145° for 1 hour. Distillation gave 26.7 g. boiling between 76 and 97° at 2.9 mm. (42% yield). Analysis indicated 11.2 meq. of ester/g. (theoretical for diacetoxy cyclopentene 10.87).

(b) **From Cyclopentenediol.**—Cyclopentenediol (108.6 g., 1.086 moles) was added over a period of 1.5 hours to 220 g. (2.16 moles) of acetic anhydride at 65–90°. After the complete addition the acetic acid was distilled through a Widmer column at 69–72° at 152 mm. until 129.4 g. had collected. Distillation of the residue afforded 195.9 g. (98% yield) of diacetate boiling between 75 and 87° (4.5 mm.). Analysis indicated 11.0 meq. of ester/g. (theoretical 10.87).

CORPUS CHRISTI, TEX.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

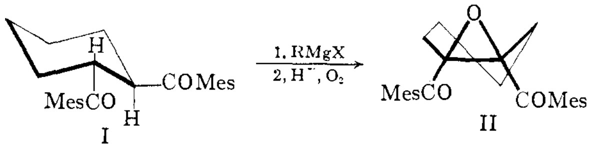
Autoxidation of the Enol Form of 1,2-Dimesitoylcyclohexane. A New Route to Epoxy Ketones[1]

BY REYNOLD C. FUSON, WILLIAM R. HATCHARD, ROGER H. KOTTKE[2] AND JAMES L. FEDRICK[3]

RECEIVED AUGUST 20, 1959

Enolization of *trans*-1,2-dimesitoylcyclohexane by treatment with a Grignard reagent followed by air oxidation of the enol in strongly acidic solution gives *cis*-1,2-dimesitoyl-1-cyclohexene oxide. Autoxidation in dilute acidic solution produces this oxide, along with 2-mesitoyl-1-cyclohexen-1-ol and mesitoic acid. Platinum-catalyzed oxidation of the monoenol of *trans*-1,2-dimesitoylcyclohexane yields 1,6-dimesitoyl-1-cyclohexene. This olefin has been made also by treatment of the dienol salt of the diketone with iodine. Epoxidation of the olefin has been accomplished with alkaline hydrogen peroxide.

Treatment of *trans*-1,2-dimesitoylcyclohexane (I) with a Grignard reagent followed by air oxidation of the resulting enol has been found to yield the symmetrical *cis*-1,2-dimesitoylcyclohexene oxide (II). When the liberation and autoxidation were conducted in strongly acidic solution, the epoxide was obtained in 89% yield.



Structure of the Oxide II.—When the oxide was treated with 48% hydrobromic acid under vigorous conditions, it was converted to *o*-dimesitoylbenzene.[4] Prolonged treatment of the oxide with zinc and hydrochloric acid regenerated the original diketone I. The oxide proved to be stable to a hot mixture of acetic and sulfuric acids as would be expected if it had the 1,2-epoxy structure, since acid cleavage of such ring systems would generate a carbonium ion adjacent to a carbonyl group.

The spectroscopic data[5] support the symmetrical structure for the epoxide. The shift produced in the ultraviolet spectrum by the formation of the oxide from *trans*-1,2-dimesitoylcyclohexane is the same as that observed when 1,2-dimesitoylethane is converted to *trans*-1,2-dimesitoylethylene oxide. The nuclear magnetic resonance spectrum of *trans*-1,2-dimesitoylcyclohexane[6] has a peak (+2.2 p.p.m.) characteristic of tertiary hydrogen atoms adjacent to carbonyl groups. This peak (+2.2 p.p.m.) was identified by the relation of the area under its curve to that under the peak for methylene hydrogen (+3.5 p.p.m.) and by the fact that this same peak appears in the spectrum of cyclohexyl phenyl ketone in the required ratio to the methylene hydrogen peak. The tertiary hydrogen peak is absent in the spectrum of the oxide. A weak tertiary hydrogen atom band is present at 1315 cm.$^{-1}$ (carbon tetrachloride)[7] in the infrared spectra of *trans*-1,2-dimesitoylcyclohexane (I), 1,6-dimesitoyl-1-cyclohexene, 1,6-dimesitoyl-1-cyclohexene oxide and Δ^4-2,6-endoxo-*exo-cis*-tetrahydrophthalic anhydride. In agreement with the symmetrical epoxide structure, this band is absent in the spectrum of the oxide from *trans*-1,2-dimesitoylcyclohexane.

