

phenylmagnesium bromide. After boiling for 15 minutes, the mixture was cooled and a saturated solution of ammonium chloride was added to decompose the addition compound. After extraction of the aqueous solution with benzene, the benzene solutions were extracted once with water, dried, and concentrated in vacuum to 20 ml. After standing several days, a white product separated. The yield was 0.95 g. It was purified by crystallization from benzene-petroleum ether (b.p. 30–60°), m.p. 268–269°.

Anal. Calcd. for $C_{36}H_{30}N_2O_4S_2$: C, 69.88; H, 4.89; N, 4.53. Found: average of 5 anal.: C, 69.64; H, 4.98; N, 4.42.

The Reaction of Butadiene with IIb, IIIb and IVb.—A. 3-Benzenesulfonimido-3-methoxy-1-phenyl-1-propene (IIb) when heated with butadiene in chloroform at 90° or in xylene at 170° or with 2,3-dimethylbutadiene in chloroform at 90° was recovered unchanged.

B. A mixture of 4 g. of 1,2-dibzenesulfonimido-1,2-dimethoxyethane (IIIb), 8 ml. of xylene and 1 g. of butadiene was heated for 21 hours at 170–175° in a sealed tube. Upon addition of ether to the cooled reaction mixture, a white substance crystallized and was recrystallized several times from benzene-ether; m.p. 145.5°. The yield was 3.2 g. (80%). The same product resulted when 2,3-dimethylbutadiene was used in place of butadiene.

Anal. Calcd. for $C_{16}H_{16}N_2O_6S_2$: C, 48.47; H, 4.07; N, 7.07. Found: C, 48.57; H, 4.04; N, 7.04; OCH_3 , 0.

The product proved to be identical with *N,N'*-dibzenesulfonyl-*N,N'*-dimethylloxamide (XV), obtained by the action of methyl iodide on the silver salt of *N,N'*-dibzenesulfonyloxamide (III) and by the reaction between benzenesulfonylmethylamide and oxalyl chloride.

No reaction took place when chloroform was used as solvent or when xylene was used without the butadiene.

C. A mixture of 4.22 g. of 1,4-dibzenesulfonimido-1,4-dimethoxy-2-butene (IVb), 8 ml. of chloroform, 1 g. of butadiene and 2 mg. of hydroquinone was heated in a sealed tube for 18 hours at 90–95°. After cooling, the substance which crystallized was removed by filtration, washed with ether and recrystallized from benzene, m.p. 238°. The yield was 3.9 g. (81.8%).

Anal. Calcd. for $C_{22}H_{24}N_2O_6S_2$: C, 55.44; H, 5.08; N, 5.88. Found: C, 55.63; H, 4.80; N, 5.64.

The infrared spectrum showed absorption for $C=N$ at 1599 cm^{-1} , $-OCH_3$ at 1098 cm^{-1} and $HC=CH$ (*cis*) at 735 cm^{-1} .

***N,N'*-Dibzenesulfonyl-*N,N'*-dimethylloxamide (XV).**—To a solution of 33 g. of benzenesulfonylmethylamide in a mixture of 50 ml. of thionyl chloride and 50 ml. of benzene, 12.3 g. of oxalyl chloride was added and the mixture heated for 4 hours. The solvents were removed by distillation under vacuum and the residue extracted with petroleum ether to remove traces of thionyl chloride. The residue was then taken up in ether and petroleum ether was added. A colorless substance crystallized and was recrystallized from benzene-petroleum ether (b.p. 30–60°); m.p. 145.5°. The yield was 26 g. (86%).

Anal. Calcd. for $C_{16}H_{16}N_2O_6S_2$: C, 48.47; H, 4.07. Found: C, 48.82; H, 4.27.

