A magnetically stirred mixture of 165 g. of 4-vinylcyclohexene, 36 g. of di-*t*-butyl peroxide and 0.3 g. of cupric chloride hydrate was gently refluxed 5 hr. under nitrogen, the pot temperature varying from 115–125°. The reaction vessel was fitted with a six-inch glass-helix-packed column and distilling head with controlled take-off. Effluent vapors were trapped and oxygen excluded by a liquid-nitrogen cooled trap and a mercury check-valve which also served to maintain the system pressure slightly above atmospheric pressure. During the course of the reaction, 27 g. of *t*-butyl alcohol and 7 g. of di-*t*-butyl peroxide were collected as distillate. After filtration of the mixture and fractionation of the filtrate, a further 0.5 g. of *t*-butyl alcohol was recovered and 2 g. of di-*t*-butyl peroxide; 110 g. of 4-vinylcyclohexene was recovered. Identification of products was not complete but 4 g. of *t*-butyl vinylcyclohexenyl ether (boiling 30° at 0.2 mm.; n_D^{20}, 1.462) and 4 g. of vinylcyclohexene dehydrodimer were isolated. The infrared spectrum of the *t*-butyl vinylcyclohexenyl ether contains the major olefinic absorptions of 4-vinylcyclohexene; the absorptions at 7.21 and 7.34 μ, assigned to *t*-butyl; a strong band at 8.40 μ, C—O stretching; and a very strong, broad band at 9.4 μ, typical of ethers. A 0.36-g. sample absorbed 85 ml. hydrogen (S.T.P.; 2.0 moles hydrogen per mole) over Adam's catalyst in ethanol at one atmosphere at room temperature.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.9; H, 11.2; mol. wt., 180. Found[13]: C, 78.4; H, 11.2; mol. wt., 192. Subsequent gas chromatographic analysis showed the presence of two as yet unrecognized impurities, totalling possibly 7% of the sample.

Acknowledgment. The authors wish to acknowledge the contribution of Dr. Lieng-huang Lee (Present address: Dow Chemical Company), who helped to establish the direction of this study and began the experimental work. This paper is based on the Ph.D. thesis of J. Neil Henderson and is a part of a research program supported by The Goodyear Tire and Rubber Co.

CLEVELAND 6, OHIO

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

The Structure of 2,6-Dibenzalcyclohexanone Dimer

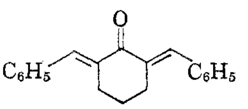
HERBERT O. HOUSE AND ALFRED G. HORTMANN

Received November 21, 1960

A solution of 2,6-dibenzalcyclohexanone in boiling toluene is converted to an equilibrium mixture of the starting ketone and its dimer. Subsequent transformations have established the structure 9 for this dimer.

Solutions of 2,6-dibenzalcyclohexanone (**1**) in boiling acetic anhydride, acetic acid, benzene and ethanol have been reported[1] to yield a colorless dimer, m.p. 187–188°. The dimer was reported[1] to exhibit an ultraviolet maximum at 292 mμ (ϵ 42,500) with infrared bands at 1695, 1608, 754, and 697 cm.$^{-1}$ and to form a dioxime, m.p. 197–198°, and a tetrahydro derivative, m.p. 217–218°. From these observations, as well as the failure to isolate benzoic acid from a permanganate oxidation, the structure II was tentatively suggested for this dimer.