Confirmation of the structure assigned to the oxide is provided by the characteristic symmetrical epoxide bands at 1240, 1175 and 840 cm.$^{-1}$ (carbon tetrachloride) in the infrared spectra.[7] These bands are identified readily by comparing the spectra of the two model compounds, 1,2-dimesitoylethane and 1,2-dimesitoylethylene oxide; the bands are present only in the epoxide. It might be mentioned that the *unsym*-epoxide bands at 1100 and 910 cm.$^{-1}$ (chloroform) are quite different as can be seen by a comparison of the spectrum of duryl α-mesitylethyl ketone with that of 1-mesityl-1-duroylethylene oxide and the spectrum of *trans*-1,2-dimesitoylcyclohexane with that of 1,6-dimesitoyl-1-cyclohexene oxide. Any other bridged ether structure that might be proposed

---

(1) This investigation was supported in part by a grant from the Office of Ordnance Research, U. S. Army (Contract No. DA-11-022-ORD-874).

(2) Visking Corporation Fellow, 1954–1955.

(3) Toms–River Cincinnati Chemical Corp. Fellow, 1957–1958.

(4) R. C. Fuson, S. B. Speck and W. R. Hatchard, *J. Org. Chem.*, **10**, 55 (1945).

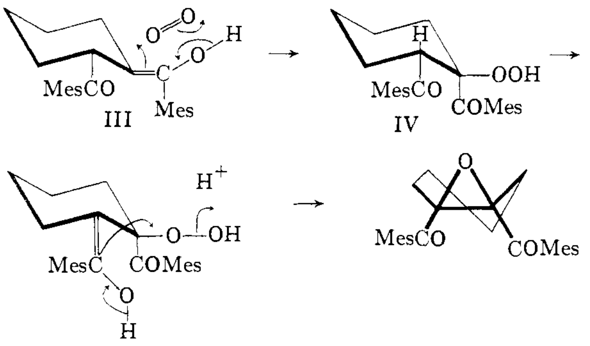
(5) The ultraviolet spectra were obtained by Mr. J. Chin with a Cary model 14 recording spectrophotometer. The spectra were measured in 1-cm., quartz cells at concentrations of about 5 × 10^{-5} mole per liter in absolute ethanol. The infrared spectra were recorded by Mr. James Brader, Mrs. Louise Griffing, Mr. Cy Portnow, Mr. Paul E. McMahon and Miss Mary DeMott. The proton magnetic resonance spectra were determined by Mr. Benjamin Shoulders at 40 mc. rf. with a Varian model V-4300 B high-resolution spectrometer fitted with a field-sensing stabilizer ("Super Stabilizer"). The measurements, were made in approximately 15% solutions. The chemical shifts expressed in p.p.m. relative to water were actually determined relative to methylene chloride by use of a concentric-tube cell with methylene chloride in the outer compartment. Subtraction of 0.65 p.p.m. from shifts relative to methylene chloride was used in calculating shifts in p.p.m. relative to water. The authors are grateful to Dr. N. F. Chamberlain and to The Humble Oil and Refining Co. for preliminary nuclear magnetic resonance studies.

(6) It was necessary to use as solvent a mixture of one part of phenol and two parts of carbon disulfide for the n.m.r. spectra of this and similar ketones; band splitting could not be determined because of poor resolution.

