colorless liquid, b.p. 94–95° (17 mm.), $n^{25}D$ 1.5590,[16] was 2.4 g.; ultraviolet λ_{max} 250 and 293 mμ, ε 8600 and 2150.

The Oxidation of 1-Methoxy-5,6-dihydronaphthalene.[17]—To a slurry of 10 g. of 1-methoxy-5,6-dihydronaphthalene[17] in 100 ml. of acetone and 100 ml. of water cooled to 0°, 16 g. of potassium permanganate dissolved in 400 ml. of water was added dropwise. The reaction mixture was stirred while chipped ice was added regularly to the flask throughout the reaction to keep the temperature below 5°. After three hours the manganese dioxide formed in the reaction was removed by filtration and washed with aqueous sodium bicarbonate which was then added to the filtrate. The clear yellow filtrate was extracted twice with chloroform. The manganese dioxide was washed with chloroform and this washing added to the chloroform extract. Evaporation of the chloroform extracts and crystallization of the residue from methyl alcohol gave 0.5 g. of a glycol, probably *cis*-1,2-dihydroxy-5-methoxytetralin, m.p. 150–151°.[18]

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.08; H, 7.41.

The filtrate from the permanganate oxidation described above, after being extracted with chloroform, was acidified and cooled overnight in a cold-room. The precipitate of cream colored needles was collected, washed with water, dried, and recrystallized from methanol to give 1.3 g. of an acid which melted 221–222° without depression by 3-(2-methoxy-6-carboxyphenyl)-propanoic acid.

(16) M. Sulzbacher, *J. Appl. Chem.*, **1**, 95 (1951).

(17) The 1-methoxy-5,6-dihydronaphthalene employed in this experiment was that prepared by methylation of the crude isomerization product of 5,8-dihydro-1-naphthol.

(18) The isomeric glycol *cis*-1,2-dihydroxy-8-methoxytetralin which could have been obtained from 1-methoxy-5,6-dihydronaphthalene melts at 125°. We are indebted to Dr. R. Pappo for furnishing us a sample of this lower melting isomeric glycol.

Kinetics of the Base-catalyzed Isomerization of 1-Methoxy-5,8-dihydronaphthalene and of Potassium 5,8-dihydro-1-naphthoxide.—In 500 ml. of dry, oxygen-free *t*-amyl alcohol there was dissolved 5.35 g. of potassium metal. The solution was maintained at 100° under a nitrogen atmosphere and 6 g. of 5,8-dihydro-1-naphthol was added to the reaction flask at time zero. At 15-minute intervals 5-ml. aliquots were removed from the reaction flask and added to 65 ml. of chilled 0.0274 *N* ethanolic hydrochloric acid in 100-ml. volumetric flasks. Each aliquot was diluted to 100 ml. with ethanol and the precipitated potassium chloride allowed to settle. A portion of each diluted aliquot was then further diluted 10:1 with ethanol. The concentration of product in each aliquot was determined spectroscopically. The spectrum of the product has a maximum at 299 mμ while the starting material absorbs negligibly at this wave length. The rate constant was determined graphically (Fig. 1). After the final aliquot had been removed, the concentration of potassium *t*-amylate in the residual reaction mixture was determined by titration with standard ethanolic hydrochloric acid, using phenolphthalein as indicator.

The kinetics of the isomerization of 1-methoxy-5,8-dihydronaphthalene were determined in the same manner except that aliquots were taken at 7.5-minute intervals. Only 4.0 g. (0.103 mole) of potassium metal was used while 6.57 g. (0.0411 mole) of 1-methoxy-5,8-dihydronaphthalene was added.

The isomerization of each compound followed first-order kinetics for the first 30% of reaction and then began to deviate slightly, Fig. 1. The rate constant for potassium 5,7-dihydro-1-naphthoxide was 0.00297 $min.^{-1}$ at the base concentration of 0.133 *N*. The rate constant for 1-methoxy-5,8-dihydronaphthalene was 0.00344 $min.^{-1}$ in 0.135 *N* base.