This method is much superior to that employing the silver salt of *N,N'*-dibzenesulfonyloxamide (III) and methyl iodide.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH CENTER OF THE NATIONAL ANILINE DIVISION OF THE ALLIED CHEMICAL & DYE CORPORATION AND THE INSTITUTE OF RESEARCH OF LEHIGH UNIVERSITY]

Rearrangement of the Double Bond in *cis*-4-Cyclohexene-1,2-dicarboxylic Anhydride

BY M. E. BAILEY¹ AND E. D. AMSTUTZ

RECEIVED DECEMBER 10, 1955

cis-4-Cyclohexene-1,2-dicarboxylic anhydride (IV) was found to undergo isomerization at elevated temperatures under the influence of acid catalysts to form progressively: *cis*-3-cyclohexene-1,2-dicarboxylic anhydride (III), 2-cyclohexene-1,2-dicarboxylic anhydride (II) and 1-cyclohexene-1,2-dicarboxylic anhydride (I). Distillation of the final product yielded pure I. Fractional crystallization of an intermediate mixture containing high concentrations of III followed by recrystallization from toluene, yielded pure III. No *trans*-4-cyclohexene-1,2-dicarboxylic anhydride (V) was detectable at any stage. Identity of the products was established and rates of the isomerization were determined at two temperatures by use of infrared absorption spectra.

cis-4-Cyclohexene-1,2-dicarboxylic anhydride (IV) is easily obtainable from maleic anhydride and butadiene. In contrast with many other diene addition products it is not thermally reversible to the dieneophile and diene from which it is derived. For these reasons and because of the unique properties of many of its derivatives, IV has come to possess considerable academic as well as commercial importance. The other cyclohexene-1,2-dicarboxylic anhydrides are known but have not been of any particular interest because their reported methods of synthesis are cumbersome and inefficient. The present paper reports a hitherto unknown chemical property of IV which provides an easy route to some of the other isomers.

When IV is heated with acid catalysts, anhydride functionality is retained and average molecular weight is unchanged, but other properties are altered substantially. Possible explanations are *cis-trans* isomerization and double bond rearrangement

which would lead to other *cis* isomers of cyclohexene-1,2-dicarboxylic anhydride.

In the first case, rupture of carbon-carbon bonds would be required, in the second, migration of a proton would need to occur. In order to determine which, if either, of these mechanisms applies, samples of the products which might be formed, *i.e.*, *trans*-4-cyclohexene-1,2-dicarboxylic anhydride (V), *cis*-3-cyclohexene-1,2-dicarboxylic anhydride (III), 2-cyclohexene-1,2-dicarboxylic anhydride (II) and 1-cyclohexene-1,2-dicarboxylic anhydride (I), were prepared for purposes of comparison, by the use of methods of synthesis already established.

The infrared absorption spectra for all five of these isomers were determined. All show strong absorptions between 5.4 and 5.9 μ which are characteristic of 1,2-dicarboxylic anhydrides. Between 6.0 and 12.0 μ there were important differences in the spectra. It was possible to distinguish the various isomeric anhydrides from each other by selection of strong absorption bands characteristic of each isomer. Their relative concentrations were deter-

(1) National Aniline Division, Allied Chemical and Dye Corporation, Buffalo, New York.

mined by the use of Beer's law. The portions of the spectra selected for each compound are shown in Fig. 1.

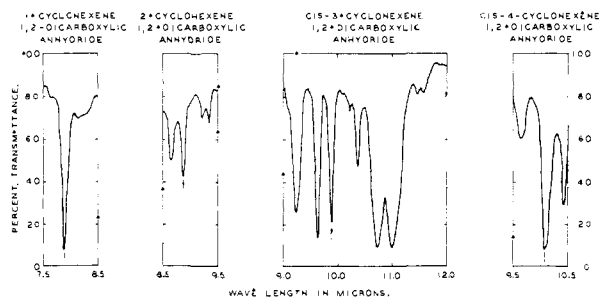


Fig. 1.—Infrared absorption bands for solutions in chloroform of the pure isomers (5 g./100 ml.), selected for analysis of the various isomers of cyclohexene-1,2-dicarboxylic anhydrides.