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd. Ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

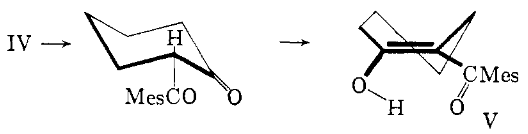
for the autoxidation product must be ruled out. Four-, five- and six-membered cyclic ethers have one strong band in the 1100 to 1000 cm.$^{-1}$ region as does Δ^4-2,6-endoxo-*exo*-*cis*-tetrahydrophthalic anhydride. Two equally strong carbonyl bands at 1705 and 1670 cm.$^{-1}$ (carbon tetrachloride) are found in the spectrum of the epoxide. *trans*-1,2-Dimesitoylethylene oxide, however, has only a single carbonyl band at 1690 cm.$^{-1}$ (chloroform). It is possible to attribute the carbonyl doublet in the epoxide to Fermi resonance; it may be peculiar to the *cis*-epoxide conformation. This same phenomenon accounts for the 60 cm.$^{-1}$ separation of the carbonyl bands in the spectra of cyclic anhydrides.[7]

Mechanism of the Oxidation.—A possible mechanism for the epoxidation involves initial hydrolysis of the dienol salt of *trans*-1,2-dimesitoylcyclohexane to the corresponding dienol. Autoxidation of the monoenol III, formed by partial ketonization of the dienol, is postulated to proceed by oxygen addition from the less hindered side of the molecule in agreement with the proposal of Zimmerman[8] to yield the diketo hydroperoxide IV.[9,10] The carbonyl function in the β-position with respect to the hydroperoxide group would be expected to undergo enolization in the strongly acidic medium; the enolic hydroperoxide, under the influence of acid, could generate a cationic transition state in which the oxonium ion may attack the double bond with simultaneous loss of water.

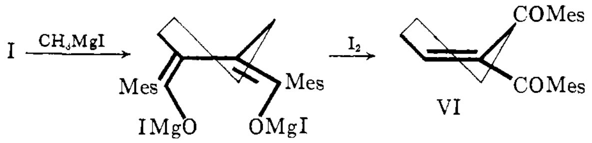


It seems necessary to assume the second enolization step since the monoenol (isolated as a waxy solid by hydrolysis of the dienol salt) gave only a small amount (3%) of the oxide when exposed to air in neutral solution, conditions unfavorable to enolization. Direct decomposition of the hydroperoxide would require hydrogen abstraction from a carbon atom by way of an unfavorable transition state.[11] 1,2-Dimesitoylethane, under the conditions used for epoxidation, failed to yield an epoxide; instead *trans*-1,2-dimesitoylethylene was isolated. Perhaps the epoxidation is dependent on the geometry of the cyclohexane system or on the presence of the tertiary hydrogen atoms adjacent to the ketone functions.

Oxidative Cleavage.—When the liberation and oxidation of the enol of *trans*-1,2-dimesitoylcyclohexane are conducted in more dilute hydrochloric acid, the chief reaction is oxidative cleavage to give mesitoic acid and 2-mesitoyl-1-cyclohexene-1-ol (V). These products might arise by decomposition of the diketo hydroperoxide.

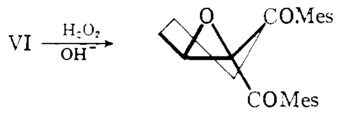


1,6-Dimesitoyl-1-cyclohexene.—In an attempt to synthesize the corresponding symmetrical olefin, the enol salt of *trans*-1,2-dimesitoylcyclohexane was treated with iodine. The oxidation product was, instead, the unsymmetrical olefin, 1,6-dimesitoyl-1-cyclohexene (VI). None of the symmetrical cyclohexene was isolated; it may be that steric requirements are too demanding for it to be stable.[12]



1,6-Dimesitoyl-1-cyclohexene undergoes dehydrogenation to yield the known compound, 1,2-dimesitoylbenzene.[4] The olefin decolorizes bromine, and its infrared spectrum has two carbonyl bands. Catalytic reduction of the olefin required one mole of hydrogen. When the reaction mixture was exposed to the air, however, an instantaneous, quantitative, catalytic oxidation of the enol to the unsymmetrical olefin occurred. A 1,4-dehydrogenation of this type had been reported previously.[13]

Epoxidation of 1,6-dimesitoyl-1-cyclohexene (VI) was accomplished by the use of alkaline hydrogen peroxide.