As it was not apparent why the reaction conditions described should convert the unsaturated ketone **1** to structure **2** or to any other dimer containing two carbonyl groups,[2] the formation and constitution of the dimer have been reinvestigated. Our attempts to prepare the dimer by refluxing an ethanol solution of **1** for 120 hours, a process reported to form the dimer in 90% yield, were uniformly unrewarding. In one instance in which an ethanol solution of 17.7 g. of the dimer had been refluxed for 121 hours, chromatography of the mother liquors remaining after separation of the starting material afforded 10 mg. of the crude dimer, m.p. 184–187°. However, the use of the higher-boiling solvents acetic anhydride, bromobenzene and toluene permitted formation of the dimer in reasonable yield. Use of boiling toluene with a reaction period of two days was found most convenient and permitted the isolation of the dimer, m.p. 192–193° dec., in 21% yield. The dimerization proceeded equally well when the reaction mixture was protected from light indicating that the dimerization was not a photochemical transformation. After a solution of the dimer in bromobenzene had been refluxed for twenty hours, the pure, monomeric unsaturated ketone **1** was isolated in 60% yield. Solutions of the ketone **1** and the dimer in boiling toluene were heated until equilibrium was established. In these toluene solutions, containing the equivalent of 0.30*M* 2,6-dibenzalcyclohexanone (**1**), equilibrium was established when 50–55% of the dimer was present.



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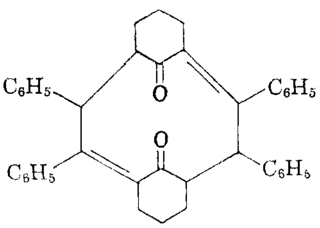

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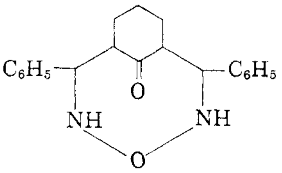
[1] (a) P. Y. Yeh, *J. Taiwan Pharm. Assoc.*, **5**, 2 (1953); (b) P. Y. Yeh, C. T. Chen, S. Y. Ro, and C. H. Wang, *J. Am. Chem. Soc.*, **77**, 3415 (1955).

[2] Although the formation of photodimers containing cyclobutane rings is well known [A. Mustafa, *Chem. Revs.*, **51**, 1 (1952)], there was no indication (ref. 1) that light was required to transform the ketone **1** to its dimer.

The spectra of our product exhibited the features previous noted[1] with an ultraviolet maximum at 293 mμ (ε 43,500) and infrared absorption at 1685 cm.$^{-1}$ but no band in the 3 μ region attributable to a hydroxyl function. Since the previously reported[1] dimer dioxime, m.p. 197–198°, had been obtained in poor yield after a long reaction period and the reported analytical values (C, 82.65; H, 6.34) did not agree with the values calculated for the molecular formula $C_{40}H_{38}N_2O_2$ (C, 83.01; H, 6.62), we were led to consider other structures for this derivative. The reported[3,4] reaction of 2,6-dibenzalcyclohexanone (1) with hydroxylamine to form a substance $C_{20}H_{22}N_2O_2$, m.p. 199–200° dec., suggested that the reported[1] dimer dioxime may have been the substance $C_{20}H_{22}N_2O_2$ formed by partial dissociation of the dimer to 2,6-dibenzalcyclohexanone (1) followed by reaction with hydroxylamine. The substance $C_{20}H_{22}N_2O_2$, which has been formulated as 3[3] or 4[4], exhibits an ultraviolet maximum at 267 mμ (ε 15,500) with broad infrared absorption at 3300 cm.$^{-1}$ as well as a weak band at 1600 cm.$^{-1}$ and, consequently, cannot have either structure 3 or 4. The close resemblance of the ultraviolet spectrum of the substance $C_{20}H_{22}N_2O_2$ to the spectrum of 2-benzalcyclohexanone oxime (5), λ_{max} 272 mμ (ε 15,100), permits the substance $C_{20}H_{22}N_2O_2$ to be assigned either structure 6 or 7, structure 6 being more probable.



