Either of these intermediates can then break up to give two molecules of the product area (or one molecule of the urea and one molecule each of phenyl isocyanate and aniline). Whether series A or series B is the more likely is difficult to predict; there is no direct experimental evidence to support one over the other.

Further studies are indicated in the direction of obtaining such direct evidence of the existence of these complexes. Perhaps spectroscopic studies of the system during the course of the reaction would show their presence. More extensive kinetic studies in the region of low concentrations of both reactants and at even higher excess concentrations of aniline than those studied here are called for.

Acknowledgment. The authors are indebted to Dr. Costas Issidorides for helpful discussions concerning the mechanism of the reaction, and to Messrs. Abdu Bardawil and Ismat Abu-Isa, who worked on some of the preliminary experiments and contributed to the development of techniques. This work was supported by grants from the Petroleum Research Fund (PRF #421-A) and from Sigma Xi-RESA. Funds for the purchase of equipment and supplies were available from the A.U.B.-Rockefeller Foundation Research Fund.

BEIRUT, LEBANON

Notes A department for short papers of immediate interest.

1,3-Diaxial Methyl Hydroxyl Interaction

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The 1,3-diaxial methyl hydroxyl interaction has been estimated to be 2.15 kcal./mole by the application of Equation 1 to the rate of acetylation of 3,3-dimethylcyclohexanol with acetic anhydride in pyridine.[1,2] In this equation K is the conformational equilibrium constant shown in Fig. 1, k is the specific rate constant for 3,3-dimethylcyclohexanol, k_e is the specific rate constant for *trans*-

$$K = (k_a - k)/(k - k_e) \qquad (1)$$

4-*t*-butylcyclohexanol, assumed to be identical with that of conformation E in Fig. 1, and k_a is taken as zero, the acetylation rate of conformation A in Fig. 1 being assumed negligible.

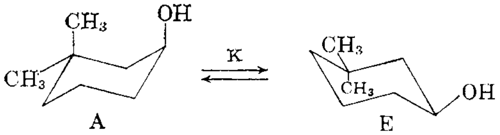
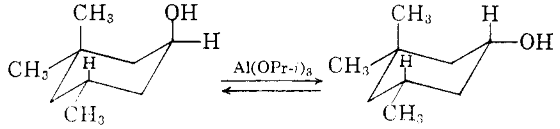


Figure 1

The present communication reports an independent determination of the 1,3-diaxial methyl hydroxyl interaction by means of the chemical equilibration of *cis*- and *trans*-3,3,5-trimethylcyclohexanol (Fig. 2).



trans (A) *cis* (E)

Figure 2

trans-3,3,5-Trimethylcyclohexanol[3] was prepared by the hydrogenation of isophorone or of 3,3,5-trimethylcyclohexanone (dihydroisophorone) in glacial acetic acid at room temperature over a platinum oxide catalyst. The catalytic reduction of dihydroisophorone under these conditions gave a mixture containing approximately 95% of the *trans* isomer. The *cis*-alcohol was prepared from commercial 3,3,5-trimethylcyclohexanol by purification through the acid phthalate.[4]

Equilibration of the 3,3,5-trimethylcyclohexanols was accomplished by boiling either isomer with aluminum isopropoxide and a small amount of acetone in anhydrous isopropyl alcohol. The equilibrium composition at 84.5° was determined by gas chromatography to be 94% *cis* and 6% *trans* starting from either isomer. The equilibrium constant for the equilibrium shown in Fig. 2 is 15.7 at 357.7°K., corresponding to a $\Delta F°$ of -1.96 kcal./mole. In isomer A (Fig. 2) the following 1,3-diaxial interactions are present: CH_3—OH, CH_3—H, and OH—H. The concentration of the conforma-

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(1) E. L. Eliel, *J. Chem. Ed.*, **37**, 126 (1960).

(2) For the derivation of an alternative form of equation (1) see S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).

(3)(a) E. G. Peppiatt and R. J. Wicker, *J. Chem. Soc.*, 3122 (1955); (b) I. Alkonyi, *Chem. Ber.*, **92**, 1130 (1959).

