 155.5°, appreciable decomposition of dimethyl sulfoxide oc-

(21) E. W. Garbisch, Jr., *J. Org. Chem.*, **26**, 4165 (1961).

(22) A sample of this material was provided by the MSA Research Corporation, Callery, Pa.

curred during the 15 min. required to reach equilibrium. Extending the equilibration time to 30 min. did not effect the equilibrium composition. The chromatographic column was calibrated with known mixtures of pure (>99.9%) III and IV.

***cis*- and *trans*-4-Methyl-1-phenylcyclohexanes (V and VI).**—*trans*- and *cis*-4-methyl-1-phenylcyclohexanols were prepared through the reaction between phenylmagnesium bromide and 4-methylcyclohexanone. The resulting mixture (10 g.) of stereoisomeric carbinols was separated by chromatography as described for I and II. The *trans*-carbinol, 4.70 g. melting at 63.5° after recrystallization from pentane, was eluted first.

*Anal.* Calcd. for C<sub>13</sub>H<sub>18</sub>O: C, 82.06; H, 9.53. Found: C, 81.87; H, 9.53.

The *cis*-carbinol, 4.22 g. melting at 68–69.5° after recrystallization from pentane, was eluted last.

*Anal.* Calcd. for C<sub>13</sub>H<sub>18</sub>O: C, 82.06; H, 9.53. Found: C, 82.15; H, 9.63.

A mixture of 1.05 g. of *cis*-4-methyl-1-phenylcyclohexanol, 6.0 g. of Raney nickel,<sup>20</sup> and 20 ml. of ethanol was stirred at room temperature<sup>10</sup> for 20 min. The mixture was then worked up as described for the preparation of III using Ni (Raney), except the pentane extract was treated with 5 g. of silica gel to remove the unreacted carbinol. Distillation of the product gave 0.6 g. of V boiling at 104° (6 mm.), *n*<sub>D</sub><sup>20</sup> 1.5190.

*Anal.* Calcd. for C<sub>13</sub>H<sub>18</sub>: C, 89.59; H, 10.41. Found: C, 89.70; H, 10.60.

The preparation of VI was carried out in the same manner as for the *cis* stereoisomer V except that the reaction mixture was refluxed for 13 min. Distillation afforded 0.8 g. of VI boiling at 90° (3 mm.), *n*<sub>D</sub><sup>20</sup> 1.5123.

*Anal.* Calcd. for C<sub>13</sub>H<sub>18</sub>: C, 89.59; H, 10.41. Found: C, 89.26; H, 10.91.

Both the n.m.r. (Fig. 4 and 5) and the infrared spectra of V and VI (obtained by the above procedure) show that these products are probably greater than 90% configurationally homogeneous.

When the hydrogenolysis of *cis*-4-methyl-1-phenylcyclohexanol was carried out by refluxing for 15 min. a mixture of 300 mg. of the carbinol, 3.0 g. of Ni (Raney), and 10 ml. of ethanol, it was apparent from the infrared spectrum of the product that equilibration had progressed to a significant extent leading to a contamination of V by roughly 20–40% of VI.

**Acknowledgment.**—Support of this work from the Louis Block Fund of the University of Chicago and from the Petroleum Research Fund (Grant No. 1536) of the American Chemical Society is gratefully acknowledged.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

## Thietane Dioxide Derivatives *via* the Interaction of Sulfonyl Chlorides with Ketene Diethylacetal<sup>1</sup>

BY WILLIAM E. TRUCE AND JOHN R. NORELL

RECEIVED JUNE 3, 1963

The formation of nine new thietane 1,1-dioxide derivatives, from the interaction of sulfonyl chlorides (RCH<sub>2</sub>SO<sub>2</sub>Cl), containing a hydrogen atom  $\alpha$  to the sulfonyl group, with ketene diethylacetal in the presence of triethylamine, is described. Cyclization products are obtained when R is an acidifying group such as phenyl but not if R is an alkyl group. The possible intermediacy of sulfenes (RCHSO<sub>2</sub>) is discussed.

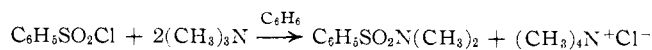
In aqueous media, as in the well-known Hinsberg test,<sup>2</sup> generally no reaction occurs between sulfonyl chlorides and tertiary amines. However, sulfonyl chlorides react with tertiary amines in nonprotic solvents to form unstable addition compounds,<sup>3</sup> or by the over-all disproportionation reaction<sup>4</sup>

(1) Abstracted from the Ph.D. Thesis of John R. Norell, Purdue University, 1963.

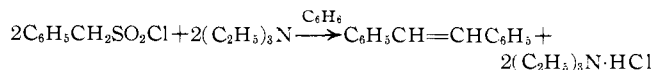
(2) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 103.

(3) (a) M. Kauffmann and D. Vorlander, *Ber.*, **43**, 2741 (1910); (b) G. L. Schwartz and W. M. Dehn, *J. Am. Chem. Soc.*, **39**, 2444 (1917); (c) L. Horner and H. Nickel, *Ann.*, **597**, 20 (1955); (d) H. Majda-Grabowska and K. Okon, *Roczniki Chem.*, **37**, 379 (1963), isolated pyridinium salts from benzenesulfonyl chlorides.

(4) L. W. Jones and H. F. Whalen, *J. Am. Chem. Soc.*, **47**, 1343 (1925).



If the sulfonyl chloride contains a hydrogen atom  $\alpha$  to the sulfonyl group, then a different reaction occurs. With benzylsulfonyl chloride in the presence of triethylamine in benzene, Wedekind and Schenk<sup>5</sup> found that *trans*-stilbene was formed in an unspecified yield.



As a reaction path these workers postulated initial abstraction of the proton by the base and loss of chlo-

(5) E. Wedekind and D. Schenk, *Ber.*, **44**, 198 (1911); recently J. F. King and T. Durst, *Tetrahedron Letters*, 585 (1963), obtained C<sub>6</sub>H<sub>5</sub>CClSO when the reaction was carried out in cyclohexane.