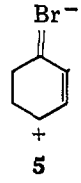
we examined the reaction of 2 with potassium *t*-butoxide in dimethyl sulfoxide in order to determine if such reaction conditions would provide a more suitable means of preparing 1 from 2. Treatment of 2 with 0.5 *M* potassium *t*-butoxide in dimethyl sulfoxide for 8 hr. at 75° gave in 35% yield a mixture of 79% 1 and 21% 2. In order to determine if this was the equilibrium mixture, 1 was treated in a similar manner; the mixture of bromocyclohexadienes obtained was identical with that obtained from 2.[10]

The difference in free energy between 1 and 2 (0.9 kcal. at 75°) appears to be the results of greater conjugation of bromine with cyclohexadiene system in 1 (*cf.* 5).



5

Although admittedly some disproportionation to bromobenzene and bromocyclohexene could have occurred, and these products, because of further reaction with potassium *t*-butoxide, escaped detection,[11] it is clear that *t*-butoxide-catalyzed disproportionation of 1 and 2 occurs considerably more slowly than the disproportionation of 1,3-cyclohexadiene to benzene and cyclohexene under similar conditions.[2] The slow step postulated for the disproportionation of 1,3-cyclohexadiene is transfer of hydride from cyclohexadienyl anion to cyclohexadiene to form benzene and cyclohexenyl anion. Apparently, substitution of bromine on the cyclohexadiene ring results in the introduction of substantial, nonbonded interactions in the transition state for hydride transfer and thereby markedly decreases the rate of disproportionation.

Experimental

Boiling points are uncorrected. Infrared spectra were obtained with a Beckman IR-4 spectrophotometer. Ultraviolet spectra of cyclohexane solutions were obtained with a Cary Model 14 recording spectrophotometer. N.m.r. spectra were obtained with a Varian Associates HR-60 system equipped with integrator and base-line stabilizer of samples as 20% solutions in carbon tetrachloride contained in 5-mm.-o.d. tubes. Resonance frequencies in n.m.r. spectra were determined relative to internal TMS using the side-band technique with a Packard CD-200 audiooscillator. Gas–liquid partition chromatograms were obtained using a 0.25 in. × 15 ft. column packed with octyl phthalate on Chromasorb W-HMDS in an Aerograph Model A-700 (Wilkens Instrument and Research, Inc., Walnut Creek, Calif.). Microanalyses were performed by Mr. V. H. Tashinian, Berkeley, Calif.

2-Bromo-1,3-cyclohexadiene (2).—A mixture of 6.0 g. (0.025 mole) of 2,3-dibromocyclohexene[4] and 150 ml. of quinoline was heated at 125° for 16 hr. The reaction mixture was allowed to cool, 300 ml. of ether was added, and the organic solution was extracted with dilute aqueous hydrochloric acid in order to remove the quinoline. The ether solution was dried and distilled to give 2.1 g. (53%) of pale yellow liquid with b.p. 43° (15 mm.), $n^{26}D$ 1.5293.

Anal. Calcd. for C_6H_7Br: C, 45.32; H, 4.44. Found: C, 44.99; H, 4.40.

1-Bromo-1,3-cyclohexadiene (1).—Following the procedure described for the preparation and isolation of 2 except that the reaction temperature was 175°, a pale yellow liquid was obtained in 40% yield. The gas–liquid partition chromatogram showed the presence of 2 and a second compound (1) in a ratio of 2:1 (assuming equal thermal conductivities). Compound 1 was obtained pure by preparative-scale g.l.p.c. It had $n^{24.5}D$ 1.5365.

Anal. Calcd. for C_6H_7Br: C, 45.32; H, 4.44. Found: C, 44.84; H, 4.30.