(4) R. S. Ro, unpublished results.

tion of isomer *A* (Fig. 2) in which the hydroxyl group is equatorial is negligible due to the relatively large dimethyl interaction energy.[5] In isomer *E* (Fig. 2) there are two CH_3—H interactions. Using 0.9 kcal./mole for CH_3—H,[6] 0.48 kcal./mole for OH—H,[7] and *X* kcal./mole of CH_3—OH, and assuming the additivity of such interaction energies,[1] *X* can be computed from the relation $1.38 + X - 1.8 = 1.96$; hence $X = 2.4$ kcal./mole. This value is in good agreement with that determined from kinetic data (*vide supra*), especially in view of the difference of solvents involved. Thus, conformation *E* in Fig. 2 would be particularly favored in hydrogen-bonding solvents such as isopropyl alcohol, in which the ring hydroxyl group can act as the hydrogen acceptor.[1] The value obtained for the diaxial methyl hydroxyl interaction lies between the value of 3.7 kcal./mole for the 1,3-diaxial dimethyl interaction obtained from the equilibration of *cis*- and *trans*-1,1,3,5-tetramethylcyclohexane,[5] and 1.9 kcal./mole for the 1,3-diaxial dihydroxyl interaction.[8]

Our value for the free energy difference between *cis*- and *trans*-3,3,5-trimethylcyclohexanol is incompatible with the report[3a] that the equilibrium (established over a nickel catalyst) between the two alcohols at 130–140° corresponds to only 70–73% *cis* isomer, unless the entropy of the *trans* isomer exceeds that of the *cis* by 23.5 entropy units. This seems highly unlikely, especially in view of the finding[3b] that sodium at 200° converts the *trans* isomer very largely to the *cis*. More likely the 70–73% figure is in error, being based on the rather dubious relationship between melting point and composition. This relationship is easily disturbed when the mixture examined is not strictly binary.

The composition of the product (79% *trans*- and 21% *cis*-3,3,5-trimethylcyclohexanol) reported[9] for the isomerization of the *trans*-alcohol with aluminum isopropoxide in isopropyl alcohol clearly is far from the equilibrium composition.

EXPERIMENTAL

Dihydroisophorone. Concentrated sulfuric acid (110 g., 1.12 moles) was added dropwise over 1.25 hr. to a well stirred mixture of 3,3,5-trimethylcyclohexanol (Eastman, 94 g., 0.66 mole) and sodium dichromate (73 g., 0.24 mole) in 600 ml. of water. The rate of addition was controlled in order to maintain the reaction temperature at 55–60°. After the addition, the reaction mixture was stirred for 2.5 hr. and extracted with ether. The ether extract was washed with saturated sodium bicarbonate solution and with water, dried over anhydrous magnesium sulfate, and concentrated. Distillation of the residue through a helix-packed column gave 75.2 g. (81%) of dihydroisophorone, b.p. 73–74° (14 mm.), n_D^{20} 1.4461.

trans-3,3,5-Trimethylcyclohexanol. Dihydroisophorone (14.0 g., 0.1 mole, n_D^{20} 1.4461) dissolved in 50 ml. of glacial acetic acid, was hydrogenated over 0.5 g. of platinum dioxide catalyst at room temperature and an initial pressure of about 50 p.s.i. Hydrogen uptake was rapid, the reaction being completed in 35 min. The catalyst was filtered and the filtrate poured into water. The product was recovered by ether extraction, washing of the ether extract with sodium bicarbonate and salt solutions, drying over magnesium sulfate, and by distillation of the ether. The white needles obtained (11.8 g., 83% yield) were recrystallized twice from petroleum ether (b.p. 30–60°). Most of the crystals melted rapidly at 58.5° (Kofler hot stage) but a small quantity of material seemed to retain some crystalline structure at higher temperatures, exceeding 64°. (Lit. reports m.p. 57.3°[3a]; 56°[3b].)

