[Contribution from the Departments of Chemistry of the University of Minnesota and Michigan State University Oakland]

Preparation of *cis*- and *trans*-1,2-Diphenyl-1,2-cyclohexanediol[1]

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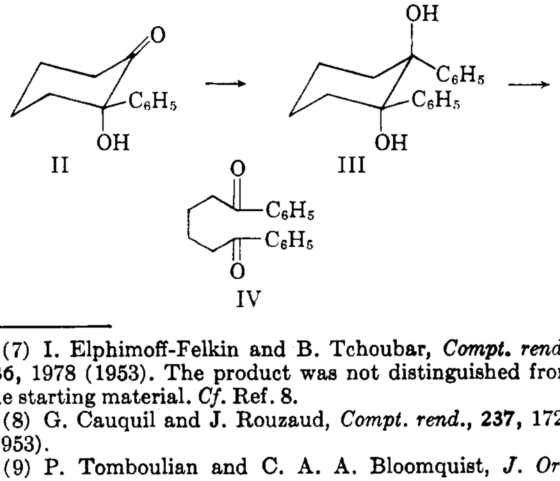
Preparative methods for the synthesis of *cis*- and *trans*-1,2-diphenyl-1,2-cyclohexanediol are described. The *cis*-isomer was formed by hydroxylation of 1,2-diphenylcyclohexene with osmium tetroxide. The *trans*-isomer was prepared from 2-hydroxy-2-phenylcyclohexanone by the action of phenyllithium. The stereochemistry of the diols and the syntheses of their precursors are also described.

As part of a program concerned with *o*-terphenyl derivatives, the unequivocal syntheses of the two isomeric 1,2-diphenyl-1,2-cyclohexanediols were undertaken. Previous to this work, no practical method for the preparation of this type of substituted glycol had been reported; especially no route involving two different aryl substituents had been described. *cis* - 1,2 - Diphenyl - 1,2 - cyclopentanediol was synthesized sixty years ago by the intramolecular reductive coupling of 1,3-dibenzoylpropane by the action of aluminum amalgam.[3] This same cyclopentanediol has been prepared by "anodic reduction" of 1,3-dibenzoylpropane in sodium iodide-pyridine solution using magnesium electrodes.[4] After similar treatment of 1,4-dibenzoylbutane, a 12% yield of *cis*-1,2-diphenyl-1,2-cyclohexanediol (VII) was isolated.[4]

A preliminary investigation of the reduction of 1,4-dibenzoylbutane using aluminum amalgam indicated that this method would not be satisfactory for the preparation of the desired diols. In this connection, it should be noted that 1,4-dianisoylbutane yielded only a linear polymeric glycol upon treatment with aluminum amalgam.[5] A second investigation involved an examination of the reaction between benzil and the Grignard reagent prepared from 1,4-dibromobutane, originally reported by Buchta and Weidinger.[6] In agreement with the original findings, no crystalline products could be isolated, and no evidence for monomeric glycols was found.

The synthesis of *trans*-1,2-diphenyl-1,2-cyclohexanediol (III) was accomplished in 75% yield by the treatment of 2-hydroxy-2-phenylcyclohexanone (II) with either phenyllithium or the phenyl Grignard reagent. The preparation of the starting material (ketol II) is of some interest. Although this ketol had been described previously as the product resulting from the base-catalyzed ring enlargement of 1 - benzoylcyclopentanol, no yield, unequivocal structure proof, or analysis was presented.[7] In the present work, the liquid ketol II was isolated in 50% yield from the reaction of 2-hydroxy-2-cyclohexen-1-one (I) with excess phenyllithium. Thus, enol I constitutes another example of a conjugated ketonic system which undergoes 1,2-addition with phenyllithium and 1,4-addition[9] with the phenyl Grignard reagent.[10,11] The structure of ketol II was established by two methods: (1) cleavage with periodic acid to give 5-benzoylpentanoic acid and (2) acid-catalyzed dehydration to yield 2-phenyl-2-cyclohexen-1-one.