KNOXVILLE, TENNESSEE

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

The Stereochemistry of Ketonization. VI. Decarboxylation of 2-Phenylcyclohexane-1,1-dicarboxylic Acid[1]

BY HOWARD E. ZIMMERMAN AND THEODORE W. CUTSHALL

RECEIVED OCTOBER 9, 1957

The decarboxylation of 2-phenylcyclohexane-1,1-dicarboxylic acid has been found to afford preferentially the *cis* isomer of 2-phenylcyclohexanecarboxylic acid, the exact isomer distribution depending on the nature of the proton donor. The stereoselectivity of ketonization of exocyclic cyclohexane enols as a function of molecular structure is discussed.

As a part of an investigation[2–5] of the relation between molecular structure and the direction and degree of stereoselectivity of the ketonization reaction of enols, it was of interest to determine the stereochemical course of decarboxylation of 2-phenylcyclohexane-1,1-dicarboxylic acid.

Previously this compound had been reported by Kipping and Perkin[6] as an unanalyzed oil obtained by saponification of the base-catalyzed condensation product of 1,5-dibromo-1-phenylpentane and diethyl malonate. The diacid was stated to afford on decarboxylation and extensive purification an unspecified yield of 2-phenylcyclohexanecarboxylic acid, m.p. 104–105°. Both *cis*- and *trans*-2-phenylcyclohexanecarboxylic acids have been synthesized unambiguously by Gutsche[7]; the *cis* isomer was reported as melting at 76–77° while the melting point of the *trans* acid was 108°. Thus the work of Kipping and Perkin seemed to suggest preferential formation of *trans*-2-phenylcyclohexanecarboxylic acid in the decarboxylation of 2-phenylcyclohexane-1,1-dicarboxylic acid. On the other hand, by analogy to the stereochemistry of decarboxylation of the 4-phenyl analog[4] and in view of the factors controlling ketonization of the enolic reaction intermediate,[2] the *cis* product would have been predicted to predominate.

In the present investigation a simple synthetic approach to the 2-phenylcyclohexanecarboxylic acid system was found in the Diels–Alder reaction of 1-phenylbutadiene with diethyl methylenemalonate. The product, diethyl 2-phenylcyclohex-3-ene-1,1-dicarboxylate (I), m.p. 78°, was converted to the desired 2-phenylcyclohexane-1,1-dicarboxylic acid (IV) in two ways. Saponification of I afforded 2-phenylcyclohex-3-ene-1,1-dicarboxylic acid (II),

(1) For Paper V of this series see H. E. Zimmerman and T. E. Nevins, THIS JOURNAL, **79**, 6559 (1957).

(2) H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955).

(3) H. E. Zimmerman, THIS JOURNAL, **78**, 1168 (1956).

(4) H. E. Zimmerman and H. J. Giallombardo, *ibid.*, **78**, 6259 (1956).

(5) H. E. Zimmerman, *ibid.*, **79**, 6554 (1957).

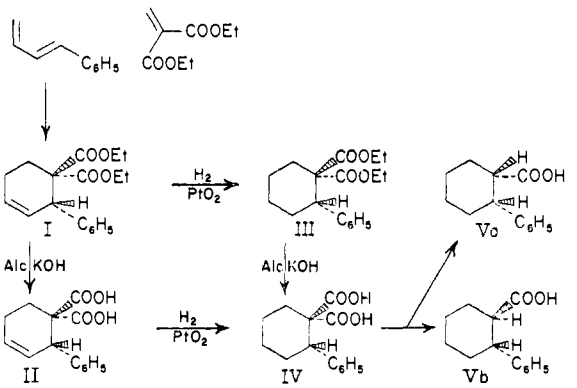
(6) F. S. Kipping and W. H. Perkin, Jr., *J. Chem. Soc.*, 315 (1890).

(7) C. D. Gutsche, THIS JOURNAL, **70**, 4150 (1948).

m.p. 186°. This, in turn, on catalytic hydrogenation led to 2-phenylcyclohexane-1,1-dicarboxylic acid (IV) of melting point 180°. Alternatively, it was found that hydrogenation of I yielded diethyl 2-phenylcyclohexane-1,1-dicarboxylate (III), m.p. 36°, which could then be saponified to give the desired 2-phenylcyclohexane-1,1-dicarboxylic acid (IV).

