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1,2-Bis-(*p*-methoxyphenyl)-cyclopentene

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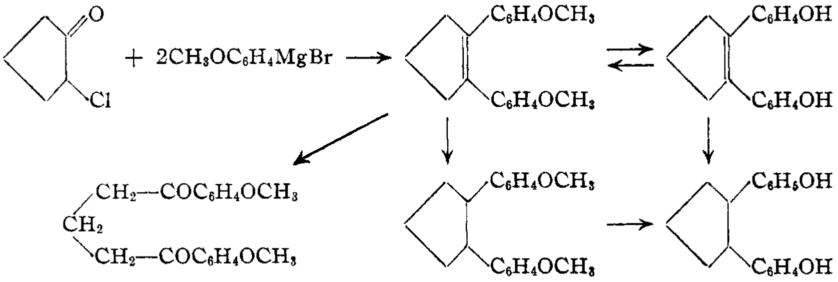
p-Methoxyphenylmagnesium bromide and 2-chlorocyclopentanone yielded 1,2-bis-(*p*-methoxyphenyl)-cyclopentene directly. Phenylmagnesium bromide with 2-phenylcyclohexanone gave a crystalline 1,2-diphenylcyclohexanol which was dehydrated to 2,3-diphenylcyclohexene. Ultraviolet absorption data indicate greater steric interference between the aryl groups in 1,2-bis-(*p*-methoxyphenyl)-cyclohexene than exists in 1,2-bis-(*p*-methoxyphenyl)-cyclopentene. 1,2-Bis-(*p*-methoxyphenyl)-cyclopentane and the corresponding phenolic compounds are reported.

In continuing our studies of diarylcycloalkanes we have synthesized 1,2-bis-(*p*-hydroxyphenyl)-cyclopentane by a route similar to that used for cyclohexestrol.[1] 2-Chlorocyclopentanone was treated with two moles of *p*-methoxyphenylmagnesium bromide and the cyclopentene isolated directly without special treatment by dehydrating agents. Again it has not been possible to isolate any intermediate carbinol.



The product from the Grignard reaction appeared from the absorption spectrum to be 1,2-bis-(*p*-methoxyphenyl)-cyclopentene and the position of the double bond was confirmed by ozonization to 1,3-bis-(*p*-methoxybenzoyl)-propane. This olefin was obtained in low yield along with anisole, *p*,*p*′-dimethoxybiphenyl, 4,4″-dimethoxy-*p*-terphenyl and a large quantity of intractable tar. Despite the presence of formidable quantities of these by-products, of which the biphenyl derivative was most difficult to remove, all fractions from several preparations were combined and carefully examined chromatographically for the presence of 2,3-bis-(*p*-methoxyphenyl)-cyclopentene, but without success. The only other identifiable product found was *p*-methoxybiphenyl, undoubtedly arising from reaction between the Grignard reagent and a trace of anisole present.[2]

It has been shown that the reaction between 2-*p*-methoxyphenyl- or 2-chlorocyclohexanone and *p*-methoxyphenylmagnesium bromide yields principally the unsymmetrical olefin, 2,3-bis-(*p*-methoxyphenyl)-cyclohexene,[3] and that the latter is isomerized during alkaline demethylation to the symmetrical olefin.[1] The anomaly attending formation of the unsymmetrical cyclohexene in view of the probable formation of a *trans* intermediary carbinol and anticipated *trans* elimination of proximate tertiary hydrogen and hydroxyl substituents has been presented. In view of this it is significant that in the present case the cyclopentene formed is the isomer to be expected on the basis of previous considerations. As the most highly conjugated and most stable isomer it was not isomerized during demethylation, as shown by comparing the absorption spectrum of the starting material with the product, 1,2-bis-(*p*-hydroxyphenyl)-cyclopentene, and by methylation of the latter to yield the original dimethyl ether.