In typical experiments, samples of IV were heated at 180 and 194° with phosphorus pentoxide. Absorption bands characteristic of IV disappeared rapidly. The first new absorption bands to appear were identified as III. These developed in considerable intensity and then disappeared. Absorption bands characteristic of II were observed to develop to small intensity and then disappear. Finally, the spectrum for I developed completely and no further change was observed. All absorption bands at all stages could be attributed to I, II, III or IV. No V was detectable at any stage in the process. All products isolated in the intermediate stages were mixtures. Compound III could be obtained in concentrations as high as about 60%. Fractional crystallization of this mixture, followed by recrystallization from toluene, yielded essentially pure III. The isomeric mixture tended to remain liquid at room temperature when the concentration of III was about 50% and I was about 35%.

The rates at which these changes occur are plotted for two temperatures in Fig. 2. The data show that change in temperature affects the rate in all steps in the process to approximately the same degree. However, in the temperature range tested, an increase in temperature appears to increase the rate of change of II to I less than the rate of formation of II.

The rate of the process was found to be affected substantially by changes in catalyst concentration. However, the magnitude of the effect of this variable was not determined.

The process is presumed to involve migration of protons and intramolecular shift of electrons to change the position of the double bond. Intermolecular hydrogen exchange, such as might occur with hydrogenation type catalysts, makes no important contribution to the process since neither cyclohexane-1,2-dicarboxylic anhydride nor dehydrogenated products were obtained. Since V was not found, cleavage of the carbon-carbon bond did not occur to any appreciable extent.

That I is formed as the final product is not surprising since it should possess the greatest thermodynamic stability of all of the isomers having *cis* configuration. However, in view of the lower rate of formation of I and II *versus* III, the activation of

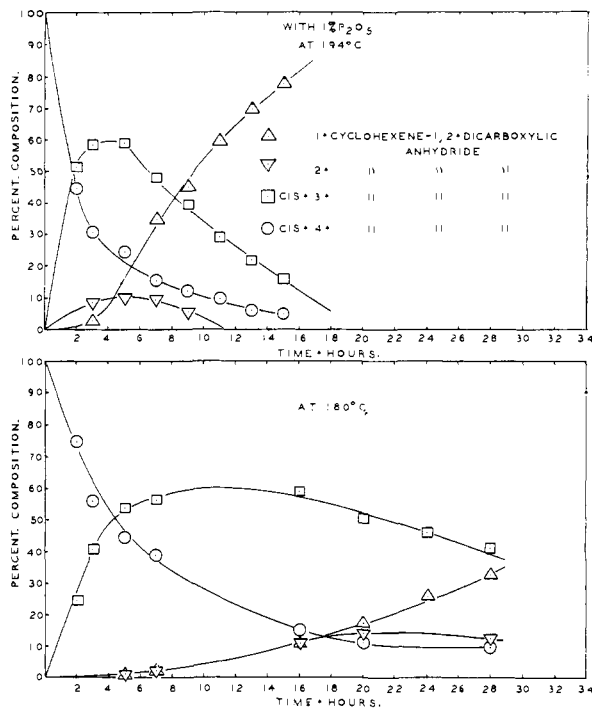


Fig. 2.—Isomerization rate of *cis*-4-cyclohexene-1,2-dicarboxylic anhydride.

the hydrogens in the 1- and 2-position would appear to require greater energy than is required in the 3-position.

Experimental

1-Cyclohexene-1,2-dicarboxylic anhydride (I) was prepared by acid hydrolysis of ethyl 2-cyano-1-cyclohexenecarboxylate which, in turn, was obtained from ethyl 2-cyclohexanecarboxylate by the cyanohydrin reaction.² The mixed acids thus obtained (corresponding to I and II) were vacuum distilled at 220–230° and crystallized from methylcyclohexane to give pure I, m.p. 70.6–72°. This compares with m.p. 74° reported by Rodd.³

2-Cyclohexene-1,2-dicarboxylic anhydride (II) was obtained by isomerization of 1-cyclohexene-1,2-dicarboxylic acid in boiling aqueous potassium hydroxide solution, followed by conversion to the anhydride with acetyl chloride; m.p. 78–79°; literature value, also 78–79°.⁴