The epoxy bands in the infrared spectrum of the unsymmetrical oxide are the same as those (1100, 900 cm.$^{-1}$) present in the spectrum of 1-duroyl-1-mesitylethylene oxide; they are absent from the spectrum of duryl α-mesitylethyl ketone.

Experimental[14]

***cis*-1,2-Dimesitoylcyclohexene Oxide.**—A solution of 5.0 g. (0.0132 mole) of *trans*-1,2-dimesitoylcylohexane in 250 ml. of benzene was added to a Grignard reagent prepared from 3.16 g. (0.130 g. atom) of magnesium and 16.4 g. (0.150 mole) of ethyl bromide in 75 ml. of ether. The mixture was stirred at room temperature for 24 hr. and poured into a slurry of crushed ice and 50 ml. of concentrated hydrochloric acid. After the surface of the hydrolysate had been exposed to air for 24 hr., the ether layer was removed, washed with 100 ml. of 5% sodium bicarbonate and two 100-ml. portions of water and dried over anhydrous sodium sulfate.

---

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

(9) E. P. Kohler, *Am. Chem. J.*, **36**, 177 (1906).

(10) J. Rigaudy, *Compt. rend.*, **226**, 1993 (1948).

(11) E. J. Corey and R. W. White, This Journal, **80**, 6686 (1958).

(12) R. E. Buckles, *Chem. Revs.*, **57**, 641 (1957).

(13) R. C. Fuson and R. E. Foster, This Journal, **65**, 913 (1943). This phenomenon might be explained by assuming that the hydrogen atom on the enol oxygen atom and one of those on the β-carbon atom are adsorbed on the platinum surface. These activated hydrogen atoms could then react with molecular oxygen to form hydrogen peroxide, leaving behind the 1,6-dimesitoyl-1-cyclohexene-1-ol.

(14) All melting points are corrected; all boiling points are uncorrected.

The solution was filtered, the solvent was evaporated, and the residual oil was crystallized from 85% ethanol. The product, dried at 100° for 24 hr., was colorless crystals (m.p. 136–137°), yield 4.5 g. (89%).

Anal.[15] Calcd. for $C_{26}H_{30}O_3$: C, 79.96; H, 7.74. Found: C, 80.07; H, 7.89.

A comparison of the ultraviolet spectra of the known compounds 1,2-dimesitoylethane ($\lambda_{\max}$ 246 mμ, log ϵ 3.75) and 1,2-dimesitoylethylene oxide ($\lambda_{\max}$ 268 mμ, log ϵ 3.76), shows a shift of 22 mμ on formation of the epoxide. This same shift is observed when the spectrum of the starting material ($\lambda_{\max}$ 248 mμ, log ϵ 4.02) is compared to that of *cis*-1,2-dimesitoyl-1-cyclohexene oxide ($\lambda_{\max}$ 270 mμ, log ϵ 4.00).

When 1.0 g. of the oxide was heated for 16 hr. in a mixture of 20 ml. of toluene and 20 ml. of 48% hydrobromic acid, a solid was obtained which, after recrystallization from benzene, melted at 230–234°. A mixed melting point with *o*-dimesitoylbenzene[4] was not depressed. Long heating (26 hr.) of the oxide with zinc and hydrochloric acid under reflux converted it in part to *trans*-1,2-dimesitoylcyclohexane, m.p. 237–240°. In one experiment the oxide was recovered unchanged after it (1.80 g.) had been heated at 50–60° for 8 hr. with a mixture of 50 ml. of acetic acid and 20 ml. of 60% sulfuric acid.