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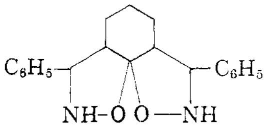

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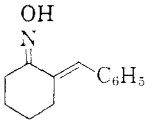

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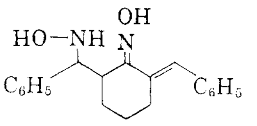

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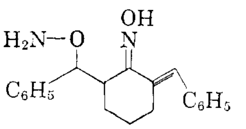


7

Reaction of the dimer with hydroxylamine in either ethanol or pyridine afforded a product, m.p. 198–199.5° dec., which proved not to be identical with the 2,6-benzalcyclohexanone-hydroxylamine product 6, but rather had the composition $C_{40}H_{37}NO_2$ corresponding to the monoxime of the dimer. This monoxime has an ultraviolet maximum at 287 mμ (ε 31,500) with broad infrared absorption at 3350 cm.$^{-1}$ as well as weak bands at 1640, 1615 and 1600 cm.$^{-1}$ The infrared spectrum lacks absorption in the 6μ region attributable to a carbonyl function indicating that the dimer is a monocarbonyl compound rather than a dicarbonyl compound as had previously[1] been supposed.

We were unable to duplicate the previously reported[1] catalytic hydrogenation of an ethanol solution of the dimer over platinum to form a tetrahydro derivative because of the insolubility of the dimer in alcohol. However, hydrogenation of an ethyl acetate solution of the dimer over platinum resulted in a relatively rapid uptake of one equivalent of hydrogen followed by a slower absorption of additional hydrogen. As the mixtures obtained after absorption of more than one and one-half molar equivalents or more proved to be extremely complex, subsequent hydrogenation reactions were stopped after approximately one and one-half equivalents of hydrogen had been absorbed. From a representative experiment of this type the materials isolated were the unchanged dimer (14.8%), a dihydrodimer A, m.p. 161.5–163° (24.5%), a second crystalline form of dihydrodimer A, m.p. 173.5–175° (6.4%), and a dihydrodimer B, m.p. 212.5–214° dec. (4.9%). The dihydrodimer A has infrared absorption at 1720 cm.$^{-1}$ with no band in the 3μ region attributable to a hydroxyl function and an ultraviolet maximum at 293 mμ (ε 28,500); similarly, the dihydrodimer B has a band at 1718 cm.$^{-1}$ in the infrared with an ultraviolet maximum at 292 mμ (ε 23,600).

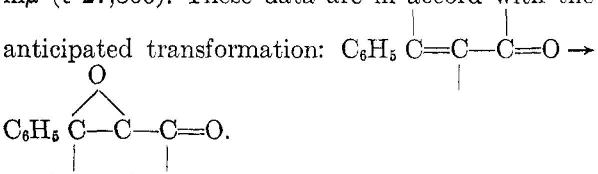
These data are compatible with the presence of the chromophores

$$C_6H_5C{=}CC{=}C \text{ and } C_6H_5C{=}CC{=}O$$

in the dimer and of the chromophores

$$C_6H_5C{=}CC{=}C \text{ and } C_6H_5CHCHC{=}O$$

in the dihydrodimers A and B.[5] Because of the similarity in analytical values for the dimer, the dihydrodimer, and the tetrahydrodimer, additional evidence for these assignments was obtained by reaction of the dimer with alkaline hydrogen peroxide in order to convert the α,β-unsaturated ketone present in the dimer to an α,β-epoxy ketone. The resulting epoxide of the dimer exhibits infrared absorption at 1725 cm.$^{-1}$ but no absorption in the 3 μ region attributable to a hydroxyl group and an ultraviolet maximum at 291 mμ (ε 27,800). These data are in accord with the anticipated transformation:



$$C_6H_5\,C{=}C{-}C{=}O \rightarrow C_6H_5\,\overset{O}{C{-}C}{-}C{=}O.$$

The ready thermal equilibration of monomer 1 and dimer in an inert medium is reasonably accommodated only if one supposes that the dimer is formed by a redistribution of multiple bonds in two molecules of the monomer. Utilizing this

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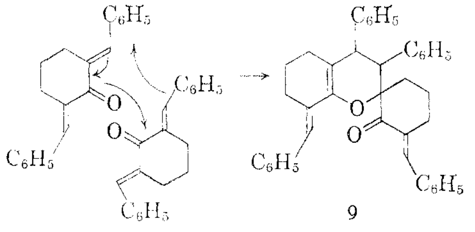
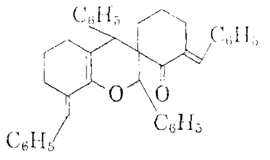
(3) R. Poggi and P. Saltini, *Gazz. chim. ital.*, **64**, 189 (1934).

