solvent mixture to afford 6.5 g (60%) of (diphenylethylidene)-diphenylphosphine, mp 114–116° (sealed capillary). The phosphine gave rise to a P$^{31}$ nmr signal (CHCl$_3$) at +24.2 ppm (relative to 85% H$_3$PO$_4$) and proton nmr signals (CDCl$_3$) centered (relative to TMS) at $\tau$ 2.6 (aromatic) and 3.1 (doublet, $J$ = 3 cps, vinyl) in the correct area ratios.

*Anal.* Calcd for C$_{26}$H$_{21}$P: C, 85.7; H, 5.7. Found: C, 85.4; H, 5.9.

The mother liquor from the above crystallization was chromatographed on alumina (Baker's neutral) under argon atmosphere. Benzene eluted an additional 1.5 g of semisolid material that was triturated with hexane and subsequently filtered to give 0.7 g of crude phosphine, mp 112–115°.

**Reactions of 2-Hydroxynonyltrimethylsilane. A. With Potassium Hydride.**—To a slurry of 5 g of 40% potassium hydride (freed of its protective coating by hexane washings) dispersed in 50 ml of tetrahydrofuran there was added 10.9 g (0.05 mole) of **9**. Within a few minutes the hydrogen evolution was complete (1.22 l.). Subsequent to stirring for 6 hr at room temperature, the reaction mixture was *carefully* hydrolyzed by pouring into chilled aqueous ammonium chloride. The ether extracts were concentrated and distilled to give 0.55 g of impure 1-nonene, bp 126–143°, and 4.03 g of pure product, bp 143–145°. The yield, based on 4.4 g, was 70%.

**B. With Triphenylmethylpotassium.**—To a red solution of triphenylmethylpotassium in 25 ml of 1,2-dimethoxyethane, prepared from 6.37 g (0.027 mole) of triphenylmethane, 3.4 g (0.05 mole) of isoprene, and 1 g (0.025 g-atom) of potassium by the method of House,[18] there was added 5.4 g (0.025 mole) of **9** which resulted in a decolorization of the solution. Subsequent to stirring for 1 hr, the reaction mixture was carefully hydrolyzed with aqueous ammonium chloride. Concentration of the ether extracts afforded a semisolid that was shown not to contain triphenylmethyltrimethylsilane by glpc analysis. A proton nmr spectrum of the mixture (in CDCl$_3$) revealed it to be composed of triphenylmethane, 1-nonene, an isoprene dimer,[18] and a small amount of hexamethyldisiloxane. No attempt was made to resolve the mixture.

**C. With Sulfuric Acid.**—To a solution of 8.68 g (0.04 mole) of **9** in 40 ml of THF there was added 3 drops of concentrated sulfuric acid. The formation of 1-nonene was slow at room temperature (reaction mixture analyzed by glpc), but became quite rapid upon heating to 65°. After 2 hr at the higher temperature, the reaction mixture was water washed and worked up in the usual manner to give 3.68 g (73%) of 1-nonene, bp 143–145°, and 0.9 g of a distillation residue which was composed of starting alcohol and small amounts of three unidentified compounds.

**Reaction of (2-Hydroxy-2,2-diphenylethyl)trimethylsilane with Sodium Hydride.**—A mixture of 2.7 g (0.01 mole) of the alcohol, 0.6 g (0.012 mole) of 50% sodium hydride, and 20 ml of tetrahydrofuran was heated at *ca.* 50° for 3 hr and then stirred overnight at room temperature. The reaction mixture was then carefully hydrolyzed with aqueous ammonium chloride and concentrated to give an oil that consisted of *ca.* 67% 1,1-diphenylethylene and 33% starting alcohol (infrared and proton nmr spectroscopy and gas phase chromatographic analyses).

**Registry No.**—**7**, 15096-08-9; **9**, 15096-09-0; diphenylethylidene methyl sulfide, 15096-10-3; (trimethylsilylmethyl)diphenylphosphine sulfide, 4451-97-2; (diphenylethylidene)diphenylphosphine sulfide, 15096-12-5; (diphenylethylidene)diphenylphosphine, 15096-13-6; 1-nonene, 124-11-8; **11**, 4451-96-1.