The *trans*-configuration was assigned tentatively to the diol III on the basis of analogy to similar systems. It is expected that the bulky aromatic groups occupy equatorial positions, thus placing the hydroxyl groups axial and *trans* to each other. Conclusive evidence for the *trans*-assignment came



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[1] Part of this work was presented at the 136th Meeting of the American Chemical Society, Atlantic City, September 1959; Abstracts, p. 2-P.

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[3] F. R. Japp and A. C. Michie, *J. Chem. Soc.*, **79**, 1019 (1901). The *cis*-configuration for the diol was recently established; see Ref. 4.

[4] W. D. Hoffman, W. E. McEwen, and J. Kleinberg, *Tetrahedron*, **5**, 293 (1959).

[5] G. P. Mueller and R. May, *J. Am. Chem. Soc.*, **71**, 3313 (1949).

[6] E. Buchta and H. Weidinger, *Ann.*, **580**, 109 (1953).

[7] I. Elphimoff-Felkin and B. Tchoubar, *Compt. rend.*, **236**, 1978 (1953). The product was not distinguished from the starting material. *Cf.* Ref. 8.

[8] G. Cauquil and J. Rouzaud, *Compt. rend.*, **237**, 1720 (1953).

[9] P. Tomboulian and C. A. A. Bloomquist, *J. Org. Chem.*, **24**, 1239 (1959).

[10] See for instance the classic work on the reaction of benzalacetophenone with phenyllithium and the phenyl Grignard reagent: H. Gilman and R. H. Kirby, *J. Am. Chem. Soc.*, **63**, 2046 (1941); A. Lüttringhaus, *Ber.*, **67B**, 1602 (1934); and E. P. Kohler, *Am. Chem. J.*, **31**, 642 (1904).

[11] The 1,2-addition of 2,3-dimethoxyphenyllithium to the enol I has been previously reported: R. A. Barnes and D. F. Reinhold, *J. Am. Chem. Soc.*, **74**, 1327 (1952).

from infrared absorption data which indicated unassociated O—H absorption at 3606 cm.$^{-1}$ (Table II). Chemical proof of the diol structure was furnished by cleavage with periodic acid or lead tetraacetate to form 1,4-dibenzoylbutane (IV). With the latter reagent, the yield was 90%.

In view of the axial alcohol groups, it is interesting that cleavage of the *trans*-diol III occurs readily. The large phenyl groups should offer a considerable energy barrier to conversion of III to the more reactive equatorial diol configuration. Especially noteworthy is the periodic acid cleavage; this reagent is supposed to react chiefly by means of an intramolecular cyclic transition state, although ditertiary alcohols (and certainly benzylic alcohols) probably react by another type of mechanism.[12]

From the distillation residue of the reaction used to prepare ketol II [phenyllithium plus 2-hydroxy-2-cyclohexen-1-one (I)] a small yield (16%) of the *trans*-diol III was isolated. The presence of this product in the reaction mixture is difficult to rationalize since the starting material (I) is 100% enolic.[9]

Preparation of *cis*-1,2-diphenyl-1,2-cyclohexanediol (VII) involved a more extensive reaction sequence. The most suitable approach appeared to be the hydroxylation of 1,2-diphenylcyclohexene (V) and this method proved successful, after the problems involved with the preparation of olefin V had been solved. The starting material for this synthesis was 2-phenylcyclohexanone, conveniently prepared by chromic acid oxidation of 2-phenylcyclohexanol.[13,14] Addition of phenyllithium or the phenyl Grignard reagent to 2-phenylcyclohexanone furnished a mixture of the 1,2-diphenylcyclohexanols in high yield. Only a partial fractionation of this mixture was achieved, although an analytically pure sample was obtained. Dehydration of the alcohol mixture with either hot phosphoric acid or thionyl chloride and pyridine yielded a mixture of 1,2-diphenylcyclohexene (V) and 2,3-diphenylcyclohexene (VI). Fortunately, the two isomers could be separated by a combination of fractional distillation and crystallization, although the net yields of the individual olefins were low. Infrared analysis of the olefin mixture from the thionyl chloride–pyridine reaction disclosed that the ratio of the 1,2-isomer (V) to the 2,3-isomer (VI) was 2:1. This result may be compared with the report of the dehydration of *cis*- and *trans*-2-phenylcyclohexanol using hot phosphoric acid.[15] The *cis*-isomer, in which *trans*-elimination of axial groups is possible, yielded 88% of 1-phenylcyclohexene; the *trans*-isomer gave only a 20% yield of this olefin in addition to at least three other products. With 1,2-diphenylcyclohexanol, however, a *trans*-elimination mechanism is not the only reaction course available, since an intermediate with considerable carbonium ion character at a benzyl position is possible. Thus the composition of the olefin mixture does not establish the configurations of the intermediate 1,2-diphenylcyclohexanols.