In the reaction between *p*-methoxyphenylmagnesium bromide and the alicylic ketones mentioned we have heretofore been unable to isolate any product corresponding to the expected carbinol but have always obtained an olefin or mixture of olefinic isomers. This has been true even with a ketone in which no adjacent tertiary hydrogen atom was present.[4] The ease of elimination of water or of MgBrOH may be due to activation of the tertiary position by the attached *p*-methoxyphenyl group. To test this assumption we repeated the reaction between phenylmagnesium bromide and 2-phenylcyclohexanone[5] and from the crude carbinol, as previously obtained, were able to isolate a crystalline product, m.p. 67–68°, analyzing correctly for 1,2-diphenylcyclohexanol. The steric configuration of this product has not yet been determined. When subjected to dehydration with potassium acid sulfate or phosphoric acid a diphenylcyclohexene, m.p. 53–54°, was obtained which may correspond with the product previously reported by Parmerter. However, the slight difference in melting points of 1,2- and 2,3-bis-(*p*-methoxyphenyl)-cyclohexenes may also exist in the diphenyl series so that it is difficult to judge whether or not our compound is identical with Parmerter's cyclohexene. The dehydration product was shown to be 2,3-diphenylcyclohexene by its absorption spectrum and by ozonization to an acid, m.p. 149.0–150.4°, having the composition of δ-phenyl-δ-benzoylvaleric acid. It is thus apparent that while the ease of dehydration in this series may be controlled by the nature of the aryl group on the carbinol carbon, the same factors control the direction of dehydration in 1,2-diphenyl- as in 1,2-bis-(*p*-methoxyphenyl)-cyclohexanol.

We have again used the ultraviolet absorption spectra of these unsaturated compounds as means of locating the position of the double bond. For example, in Fig. 1 the spectrum of 2,3-diphenylcyclohexene shows a maximum occurring at almost the same wave length as that of styrene, 246 mμ,

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(1) G. P. Mueller and R. May, This Journal, **71**, 3313 (1949).

(2) *Cf.* C. C. Price and G. P. Mueller, *ibid.*, **66**, 632 (1944).

(3) G. P. Mueller and D. Pickens, *ibid.*, **72**, 3626 (1950).

(4) G. P. Mueller and C. B. Honaker, *ibid.*, **73**, 2377 (1951).

(5) S. M. Parmerter, *ibid.*, **71**, 1127 (1949).

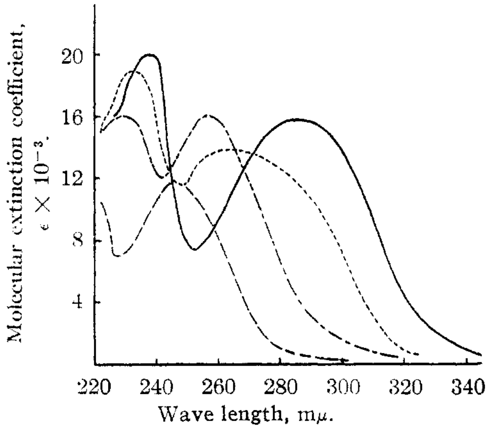

Fig. 1.—Ultraviolet absorption spectra of 1,2-bis-(*p*-methoxyphenyl)-cyclopentene, —; 1,2-bis-(*p*-methoxyphenyl)-cyclohexene, - - - -; 2,3-bis-(*p*-methoxyphenyl)-cyclohexene, - — - —; 2,3-diphenylcyclohexene, — — —.

and appearing in almost exactly the same relationship to that of 2,3-bis-(*p*-methoxyphenyl)-cyclohexene as found for styrene relative to anethole.

The conclusion was drawn earlier from examination of molecular models and comparison of absorption curves that the two aryl groups in 1,2-bis-(*p*-methoxyphenyl)-cyclohexene were more crowded than those in *cis*-stilbene. The opposite effect would be expected where the double bond must conform to the geometry of the five-membered ring, resulting in deformed valence angles and consequently more spread between the aryl substituents than exists in *cis*-stilbene. The argument follows that used in describing the Mills–Nixon effect.[6] Thus in Fig. 2 we have drawn to scale a model of 1,2-diphenylcyclohexene in which as a first approximation the cyclohexene ring is considered planar and the angles adjacent to the double bond are normal.[7] These assumptions result in very little deviation of the internal angles of cyclohexene from the normal and indicate that an actual picture of this ring with its facility of assuming a puckered configuration would show little deformation of the double bond. The interference between ortho positions of the benzene rings, however, is considerable when compared with the 1,2-diphenylcyclopentene model. In constructing the latter it was found impossible to keep the 122 and 116° angles and still construct a closed pentagon of regular form. The figure presented is an attempt to make the polygon as nearly regular as possible with minimum deformation of the 122° bond angles. The result shows very much less interference between the ortho hydrogen atoms. This effect is apparent in the curves of Fig. 1 where we have a diffuse maximum at 265 mμ for 1,2-bis-(*p*-methoxyphenyl)-cyclohexene, and a more sharply defined peak at 285 mμ for 1,2-bis-(*p*-methoxyphenyl)-cyclopentene. The corresponding values for *cis*- and *trans*-stilbene are 278 mμ, ϵ 10.4 × 10^{-3}, and 295 mμ, ϵ 24.5 × 10^{-3}, respectively.[8]