Equilibration of 1 and 2.—A mixture of 3.0 g. (0.027 mole) of potassium *t*-butoxide, 50 ml. of dimethyl sulfoxide, and 2.0 g. (0.013 mole) of 2 was heated at 75° for 8 hr. The dark mixture was cooled, water and ether were added, and the phases were separated. The ether solution was dried with magnesium sulfate and concentrated by distillation. Analysis of the concentrate by g.l.p.c. showed the presence of 1 and 2 in a ratio of 79:21. Continued distillation gave 0.7 g. (35%) of a mixture of 1 and 2, the infrared spectrum of which was consistent with the analysis obtained by g.l.p.c.

1-Bromo-1,3-cyclohexadiene (1, 0.4 g.) was treated as described for 2. Analysis of the resulting ether concentrate by g.l.p.c. showed the presence of 1 and 2 in a ratio of 79:21.

(10) (a) From consideration of results of base-catalyzed equilibrations of cyclohexadienes,[10b,c] equilibration of 1 and 2 is likely to occur through the intermediacy of 1-bromo-1,4-cyclohexadiene (4). Interestingly, although the equilibrium constant for the 1,3- ⇌ 1,4-cyclohexadiene interconversion is ~0.5, the 1 and 2 appeared to be essentially free of 4. (b) W. v. E. Doering, G. Schroeder, K. Trautner, and S. Staley, 144th National Meeting of The American Chemical Society, Los Angeles, Calif., April 1963, Abstracts of Papers, p. 14 m. (c) R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Am. Chem. Soc.*, **85**, 3032 (1963).

(11) Treatment of bromobenzene with potassium *t*-butoxide in dimethyl sulfoxide has been reported to yield *t*-butyl phenyl ether.[12] The fate of 1-bromocyclohexene on similar treatment remains to be determined; however, likely products include *t*-butyl cyclohexenyl ethers, and cyclohexadiene and its disproportionation products. The 1 and 2 obtained from the equilibrations were essentially free (<2%) of *t*-butyl ethers and carbonyl compounds, but it is conceivable that minor amounts (<10% yield) of volatile hydrocarbons could have escaped detection.

(12) D. J. Cram, B. Rickborn, and G. R. Knox, *J. Am. Chem. Soc.*, **82**, 6412 (1960).

A Convenient Method for the Preparation of 1,3-Cyclohexanedione[1]

J. C. SIRCAR AND A. I. MEYERS

Department of Chemistry,
Louisiana State University in New Orleans,
New Orleans, Louisiana 70122

Received June 2, 1965

In connection with some steroidal studies, it became necessary to have on hand substantial quantities of the useful intermediate,[2] 1,3-cyclohexanedione. Existing procedures[3] for obtaining this compound require rather tedious techniques, among them, high pressures (90–100 atm.) and complex nickel catalysts. Employing milder conditions result in poor yields and considerable recovery of starting materials.

It has been observed that 1,3-cyclohexanedione can be readily prepared by room-temperature, low-pressure hydrogenation of resorcinol in aqueous alkaline solution in the presence of rhodium on alumina. The yield of the diketone, after 16–18 hr., was 85%. The use of ethanol or acetic acid solvent in the absence of alkali results in the complete reduction to 1,3-cyclohexanediol. When the rhodium catalyst was first preconditioned[4] by suspension in acetic acid for 2 hr. and sub-

(1) This study supported by the National Institutes of Health (GM-06248-06).

(2) V. I. Gunar and S. I. Zavyalov, *Vopr. Khim. Terpenov i Terpenoidov*, 213 (1960) [*Chem. Abstr.*, **55**, 14714a (1961)], and other references cited therein.

(3) "Organic Synthesis," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p. 278. References for other methods of preparation are also cited.

(4) A. I. Meyers, W. Beverung, and G. Garcia-Munoz, *J. Org. Chem.*, **29**, 3427 (1964).

jected to a hydrogen atmosphere, the effect upon the reduction of resorcinol was inconclusive. Although only 1 equiv. of hydrogen was absorbed, no diketone could be isolated from the oily mixture of products.