(4) P. Dreyfuss, *Rend. seminario facolta sci. univ. Cagliari*, **4**, 55 (1934); *Chem. Zentr.*, **106 II**, 46 (1935); *Chem. Abstr.*, **30**, 6340 (1936).

principle (e.g., **8**), only two rational structures **9** and **10** for the dimer can be drawn which contain the necessary functional groups. Either structure explains satisfactorily the remaining chemical transformations. For example, if the dimer has structure **9**, the oxime would be **11**, the epoxide would be **12**, and the dihydrodimers A and B would be epimers of structure **13**.



8 9



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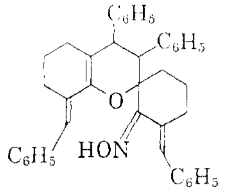

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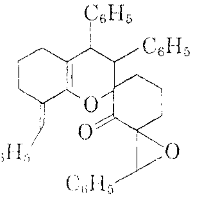

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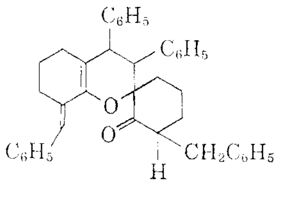
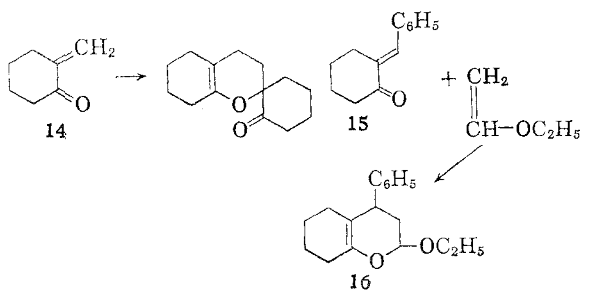


13

The dimerization of ketones possessing an adjacent vinylidene group to form dihydropyran derivatives is well known,[6] the dimerization of methylenecyclohexanone **14** being a typical example. However, we are not aware of previous examples of this type of dimerization of α,β-unsaturated ketones such as **1** which do not possess a terminal methylene group. However, the Diels-Alder reaction of 2-benzacyclohexanone (**15**) with ethyl vinyl ether to form the dihydropyran **16** has been reported.[7]



Although previous analogies[6,7] suggest that the dimer should be formulated as structure **9** rather than **10**, we considered additional evidence to be desirable. Accordingly, a solution of the dihydrodimer A **13** in boiling acetic acid was treated with zinc dust in an effort to reductively cleave the carbon-oxygen bond *alpha* to the carbonyl function in structure **13**. However, the only compounds which could be isolated from this reaction were the unchanged dihydrodimer A and the dihydrodimer B. While these results confirm the epimeric nature of the two dihydrodimers, they provide no evidence to distinguish between structures **9** and **10** for the dimer. The question has been resolved by measuring the NMR spectrum of the dimer (Fig. 1). This spectrum (60 mc.) exhibits a series of partially resolved peaks in the region of 2.87 τ (60% of total area) attributable to the twenty-two vinyl and aryl protons present in the dimer, a series of partially resolved peaks in the region 7.12 to 8.58 τ (35% of total area) attributable to the twelve methylene protons present in the dimer, and two doublets (5% of total area, J = 9 c.p.s.) located at 6.57 and 6.42 τ and at 6.32 and 6.17 τ attributable to the two benzylic protons present in the dimer. The splitting pattern observed is consistent with the presence of adjacent C_6H_5CH groupings as in structure **9** but not with the location of these groupings as shown in structure **10**.