Authentic samples of *cis*- and *trans*-2-phenylcyclohexanecarboxylic acids were obtained by silica gel chromatography of the mixture resulting from thermal decarboxylation of IV. The *cis*-acid fraction comprised 64% of the monoacid product. By use of the infrared analytical procedure described previously[5] it proved possible to determine the percentage of *cis* isomer in a mixture with an infrared uncertainty of ±0.5% *cis* isomer (note Table II).

CHART I



Before infrared analysis it was necessary to separate unreacted 2-phenylcyclohexane-1,1-dicarboxylic acid from *cis*- and *trans*-2-phenylcyclohexanecarboxylic acids; this was effected by a fractional extraction process using ether and *p*H 7 buffer phases.

In agreement with the product distribution indicated by chromatography (*vide supra*), infrared analysis of the product of thermal decarboxylation (Table I, run 5) showed this to contain 65.5% *cis*-2-phenylcyclohexanecarboxylic acid (Va). Since under the reaction conditions Va was found to be unchanged, this represents the isomer distribution resulting from kinetic control.

TABLE I

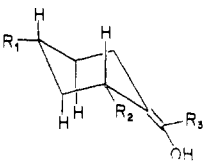
Run	Reactant	Solvent	*T*, °C.	Time	*cis*-Acid, %	*cis*-Acid,[a] %
1	Diacid	Collidine	60	60 min.	72.5	76.0
2	Diacid	Collidine	90	30 min.	71.4	73.5
3	Diacid	Collidine	130	20 min.	71.3	75.3
4	Diacid	Collidine	165	20 min.	69.7	74.8
5	Diacid	None	195	8 min.	65.5	65.5
6	*cis*-Acid	None	200	64 hr.	13.7	..
7	*cis*-Acid	None	200	102 hr.	8.5	..
8	*trans*-Acid	None	200	102 hr.	8.9	..

[a] Corrected for any isomerization of *cis*-acid under reaction conditions.

Decarboxylation experiments also were carried out in collidine solution at temperatures ranging from 60 to 165°. A small temperature dependence was noted; however, when corrections had been made for the small amounts of isomerization of Va under reaction conditions an average of 74.9 ± 1.4% *cis*-2-phenylcyclohexanecarboxylic acid was obtained. The greater scattering than found in analysis of synthetic mixtures may be due to slight random losses during the purification processes.[8]

When either *cis*- or *trans*-2-phenylcyclohexanecarboxylic acid was heated to 200° for 102 hours (Table I, runs 7 and 8) an equilibrium mixture of the stereoisomers containing 8.7% *cis*-2-phenylcyclohexanecarboxylic acid resulted. Thus the equatorial-phenyl, equatorial-carboxyl situation of the *trans* isomer is favored by 2.2 kcal./mole free energy over the *cis* equilibrium mixture[9] composed of equatorial-phenyl, axial-carboxyl and equatorial-carboxyl, axial-phenyl conformations.

Thus ketonization of the enolic reaction intermediate VIb yields the less stable of two possible stereoisomers in analogy to ketonization of the similar enolic intermediates studied previously[1-5] (*i.e.*, VIa, c, d). Particularly of interest is a consideration of the effect of changes in molecular structure in the series VIa, VIb, VIc and VId.



VIa, $R_1 = C_6H_5$, $R_2 = H$, $R_3 = OH$
VIb, $R_1 = H$, $R_2 = C_6H_5$, $R_3 = OH$
VIc, $R_1 = H$, $R_2 = C_6H_5$, $R_3 = CH_3$
VId, $R_1 = H$, $R_2 = C_6H_5$, $R_3 = C_6H_5$

The least stereoselective of these systems was VIa, the intermediate in the decarboxylation of 4-phenylcyclohexane-1,1-dicarboxylic acid.[4] Where the proton donor was a small species as a carboxyl group there was a complete absence of selectivity, 50% of the product being *cis*-acid.[4] When a proton donor presenting greater steric demands was used, as in decarboxylation in collidine where the donor was either the bulky collidinium–carboxylate ion pair or the hydrogen bonded equivalent, 61% of the less stable *cis* product was obtained. From this it is apparent that the selectivity due to the hindrance to prototopic attack derived from the 3 and 5 axial hydrogen atoms *per se* is slight. This is not unexpected, since the proton donor on ap-