The styrene analog (VI) proved to be relatively unstable, decomposing extensively during distillation or after a few weeks at room temperature; this behavior is typical of the styrene system.[16]

Aside from conversions of olefins V and VI to the corresponding diols discussed below, the chemical proof for the cyclohexene structures consisted in conversion to *o*-terphenyl by aromatization with sulfur. Physical evidence for the position of the double bonds came from an examination of the infrared and ultraviolet spectra. A weak olefinic double bond absorption at 1635 cm.$^{-1}$ is exhibited only by 2,3-diphenylcyclohexene (VI). The ultraviolet absorption maxima of the olefins are listed in Table I along with reference compounds.

TABLE I

ULTRAVIOLET ABSORPTION

Compound	λ_{max} in mμ	log ϵ
Styrene	244	4.0
	282, 292	3.78
cis-Stilbene	222	4.36
	280	4.13
1,2-Diphenylcyclohexene(V)	220	4.48
	253(shoulder)	4.02
2,3-Diphenylcyclohexene(VI)	246	4.03

A compound described as 1,2-diphenylcyclohexene had been previously synthesized by the same method as used here.[17] There seems little doubt, however, that the olefin prepared by Parmerter actually was the 2,3-isomer.[18] The melting point, the method of preparation (phosphoric acid dehydration), and the manner of isolation (distillation plus crystallization) are further evidence for this reassignment. The higher melting point, higher boiling point, and lower solubility of the 2,3-isomer favor its isolation. Without analyses and careful fractional distillation techniques, the existence of two isomers is not apparent. The successful separation of 1,2- and 2,3-dianisylcyclohexene has been

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(12) S. J. Angyal and R. J. Young, *J. Am. Chem. Soc.*, **81**, 5251 (1959).

(13) J. W. Cook, C. L. Hewett, and C. A. Lawrence, *J. Chem. Soc.*, 71 (1936).

(14) An alternate synthesis involving the reaction of 2-chlorocyclohexanone with the phenyl Grignard reagent gave less consistent results: M. S. Newman and M. D. Farbman, *J. Am. Chem. Soc.*, **66**, 1550 (1944); *cf.* W. E. Bachmann, G. I. Fujimoto, and L. B. Wick, *J. Am. Chem. Soc.*, **72**, 1995 (1950).

(15) E. L. Eliel, J. W. McCoy, and C. C. Price, *J. Org. Chem.*, **22**, 1533 (1957).

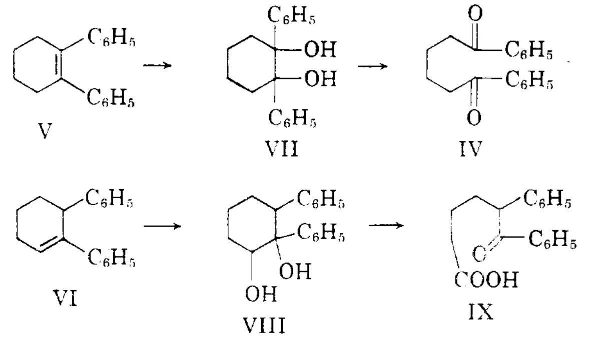
(16) For a recent example, see the study of the oxidative decomposition of α-methyl styrene: F. R. Mayo and A. A. Miller, *J. Am. Chem. Soc.*, **80**, 2480 (1958).