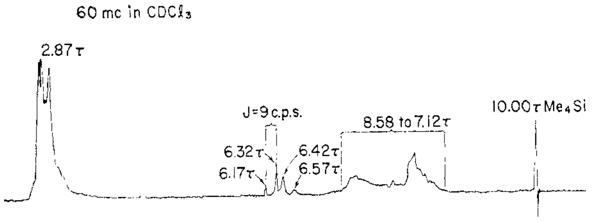


Fig. 1. NMR spectrum of 2,6-dibenzalcyclohexanone dimer

From the mode of formation of the dimer **9**, its stereo chemistry may be ascertained by the application of Alder's rules (represented in structure **17**) as previously discussed,[6c] as the ultraviolet absorption [λ_{max} 232 mμ (ϵ 15,600) and 323 mμ (ϵ 20,200)] of the starting 2,6-dibenzalcyclohexanone leaves no doubt that the material possesses the *trans, trans*-configuration[8] indicated in structure **1**. Consequently, the stereochemistry of the dimer is represented by structure **18**. It should be noted that the magnitude of the coupling con-

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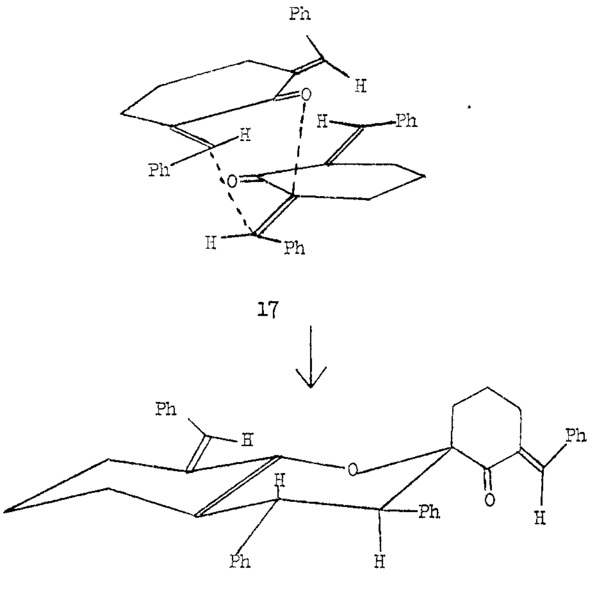
(5) The ultraviolet spectra of 2-benzalcyclohexanone [H. O. House and R. L. Wasson, *J. Am. Chem. Soc.*, **78**, 4394 (1956)] and *trans*-1-phenyl-1,3-butadiene [E. A. Braude, E. R. H. Jones, and E. S. Stern, *J. Chem. Soc.*, 1087 (1947); O. Grummitt and F. J. Christoph, *J. Am. Chem. Soc.*, **73**, 3479 (1951)] have maxima at 290 mμ (ϵ 16,200) and 280 mμ (ϵ 28,300), respectively.

(6) For example, see (a) C. Mannick, *Ber.*, **74**, 557 (1941); (b) H. Fiesselmann and J. Ribka, *Chem. Ber.*, **89**, 40 (1956); (c) E. Romann, A. J. Frey, P. A. Stadler, and A. Eschenmoser, *Helv. Chim. Acta*, **40**, 1900 (1957).

(7) W. S. Emerson, G. H. Birum, and R. I. Longley, Jr., *J. Am. Chem. Soc.*, **75**, 1312 (1953).

(8) For a discussion see P. Yates, N. Yoda, W. Brown and B. Mann, *J. Am. Chem. Soc.*, **80**, 203 (1958).

stant (J = 9 c.p.s.) observed in the NMR spectrum of the dimer is consistent with the location of the two benzylic hydrogen atoms in a *trans*, diaxial conformation[9] as shown in structure **18**.