A gas chromatogram of the twice-recrystallized *trans*-alcohol on a Tide column, column temperature 156°, helium flow rate 53 ml./min. showed no trace of *cis*-alcohol.

Contrary to a previous report,[3b] Drs. R. Ro and R. P. Gerber in our laboratories were able to obtain the *p*-toluenesulfonate of the *trans*-alcohol; m.p. 66–67.5° after two recrystallizations from petroleum ether (b.p. 30–60°).

Anal. Calcd. for $C_{16}H_{24}O_3S$: C, 64.84; H, 8.16. Found: C, 64.67; H, 8.37.

The crude product of hydrogenation of dihydroisophorone was shown by gas chromatography to be an alcohol mixture containing approximately 95% of the *trans* isomer.

cis-3,3,5-Trimethylcyclohexanol.[4] Commercial 3,3,5-trimethylcyclohexanol (Eastman, 56 g., 0.4 mole) was converted to the acid phthalate with 60 g. of phthalic anhydride in 200 ml. of pyridine. The crude solid residue (107 g., 92%) was recrystallized from petroleum ether–ethyl acetate yielding 70 g. of the *cis*-acid phthalate, m.p. 127–5–129° (lit. m.p. 129°[3a,b]).

A mixture of the acid phthalate and 200 ml. of 10% sodium hydroxide solution was steam distilled. The distillate was extracted with ether, and the ether extract washed with salt solution and dried over magnesium sulfate. Distillation of the ether left 30 g. of a white solid residue which was purified by low-temperature crystallization from a small amount of petroleum ether (b.p. 30–60°) to give the *cis*-alcohol, m.p. 36–38° (lit. m.p. 37.3°[3a], 34°[3b]).

The *p*-toluenesulfonate ester was prepared by reaction of the *cis*-alcohol with *p*-toluenesulfonyl chloride in pyridine, m.p. 81–82° (lit. m.p. 81°[3b], 80–81°[4]).

Anal. Calcd. for $C_{16}H_{24}O_3S$: C, 64.84; H, 8.16; S, 10.83. Found: C, 64.82; H, 8.13; S, 10.58, 10.72.

Equilibration of the 3,3,5-trimethylcyclohexanols. The *cis*-alcohol (4.0 g.) was boiled with 4.3 g. of aluminum isopropoxide and 1–1.5 ml. of acetone in 100 ml. of anhydrous isopropyl alcohol under reflux for 144 hr. The reaction mixture was poured into 30 ml. of concd. hydrochloric acid diluted with 500 ml. of water and the product extracted with five 100-ml. portions of ether. The ether extract was washed with 50 ml. of saturated salt solution, 50 ml. of saturated sodium bicarbonate solution and twice with 50-ml. portions of salt solution, and dried over anhydrous magnesium sulfate. The solution was concentrated to 7 g. and analyzed by gas chromatography on a 10-ft. Tide column, column temperature 159–161°, helium flow rate 42 ml./min. The alcohol mixture consisted of 94 ± 0.5% *cis*- and 6 ± 0.5% *trans*-alcohol.

The *trans*-alcohol was equilibrated in a similar manner and also gave 94 ± 0.5% *cis*- and 6 ± 0.5% *trans*-alcohol. A duplicate equilibration of the *trans*-alcohol, in which boiling was continued for 167 hr. gave the same result.

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(6) W. G. Dauben and K. S. Pitzer in M. S. Newman, *Steric Effects in Organic Chemistry*, John Wiley & Sons, Inc., New York, 1956, p. 18; E. L. Eliel and M. N. Rerick, *J. Am. Chem. Soc.*, **82**, 1367 (1960); see also ref. (1) for a review of present values and methods of determination of conformational equilibrium constants.

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The temperature of the equilibration was 84.5°. The gas chromatographic analyses of the equilibration products are averages of several determinations.