***cis*-3-Cyclohexene-1,2-dicarboxylic anhydride (III)** was obtained by condensation of *trans*-butadiene-1-carboxylic acid with acrylic acid, followed by dehydration in boiling acetic anhydride; m.p. 58–59°; literature value, also 58–59°.⁵

***trans*-4-Cyclohexene-1,2-dicarboxylic anhydride (V)** was obtained by condensation of fumaryl chloride with butadiene, followed by hydrolysis and dehydration to the anhydride in boiling acetic anhydride; m.p. 183.5–184.5°; Alder reported m.p. 186°.⁵

Partial Isomerization of *cis*-4-Cyclohexene-1,2-dicarboxylic Anhydride (IV). 1. **With Phosphorus Pentoxide.**—Five hundred grams of IV (99.5% purity; National Aniline Division, Allied Chemical and Dye Corporation) was heated at 220° for 10 hr. with 2 g. of phosphorus pentoxide. The product was distilled at 34 mm. and 165° to yield 447 g. of liquid distillate and 40 g. of tarry residue. Neutralization equivalent of the distillate was 75.8; molecular weight, measured by depression of freezing point of benzene, was 150.

Anal. Calcd. for C₈H₈O₃: C, 63.15; H, 5.30. Found: C, 63.25; H, 5.32.

(2) D. T. Mowry and A. G. Rossow, *THIS JOURNAL*, **67**, 926 (1945).

(3) E. H. Rodd, "Chemistry of Carbon Compounds," Elsevier Publishing Co., Amsterdam, 1953, Vol. II, p. 236.

(4) A. von Baeyer, *Ann.*, **258**, 145 (1890).

(5) K. Alder, M. Schumacher and O. Wolff, *ibid.*, **564**, 79 (1949).

The rate of the isomerization process is affected by temperature and per cent. of catalyst. The solidification point decreases from 100° (for pure IV) to a minimum of about 0°, under any of the following conditions.

Time, hr.	Temp., °C.	P ₂ O ₅ , %
36	200	0.5
5	200	1.0
2	200	1.5
1	230	1.0
84	170	1.0

The product obtained after 4 hours heating at 194° with 1% P₂O₅ contained 60% III. This mixture was fractionally crystallized and the crystals obtained were crystallized twice from toluene to yield essentially pure III (m.p. 57°; mixed m.p. with authentic III, 58°). The product obtained after 7 hr. heating at 194° was liquid at room temperature. However, crystals tended to form on standing.

2. **With Sulfuric Acid.**—Six hundred grams of IV was heated at 200° for 18 hr. with 6 g. of sulfuric acid. The product was vacuum distilled as above to yield 570 g. of liquid distillate and 29 g. of residue. The neutralization equivalent of the distillate was 76.0.

Complete Isomerization of IV.—Six hundred grams of IV was heated at 200° with 9 g. of phosphorus pentoxide for 48 hr. The product was distilled at 5–9 mm. and 140–145° to yield 481 g. of solid distillate and 87 g. of tarry residue. Neutralization equivalent of the distillate was 76.2, m.p. 71–72°.

Determination of Isomer Concentration by Infrared Absorption.—Two 1000-g. samples of IV were agitated with

10 g. of P₂O₅ at 180 and 194°, respectively. Fifty-gram samples were withdrawn after various time intervals and distilled rapidly *in vacuo* at 150°. Samples of distillates were dissolved in chloroform (5.00 g./100 ml.) and their infrared absorption spectra determined using a Baird spectrophotometer. The relative concentrations of the various isomers were determined by comparison of these spectra with the spectra of the pure isomers (dissolved in chloroform, (5.00 g./100 ml.)). A principal absorption band was selected for each material such that there was no substantial interference from other isomers (Fig. 1). Compound I was determined by measuring the absorbancy of the bands at 7.9 μ referred to 7.7 μ basing point, *versus* the absorbancy for the pure isomer; II was determined using the 8.9 μ band referred to a base line constructed tangent to the inflection points near 8.8 and 9.0 μ; III, by using the 9.9 μ band referred to a base line tangent to the inflection points near 9.0 and 12.0 μ; IV, by using the band at 10.1 μ referred to a basing point at 10.0 μ. The results are shown graphically for the two temperatures in Fig. 2.