(8) Of interest is the absence of a marked temperature dependence of stereoselectivity. The product distribution corresponds to a transition state for formation of *cis* isomer which is 0.81 kcal./mole lower in free energy than that for *trans* product (*i.e.*, $\Delta\Delta F^{\ddagger} = 0.81$ kcal./mole). Now if this resulted entirely from a difference in enthalpies of activation for the two competing stereochemical courses then a change of 5.5% *cis* isomer could be expected for a 100° temperature change. Since such an effect is not observed it is tempting to conclude that at least a sizable fraction of the difference in free energies of activation stems from an entropy effect. However, in view of the small temperature dependence expected it is entirely possible that such an effect is obscured by the experimental scatter. An answer must await data for a system allowing greater analytical precision and a larger temperature range.

(9) The equilibrium concentration of *cis* isomer is enhanced by the occurrence of two conformations. The equilibrium constant for formation of *cis* isomer from *trans* is the sum of the individual equilibrium constants for formation of each of the *cis* conformations from *trans*-acid; that is, the standard free energy of a rapidly equilibrated mixture of two isomers is less than that of the more stable of the isomers by the amount $RT \ln (1 + K)$ where K is the equilibrium constant for formation of the less stable from the more stable isomer.

proaching the more hindered side of the molecule can find an orientation in which the 3 and 5 axial hydrogen atoms are avoided.

In the present study, ketonization of the decarboxylation intermediate VIb is seen to proceed with a selectivity depending again on the bulk of the proton donor; however, with each donor *ca.* 12% more *cis* product was obtained than from intermediate VIa. Although the 2-phenyl group is only slightly out of the plane of the enolic double bond and does not offer selective steric hindrance, it does tend to enforce a direct approach by the proton donor with consequent amplification of the selective effect of the 3 and 5 hydrogen atoms.

Ketonization of the enol VIc, in which one OH is replaced by CH_3, proceeds[5] with still greater selectivity, 89% *cis*-product resulting.[10]

In the case of enol VId where a second phenyl group is introduced into the plane of the enolic double bond, selectivity was observed to be enhanced even further.[11] It is postulated that the trend in selectivity in this series may be attributed to the increasingly important role of non-selective steric hindrance in preventing a sidewise approach to the enolic double bond.[12]

Experimental[13]

Diethyl methylenemalonate was prepared essentially by the method of Bachman;[14] it was found that polymerization of the product was inhibited by addition of a small amount of phosphorus pentoxide and storing at 5°.

1-Phenylbutadiene was prepared according to the procedure of Grummitt and Becker.[15]

Diethyl 2-Phenylcyclohex-3-ene-1,1-dicarboxylate.—A solution of 64.2 g. (0.497 mole) of 1-phenylbutadiene and 85.0 g. (0.497 mole) of diethyl methylenemalonate in 150 ml. of benzene was prepared. This was observed to warm slightly. The mixture was refluxed for 2.5 hr. The solution was then concentrated under reduced pressure. Recrystallization of the residue from hexane yielded 89.2 g. of diethyl 2-phenylcyclohex-3-ene-1,1-dicarboxylate, m.p. 77–78°.

Anal. Calcd. for $C_{15}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.17; H, 7.76.

Diethyl 2-Phenylcyclohexane-1,1-dicarboxylate.—Hydrogenation of 15.7 g. (0.051 mole) of diethyl 2-phenyl-cyclohex-3-ene-1,1-dicarboxylate in 100 ml. of ethyl acetate with 300 mg. of platinum dioxide catalyst resulted in the theoretical uptake. The mixture was filtered, concentrated and the residue crystallized from hexane to yield 8.2 g. of diethyl 2-phenylcyclohexane-1,1-dicarboxylate, m.p. 34–36°.

Anal. Calcd. for $C_{18}H_{24}O_4$: C, 71.02; H, 7.95. Found: C, 71.32; H, 7.72.

2-Phenylcyclohexane-1,1-dicarboxylic Acid.—A mixture of 10.0 g. (0.033 mole) of diethyl 2-phenylcyclohexane-1,1-dicarboxylate and 11.2 g. (0.200 mole) of potassium hydroxide in 50 ml. of 95% ethanol was refluxed for five hours; during this time precipitation of the potassium salt was observed. The mixture was then cooled, diluted with 200 ml. of water and ether extracted. The aqueous phase was acidified with 50% hydrochloric acid to congo red paper and then ether extracted. The extracts were washed with water, dried over sodium sulfate and concentrated *in vacuo*. The residual oil was crystallized from ethyl acetate–ligroin (86–100°) to yield 2.10 g. of 2-phenylcyclohexane-1,1-dicarboxylic acid, m.p. 179–180°.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.42; H, 6.63.