**Acknowledgments.**—The author is grateful to Dr. T. J. Logan for helpful discussions of this work and to Mr. T. E. Knorr for technical assistance.

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[18] H. O. House and V. Kramar, *J. Org. Chem.*, **27**, 4146 (1962).

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# Conformational Analysis. LIX. The Relative Stabilities of the *cis*- and *trans*-Dimethylcyclohexanes[1,2]

NORMAN L. ALLINGER, WILLIAM SZKRYBALO, AND FREDERIC A. VAN-CATLEDGE[3]

*Department of Chemistry, Wayne State University, Detroit, Michigan 48202*

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The equilibration of the *cis* and *trans* isomers of the 1,2-, 1,3-, and 1,4-dimethylcyclohexanes has been carried out using palladium catalyst at elevated temperatures. The thermodynamic quantities for the isomerization of the diequatorial to the equatorial-axial conformations are as follows: for the 1,2 isomer, $\Delta H^\circ = +1.72$ kcal/mole, $\Delta S^\circ = +0.79$ eu; for the 1,3 isomer $\Delta H^\circ = +1.81$ kcal/mole, $\Delta S^\circ = +1.16$; and for the 1,4 isomer, $\Delta H^\circ = +1.78$ kcal/mole, $\Delta S^\circ = +1.14$ eu. The experimental values for the 1,3 and 1,4 isomers are in agreement with both theoretical and thermochemical values. The values for the 1,2 isomer are somewhat anomalous with reference to the theoretical quantities but in agreement with the thermochemical data.

The conformational energies of the simple alkyl groups are of considerable importance in quantitative conformational analysis, and that of the methyl group is really the cornerstone of the whole subject.[4] From calorimetric studies on the isomers of the 1,3- and 1,4-dimethylcyclohexanes, the conformational enthalpy of the methyl group was determined to be 1.94 ± 0.2 kcal/mole in the gas phase,[5] and 1.66 ± 0.2 kcal/mole in the liquid phase.[6] By direct equilibration methods the value in the liquid phase was determined from these same compounds as 1.97 ± 0.3 kcal/mole.[7]

## Results and Discussion

Since we have obtained considerable experience in the equilibrium method during the last few years, it seemed that it would now be desirable to redetermine the value in this way with a higher accuracy. In the present work, the type of experiment and the measurements were the same in principle as previously, but great attention was paid to achieving accuracy. The equilibrations were carried out in sealed tubes with a small amount of palladium catalyst at elevated tem-

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[1] Paper LVIII: N. L. Allinger, J. A. Hirsch, and M. A. Miller, *Tetrahedron Letters*, 3729 (1967).

[2] This research was supported by grant PRF 2916 from the Petroleum Research Fund administered by the American Chemical Society.

[3] National Aeronautics and Space Administration Predoctoral trainee, 1964–1967.

[4] For a recent review, see E. L. Eliel and T. J. Brett, *J. Am. Chem. Soc.*, **87**, 5039 (1965). For a complete literature summary, see J. A Hirsch in "Topics in Stereochemistry," Vol. I, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, Inc., New York, N. Y., 1967, p 199.

[5] (a) C. W. Beckett, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2488 (1947); (b) K. S. Pitzer and C. W. Beckett, *ibid.*, **69**, 977 (1947).

[6] (a) E. J. Prossen, W. H. Johnson, and F. D. Rossini, *Bur. Std. J. Res.*, **39**, 49 (1947); (b) *ibid.*, **39**, 173 (1947).

[7] N L. Allinger and S. Hu, *J. Org. Chem.*, **27**, 3417 (1962).

peratures. Care was taken to fill the tubes sufficiently so that when they reached the equilibrium temperature the volume not occupied by the liquid was essentially zero. This avoids the problem of the presence of a gas phase in which the equilibrium constant differs from that in the liquid.[8]

Equilibrium was usually approached from both sides. The equilibrations were quenched, and the equilibrium mixture was analyzed by gas phase chromatography. The equilibrations were carried out at five to eight different temperatures over a range of 100°, and each sample was analyzed several times. From the slope and intercept of a plot of log $K$ against $1/T$, the enthalpies and entropies of isomerization were found. From a statistical treatment of the data, probable errors of about $\pm 0.1$ kcal/mole for the enthalpies of isomerization were calculated for each isomeric pair. The numerical values found for the enthalpies and entropies of isomerization are in agreement with the liquid phase thermochemical values, but the probable errors in the present enthalpy measurements are much smaller. The results are summarized in Table I.