(17) S. M. Parmerter, *J. Am. Chem. Soc.*, **71**, 1127 (1949).

(18) This reassignment also explains the discrepancy in the melting points reported for the reduction product "*cis*"-1,2-diphenylcyclohexane; *cf.* G. F. Wright, *J. Org. Chem.*, **19**, 940 (1954).

described by Mueller and May,[5] who used a combination of distillation and crystallization procedures similar to those employed here. Their assignment of structure, however, must be questioned because of the results described above.

Osmium tetroxide hydroxylation of 1,2-diphenylcyclohexene furnished the desired *cis*-glycol (VII), m.p. 87–88°, in 47% yield. A lower melting form of this diol, m.p. 73.2–73.9°, has been prepared by the anodic reduction of 1,4-dibenzoylbutane.[4] A comparison of the infrared spectra shows that the two glycols apparently are dimorphic forms of the same *cis*-diol (VII).[19] The chemical structure proof for *cis*-1,2-diphenyl-1,2-cyclohexanediol (VII) consisted of lead tetraacetate cleavage to form 1,4-dibenzoylbutane (IV) in 100% yield.



Treatment of 2,3-diphenylcyclohexene (VI) with osmium tetroxide gave one of the isomeric 2,3-diphenyl-1,2-cyclohexanediols (VIII), m.p. 133–134°, presumably a *cis*-diol. Oxidation of this glycol with lead tetraacetate yielded a ketoaldehyde, probably 5-phenyl-5-benzoylpentanal. This unstable material underwent air oxidation to furnish a ketoacid, which has been assigned the structure 5-phenyl-5-benzoylpentanoic acid (IX) on the basis of infrared analysis and combustion data.

Table II lists the infrared absorption maxima of various 1,2-glycols related to the present work. The higher frequency band (near 3600 cm.$^{-1}$) is usually assigned to the unbonded O—H absorption, whereas the lower band is characteristic of intramolecular hydrogen bonded O-H absorption.[20–22]

TABLE II

INFRARED ABSORPTION

Substituted 1,2-Cyclohexanediol	ν_{max} (cm.$^{-1}$)	$\Delta\nu$
cis-1,2-Diphenyl (VII)	3607, 3571	36
trans-1,2,-Diphenyl (III)	3606	—
cis-2,3-Diphenyl (VIII)	3592, 3574	18
cis-1,3-Diphenyl[a]	3602, 3574	28
cis-1-Phenyl[b]	3600, 3575	25

[a] Reference 9. [b] T. H. Fife, Ph.D. Dissertation, University of Minnesota, 1959.

No hydrogen bonding is observed for the *trans*-glycol (III) since the hydroxyl groups are axially oriented. In the other diols, hydrogen bonding can exist. Thus, the infrared measurements offer conclusive evidence for the structures of the *cis*- and *trans*-diols, VII and III.

EXPERIMENTAL[23]

Attempted reduction of 1,4-dibenzoylbutane with aluminum amalgam.[3,5,24] No discrete products could be isolated from several experiments in which the diketone was treated with amalgamated aluminum. Large amounts of starting material were recovered. This reaction is under further investigation.

Reaction of benzil with the Grignard reagent prepared from 1,4-dibromobutane.[6] Under several sets of conditions, resinous yellow oils were obtained which were analyzed by infrared and chromatographic methods. The infrared spectra revealed the presence of alcohol and ketone components, but as shown by comparison with subsequently prepared authentic samples, neither the *cis*-diol VII nor the *trans*-diol III was present. The chromatography yielded no crystalline substances other than benzil.

Reaction of 2-hydroxy-2-cyclohexen-1-one (I) *with phenyllithium; 2-hydroxy-2-phenylcyclohexanone* (II). Seven grams (0.0625 mole) of freshly prepared crystalline enol I in 50 ml. of benzene was added dropwise to a chilled solution of phenyllithium. The lithium reagent was prepared from 45 g. (30 ml., 0.29 mole) of bromobenzene and 3.50 g. (0.505 g.-atom) of lithium wire in 45 ml. of ether and 100 ml. of benzene. After 40 hr. under reflux, the mixture was hydrolyzed with ice and dilute hydrochloric acid. The organic layer was removed and distilled at reduced pressure; 5.95 g. (50% yield) of 2-hydroxy-2-phenylcyclohexanone (II) was collected as the main fraction, b.p. 87°/0.1 mm., n^{26} 1.5493. (A reaction period of 20 hr. at room temperature gave essentially the same results).