Autoxidation of the Enol Form of *trans*-1,2-Dimesitoylcyclohexane in the Presence of Dilute Hydrochloric Acid.—To a Grignard reagent, prepared from 4.42 g. (0.182 g. atom) of magnesium and 23.0 g. (0.211 mole) of freshly distilled ethyl bromide in 100 ml. of ether, was added 7.00 g. (0.0186 mole) of *trans*-1,2-dimesitoylcyclohexane in 350 ml. of benzene. The mixture, which after being stirred at room temperature for 24 hr. was olive-green, was poured into a slurry of 50 ml. of concentrated hydrochloric acid and crushed ice in a 1-l. beaker. The resulting mixture was allowed to stand for 5 days with the organic phase exposed to air. From this layer was obtained an oil which crystallized from 40 ml. of 70% ethanol as a yellow solid (5.25 g., m.p. 129–143°). Trituration of this solid with 40 ml. of absolute ethanol left 2.48 g. of a solid melting at 162–167°. One recrystallization of the material from ethanol raised the melting point to 170–171° (2.06 g., 29%). The infrared spectrum of the compound was superimposable on that of the known *cis*-1,2-dimesitoylcyclohexane. Treatment of the dark brown oil, obtained by concentration of the filtrate, with 5 ml. of absolute ethanol precipitated 90 mg. (13%) of a colorless solid (m.p. 136–137°). A mixed melting point with *cis*-1,2-dimesitoyl-1-cyclohexene oxide was not depressed. The residual oil was taken up in 100 ml. of chloroform and extracted with two 50-ml. portions of 5% sodium bicarbonate. Acidification of the basic extract and purification of the precipitate gave 156 mg. (3%) of mesitoic acid, m.p. 153–154°. A mixed melting point with an authentic sample was not depressed.

Chloroform was removed from the organic phase by low-pressure distillation, and the residual, dark-brown oil was dried (2.60 g.). A solution of this oil in 40 ml. of acetone was added to a solution of 0.950 g. (0.00475 mole) of copper (II) acetate in 100 ml. of 80% aqueous acetone. The light blue color of the hydrated cupric ion disappeared, and a green curdy precipitate, typical of copper chelates, formed. After this mixture had been stirred for 24 hr., the precipitate was removed, washed with four 250-ml. portions of 50% ethanol and dried 12 hr. at 100°. A solution of the green solid (1.90 g.) in 300 ml. of chloroform was washed with an equal volume of water and dried over sodium sulfate. The mass left after removal of solvent was dissolved in a mixture of 5 ml. of chloroform and 15 ml. of high-boiling petroleum ether, and the solution was concentrated to 10 ml. The cooled mixture yielded 570 mg. (6%) of a green solid, m.p. 245–247°. A perturbed carbonyl band (1565 cm.$^{-1}$) was present in the infrared spectrum. The properties of the product are those to be expected for the copper chelate of 2-mesitoyl-1-cyclohexene-1-ol.

Anal. Calcd. for $C_{32}H_{38}O_4Cu$: C, 69.85; H, 6.96. Found: C, 69.72; H, 6.92.

The filtrate and the copper chelate were combined and heated at reflux with a two-phase system of 50 ml. of ether and 50 ml. of water containing 6 ml. of concentrated hydrochloric acid until solution had taken place. The organic phase was removed, washed with 60 ml. of 5% aqueous sodium bicarbonate and 60 ml. of water, then dried over sodium sulfate. The brown oil, obtained by concentration of the organic phase, could not be distilled on a micro distillation apparatus at a pot temperature of 240° (0.5 mm.); however, 436 mg. (10%) of a clear, light-yellow distillate (n^{25}D 1.5620) was collected when a free flame was applied to the reaction flask. The 2-mesitoyl-1-cyclohexen-1-ol gave a purple-red color in the ferric chloride test. The infrared spectrum had the usual chelated carbonyl peak (1610-1550 cm.$^{-1}$).

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.69; H, 8.19.