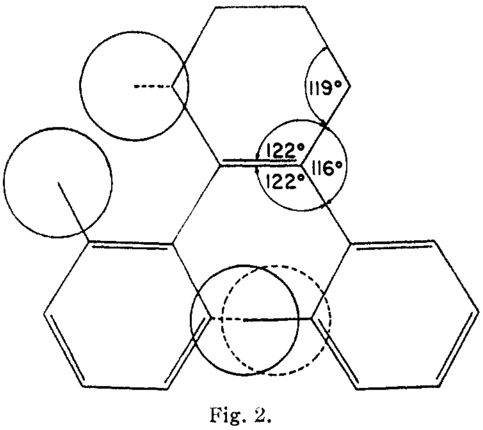

Fig. 2.

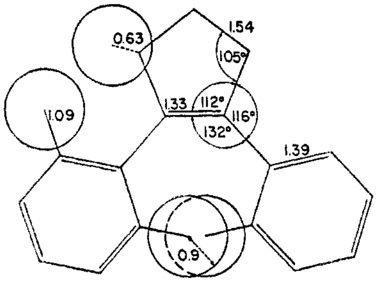

Fig. 3.

Qualitatively, the cyclopentene structure allows the two aryl groups to approach a coplanar configuration with the result that the contribution of the longest conjugated system to the excited state is greater and the spectrum has more of the characteristics of *trans*-stilbene absorption. Conversely the 1,2-diarylcyclohexenes show great damping of this contribution and are intermediate between styrene and *cis*-stilbene in character.

Any complete explanation of the apparent anomaly existing between dehydration of the cyclopentanol and cyclohexanol structures requires knowledge of their steric configurations. However, we believe that the ability of the double bond to enter more completely into conjugation with both aryl groups is part of the reason for its assuming the most highly substituted position in the five-membered ring.

Experimental

1,2-Bis-(*p*-methoxyphenyl)-cyclopentene.—A solution containing 57.5 g. (0.487 mole) of 2-chlorocyclopentanone[9] in 150 ml. of dry ether was added dropwise with stirring to the Grignard reagent prepared from 24.3 g. of magnesium turnings and 187 g. (1.0 mole) of *p*-bromoanisole in 250 ml. of dry ether. The heat of reaction caused gentle refluxing which was continued for one hour after the addition. The solution, from which a red, viscous oil had separated, was poured into 300 g. of ice and 75 ml. of concentrated hydrochloric acid. A solid separating at the interface was collected and proved to be 0.3 g. of 4,4″-dimethoxy-*p*-terphenyl, m.p. 272–275° after recrystallization from benzene.[2] The ether layer was separated, dried over magnesium sulfate and concentrated to yield 170 g. of a dark oil. On distillation this yielded 9.4 g. of oily crystals boiling up to 140° (0.02 mm.) and consisting mainly of 4,4′-dimethoxybiphenyl, m.p. 179.5–180.5°.[10] The next fraction, b.p. 140–180° (0.02 mm.), amounted to 44.9 g. of an orange oil

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(6) W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 2510 (1930); A. E. Remick, "Electronic Interpretations of Organic Chemistry," second ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 308.

(7) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice–Hall Co., New York, N. Y., 1945, p. 122.

(8) U. V. Solmssen, This Journal, **65**, 2370 (1943).

(9) M. Godchot and F. Taboury, *Compt. rend.*, **156**, 332 (1913).