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 76.03; H, 7.45.

The infrared spectrum of ketol II exhibits alcohol absorption at 3500 cm.$^{-1}$ and ketone absorption at 1713 cm.$^{-1}$.

Dehydration of ketol II occurred during the preparation of the *2,4-dinitrophenylhydrazone* by the usual method. The product obtained was the derivative of 2-phenyl-2-cyclohexen-1-one, m.p. 163–163.5°; reported[25] m.p. 165–166°.

Anal. Calcd. for $C_{18}H_{16}N_4O_4$: C, 61.36; H, 4.58; N, 15.90. Found: C, 61.46; H, 4.73; N, 15.62.

Dehydration could also be effected by warming an acidic solution of ketol II: 0.34 g. (1.8 mmoles) in 3 ml. of acetic acid containing 0.3 ml. of concd. hydrochloric acid was heated at 75° for 4 hr. Chromatographic separation of the reaction mixture followed by sublimation and crystallization from heptane furnished 0.12 g. (39% yield) of 2-phenyl-2-cyclohexen-1-one, m.p. 90–91°. One additional crytallization of the ketone gave a sample of m.p. 91.5–93.5°, which when mixed with an authentic sample melted at 92–95°.

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[19] W. E. McEwen, private communication.

[20] L. P. Kuhn, *J. Am. Chem. Soc.*, **76**, 4323 (1954).

[21] A. R. H. Cole and P. R. Jefferies, *J. Chem. Soc.*, 4391 (1956).

[22] J. S. Brimacombe, A. B. Foster, M. Stacey, and D. H. Whiffen, *Tetrahedron*, **4**, 351 (1958).

[23] Elemental analyses were performed by Mrs. Olga Hamerston, William Kuryla, and the Clark Microanalytical Laboratory, Urbana, Ill. The infrared spectra of carbon disulfide solutions or liquid films were measured with Perkin-Elmer Model 21 and Model 137 spectrophotometers. The ultraviolet spectra of methylene chloride solutions were determined on a Cary Model 11 spectrophotometer. All melting points are corrected.

[24] E. D. Bergmann and R. Ikan, *J. Am. Chem. Soc.*, **80**, 208 (1958).

[25] D. Ginsburg and R. Pappo, *J. Chem. Soc.*, 516 (1951).

Treatment of 0.23 g. (1.2 mmoles) of 2-hydroxy-2-phenylcyclohexanone (II) with 0.30 g. of periodic acid in 2 ml. of water and 1 ml. of dioxane for 16 hr. at 30° gave 0.21 g. (84% yield) of 5-benzoylpentanoic acid, m.p. 75–77°. The ketoacid was identified by its infrared spectrum and by a mixture melting point determination with an authentic sample.

A second product was isolated from the reaction of phenyllithium with enol I. After the main product, ketol II, had been removed by distillation, the red-brown distillation residue (4.83 g.) was treated with a mixture of hexane and ether and subjected to chromatographic analysis. A total of 2.76 g. (16% yield) of *trans*-1,2-diphenyl-1,2-cyclohexanediol (III) was collected, m.p. 120–122°. The identification of this diol is described subsequently.

TRANS-*1,2-Diphenyl-1,2-cyclohexanediol* (III). Phenyllithium was prepared from 17.2 g. (11.5 ml., 0.110 mole) of bromobenzene and 1.55 g. (0.224 g.-atom) of lithium wire in 30 ml. of ether. To this mixture, a solution of 2.65 g. (0.0140 mole) of 2-hydroxy-2-phenylcyclohexanone (II) in 60 ml. of benzene was added slowly. After a reflux period of 20 hr., hydrolysis was effected with ice and hydrochloric acid. Removal of solvent from the organic layer left 4.34 g. of crystals. Recrystallization from heptane followed by chromatography of the crystallization residues furnished a total of 2.82 g. (75% yield) of *trans*-diol III, m.p. 121–122°, in the form of needles.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.44; H, 7.67.