17

18

EXPERIMENTAL[10]

2,6-Dibenzalcyclohexanone dimer (9). A solution of 45 g. (0.16 mole) of 2,6-dibenzalcyclohexanone, m.p. 116.5–118° (lit.[11] m.p. 117–118°), λ_{max} 232 mμ (ϵ 15,600) and 323(mμ, (ϵ 20,200),[12] in 75 ml. of toluene was refluxed for 72 hr. and then concentrated under reduced pressure. The residual solid was extracted with 350 ml. of boiling ethanol to leave the crude dimer which was recrystallized from ethyl acetate. The dimer separated as white, cotton-like needles, m.p. 192.3–193.3° dec., yield 9.5 g. (21%). An additional crystallization afforded to dimer as white needles, m.p. 194.3–195° dec. (lit.[1] m.p. 187–188°), which exhibit infrared absorption[13] at 1685 cm.$^{-1}$ (conj. C=O) with no absorption in the 3 μ region attributable to a hydroxyl function and an ultraviolet maximum[12] at 293 mμ (ϵ 43,500).

Anal. Calcd. for $C_{40}H_{36}O_2$: 87.56; H, 6.61; mol. wt. 549. Found: C, 87.69; H, 6.70; mol. wt. (Rast), 528.

A solution of 200 mg. of the dimer in 15 ml. of bromobenzene was refluxed for 20 hr. and then concentrated under reduced pressure. Recrystallization of the residue from ethanol afforded 120 mg. (60%) of 2,6-dibenzalcyclohexanone, m.p. 117–118.5°. To study the equilibration of the monomer and dimer solutions of 2.0712 g. (0.00756 mole) of the monomer and 2.0869 g. (0.00379 mole) of the dimer in 25-ml. portions of toluene were boiled under reflux, aliquots being removed from the solutions periodically for analysis by ultraviolet spectroscopy. After 213.5 hr., the solution originally containing pure monomer contained 55% of the monomer and the solution originally containing pure dimer contained 46% of the monomer. Extrapolation of the composition *vs.* time curves for the two solutions indicated that at equilibrium 50–55% of the dimer would be present.

Reaction of 2,6-dibenzalcyclohexanone (1) *with hydroxylamine.* A solution of 4.0 g. (0.015 mole) of 2,6-dibenzalcyclohexanone, 8.0 g. (0.12 mole) of hydroxylamine hydrochloride and 16 g. of sodium acetate in a mixture of 55 ml. of ethanol and 34 ml. of water was refluxed for 1.75 hr. and allowed to cool. The cold solution deposited 2.44 g. (54%) of the crude derivative, m.p. 177–181.5° dec. Recrystallization from ethanol afforded the pure derivative as white needles, m.p. 198.7–199.7° dec. (lit.[3] m.p. 199–200°), which exhibit infrared absorption[14] at 3300 cm.$^{-1}$ (broad, OH and NH) with no absorption in the 6 μ region attributable to a carbonyl function and an ultraviolet maximum[12] at 267 mμ (ϵ 15,500).

Anal. Calcd. for $C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.88; N, 8.69; mol. wt., 322. Found: C, 74.26; H, 7.08; N, 8.58; mol. wt. (Rast), 312.

For comparison, the *oxime of 2-benzalcyclohexanone* was prepared. The product, which crystallized from aqueous ethanol as colorless plates melting at 127–128.5° (lit.[15] m.p. 126.5°), has infrared bands[13] at 3600 cm.$^{-1}$ (unassoc. OH), 3300 cm.$^{-1}$ (assoc. OH), and 1640 cm.$^{-1}$ (very weak, C=N) with an ultraviolet maximum[12] at 272 mμ (ϵ 15,100).

Anal. Calcd. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.48; H, 7.45; N, 6.71.

Monoxime of the dimer 9. A mixture of 0.275 g. (0.5 mmole) of the dimer, 0.278 g. (2.0 mmoles) of hydroxylamine hydrochloride, and 5 ml. of pyridine was heated on a steam bath for 90 min. and then concentrated. Fractional crystallization of the crude product from ethanol and aqueous ethanol separated 0.137 g. (50% recovery) of the dimer and 0.50 g. (18%) of the crude oxime, m.p. 196.5–201° dec. Two additional crystallizations from ethanol–ethyl acetate mixtures afforded the pure oxime as white needles, m.p. 198–199.5° dec. The product has broad infrared absorption[14] at 3350 cm.$^{-1}$ with weak bands at 1640 cm.$^{-1}$ (C = N) and 1615 cm.$^{-1}$ (conj. C=C) and no absorption in the 6 μ region attributable to a carbonyl function; the material has an ultraviolet maximum[12] at 287 mμ (ϵ 31,500).