TABLE I

DIFFERENCES IN THERMODYNAMIC PROPERTIES BETWEEN *cis*- AND *trans*-DIMETHYLCYCLOHEXANES[a]

| | Thermochemical (25°)[b,c] | | Present work (260°)[d] | |
|---|---|---|---|---|
| Isomer | $\Delta H°$ | $\Delta S°$ | $\Delta H°$ | $\Delta S°$ |
| 1,2 | $1.54 \pm 0.22$ | 0.72 | $1.49 \pm 0.03$ | $0.20 \pm 0.06$ |
| 1,3 | $1.72 \pm 0.22$ | 1.24 | $1.80 \pm 0.05$ | $1.13 \pm 0.09$ |
| 1,4 | $1.62 \pm 0.22$ | 1.19 | $1.74 \pm 0.06$ | $1.03 \pm 0.12$ |

[a] The enthalpy values are in kcal/mole and entropy values in eu. All values are for the liquid phase. The differences are always in the direction diequatorial ⇌ equatorial–axial. [b] The entropy values are taken from the thermochemical data of Huffman.[c] Our estimate of the probable experimental error in that work is $\pm 0.3$ eu. [c] H. M. Huffman, S. S. Todd, and G. O. Oliver, *J. Am. Chem. Soc.*, **71**, 584 (1949). [d] The errors listed are the standard deviations in the least-squares values. We estimate our experimental error to be $\pm 0.1$ kcal/mole for $\Delta H°$ and $\pm 0.2$ eu for $\Delta S°$.

Of more general interest than the isomerization equilibria of the dimethylcycloalkanes themselves (Table I) is the equilibrium between the diequatorial (ee) and equatorial–axial (ea) conformations. Since the equilibrations were carried out at rather high temperatures, diaxial and boat conformations which are negligible at room temperature may alter significantly the observed equilibrium constant ($K_{\text{obsd}}$) from that in which we are really interested ($K_{\text{eq}}$). Thus while

$$K_{\text{eq}} = \frac{(\text{ea})}{(\text{ee})}$$

$$K_{\text{obsd}} = \frac{(\text{ea}) + (\text{boats})}{(\text{ee}) + (\text{aa}) + (\text{boats})}$$

In order to determine $K_{\text{eq}}$, it was necessary to calculate the concentrations of the extraneous conformers present. To do this, the enthalpy and entropy of each such conformer, relative to the stable conformer, must be known. Since these corrections prove to be fairly small, these quantities can be adequately calculated by rather rough approximations.

For the diaxial isomers, the 1,2, 1,3, and 1,4 were assigned, respectively, the following enthalpies relative to the diequatorial isomers: 2.7,[4] 5.5,[9] and 3.6[4] kcal/mole. The entropies of the diaxial conformers are taken to be the same as those of their diequatorial conformers.

It is a little more complicated to correct for the boat forms present. The enthalpy of the unsubstituted boat was taken as 5.02 kcal/mole at the pseudo-rotational minimum,[10] and 6.75 kcal/mole at the pseudorotational maximum. The contribution by each methyl group to the total energy of a particular boat was then calculated by considering that substitution of a hydrogen by a methyl converted a propane to a butane unit and by using the energy function for the rotation of butane as given by Eliel[11] (Table II) and a simple threefold cosine function for propane ($V_0$ = 3.3 kcal/mole). The energy of the boat form was calculated for each isomer for values of the pseudo-rotational parameter (Θ) from 0 to 360° in 30° increments. (Details are given in the Appendix.)