Attempts to produce 1,4-cyclohexanedione similarly by reduction of hydroquonine failed, although good yields of 1,4-cyclohexanediol were obtained.

Experimental[5]

1,3-Cyclohexanedione.—A solution of resorcinol (11.0 g.) in sodium hydroxide solution (4.8 g. of sodium hydroxide in 20 ml. of water) was hydrogenated in the presence of 1.1 g. of 5% rhodium-on-alumina for 16–18 hr. at 50 p.s.i. in a Parr apparatus. The reduction ceased after the absorption of 1 equiv. of hydrogen. The catalyst was removed by filtration and the aqueous solution was carefully acidified with concentrated hydrochloric acid at 0°. The crude product, 9.1 g. (m.p. 104–106°), was recrystallized from benzene to yield pure 1,3-cyclohexanedione, m.p. 105–107°.

Reduction of Resorcinol to *cis*- and *trans*-1,3-Cyclohexanediol.—A solution of 11.0 g. of resorcinol in ethanol or acetic acid (50 ml.) was hydrogenated in the presence of 1.1 g. of rhodium on alumina at 52 p.s.i. for 2.6 hr. The system absorbed 3 equiv. of hydrogen. After removal of the catalyst and evaporation of the solvent, a viscous oil remained which showed strong –OH absorption in the infrared. The yield of the mixture of diols was 11.1 g.

Reduction of Hydroquinone to *cis*- and *trans*-1,4-Cyclohexanediol. A.—A solution of hydroquinone (11.0 g.) in aqueous alkali (as above) was hydrogenated using 1.1 g. of rhodium catalyst. After 24 hr. the catalyst was removed and the aqueous solution was acidified to yield 6.0 g. of starting material.

B.—When the same amount of hydroquinone and rhodium catalyst was hydrogenated in ethanol or acetic acid solvent, a rapid absorption of 3 equiv. of hydrogen was observed. Removal of the catalyst and evaporation of the solvent yielded 11.7 g. of a viscous oil showing the –OH stretching frequency of the isomeric 1,4-diols, and the absence of any carbonyl absorption.

(5) Melting points were determined on a Fisher-Johns apparatus and are corrected.

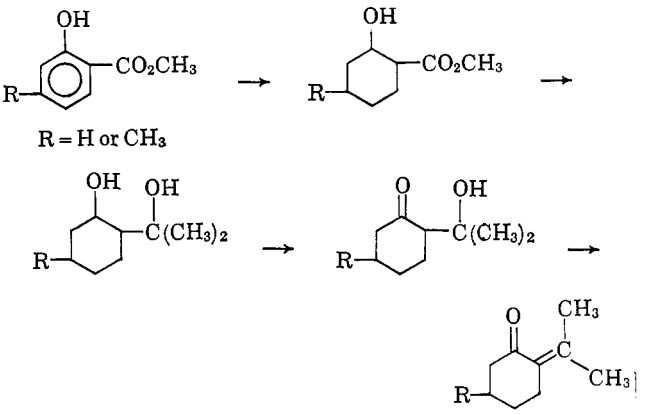
Synthesis of 2-Isopropylidenecyclohexanones. (±)-Pulegone

JOSEPH WOLINSKY, MICHAEL SENYEK, AND STUART COHEN

Department of Chemistry, Purdue University, Lafayette, Indiana

Received April 6, 1965

Samples of 2-isopropylidenecyclohexanones, particularly (±)-pulegone, were desired in connection with other investigations being conducted in this laboratory.[1,2] (±)-Pulegone has been prepared by cyclization of citronellic acid[3] and by hydrolysis of the product derived from the reaction of methylmagnesium iodide with the ethylene ketal of 2-carboethoxy-5-methylcyclohexanone.[4,5] 2-Isopropylidenecyclohexanone can also be obtained from the ethylene ketal of 2-carboethoxycyclohexanone, but is only a minor product in the cyclization of 7-methyloct-6-enoic acid.[6] The lack of a general synthetic method and the relative unavailability of certain of the above-mentioned starting materials prompted us to devise a convenient synthesis of 2-isopropylidenecyclohexanones from commercially available salicylic or cresotic acids as outlined below.