2-Phenylcyclohex-3-ene-1,1-dicarboxylic Acid.—A solution of 54.2 g. (0.18 mole) of diethyl 2-phenylcyclohex-3-ene-1,1-dicarboxylate and 78.5 g. (1.4 moles) of potassium hydroxide in 250 ml. of 95% ethanol was refluxed for 4.5 hr. During this time some potassium salt precipitated. The cooled mixture was diluted with 500 ml. of water and ether extracted. Acidification of the aqueous phase to a congo red end-point with 50% hydrochloric acid followed by ether extraction, washing the extracts and drying over sodium sulfate and finally concentration yielded 26.0 g. of acidic material. Crystallization from ethyl acetate–ligroin (86–100°) gave 18.3 g. of 2-phenylcyclohex-3-ene-1,1-dicarboxylic acid, m.p. 180–182°. Further crystallization brought the melting point to 185–186°.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.40; H, 5.56.

Hydrogenation of 2-Phenylcyclohex-3-ene-1,1-dicarboxylic Acid to Yield 2-Phenylcyclohexane-1,1-dicarboxylic Acid.—A solution of 15.0 g. of phenylcyclohex-3-ene-1,1-dicarboxylic acid (0.061 mole) in 100 ml. of ethyl acetate was hydrogenated in a Parr apparatus with 500 mg. of PtO_2 catalyst. After the theoretical uptake of hydrogen, the mixture was filtered and concentrated. Crystallization from ethyl acetate–ligroin (86–100°) afforded 10.5 g. of essentially pure 2-phenylcyclohexane-1,1-dicarboxylic acid, m.p. 177–179°. Additional material could be obtained from the filtrates.

***cis*- and *trans*-2-Phenylcyclohexanecarboxylic Acids.**—A 1.00-g. sample of 2-phenylcyclohexane-1,1-dicarboxylic acid was heated in a vacuum sublimation apparatus to 194–199° at 1 mm. for 7 min. From the cold finger was obtained a colorless, viscous oil weighing 0.81 g. This was chromatographed on silica gel (22 × 300 mm.) by elution with 15% ether in hexane. A first fraction of 250 ml. was collected followed by thirteen 50-ml. fractions and finally by two 100-ml. fractions obtained by ether elution. The weights and melting points were as follows: Fraction 1, 0.08 g., m.p. 67–70°; 2, 0.24 g., m.p. 76–77°; 3, 0.12 g., m.p. 70–71°; 4, 0.08 g., m.p. 52–54°; 5, 0.06 g., m.p. 77–81°; 6, 0.05 g., m.p. 104–106°; 7, 0.05 g., m.p. 105–106°; 8, 0.05 g., m.p. 105–106°; 9, 0.04 g., m.p. 105–106.5°; 10, 0.04 g., m.p. 105–106°; 11, 0.02 g., m.p. 104–105°; 12, 0.01 g.; 13, 0.02 g.; 14, 0.03 g., m.p. 102–104°; 15, 0.01 g., m.p. 95–98°; 16, 0.04 g., m.p. 85–95°.

Fractions 1 through 5 consisted of *cis*-acid and were dried. Recrystallization from hexane brought the melting point to 75.0–75.5°. The combined fractions 6 through 14, consisted of *trans*-acid. Recrystallization brought the melting point to 107.0–108.0° (reported for *cis*-2-phenylcyclohexanecarboxylic acid: 76–78°,[16] 76.0–76.5°,[17] 76–77°[7]; reported for *trans*-2-phenylcyclohexanecarboxylic acid: 103–107°,[16] 108°[7]).

Decarboxylation of 2-Phenylcyclohexane-1,1-dicarboxylic Acid in Collidine.—A solution of 500 mg. of 2-phenylcyclo-

(10) Part of this increase may be attributed to an increased importance of delocalization of the bonding electrons in the ketonization transition state and hence a closer approximation to SP^2 hybridization (for case VIc) compared to VIb where interaction of the extra hydroxyl group's unshared electrons with the incipient carbonyl group diminishes the demand of the latter for electrons.