TABLE II

ENTHALPY CONTENT OF CONFORMERS OF *n*-BUTANE

| Dihedral angle, $\omega$ ($C_1C_2C_3C_4$) | $\Delta H°$, kcal/mole |
|---|---|
| 0 | 5.25 |
| 30 | 3.08 |
| 60 | 0.90 |
| 90 | 2.20 |
| 120 | 3.50 |
| 150 | 1.75 |
| 180 | 0.0 |

It was found that there were minima in the pseudorotational curve at 30, 90°, etc., and each of those which had a calculated enthalpy of less than 8 kcal/mole (relative to the corresponding chair) was considered as a separate conformation contributing to the conformational mixture. The symmetry properties of each conformer were considered separately, and their effect on the entropy was taken into account. With these corrections, $K_{\text{eq}}$ was then calculated for each experimental point, and then the thermodynamic properties for that equilibrium were calculated from the points (ln $K$ *vs.* $1/T$), and the results are given in Table III.

The enthalpy values obtained in this work are appreciably more accurate and slightly lower than those obtained previously by the same method.[7] They are also in agreement with the thermochemical values to within the combined experimental errors, but are believed to be of greater accuracy.

There are theoretical reasons for expecting the conformational enthalpy of the axial methyl to be greater in the 1,3 than in the 1,4 isomer by 0.1–0.2 kcal/mole,[12] and such has been observed in other systems.[4] The probable errors in the enthalpy changes found in the present work, though relatively small, are still large enough to obscure this difference. For the 1,2 isomers, first-order theory predicts for the axial–equa-

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(8) N. L. Allinger and J. L. Coke, *J. Am. Chem. Soc.*, **81**, 4080 (1959).

(9) N. L. Allinger and M. A. Miller, *ibid.*, **83**, 2145 (1961).

(10) P. Hazebroek and L. J. Osterhoff, *Discussions Faraday Soc.*, **10**, 87 (1951).

(11) (a) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 126; (b) see Table I, footnote *c*.

(12) N. L. Allinger, M. A. Miller, F. A. Van-Catledge, and J. A. Hirsch, *J. Am. Chem. Soc.*, **89**, 4345 (1967).

TABLE III

THERMODYNAMIC DATA FOR THE EQUILIBRIUM DIEQUATORIAL $\rightleftharpoons$ AXIAL–EQUATORIAL DIMETHYLCYCLOHEXANE[a]

| | Theoretical[b] | | Thermochemical[c] (298°K) | | Present work[d] | | |
|---|---|---|---|---|---|---|---|
| Isomer | $\Delta H°$ | $\Delta S°$ | $\Delta H°$ | $\Delta S°$ | $\Delta H^\circ_{540}$ | $\Delta S^\circ_{540}$ | $\Delta G^\circ_{298}$ |
| 1,2 | 1.80 | 1.38 | 1.54 ± 0.22 | 0.49 | 1.72 ± 0.1 | 0.79 ± 0.2 | 1.46 |
| 1,3 | 1.80 | 1.38 | 1.72 ± 0.22 | 0.87 | 1.81 ± 0.1 | 1.16 ± 0.2 | 1.47 |
| 1,4 | 1.80 | 1.38 | 1.62 ± 0.22 | 0.72 | 1.78 ± 0.1 | 1.14 ± 0.2 | 1.43 |

[a] The enthalpy and free energy values are in kcal/mole, the entropy values in eu (for the liquid phase). [b] From ref 11a. [c] The enthalpy values are from ref 6. The entropy values are taken from thermochemical studies by Huffman, *et al.*[11b] Our estimate of that experimental error is ±0.3 eu. [d] The probable errors listed are our estimates. The standard deviations of the least-squares values for the 1,2, 1,3, and 1,4 isomers in $\Delta H°$ are ±0.03, ±0.03, ±0.07, respectively, and in $\Delta S°$ are ±0.06, ±0.05, and ±0.13.

torial conformer a conformational enthalpy of 1.8 kcal/mole from two additional *gauche* interactions, and a conformational entropy of 1.38 eu, resulting from $\sigma = 1$ (compared with $\sigma = 2$ for the diequatorial conformer). The thermochemical values indicate both the enthalpy and entropy are somewhat smaller than the first-order theory predicts, but in a compensating way so that the conformational free energy is as calculated. These results have been attributed to a cogwheeling of the methyl groups to a greater extent in the ea isomer than in the ee, which decreases both the enthalpy and entropy.[5] Why this should be true is unclear, but the present work supports the thermochemical values.