Autoxidation of the Enol Form of *trans*-1,2-Dimesitoylcyclohexane in the Absence of an Acid Catalyst.—*trans*-1,2-Dimesitoylcyclohexane, (3.76 g., 0.0100 mole) was enolized with 0.1 mole of the ethyl Grignard reagent in the manner previously described. The reaction mixture was hydrolyzed by the addition of 1.3 ml. of concentrated hydrochloric acid in 100 ml. of water. The organic phase was washed with 100 ml. of 5% sodium bicarbonate solution and twice with water, then dried over sodium sulfate. Low-pressure distillation of this solution left 3.5 g. of a colorless, waxy solid, the infrared spectrum of which contained bands for hydroxyl (3350 cm.$^{-1}$) and carbonyl (1690 cm.$^{-1}$) groups. The reaction and as much of the work-up as possible were carried out under nitrogen. A solution of the solid in 400 ml. of ether was cooled to 5°, and oxygen was passed through it for 10 hr. The colorless solution was concentrated to an oil which partially crystallized from aqueous ethanol; a colorless solid (0.872 g., m.p. 172–190°) was isolated. When it was treated with aqueous ethanol, 0.134 g. (3.4%) of colorless crystals (m.p. 132–136°) separated. A mixed melting point with *cis*-1,2-dimesitoyl-1-cyclohexene oxide was not depressed.

1,6-Dimesitoyl-1-cyclohexene.—The procedure was modelled after that used for the synthesis of 1,2-dimesitoylethylene.[16] A solution of 16.0 g. (0.0424 mole) of *trans*-1,2-dimesitoylcyclohexane in 800 ml. of toluene was added to a Grignard reagent prepared from 11.6 g. (0.476 g. atom) of magnesium and 80.0 g. (0.564 mole) of methyl iodide in 600 ml. of anhydrous ether. The reaction mixture was heated at reflux for 12 hr. Iodine in ether solution was then added to the mixture until a brown, iodine color persisted. After destruction of excess iodine with a solution of sodium bisulfite, the reaction mixture was washed with 500 ml. of 5% sodium bicarbonate and 500 ml. of water. The resulting clear, yellow solution developed a bright-green color when dried over sodium sulfate for 6 hr. Removal of solvent by low-pressure distillation left 16.9 g. of dark-green crystals. This product was taken up in 50 ml. of chloroform, and the chloroform replaced by 200 ml. of high-boiling petroleum ether on a steam-bath. When the solution was allowed to stand at 5° for 12 hr., 8.61 g. of a light-yellow solid (m.p. 201–204°) separated. Recrystallization from the same solvent gave 6.76 g. (43%) of 1,6-dimesitoyl-1-cyclohexene as colorless crystals, m.p. 204–206°. A second recrystallization gave a pure sample, m.p. 205–206°. Carbonyl bands appear in the infrared spectrum at 1650 and 1685 cm.$^{-1}$, as would be expected if one carbonyl group was conjugated with a double bond and the other was not. The tertiary hydrogen atom absorption peak (1310 cm.$^{-1}$) is present but is weaker than that in the spectrum of the starting material. The increase in the intensity of the mesitylene peak at 1610 cm.$^{-1}$ presumably is due to absorption by the olefin bond. The compound decolorized bromine in carbon tetrachloride.

Anal. Calcd. for $C_{26}H_{30}O_2$: C, 83.38; H, 8.07. Found: C, 83.33; H, 8.04.

In a second experiment, run with 4.00 g. (0.0106 mole) of the diketone, the crude reaction product was chromatographed on 120 g. of alumina in a 30-cm. column. The crude olefinic ketone was obtained in a yield of 2.17 g. (68%), m.p. 194–200°.

Dehydrogenation of 1,6-Dimesitoyl-1-cyclohexene.—A mixture of 60.0 mg. of 10% palladium-on-charcoal and 374 mg. of the diketone was heated under nitrogen at 300° for 2 hr. When cool, the product was taken up in chloroform, and the solution was filtered. The solid (m.p. 182–205°) obtained by removal of solvent was recrystallized once from a mixture of 2 ml. of chloroform and 10 ml. of high-boiling petroleum ether and once from 10 ml. of ethanol. It separated as colorless crystals, yield 45.4 mg. (12%), m.p. 226–

---

(15) The microanalyses were performed by Mr. Josef Nemeth, Miss Claire Higham and Mrs. Frederick Ju.

(16) R. E. Lutz and W. G. Reveley, THIS JOURNAL, **61**, 1854 (1939).

230°. The infrared spectrum of the product and that of *o*-dimesitoylbenzene were superimposable.