(11) Although *quantitative* infrared analysis was not employed in the 1-benzoyl-2-phenylcyclohexane study, the fact that the crude ketonization product melted within one degree of the m.p. of pure *cis* isomer and that the infrared spectrum was essentially superimposable with that of *cis* isomer despite sharp differences in the spectrum of the *trans* isomer is taken as evidence that little if any *trans* product was formed.

(12) It is of some interest to consider whether the decreased selectivity in the 4-phenyl enol (VIa) compared to the 2-phenyl enols (VIb, c, d) can be related to the expectation that for the former the axial-phenyl conformation should ketonize with a product distribution which is precisely the reverse of that for the equatorial-phenyl conformation; for the 2-phenyl enols the axial-phenyl conformation might be anticipated to yield the less stable isomer due to the hindrance offered by the 2-phenyl group which in this conformation is no longer in the enolic double bond plane. However, the axial-phenyl conformations probably participate only negligibly in the reaction. ΔF (axial-equat.) for the *i*-Pr group (W. G. Dauben and K. S. Pitzer in "Steric Effects in Organic Chemistry," by M. S. Newman, p. 54) is 3.3 kcal./mole. If this is taken as an approximation to that for the phenyl group, the concentration of axial-phenyl molecules will be less than 1%.

(13) All melting points were taken on a Fisher–Johns block checked with compounds of known melting point.

(14) G. B. Bachman and H. A. Tanner, *J. Org. Chem.*, **4**, 493 (1939).

(15) O. Grummitt and E. I. Becker, *Org. Syntheses*, **30**, 75 (1950).

(16) J. Meek, F. Lorenzi and S. Cristol, THIS JOURNAL, **71**, 1830 (1949).

(17) G. Ropp and E. Coyner, *ibid.*, **71**, 1832 (1949).

hexane-1,1-dicarboxylic acid in 7.5 ml. of collidine was heated to the given temperature for the desired time. The cooled solution was taken up in 100 ml. of ether and extracted with two 40-ml. portions of 10% sodium hydroxide solution. The aqueous layer was acidified with 20% hydrochloric acid to a congo red end-point and extracted twice with 75-ml. portions of ether. The ether phase was washed twice with water and subjected to an eight funnel fractional extraction using in each flask 50 ml. of ether and 50 ml. of a *p*H 7.0 buffer prepared from 41.20 ml. of 0.2 *M* disodium phosphate and 8.80 ml. of 0.1 *M* citric acid as described previously.[4] When all eight funnels had been utilized, each aqueous phase was acidified with hydrochloric acid to a congo red end-point and extracted with the accompanying ether phase. The monoacids were found in the first two or three fractions; fractions four and five contained negligible material. Unreacted diacid was found in the last two or three fractions. The monoacid fraction was analyzed by the quantitative infrared method.

Equilibration of *cis*- and *trans*-2-Phenylcyclohexanecarboxylic Acids.—A sample of 60 mg. of *cis*-2-phenylcyclohexanecarboxylic acid was sealed in a Pyrex tube which was then heated to 200° for 102 hr. Infrared analysis indicated the mixture of *cis*- and *trans*-2-phenylcyclohexanecarboxylic acids to contain 8.5% *cis* isomer.

When the time of heating was only 64 hr. the product contained 13.7% *cis*-acid. At the end of 20 hr. 39.2% *cis*-acid was indicated while after 6 hr. there was 74.0% *cis* isomer. On this basis less than 2% isomerization of *cis*-acid is calculated for heating for 8 minutes.

Similarly, heating of 60 mg. of *trans*-2-phenylcyclohexanecarboxylic acid to 200° for 102 hr. resulted in a mixture containing 8.9% *cis* isomer.

Stability of *cis*-2-Phenylcyclohexanecarboxylic Acid in Collidine under Decarboxylation Conditions.—Four 60.0-mg. samples of *cis*-2-phenylcyclohexanecarboxylic acid in 1.0 ml. of collidine were heated to 60°, 90°, 110° and 160° for 60, 30, 20 and 20 minute periods, respectively. The acidic product was separated from the collidine as in the decarboxylation experiments except that the fractional extraction was omitted. Analysis by infrared indicated the fractions converted to *trans*-2-phenylcyclohexanecarboxylic acid to be 0.0472, 0.0298, 0.0396, 0.0698 in the four runs, respectively. These were used in correcting the percentage *cis*-2-phenylcyclohexanecarboxylic acid obtained from the collidine decarboxylation experiments for isomerization.