Catalytic hydrogenation of methyl 2-hydroxy-4-methylbenzoate using Raney nickel catalyst afforded a mixture of isomeric methyl 2-hydroxy-5-methylcyclohexanecarboxylates. This isomeric mixture was converted into the corresponding mixture of glycols with methyllithium. Oxidation of the glycols according to the Jones procedure[7] gave 2-(α-hydroxyisopropyl)-5-methylcyclohexanone which was converted into (±)-pulegone by distillation from a trace of iodine.

2-Isopropylidenecyclohexanone and 2-isopropylidene-4-methylcyclohexanone were prepared in a similar manner from methyl salicylate and methyl 2-hydroxy-5-methylbenzoate, respectively. It is seen that this procedure is general for the synthesis of substituted 2-isopropylidenecyclohexanones from available salicylic acid derivatives.

Experimental[8]

Methyl 2-Hydroxy-4-methylbenzoate.—A solution of 120 g. (0.789 mole) of 2,4-cresotic acid in 600 ml. of methanol and 10 ml. of concentrated sulfuric acid was heated at reflux for 184 hr. The dark orange mixture was poured into 800 ml. of water and the layers were separated. The aqueous phase was extracted with ether. The combined ether extracts and organic layer were dried and then distilled to give 116.3 g. (88.8%) of a colorless liquid, b.p. 75–76° (1.5 mm.), $n^{18}D$ 1.5360 (lit.[9] b.p. 242–244°, $n^{15}D$ 1.5378).

Methyl 2-Hydroxy-4-methylcyclohexanecarboxylate.—A mixture of 102.3 g. (0.616 mole) of methyl 2-hydroxy-4-methylbenzoate, 12 g. of W-2 Raney nickel,[10] and 25 ml. of methanol was stirred for 4 days in a 250-ml. hydrogenation bomb at 150° under 1500 p.s.i. of hydrogen. The catalyst was removed by filtration and distillation gave 69.5 g. (65.6%) of a colorless oil, b.p. 79–80° (0.7 mm.), $n^{22}D$ 1.4596, ν_{max} 2.90 and 5.88 μ. Vapor phase chromatography on a Carbowax 20M column indicated the presence of a mixture of stereoisomers.

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.59; H, 9.66.

(1) J. Wolinsky, T. Gibson, H. Wolf, and D. Chan, *Tetrahedron*, **21**, 1247 (1965).

(2) M. Senyek, M.S. Thesis, Purdue University, June 1964.

(3) W. Kuhn and H. Schinz, *Helv. Chim. Acta*, **36**, 161 (1953); J. C. Bardhan and K. C. Bhattacharyya, *Chem. Ind.* (London), 800 (1951).

(4) C. Black, G. L. Buchanan, and A. W. Jarvie, *J. Chem. Soc.*, 2971 (1956).

(5) S. M. Mukherji, R. P. Gandhi, and O. P. Vig, *J. Indian Chem. Soc.*, **33**, 853 (1956); O. P. Vig, *et al.*, *ibid.*, **41**, 420 (1964).

(6) M. F. Ansell and S. F. Brown, *J. Chem. Soc.*, 2955 (1958).

(7) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

(8) All boiling and melting points are uncorrected. N.m.r. spectra were measured at 60 Mc. by Mr. W. E. Baitinger with the Varian Associates A-60 spectrometer. Chemical shifts are given with reference to tetramethylsilane. The microanalyses were performed by Dr. C. S. Yeh and associates.

(9) C. Guillaumin, *Bull. soc. chim. France*, [4] **7**, 374 (1910).

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