## Experimental Section

**1,3-Dimethylcyclohexane.**—This compound was obtained by hydrogenation of *m*-xylene.[7] Gas phase chromatography showed that the product was 77% *cis*-1,3-dimethylcyclohexane. Five samples of this mixture were used in the equilibration experiments. Percentage compositions are given in Table IV.

*trans*-Enriched 1,3-dimethylcyclohexane was obtained by distilling the above mixture through a 3-ft Podbielniak column. When the temperature rose to 124°, the distillation was stopped and the residue analyzed by gas phase chromatography. The analysis showed that >30% of the *trans* isomer was present (lit.[13] *cis* bp 120.1°, *trans* bp 124.4°).

TABLE IV

PERCENTAGE COMPOSITION OF EQUILIBRATED DIMETHYLCYCLOHEXANES

| Temp, °K | % major isomer | Time, hr |
|---|---|---|
| | 1,2 Isomer | |
| 482.1[a] | 81.20 | 168 |
| 496.1 | 80.31 | 168 |
| 511.4 | 79.72 | 120 |
| 528.6 | 78.75 | 96 |
| 543.7 | 78.27 | 96 |
| 559.0 | 77.68 | 120 |
| 571.0 | 77.02 | 72 |
| 585.4 | 76.56 | 72 |
| | 1,3 Isomer | |
| 496.2[b] | 77.75 | 200 |
| 527.7 | 75.68 | 198 |
| 543.2 | 74.99 | 103 |
| 552.7 | 74.38 | 104 |
| 566.3 | 73.89 | 48 |
| 583.2 | 72.54 | 24 |
| 598.5[b] | 71.83 | 9 |
| | 1,4 Isomer[c] | |
| 483.2 | 78.45 | 200 |
| 512.7 | 76.74 | 180 |
| 529.0 | 75.96 | 160 |
| 548.8 | 74.36 | 100 |
| 582.2 | 72.90 | 24 |

[a] The analysis was obtained from one sample starting at 83% *cis*. All others were obtained starting at both 83% *cis* and 75% *trans*. [b] These two analyses were obtained starting at 30% *trans*. The remaining samples contained less than 22% *trans*. [c] Each analysis is based on three samples, one of which had been enriched in the *trans* isomer.

**1,4-Dimethylcyclohexane.**—The compound was prepared as previously described.[7] Gas phase chromatography showed that the *cis* isomer was present to the extent of 78%.

A *cis*-enriched mixture was prepared as described above and was used in all equilibrations (lit.[13] *cis* bp 124.3°, *trans* bp 119.4°).

**1,2-Dimethylcyclohexane.**—The compound was prepared by a method strictly analogous to the one previously described.[7] The reduction product was distilled through a 2-ft spinning-band column and collected over the range 122–127°, $n^{25}\text{D}$ 1.4315 (lit.[13] *cis*, $n^{25}\text{D}$ 1.4336, bp 129.7°; *trans*, $n^{25}\text{D}$ 1.4247, bp 123.4°). Gas phase chromatography showed the mixture to be >83% *cis*.

Preparation of a *trans*-rich mixture was carried out by placing 15 g of the reduction product and 1.5 g of 10% palladium on carbon in a sealed tube and equilibrating at 523°K for 48 hr. The resulting mixture was shown to contain more than 75% of the *trans* isomer by gas phase chromatography.

**Equilibrations.**—Samples of *ca.* 100 mg of dimethylcyclohexane and 20 mg of 10% palladium-on-carbon catalyst were sealed in 6 mm × 1 in. pyrex glass tubes leaving only enough air space to allow for expansion of the liquid ($^2/_3$ to $^3/_4$ full). The tubes were placed in a constant-temperature furnace for a suitable length of time (predetermined by preliminary experiments) following the general procedure which was outlined earlier.[7]

Equilibrium concentrations of the *cis*- and *trans*-dimethylcyclohexanes were determined by gas phase chromatography on an instrument equipped with a Disc chart integrator. The column used was 6 mm × 12 ft filled with 20% $\gamma$-methyl-$\gamma$-nitropimelonitrile on 48–60 mesh firebrick with a helium flow rate of *ca.* 25 cc/min.