Hydrogenation of 1,6-Dimesitoyl-1-cyclohexene.—A solution of 374 mg. (0.00100 mole) of the ketone in 60 ml. of absolute ethanol was treated with hydrogen in the presence of a catalyst prepared from 60 mg. of platinum oxide in 15 ml. of absolute ethanol in an Adams micro-hydrogenation apparatus. The volume of hydrogen taken up was 22.4 ml. (0.00100 mole). The reaction vessel was opened to the air with the catalyst still present. When the solution was concentrated, a quantitative amount of the starting material was recovered as a colorless solid.

1,6-Dimesitoyl-1-cyclohexene Oxide.—To a solution of 2.00 g. (0.00535 mole) of 1,6-dimesitoyl-1-cyclohexene and 1 l. of absolute ethanol was added 10.0 ml. (0.0835 mole) of 30% hydrogen peroxide and 12 ml. (0.0300 mole) of 10% sodium hydroxide, with stirring. The addition of hydrogen peroxide caused the solution to develop an orange color and to deposit a colorless solid. The reaction mixture was stirred at room temperature for 48 hr., a portion of 5 ml. of 30% hydrogen peroxide being added every 12 hr. A colorless precipitate was removed by filtration, and an equal volume of water was added to the clear, colorless filtrate; a solid precipitated (700 mg., m.p. 213–225°). Two recrystallizations of this solid from high-boiling petroleum ether–methylene chloride followed by two recrystallizations from chloroform–ethanol yielded 162 mg. (7.9%) of colorless crystals, m.p. 248–251°. The infrared spectrum of this product has one carbonyl band (1685 cm.$^{-1}$), two unsymmetrical epoxide peaks (1100 and 900 cm.$^{-1}$) and a weak band (1310 cm.$^{-1}$) for a tertiary hydrogen atom. The ultraviolet spectrum in ethanol (λ_{max} 235 mμ, log ϵ, 4.10) exhibits no appreciable shift from the peak in the spectrum of *trans*-1,2-dimesitoylcyclohexane.

Anal. Calcd. for $C_{26}H_{30}O_3$: C, 79.96; H, 7.74. Found: C, 80.23; H, 7.89.

Ethyl Hexahydrophthalate.—A solution of 100 g. (0.650 mole) of *cis*-hexahydrophthalic anhydride, 100 ml. (21.8 moles) of absolute ethanol, 300 ml. of anhydrous benzene and 1 ml. of concentrated sulfuric acid was heated at vigorous reflux under conditions that permitted removal of the water as it formed. At the end of 12 hr., water ceased to come over; the ester, purified by conventional procedures, was a clear, colorless oil, yield 94%. The infrared spectrum indicated that the product was contaminated with a small amount of the anhydride used as a starting material. This procedure was found to be superior to the one previously described.[4]

***trans*-1,2-Dimesitoylcyclohexane.**—The ethyl hexahydrophthalate was converted by hydrolysis under conditions known to isomerize the *cis*- acid to the *trans* form. The *trans*-hexahydrophthalic acid (79% yield) was transformed into the acid chloride (97% yield) by use of phosphorus pentachloride.[4] A mixture of 67.3 g. (0.560 mole) of mesitylene and 29.3 g. (0.140 mole) of the acid chloride was allowed to react in the presence of aluminum chloride. From the crude solid 28.1 g. (53%) of pure diketone was isolated after four extractions with boiling benzene; m.p. 241–242°. A mixture melting point (238–239°) with an authentic sample (m.p. 234–235°)[4] was not depressed; the infrared spectrum of the product and that of *trans*-1,2-dimesitoylcyclohexane were superimposable. A hindered aroyl carbonyl band (1695 cm.$^{-1}$) and a peak for tertiary hydrogen (1315 cm.$^{-1}$) are also consistent with the structure. Peaks for the α,α'-tertiary hydrogen atoms in the 1,4-diketone appeared at + 2.2 p.p.m. in the nuclear magnetic resonance spectrum. When the area under the + 2.2 p.p.m. curve was compared to that under the + 3.45 p.p.m. peak (methylene hydrogen), the ratio was found to be 1:4. Evidence for the validity of this assignment was obtained from the spectrum of benzoylcyclohexane. Tertiary hydrogen and methylene hydrogen adsorb at + 1.95 and + 3.5 p.p.m., respectively; the ratio of the areas under these curves is 1:10. In addition, the ultraviolet spectrum of *trans*-1,2-dimesitoylcyclohexane is characteristic of hindered aroyl ketones; λ_{max} 243 mμ, log ϵ 4.02.