Infrared spectral analysis[26] of this diol demonstrated the existence of a single O—H absorption band at 3606 cm.$^{-1}$.

Substitution of the phenyl Grignard reagent for phenyllithium resulted in lower yields of the diol.

Cleavage of the *trans*-diol III (0.345 g., 1.29 mmoles) with lead tetraacetate (0.62 g., 1.40 mmoles) in 5 ml. of benzene for 15 min. at room temperature gave 1,4-dibenzoylbutane (IV). One crystallization of the crude reaction product from heptane gave 0.310 g. (90% yield) of the diketone (IV), m.p. 105–106.5°, identified by mixture melting point data and infrared spectral comparisons with an authentic sample. Cleavage with periodic acid also gave the diketone (IV), but the best yield obtained was 38%.

2-Phenylcyclohexanone was prepared from *trans*-2-phenylcyclohexanol by chromic acid oxidation.[13,27] Consistent 50–60% yields of the crude ketone were obtained by use of the following modified procedure. Thirty grams (0.170 mole) of 2-phenylcyclohexanol[13] in 70 ml. of acetic acid was chilled in an ice bath. A solution of 24 g. (0.24 mole) of chromium trioxide dissolved in 20 ml. of water and 80 ml. of acetic acid was added dropwise, while the temperature was held at 3–4°. The mixture was warmed slowly, then heated at 70–80° for 0.5 hr. before it was added to ice. Following addition of benzene, the organic layer was removed, washed with saturated potassium carbonate solution, and the solvent was distilled to furnish the impure crystalline ketone.

1,2-Diphenylcyclohexanol. Phenyllithium was prepared from 24.7 g. (16.5 ml., 0.157 mole) of bromobenzene, 2.10 g. (0.303 g.-atom) of lithium, and 50 ml. of ether. A solution of 9.15 g. (0.0526 mole) of crystalline 2-phenylcyclohexanone in 25 ml. of benzene was added. The resulting mixture was stirred under reflux for 12 hr. before addition to ice and hydrochloric acid. Removal of the solvent from the organic layer left 17.7 g. of a red-brown oil, 40% of which could be induced to crystallize. (Distillation of the alcohol mixture gave a white waxy solid, b.p. 152–166°/0.6 mm., in a yield of about 50%.) Crystallization of the crude reaction product or the waxy distillate from ligroin gave crystals which melted in the range of 66–70°. The analytical sample melted at 67–69°.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.38; H, 8.14.

Several additional crystallizations changed the melting point of the product to 74–79°, but failed to alter the infrared spectrum significantly. Repeated fractional crystallizations furnished an alcohol sample which melted at 95–104°, and exhibited a strong infrared absorption (C—OH stretch) at 1010 cm.$^{-1}$. The lower-melting samples absorbed strongly at 978 cm.$^{-1}$, with only weak absorption at 1010 cm.$^{-1}$ The two modifications of the alcohol may well be epimers, the higher melting form perhaps having the hydroxyl group in the equatorial position.[28]

Treatment of 2-phenylcyclohexanone with the phenyl Grignard reagent gave essentially the same results as described above, except that some of the starting material was recovered, as indicated by the infrared spectrum of the crude product.