**Determination of $K_{\text{obsd}}$.**—The relative areas of the *cis* and *trans* peaks were determined by use of the disk integrator in the case of the 1,4 isomers; the values for the 1,2 and 1,3 isomers were determined by the half-band-width technique. Half-band-width treatment of the curves, obtained from the analysis of the 1,4 compound, yielded percentage values whose average deviation was ±0.5% from those obtained from the disk integration. Samples of known composition were analyzed, and it was found that the areas under the peaks corresponded to the amount of material present to within experimental error. The only side products detected were the aromatic hydrocarbons, which were easily separated and did not interfere. Olefinic products were not anticipated, as they would be expected to disproportionate. The nmr spectra were checked for the 1,2 isomers, and no allyl or vinyl absorption could be detected.

## Appendix[14]

The calculations required to obtain $K_{\text{eq}}$ from $K_{\text{obsd}}$ for the 1,2 isomer are outlined as follows.

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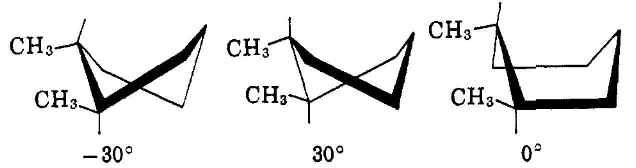
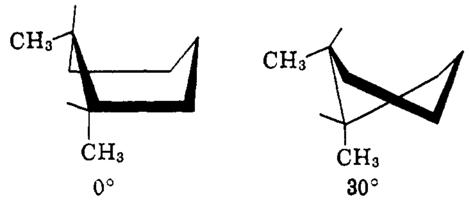
(13) F. D. Rossini, "Selected values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

(14) The notation used is as follows: $\Delta G_{cis}$ means $\Delta G$ for the reaction chair $\rightleftharpoons$ boat for the *cis* isomer; ba and bb designate boat a and boat b, respectively; $H^\circ_c$ is the enthalpy of the chair mixture; $K_t$, $K_c$ are the equilibrium constants for the reaction chair $\rightleftharpoons$ boats for the *trans* and *cis* isomers, respectively; ee, aa, and ae are diequatorial, diaxial, and axial–equatorial respectively.

1,2-*trans*



1,2-*cis*



1,2-*cis*

Chair: $H^\circ = 2.70$ kcal/mole, $\sigma = 1$; *dl*
Boat: $H^\circ = 8.89$ kcal/mole, $\sigma = 1$; *dl*($\Theta = 30°$)

For chair ⇄ boat:

$$\Delta G^\circ_{\mathrm{cb}} = 6.19 \text{ kcal/mole},\ K_{\mathrm{cb}} = \exp(-6.19/\mathrm{RT})$$
$$N_{\mathrm{ea}} = 1/(1 + K_{\mathrm{cb}})$$

1,2-*trans*

Chairs: ee, $H^\circ = 0.9$ kcal/mole, $\sigma = 2$; *dl*
aa, $H^\circ = 3.6$ kcal/mole, $\sigma = 2$; *dl*

Boats: ba, $H^\circ = 6.57$ kcal/mole, $\sigma = 2$; *dl* ($\Theta = 30°$)
bb, $H^\circ = 8.66$ kcal/mole, $\sigma = 1$; *dl* ($\Theta = -30°$)

For chairs:

$$K = \exp(-2700/\mathrm{RT})$$
$$N_{\mathrm{ee}} = 1/(1 + K) \qquad N_{\mathrm{aa}} = 1 - N_{\mathrm{ee}}$$
$$H^\circ_{\mathrm{c}} = \Sigma N_{\mathrm{i}} H^\circ_{\mathrm{i}}$$
$$S_{\mathrm{c}} = -R\,\Sigma(N_{\mathrm{i}} \ln N_{\mathrm{i}})$$

For boats:

$$K = 2 \times \exp(-2090/\mathrm{RT})$$
$$N_{\mathrm{ba}} = 1/(1 + K) \qquad N_{\mathrm{bb}} = 1 - N_{\mathrm{ba}}$$