Anal. Calcd. for $C_{40}H_{37}NO_2$: C, 85.22; H, 6.62. Found C, 85.05; H, 6.78.

In another experiment a solution of 0.550 (1.0 mmole) of the dimer and 0.420 g. (6 mmoles) of hydroxylamine hydrochloride in ethanol was refluxed for 28 hr. and then concentrated. A series of fractional crystallizations from ethanol separated 8 mg. (1%) of the oxime, m.p. 198.7–199.7°, which was shown to be identical with the previously described derivative by comparison of the infrared spectra of the two samples.

Epoxidation of the dimer. To a solution of 2.22 g. (0.004 mole) of the dimer in 320 ml. of acetone was added 4.0 ml. (0.024 mole) of 6*N* aqueous sodium hydroxide and 6.0 ml. (0.063 mole) of 30% hydrogen peroxide. After the resulting mixture had been stirred at room temperature for 36 hr., an additional 2.0 ml. (0.021 mole) of 30% hydrogen peroxide, and 1.5 ml. (0.009 mole) of 6*N* aqueous sodium hydroxide were added. Stirring was continued for a total reaction time of 144 hr. at which time the reaction mixture was diluted with water and filtered to leave 2.010 g. of crude material, m.p. 184–197°. A 1.556-g. portion of this residue was subjected to a series of fractional crystallizations from ethanol to separate 1.10 g. (70% recovery) of the unchanged dimer and 0.186 g. (11.6%) of the crude epoxide, m.p. 182.5–185.6°. Additional recrystallization from ethanol afforded the pure

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(9) H. Conroy in R. A. Raphael, E. C. Taylor, and H. Wynberg, ed., *Advances in Organic Chemistry, Methods and Results*, Vol. 2, Interscience, New York, 1960, pp. 265–328.

(10) All melting points are corrected. The infrared spectra were determined with either a Baird, Model B, or a Perkin Elmer Model 21, infrared recording spectrophotometer fitted with a sodium chloride prism. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 11MS. The microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory. The NMR spectrum was determined in deuterochloroform by LeRoy F. Johnson of Varian Associates.

(11) D. Vorlander and K. Kunze, *Ber.*, **59**, 2078 (1926).

(12) Determined in ethanol solution.

(13) Determined in chloroform solution.

(14) Determined as a Nujol mull.

(15) R. Poggi and V. Guastalla, *Gazz. chim. ital.*, **61**, 405 (1931).

epoxide as colorless plates, m.p. 185.6–186.1°. The product exhibits infrared absorption[13] at 1725 cm.$^{-1}$ (unconj. C=O) with an ultraviolet maximum[12] at 291 mμ (ϵ 27,800).

Anal. Calcd. for $C_{40}H_{36}O_3$: C, 85.07; H, 6.43. Found: C, 84.96; H, 6.52.

Catalytic hydrogenation of the dimer. A solution of 5.97 g. (0.0108 mole) of the dimer in 200 ml. of ethyl acetate was hydrogenated at room temperature and atmospheric pressure over the catalyst obtained from 0.315 g. of platinum oxide. The reaction was stopped after the absorption of 354 ml. (1.58 equiv.) of hydrogen. After the catalyst had been removed by filtration, the filtrate was concentrated under reduced pressure. A combination of fractional recrystallization from ethanol and chromatography on Merck acid-washed alumina separated 0.8872 g. (14.8% recovery) of the unchanged dimer, 1.4615 g. (24.5%) of one crystalline modification of the dihydrodimer A, m.p. 159–162°, 0.3796 g. (6.4%) of a second crystalline modification of the dihydrodimer A, m.p. 171–172.5°, and 0.2914 g. (4.9%) of the dihydrodimer B, m.p. 208–211°.