Acknowledgment.—The authors wish to express their gratitude to Messrs. B. M. Helfaer and E. B. Punnett for their helpful suggestions and advice and to Dr. Wesley Minnis for his guidance and encouragement during the course of this research. The assistance and suggestions of Mr. Richard Seeber, Dr. A. Semetsov and Mr. Richard Spanburgh are acknowledged as well.

BUFFALO 5, NEW YORK

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY, THE STATE UNIVERSITY OF NEW JERSEY]

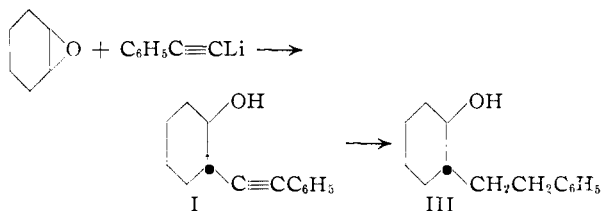
The Cyclization of Optically Active 2-(2-Phenylethyl)-cyclohexanol

BY RODERICK A. BARNES AND ARTHUR D. OLIN¹

RECEIVED DECEMBER 27, 1955

Optically active *trans*-2-(2-phenylethyl)-cyclohexanol has been prepared and cyclized with 90% sulfuric acid. The formation of optically active *cis*-1,2,3,4,4a,9,10,10a-octahydrophenanthrene eliminates both the olefin and tertiary carbonium ion as possible intermediates in this reaction. In addition to the expected ketone, there resulted from the oxidation of the cyclization product, a substance which has been characterized as an unsaturated ketone; a possible mechanism for its formation has been suggested.

As a result of previous studies on the cyclization of 2-arylethylcyclohexanols,² it was suggested that one of three intermediates may react with the aromatic nucleus depending on the experimental conditions and the reactivity of the nucleus. In order to obtain information which could serve to further elucidate the mechanistic details of these cyclizations, it was believed necessary to prepare optically active alcohols of known stereochemical configuration. The first of the required alcohols, the *trans* form of 2-(2-phenylethyl)-cyclohexanol (III), has been prepared from cyclohexene oxide.



The reaction of cyclohexene oxide with either sodium or potassium phenylacetylide failed com-

pletely, perhaps due to the insolubility of these salts in the organic solvents which were used. Lithium phenylacetylide did react; however the maximum yield was only 21%. The acid phthalate of alcohol I could not be resolved with brucine, cinchonine or quinine. Finally, treatment of the acid phthalate with *d*-α-phenylethylamine yielded a salt which was readily recrystallized to constant rotation. The levorotatory form of alcohol I, obtained by decomposition of the salt, was easily reduced by hydrogen and platinum to the desired optically active 2-(2-phenylethyl)-cyclohexanol. Alcohols I and III must have the *trans* configuration because the opening of the oxide ring is certainly a bimolecular displacement.

A sample of inactive alcohol III prepared by hydrogenation of unresolved I yielded a phenylurethan melting at 117.5–118.5°. The 2-(2-phenylethyl)-cyclohexanol prepared by sodium and alcohol reduction³ of 2-(2-phenylethyl)-cyclohexanone probably was mostly the *trans* isomer since its phenylurethan was reported³ to melt at 115–116°. Although stereospecific reduction of ketones by lithium aluminum hydride frequently has been ob-

(1) Abstracted from a thesis presented by A. D. Olin to the Graduate School for the Ph.D. degree, December, 1955.

(2) R. A. Barnes, *THIS JOURNAL*, **75**, 3004 (1953); R. A. Barnes and M. T. Beachem, *ibid.*, **77**, 5388 (1955).

(3) J. C. Bardhan and S. C. Sengupta, *J. Chem. Soc.*, 2520, 2278 (1932).