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Preparation of Trichloromethanesulfonyl Chloride[1]

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Recently, it has been shown[2] that trichloromethanesulfonyl chloride is a very useful chlorinating agent. For instance, toluene was converted to benzyl chloride in high yield, *p*-bromotoluene was converted to *p*-bromobenzyl chloride without halogen interchange, and cyclohexane was chlorinated to cyclohexyl chloride. Chlorine and sulfuryl chloride react with *n*-alkanes and alkylbenzenes under free radical conditions to give a mixture of isomers, but trichloromethanesulfonyl chloride shows great selectivity. Thus, with *n*-hexane and ethylbenzene it gave only 2-chlorohexane and α-chloroethylbenzene, respectively. This work has prompted us to publish the present communication dealing with the preparation of trichloromethanesulfonyl chloride.

Trichloromethanesulfonyl chloride can be prepared by the action of moist chlorine on carbon disulfide[3,4] or by oxidation of trichloromethanesulfenyl chloride with nitric acid,[5,6] calcium hypochlorite,[7] or hydrogen peroxide.[8,9] The best yields and product quality are obtained by the peroxide oxidation, which was therefore investigated in more detail.

Peracetic acid was brought into contact with trichloromethanesulfenyl chloride at varying temperatures. The sulfenyl chloride was not attacked by 40% peracetic acid in acetic acid at 25–35°. It was oxidized smoothly to the sulfonyl chloride in *ca.* 40% yield when the peracetic acid was added slowly at 100°.

A 30% solution of hydrogen peroxide oxidized the sulfenyl chloride to the sulfonyl chloride in yields up to 78%. The sulfenyl chloride was dissolved in acetic acid and maintained at reflux during the peroxide addition.

Urea–hydrogen peroxide addition compound can also be used advantageously for this oxidation. A solution of the sulfenyl chloride in glacial acetic acid was heated to 110°, and solid urea–hydrogen peroxide was added at a rate to keep the reaction mixture boiling. Trichloromethanesulfonyl chloride was obtained in 50% yield. It is important that this reaction be carried out as rapidly as possible at 110°, as prolonged reaction (e.g., 10 hr.) lowers the yield appreciably.

During the course of these experiments no explosions occurred. Therefore, the reactions are regarded as safe under the described conditions.

EXPERIMENTAL

With 30% aqueous hydrogen peroxide. A solution of trichloromethanesulfenyl chloride (18.6 g., 0.1 mole) in glacial acetic acid (50 ml.) was brought to boiling, and 30% aqueous hydrogen peroxide solution was added slowly, with the reaction mixture being maintained at reflux. The addition of hydrogen peroxide (50 ml.) was stopped when a white sublimate appeared in the reflux condenser. The reaction mixture was diluted with water, and the snow-white product (17 g., 78%) was collected, dried, and recrystallized from alcohol, m.p. 140–141°.

With a 40% solution of peracetic acid in glacial acetic acid. A solution of trichloromethanesulfenyl chloride (5.16 g., 0.028 mole) in glacial acetic acid (5 ml.) was heated to 100°. A 40% solution (18 ml.) of peracetic acid in acetic acid was added drop by drop over a period of 8 hr. to the sulfenyl chloride solution. At this point the reaction mixture became nearly colorless, and it was cooled and diluted with water. The white precipitate collected (2.4 g., 40%) was identical with that prepared by the previous method.

With urea–hydrogen peroxide addition compound. To a solution of trichloromethanesulfenyl chloride (1.74 g., 0.0093 mole) in acetic acid (4 ml.) at 110° was slowly added powdered urea–hydrogen peroxide compound (2 g.). The rate of addition was adjusted to maintain the reaction mixture at boiling. The reaction mixture was diluted with water and the product (1 g., 50%) collected by filtration.

Acknowledgment. We are grateful to the Food Machinery and Chemical Corporation for samples of peracetic acid and urea–hydrogen peroxide compound and to Stauffer Chemical Company for a sample of trichloromethanesulfenyl chloride.

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(1) The work was carried out in part at the Central Research Laboratories of Imperial Chemical Industries Ltd., Melbourne, Australia, and in part at Armour Research Foundation, Chicago, Ill.

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