One pure crystalline modification of the dihydrodimer A was obtained as white needles, m.p. 161.5–163°, by recrystallization from an ethanol-ethyl acetate mixture. The product exhibits infrared absorption[13] at 1720 cm.$^{-1}$ (unconj. C=O) with no absorption in the 3 μ region attributable to a hydroxyl function; the ultraviolet spectrum[12] exhibits a maximum at 293 mμ (ϵ 28,500).

Anal. Calcd. for $C_{40}H_{38}O_2$: C, 87.23; H, 6.96. Found: C, 86.91; H, 6.87.

The dihydrodimer A occasionally separated in a second crystalline modification as white prisms, m.p. 173.5–175°, which exhibit the same infrared and ultraviolet absorption as the crystalline form melting at 161.5–163°.

Anal. Calcd. for $C_{40}H_{38}O_2$: C, 87.23; H, 6.96. Found: C, 86.96; H, 6.98.

The pure dihydrodimer B crystallized from an ethanol-ethyl acetate mixture as colorless prisms, m.p. 212.5–214° dec., which exhibit infrared[13] absorption at 1718 cm.$^{-1}$ (unconj. C=O) with no absorption in the 3 μ region attributable in a hydroxyl function and an ultraviolet maximum[12] at 292 mμ (ϵ 23,600).

Anal. Calcd. for $C_{40}H_{38}O_2$: C, 87.23; H, 6.96. Found: C, 87.16; H, 6.84.

Treatment of the dihydrodimer **13** *with zinc and acetic acid.* A mixture of 0.8292 g. (0.0015 mole) of the dihydrodimer A, m.p. 161–163°, and 1.078 g. (0.019 g.-atom) of zinc dust in 20 ml. of acetic acid was refluxed with stirring for 1 hr. and then poured into cold water and filtered. Fractional crystallization of the residue from ethanol–ethyl acetate mixtures separated 0.6225 g. (75% recovery) of unchanged dihydrodimer A and 0.0557 g. (6.7%) of dihydrodimer B, m.p. 211–213° dec., identified by a mixed melting-point determination.

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Asymmetric Induction

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(−)-Menthyl *p*-benzoylbenzoate, a vinylog of an optically active α-keto ester has been subjected to the action of reducing agents and Grignard reagents to see if optical activity appears at the new asymmetric center produced at the benzoyl group after subsequent removal of the (−)-menthyl moiety. If asymmetric induction operates as do ordinary inductive forces through an aromatic nucleus, the ultimate products of such reactions should be optically active. If purely steric effects are responsible for asymmetric synthesis the products of such reactions should be optically inactive. In none of our experiments were we able to detect optical activity in the final reaction products, indicating that asymmetric induction if it exists is incapable of transmission through an aromatic nucleus.

Two distinct concepts of the mechanism of asymmetric synthesis are to be found in the literature. The first, that of "Asymmetric Induction," based on early suggestions of LeBel[1] and Erlenmeyer,[2] was developed in the hands of Kortum,[3] Lowry,[4] Ritchie,[5] Turner,[6] and Phillips[7] to explain not only McKenzie's classic asymmetric syntheses in the α-keto ester series[8,9] but also certain mutarotation[8,10] and anomalous rotatory dispersion[5,7] phenomena. This concept, in brief, postulates the asymmetric polarization of a symmetrical center in a molecule, under the influence of a nearby preexisting center of asymmetry. Such polarization is assumed to produce differing quantities of two diastereomeric "activated species," which ultimately react chemically to yield unequal amounts of diastereomeric products, and which are also responsible for anomalous mutarotation or rotatory dispersion properties. The second and more recent mechanism rationalizing asymmetric synthesis is one in which purely steric interactions between the symmetrical and asymmetric reactants lead to a stereochemically favored reaction path and to the ultimate production of unequal amounts

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