$H_{\mathrm{b}}$ and $S_{\mathrm{b}}$ are calculated as for chairs

For chair ⇄ boat:

$$\Delta G^\circ = H^\circ_{\mathrm{boat}} - H^\circ_{\mathrm{chair}} - T(S^\circ_{\mathrm{boat}} - S^\circ_{\mathrm{chair}})$$
$$K_{\mathrm{t}} = \frac{(\text{boats})}{(\text{chairs})} = \exp(-\Delta G^\circ/\mathrm{RT})$$
$$N_{\mathrm{chairs}} = 1/(1 + K_{\mathrm{t}})$$

The mole fraction of diequatorial chair ($N_{\mathrm{ee}}'$) in the mixture then is

$$N_{\mathrm{ee}}' = N_{\mathrm{ee}}' N_{\mathrm{chairs}}$$

Then for axial–equatorial ⇄ diequatorial

$$K_{\mathrm{eq}} = \frac{N_{\mathrm{ee}}'}{N_{\mathrm{ea}}} K_{\mathrm{obsd}}$$

Similar calculations were carried out for the 1,3 and 1,4 isomers.

Enthalpy and entropy values were obtained by a least-squares fit of ln $K$ *vs.* $1/T$. All correlation coefficients were $\geq 0.996$.

**Registry No.**—*cis*-1,2-Dimethylcyclohexane, 2207-01-4; *trans*-1,2-dimethylcyclohexane, 6876-23-9; *cis*-1,3-dimethylcyclohexane, 638-04-0; *trans*-1,3-dimethylcyclohexane, 2207-03-6; *cis*-1,4-dimethylcyclohexane, 624-29-3; *trans*-1,4-dimethylcyclohexane, 2207-04-7.

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# Directional Effects of Substituents in the Ozonolysis of Naphthalenes. Synthesis of *o*-Phthalaldehydes

JAMES J. PAPPAS, WILLIAM P. KEAVENEY, MELVIN BERGER, AND RAYMOND V. RUSH

*Central Research Laboratories, Interchemical Corporation, Clifton, New Jersey 07015*

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A number of substituted naphthalenes have been ozonized and the selectivity of ozone attack determined quantitatively by conversion to the phthalic acids. Naphthalenes with electron-withdrawing substituents give predominance of attack on the ring not containing these substituents. Triphenylphosphine reduces these ozonolyses mixtures at low temperatures and results in good yields of the isolated *o*-phthalaldehydes. The cyclic peroxides that can be isolated from various naphthalenes are also reduced with triphenylphosphine to the corresponding *o*-phthalaldehydes.

Numerous investigations into the ozonolysis of naphthalene[1] and substituted naphthalenes[2] have been reported. These systems absorb 2 moles of ozone and lead to various *ortho*-disubstituted derivatives of benzene depending on reaction conditions and method of work-up. Further attack on the benzene ring is found to be extremely sluggish and for practical purposes may be considered to be negligible relative to the uptake of the first 2 mole equiv of ozone.

The majority of studies have been concerned with substituted naphthalenes in which the substituents are electron releasing. These are attacked by ozone predominantly, and in some cases exclusively, in the substituted ring. The net result is that one generally isolates the same products from these naphthalene derivatives that can be obtained from the ozonolysis of naphthalene itself. On the other hand, little is recorded[3] in the literature on the ozonolysis of naphthalene derivatives containing electron-attracting substituents, which would be expected to give greater attack of ozone on the unsubstituted ring. One purpose of this work was to determine quantitatively the selectivity of ozone attack on a variety of naphthalenes with electron-withdrawing substituents. Since a high selectivity is desirable in order to avoid mixtures of products, this information would be of value in choosing appropriate naphthalene systems for conversion to a number of difficultly available benzene derivatives. Of particular interest was the synthesis of *o*-phthalaldehydes and certain phthalic acids.

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[1] (a) P. S. Bailey, S. S. Bath, F. Dobinson, F. J. Garcia-Sharp, and C. D. Johnson, *J. Org. Chem.*, **29**, 697 (1964); (b) C. D. Johnson and P. S. Bailey, *ibid.*, **29**, 703 (1964).

[2] P. S. Bailey, *Chem. Rev.*, **58**, 959 (1958). Reference 1a has a review of more recent work.

[3] Most simple monosubstituted naphthalenes with electron-withdrawing substituents have never been treated with ozone.