1,2-Diphenylcyclohexene (V) *and 2,3-diphenylcyclohexene* (VI). To a solution of 41.0 g. of crude 1,2-diphenylcyclohexanol in 50 ml. of methylene chloride kept at 5–10° in an ice bath, a solution of 12 ml. of thionyl chloride in 30 ml. of pyridine was added dropwise with stirring. The mixture was stirred at 5° for 0.5 hr. and at room temperature for 0.5 hr. before addition to ice. The organic components were removed by methylene chloride extraction, and the solvent was distilled to yield a viscous brown oil, which exhibited only aromatic and olefinic infrared absorption bands; the ratio of the 1,2-isomer (V) to the 2,3-isomer (VI) was 2:1. Rapid distillation of the reaction product under reduced pressure gave a forerun (b.p. up to 120°/0.5 mm.) of 9.7 g., and a main fraction (b.p. 120–180°/0.5 mm.) of 24.0 g. The main fraction contained only 1,2-diphenylcyclohexene (70–75%) and 2,3-diphenylcyclohexene (25–30%), according to infrared analysis. Redistillation of the main fraction through a spiral-wire column effected a partial separation of the two olefins: 1,2-isomer, b.p. 169–171°/10 mm.; 2,3-isomer, b.p. 180–182°/10 mm. Distillation was accompanied by some polymerization in the distillation flask, and a detectable loss of the 2,3-isomer. Cooling of the distillates or treatment with methanol resulted in partial crystallization of each fraction. Several recrystallizations from methanol usually furnished pure samples of each olefin in the form of long needles: yield of crystalline 1,2-diphenylcyclohexene, 4%; yield of crystalline 2,3-diphenylcyclohexene, 6%. An analytical sample of the 1,2-isomer melted at 48–48.5°; that of the 2,3-isomer melted at 51–53°.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found (1,2-isomer): C, 92.94; H, 7.37. Found (2,3-isomer): C, 91.88; H, 7.69.

Crystallization of the crude olefin mixture always yielded the less soluble 2,3-diphenylcyclohexene. Crystalline samples of this isomer became partially liquid after standing for several weeks. This change was accompanied by the appearance of carbonyl and alcohol absorption bands in the infrared spectrum.

The ultraviolet absorption data for the two olefins are shown in Table I. The infrared spectrum of 1,2-diphenylcyclohexene exhibited characteristic absorption maxima at 1132, 1068, and 905 cm.$^{-1}$ For the 2,3-isomer, identifying bands occurred at 1635, 1077, 894, 793, and 770 cm.$^{-1}$

Dehydration of 1,2-diphenylcyclohexanol with hot phosphoric acid also furnished a mixture of the two olefins, but the yields were lower, and more tar formation was observed.

Treatment of 80 mg. of 1,2-diphenylcyclohexene with 22 mg. of sulfur at 205° for 3 hr. followed by a chromatographic separation of the reaction mixture gave 48 mg. (61%) of *o*-terphenyl, identified by a mixture melting point determination with an authentic sample. Similar treatment of 280 mg. of 2,3-diphenylcyclohexene yielded 160 mg. (58%)

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[26] High-resolution spectra were measured on a calibrated Beckman Model DK spectrophotometer using 0.001*M* solutions of the diols in carbon tetrachloride.

[27] *Cf.* C. C. Price and J. V. Karabinos, *J. Am. Chem. Soc.*, 62, 1159 (1940).

[28] R. A. Pickering and C. C. Price, *J. Am. Chem. Soc.*, 80, 4931 (1958).

of *o*-terphenyl, identified by its melting point and an infrared spectral comparison with an authentic sample.

cis-*1,2-Diphenyl-1,2-cyclohexanediol* (VII). One gram (0.0039 mole) of osmium tetroxide was added to a solution of 0.94 g. (0.0040 mole) of 1,2-diphenylcyclohexene in 50 ml. of ether and 1.5 ml. of pyridine. After 48 hr. at room temperature, the solvent was evaporated. The gummy solid was boiled with 6 g. of sodium sulfite in 80 ml. of 50% ethanol for one hour. The mixture was filtered and the organic components were removed by extraction with methylene chloride. Removal of the solvent left 0.99 g. of a brown oil which was subjected to chromatography on alumina. A total of 0.51 g. (47%) of the *cis*-glycol (VII) was obtained, m.p. 85–86°. The analytical sample crystallized from ligroin in large prisms, m.p. 86–87°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.82; H, 7.39.

Treatment of 0.11 g. of glycol VII in 5 ml. of benzene with 0.19 g. of lead tetraacetate for 0.5 hr. at room temperature furnished 0.11 g. (100%) of 1,4-dibenzoylbutane (IV), m.p. 105–106°. The diketone was identified by a mixture melting point determination with a known sample.