Infrared Analyses.—The method was that described earlier[5] except that carbon disulfide was used. The analytical wave lengths used were 7.71 and 7.98 μ. Calibration data are recorded in Table II. The optical density of all mixtures, known and unknown, was taken as zero at 2.0 μ.

TABLE II

KNOWN MIXTURES

Actual % *cis*-isomer	D'	D''	Q	Actual R	Calcd. F	Calcd. R	Calcd. % *cis*-isomer
0.0	0.431	0.136	...	...	..	...	..
25.0	.337	.251	0.314	0.333	1.06	0.327	24.6
50.0	.296	.408	0.979	1.00	1.02	1.02	50.4
75.0	.244	.569	2.86	3.00	1.05	2.98	74.8
100.0	.180	.720	...	...	..	...	..

Here D' and D'' are the optical densities at 7.71 and 7.98 μ, respectively. $Q = \frac{D''_m D'_t - D'_m D''_t}{D'_m D''_c - D''_m D'_c}$ where the subscripts c, t and m refer to pure *cis* isomer, *trans* isomer and a given mixture, respectively. R is the ratio of *cis* to *trans* isomer in a mixture. F is defined by $R = QF$ and determined empirically from values of Q and R for known mixtures. The average value of $F = 1.04$ was used in calculating the results in the last two columns of Table II and the composition of unknown mixtures.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS]

Reduction of Organic Compounds by Mixed Hydrides. II. Hydrogenolysis of Ketones and Alcohols[1]

BY ROBERT F. NYSTROM AND C. RAINER A. BERGER

RECEIVED OCTOBER 28, 1957

Diaryl ketones, alkyl aryl ketones and certain aryl alcohols are smoothly reduced to the corresponding hydrocarbon by the lithium aluminum hydride–aluminum chloride reagent in ether solution at 35°. There are notable differences in the ease and extent of reduction which varies with the order of mixing the reactants and with the groups present in the organic component.

The mixed hydride, prepared from equimolar quantities of aluminum chloride and lithium aluminum hydride,[2] has been found effective in promoting hydrogenolysis reactions. Certain aromatic ketones and alcohols were reduced in high yield to the corresponding hydrocarbon, using one to four hour reaction times at 35°. Other methods, such as the Clemmensen, Wolff–Kishner, or palladium–hydrogen, can now be considered obsolete for the small-scale reduction of diaryl and alkyl aryl ketones. Dialkyl ketones, however, are reduced only to the alcohol stage.

Conover and Tarbell[3] have reported the conversion of aromatic acid and carbonyl compounds to the hydrocarbons in moderate yield, when treated with a large excess of lithium aluminum hydride, at 60 to 90°, for periods ranging from one hour to eleven days. Recently, the hydrogenolysis of aromatic carbonyl compounds and alcohols by aluminum chloride and lithium aluminum hydride has been reported. In one publication,[4] reduction was accomplished by adding an aluminum chloride solution of the ketone to the lithium aluminum hydride in ether. In another,[5] one mole of lithium aluminum hydride was introduced into a solution containing two moles of aluminum chloride before addition of the organic compound.

In this Laboratory we have found that the extent of hydrogenolysis of aryl and alkyl aryl ketones by the lithium aluminum hydride–aluminum chloride reagent varies with the experimental operations and nature of the organic compound. Some

(1) C. R. A. Berger and R. F. Nystrom, Abstracts of Papers, 131st Meeting, American Chemical Society, Miami, Fla., April 7–12, 1957, 51-O.

(2) R. F. Nystrom, THIS JOURNAL, **77**, 2544 (1955).

(3) L. H. Conover and D. S. Tarbell, *ibid.*, **72**, 3586 (1950).

(4) J. Broome and B. R. Brown, *Chemistry & Industry*, 1307 (1956).

(5) B. R. Brown and A. M. S. White, *J. Chem. Soc.*, 3755 (1957).