The *trans*-diketone remained unchanged after being heated with an equivalent amount of selenium dioxide for 96 hr. in acetic acid and in the presence of an equivalent amount of sodium acetate.

Cyclohexyl Mesityl Ketone.—A Grignard reagent prepared from 4.25 g. (0.175 g. atom) of magnesium, 2.94 g. (0.180 mole) of cyclohexyl bromide and 100 ml. of ether was added during 30 min., with stirring, to a solution of 34.5 g. (0.188 mole) of mesitoyl chloride in 50 ml. of ether and 50 ml. of benzene. The reaction mixture was heated under reflux for 90 min. and decomposed with a mixture of ice and hydrochloric acid. The cyclohexyl mesityl ketone, recrystallized from low-boiling petroleum ether at −50°, melted at 41.0–41.5°. The infrared spectrum has bands at 1695 and 850 cm.$^{-1}$, assignable, respectively, to a carbonyl group and a mesityl nucleus.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 6.93. Found: C, 83.57; H, 6.97.

Other products isolated were mesitoic acid and mesitil. An attempt to form an epoxy derivative of cyclohexyl mesityl ketone was not successful.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Photochemical Reactions. IX.[1] Isomerization of Eucarvone

BY G. BÜCHI AND EDWARD M. BURGESS

RECEIVED JANUARY 25, 1960

Irradiation of eucarvone in alcoholic solution gave mainly 1,4,4-trimethylbicyclo[3.2.0]hept-6-en-2-one which on pyrolysis at 320° was reconverted to eucarvone. Further irradiation of the first photoproduct produced 4,4,6-trimethylbicyclo-[3.2.0]hept-6-en-2-one by a novel photochemical rearrangement whose mechanism is discussed. The structure of the second photoisomer was established by pyrolysis at 380° to 3,3,5-trimethylcyclohepta-4,6-dien-1-one and reduction to 3,3,5-trimethylcycloheptanone. The striking acid-catalyzed isomerization of the first to the second photoproduct can be rationalized in terms of a non-classical cationic intermediate.

Substituted cyclobutanes can be prepared conveniently by photochemical dimerization of appropriately activated olefins.[2] Ring formation becomes especially facile in intramolecular cyclizations, provided the two unsaturated systems involved in the bond-forming process are in spatial proximity. To exemplify we may cite the intramolecular cyclizations leading to carvonecamphor,[3] the photopyrocalciferols,[4] the lumicolchicins,[5]

---

[1] Part of a program of research supported by a grant from the Godfrey L. Cabot Fund, Publication No. 68, M. I. T. Solar Energy Conversion Project. Paper VIII, D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger and L. J. Krebaum, *Helv. Chim. Acta*, **40**, 1732 (1957).

[2] A. Mustafa, *Chem. Revs.*, **51**, 1 (1952).

[3] (a) G. Ciamician and P. Silber, *Ber.*, **41**, 1928 (1908); (b) E. Sernagiotto, *Gazz. chim. ital.*, **48**, 52 (1918); **47**, 153 (1917); (c) G. Büchi and I. M. Goldman, THIS JOURNAL, **79**, 4741 (1957).

[4] (a) A. Windaus, K. Dimroth and W. Breywisch, *Ann.*, **543**, 240 (1940); (b) W. G. Dauben and G. J. Fonken, THIS JOURNAL, **81**, 4060 (1959).

[5] (a) R. Grewe and W. Wulf, *Chem. Ber.*, **84**, 621 (1951); (b) E. J. Forbes, *J. Chem. Soc.*, 3864 (1955).