(10) This and all subsequent melting points were observed at fifty magnifications with the Kofler apparatus and are corrected.

which slowly crystallized with standing. This was recrystallized from 300 ml. of alcohol and 34.5 g. of tan crystals obtained, which became nearly colorless after several washings with cold alcohol, m.p. 80–120°. Repeated treatment with Norite and fractional crystallization from 50% aqueous methanol eliminated much 4,4′-dimethoxybiphenyl and gave 12.5 g. or 9% of 1,2-bis-(*p*-methoxyphenyl)-cyclopentene, m.p. 87.5–89.0°. The material crystallized variously in the form of needles or hexagonal plates, both having the same melting point and mixed melting point. Its solution in carbon tetrachloride slowly absorbed bromine. In alcohol, $\lambda_{\text{max.}}$ were 238 mμ (ε 20,400), and 285 mμ (ε 15,800).

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.51; H, 7.04.

Among various attempts to isolate 2,3-bis-(*p*-methoxyphenyl)-cyclopentene the collected liquors from several preparations of the 1,2-isomer were concentrated and in ethereal solution extracted with sodium hydroxide to remove phenolic constituents. After washing with dilute acid and water the ether solution was concentrated and the residue distilled to yield fractions boiling at 107–111°, 122–130°, 165–200° at 0.1 mm. with considerable residue remaining. Each fraction was treated by sublimation, chromatography and crystallization, but the only new compound isolated in addition to those already mentioned was *p*-methoxybiphenyl, m.p. 90°, found in the first fraction by absorption on alumina and identified through its analysis, absorption spectrum and melting point with an authentic sample.

Oxidation of 1,2-Bis-(*p*-methoxyphenyl)-cyclopentene.—Ozonization of 100 mg. as previously described[3] and recrystallization of the product from methanol yielded 82 mg. of 1,3-bis-(*p*-methoxybenzoyl)-propane,[11] m.p. 95–97°. After further purification the needles melted at 99.8–100.2°.

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.98; H, 6.20.

The 2,4-dinitrophenylhydrazone was prepared. This crystallized poorly from ethyl acetate but yielded red micro needles readily from 15% of methanol in pyridine; m.p. 245–246° (dec.).

Anal. Calcd. for $C_{31}H_{28}N_8O_{10}$: C, 55.34; H, 4.30. Found: C, 55.65; H, 4.35.

1,2-Bis-(*p*-hydroxyphenyl)-cyclopentene.—Demethylation was carried out as before[1] using 0.50 g. of the dimethyl ether and 1.25 g. of potassium hydroxide in 10 ml. of ethyl alcohol. Completion of the reaction yielded 0.49 g., m.p. 195–205°, of material which after several recrystallizations from aqueous ethanol melted at 209.5–211° (dec.). This diphenol was soluble in dilute alkali but not in sodium bicarbonate solution; $\lambda^{95\%\ \text{alc.}}_{\text{max.}}$ 237 mμ (ε 17,900), 280 mμ (ε 14,460).

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 81.12; H, 6.38.

Acetylation of 30 mg. of the phenol with 0.05 g. of anhydrous sodium acetate in 2 ml. of acetic anhydride gave 35 mg. of crude diacetate. Purification from aqueous methanol gave 1,2-bis-(*p*-acetoxyphenyl)-cyclopentene, m.p. 136.2–137.0°, $\lambda^{95\%\ \text{alc.}}_{\text{max.}}$ 230 mμ (ε 18,770), 279 mμ (ε 13,140).

Anal. Calcd. for $C_{21}H_{20}O_4$: C, 74.97; H, 5.99. Found: C, 74.97; H, 5.94.

Methylation of 1,2-bis-(*p*-hydroxyphenyl)-cyclopentene in 20% sodium hydroxide with dimethyl sulfate gave the corresponding dimethyl ether, m.p. and m.m.p. 86.5–88.0°.

1,2-Bis-(*p*-methoxyphenyl)-cyclopentane.—A solution of 3.1 g. of 1,2-bis-(*p*-methoxyphenyl)-cyclopentene in 100 ml. of acetone was shaken with 0.20 g. of palladium–charcoal catalyst[12] for 20 hours at 45 p.s.i. The removal of catalyst and solvent left a waxy oil which crystallized from 50% aqueous ethanol to give 2.7 g. of white plates which after further purification melted at 56.5–57.5°, $\lambda^{95\%\ \text{alc.}}_{\text{max.}}$ 227 mμ (ε 19,610) and 278 mμ (ε 3,610).

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.80; H, 7.85. Found: C, 80.70; H, 7.55.