One of the *2,3-diphenyl-1,2-cyclohexanediols* (VIII) was prepared from 2,3-diphenylcyclohexene (VI) in 51% yield by the osmium tetroxide hydroxylation method described above; the crude product melted at 129–131°. Sublimation of the diol followed by crystallization from a mixture of benzene and ligroin gave fine, colorless needles, m.p. 132–132.5°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.47; H, 7.76.

This same diol was obtained in 16% yield by the performic acid method.[29] A mixture of 2.00 g. of 2,3-diphenylcyclohexene, 5.2 ml. of 88% formic acid, and 1.2 ml. of 30% hydrogen peroxide was stirred for 9 hr. at room temperature. The formic acid was distilled under reduced pressure and the residue was treated with 10 ml. of 20% sodium hydroxide solution for 2 hr. on a steam bath. Extraction of the product followed by crystallization from ligroin gave 0.37 g. of glycol VIII, m.p. 131–133°.

Glycol VIII (50 mg.) was treated with 92 mg. of lead tetraacetate in 3 ml. of benzene for 20 min. at room temperature. The crude product (exhibiting conjugated ketone absorption at 1682 cm.$^{-1}$ and aldehyde bands at 2700 and 1723 cm.$^{-1}$) was oxidized in an air stream to give an acidic crystalline material. Recrystallization from ligroin yielded 34 mg. (65%) of *5-benzoyl-5-phenylpentanoic acid* (IX), m.p. 145–146°. The infrared spectrum contained typical acid absorption bands, as well as carbonyl absorption at 1705 cm.$^{-1}$ (acid) and 1682 cm.$^{-1}$ (conjugated ketone). An analytical sample crystallized from ligroin in the form of fine needles, m.p. 147–148°.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43; neut. equiv. 282. Found: C, 76.87; H, 6.43; neut. equiv. 285.

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Rochester, Mich.

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(29) J. English, Jr., and J. D. Gregory, *J. Am. Chem. Soc.*, 69, 2120 (1947).

[Contribution from the Department of Chemistry University of Missouri]

The Reaction of Aldoketene Dimers with Grignard Reagents[1]

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When an excess of phenylmagnesium bromide reacted with *n*-butylketene dimer, two simple ketones, 6-undecanone and benzophenone, and a di-addition compound, 5-(diphenylhydroxymethyl)-6-undecanone, were isolated from the reaction products. Analogous compounds were obtained from phenylmagnesium bromide and *n*-octylketene dimer, but from *n*-hexylketenedimer, the only identified product isolated from the reaction mixture was the di-addition compound. Only two simple ketones could be isolated from the reaction product of aliphatic Grignard reagents with the ketene dimers.

Many investigations of the reactions of the aldoketene dimers have been carried out, but only one reference has been found to the reaction of these compounds with a Grignard reagent. Reid and Groszos[4] have reported that solid ethylketene dimer, which is stated to have the 2,4-diethyl-1,3-cyclobutanedione structure, behaved abnormally in a Grignard machine yielding 1.3 active hydrogens and 1.7 carbonyls. We have found no mention of the reaction of Grignard reagents with the more common liquid aldoketene dimers for which the 3-butanoic-β-lactone structure[5] is generally accepted. The results of a study of the reaction of some Grignard reagents with the latter class of compounds are reported in this paper.

When an excess of phenylmagnesium bromide reacted with *n*-butylketene dimer, three products were isolated and identified: 6-undecanone (16%), benzophenone (16%), and 5-(diphenylhydroxymethyl)-6-undecanone (43%).

n-Hexylketene dimer reacted with an excess of phenylmagnesium bromide, but only 7-(diphenylhydroxymethyl)-8-pentadecanone could be isolated. The remainder of the reaction product was a

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(4) E. B. Reid and S. J. Groszos, *J. Am. Chem. Soc.*, 75, 1655 (1953).

(5) J. Bergman and S. H. Bauer, *J. Am. Chem. Soc.*, 77, 1955 (1955).