1,2-Bis-(*p*-hydroxyphenyl)-cyclopentane.—Alkaline demethylation of 5.1 g. of the dimethyl ether with 12.5 g. of potassium hydroxide in 100 ml. of ethyl alcohol at 210° for 24 hours gave an alkaline solution which was concentrated, diluted with water, extracted with ether and then acidified to precipitate an oil which was taken into ether. The latter solution was washed with aqueous sodium bicarbonate and water and evaporated, leaving 4.5 g. of brown crystalline product, m.p. 110–160°. On crystallization from benzene 0.9 g. of material first appeared which on further purification proved to be 1,2-bis-(*p*-hydroxyphenyl)-cyclopentene, m.p. 206–209° (dec.). Crystallization of the remainder of material from ethanol, aqueous ethanol, benzene, carbon tetrachloride and ligroin gave white needles, m.p. 109–111°. Until highly purified, this product melted at 50–54° with resolidification and final melting at the higher temperature. It was soluble in alkali and insoluble in aqueous sodium bicarbonate. As other phenols in this series the ferric chloride test was negative. In alcohol the $\lambda_{\text{max.}}$ were 226 mμ (ε 13,740), 279 mμ (ε 3,220).

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.17. Found: C, 80.03; H, 7.11.

Hydrogenation of 115 mg. of 1,2-bis-(*p*-hydroxyphenyl)-cyclopentene in 25 ml. of acetone over palladium–charcoal catalyst as before yielded, after recrystallization from aqueous ethanol, 112 mg. of white plates melting at 49–54°, solidifying and remelting at 106–109°. After one recrystallization from ligroin the m.p. and m.m.p. with the above was 107–109°.

Acetylation of 0.60 g. gave 0.65 g. of 1,2-bis-(*p*-acetoxyphenyl)-cyclopentane, m.p. 69.5–70.8° after six recrystallizations from methanol and aqueous methanol.

Anal. Calcd. for $C_{21}H_{22}O_4$: C, 74.53; H, 6.55. Found: C, 74.71; H, 6.44.

1,2-Diphenylcyclohexanol.—Phenylmagnesium bromide was treated with 2-phenylcyclohexanone exactly as described[5] and 73 g. (77%) of a viscous yellow oil was obtained from the ethereal extract. After three days 20 g. of crystalline material had separated which was isolated and recrystallized twice from *n*-hexane. This was 1,2-diphenylcyclohexanol, m.p. 67–68°.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 85.67; H, 7.99. Found: C, 85.81, 85.86; H, 7.99, 8.04.

2,3-Diphenylcyclohexene.—Crystalline 1,2-diphenylcyclohexanol, 7.0 g., was stirred for four hours at 100° with an equal volume of 85% phosphoric acid and the mixture diluted with water and extracted with benzene. The benzene extract was concentrated and distilled, the fraction boiling at 158–170° (2 mm.) being redistilled to yield 2.5 g. of the olefin, b.p. 145–150° (2 mm.) which crystallized in three days. Recrystallization of this from methanol gave needles, m.p. 53.2–53.8°, which reacted rapidly with potassium permanganate in acetone, $\lambda_{\text{max.}}$ 246 mμ (ε 11,680).

Anal. Calcd. for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.29; H, 7.75.

Dehydration of the oil from which the crystalline carbinol was obtained also gave the same product. For example, the phosphoric acid procedure as described yielded 30% of crystalline material which on further purification gave 2,3-diphenylcyclohexene. Again, heating a mixture of 25 g. of potassium acid sulfate with 25 g. of oily carbinol at 150–160° for three hours with removal of the water formed, dissolving the product in benzene and distilling as before gave 8.5 g. (36%) of the same crystalline olefin. This required further purification.

Ozonization of 2,3-diphenylcyclohexene, 2.3 g., was carried out in 80 ml. of ethyl acetate and the ozonide treated as described for the formation of acids.[13] An oil obtained from the washed ethereal extract crystallized on standing and was recrystallized three times from benzene–petroleum ether to give 0.3 g. of an acid, m.p. 149.0–150.4°. Analytical values agree with those calculated for the expected but unrecorded δ-phenyl-δ-benzoylvaleric acid.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.79; H, 6.46.

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[11] S. G. P. Plant and M. E. Tomlinson, *J. Chem. Soc.*, 856 (1935).

[12] W. H. Hartung, THIS JOURNAL, **50**, 3370 (1928).

[13] A. L. Henne and P. Hill, *ibid.*, **65**, 752 (1943).