isomer and of the eutectic mixture are nearly the same, and the curves appear actually to cross to about 100 mm. and 120°; therefore, fractional distillation at reduced pressure could not be expected to be efficient.

In connection with some studies of elimination reactions we have obtained or reinterpreted kinetic, spectroscopic and phase equilibrium data all of which indicate that the eutectic material contains about 20% of the *trans* isomer.

**Kinetic Evidence.**—We have found that a solution of the eutectic material in methanol will react at 25° with only 75 to 80% of a stoichiometric quantity of methoxide ion. Among other products, the final solution contains diiodoacetylene and *trans*-diiodoethylene, identified by chemical analysis and infrared absorption spectrum. The pure *trans* isomer does not react with methoxide ion under these conditions.

At elevated temperatures in methanol *trans*-diiodoethylene undergoes an elimination reaction with sodium iodide. Under the same conditions the eutectic mixture undergoes a similar but slower reaction, and kinetic measurements suggest that only about 20% of the material is reactive.

The detailed kinetic evidence will be included in a paper concerned with the mechanism of these elimination reactions.

**Spectroscopic Evidence.**—Infrared absorption studies between 700 and 1300 cm.$^{-1}$ showed that all bands associated with *trans*-diiodoethylene were also observed in the eutectic mixture. Quantitative measurements on the band at 918 cm.$^{-1}$ with carbon tetrachloride solutions of the two materials gave 20.1, 20.5 and 20.6% of *trans* in the eutectic mixture used to prepare three different solutions. Some of these observations are illustrated in Fig. 1.

A methanol solution of the eutectic mixture was heated with sodium iodide, and the remaining diiodoethylene was isolated and analyzed by the same technique. It appeared to contain only about 15% of *trans* isomer.

**Evidence from Phase Equilibria.**—If A represents a pure substance which crystallizes without solid solutions, then for an equilibrium with an ideal solution we can write

$$-\ln N_A = \frac{\Delta H(T_0 - T)}{RTT_0}$$

In this equation $N_A$ is the mole fraction of A in the solution in equilibrium at temperature $T$ with pure solid A, $T_0$ is the freezing point of pure A, and $\Delta H$ is the heat of fusion of pure solid A. This equation assumes that the solution is ideal and that $\Delta H$ is independent of temperature. Ordinarily this equation is used to calculate the freezing point depression of A; but if both $T$ and $N_A$ are measured, it permits a calculation of $\Delta H$.

Latiers[4] reports the freezing points of several mixtures of *trans* and eutectic diiodoethylene. His data are in agreement with a smaller number of measurements by Chavanne and Vos.[2] We have used Latiers' data to calculate values of $\Delta H$ for the fusion of *trans*-diiodoethylene. If it is assumed that the eutectic is pure *cis*, calculated values of $\Delta H$ show a steady drift from 4470 cal./mole for a mixture containing 5.5% eutectic and freezing at 69° to 6170 cal./mole for a mixture containing 87.5% eutectic and freezing at 7.2°. If it is assumed that the eutectic contains 20.5% of *trans*, the calculated values of $\Delta H$ from these extreme concentrations are 3510 and 3540 cal./mole, respectively, and the values calculated for intermediate concentrations vary between the extremes of 3290 and 3690 cal./mole with little if any trend. We have also made rough freezing point measurements on a few mixtures prepared by adding small amounts of iodobenzene to pure *trans*-diiodoethylene. These measurements indicate that $\Delta H$ is between 3000 and 3500 cal./mole and is certainly less than 4000 cal./mole.

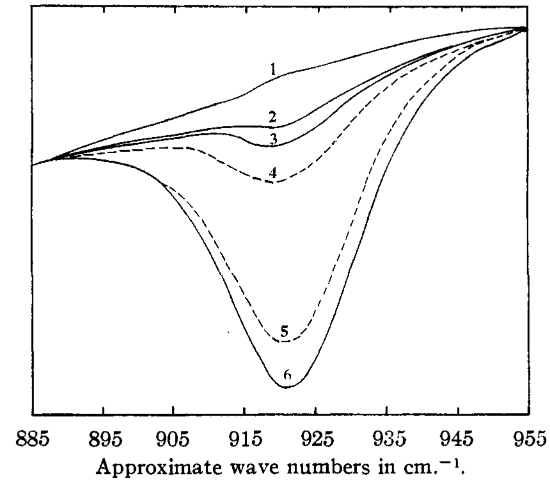

Fig. 1.—Infrared spectra of solutions of *trans* and eutectic diiodoethylene in carbon tetrachloride: 1, solvent alone; 2, 0.0057 g. *trans* per ml.; 3, 0.0107 g. *trans* per ml.; 4, 0.0830 g. eutectic per ml.; 5, 0.3083 g. eutectic per ml.; 6, 0.0824 g. *trans* per ml.

As a result of all the above evidence, we conclude that the "cis-diiodoethylene" of the literature is a eutectic mixture containing 20–21% of the *trans* isomer. Experiments are being undertaken to fractionate this material to obtain the pure *cis* isomer and to determine various properties to replace values now reported for the eutectic mixture.

**Acknowledgment.**—We are indebted to Professor W. E. Doering for suggesting the above interpretation of the kinetic results and for many helpful discussions during the investigation. We are indebted to Professor R. S. Halford and to several of his students for assistance with the infrared measurements.

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[4] G. Latiers, *Bull. soc. chim. Belg.*, **31**, 73 (1922).

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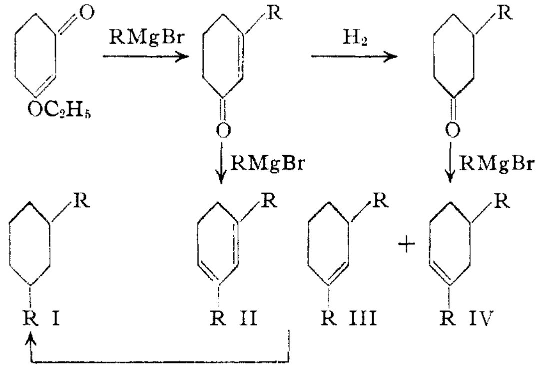
## 1,3-Bis-(*p*-methoxyphenyl)-cyclohexane

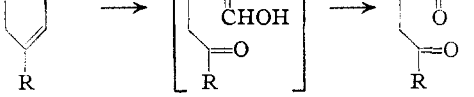
By George P. Mueller and Carl B. Honaker

Toward developing a series of diarylcycloalkanes bearing some structural relationship to the synthetic estrogens we have adapted the procedure involving dihydroresorcinol ethyl ether as an intermediate.[1] The reaction of this ketone with *p*-methoxyphenylmagnesium bromide yielded 3-*p*-methoxyphenylcyclohexene-2-one, and subsequent hydrogenation the saturated ketone, both of which corresponded in properties with the previous preparations of these ketones by ring closure.[2]

3-*p*-Methoxyphenylcyclohexene-2-one with *p*-methoxyphenylmagnesium bromide gave II which was dehydrogenated to 4,4″-dimethoxy-*m*-terphenyl, and also hydrogenated to give 1,3-bis-(*p*-methoxyphenyl)-cyclohexane (I); the latter yielded the corresponding phenol by alkaline demethylation. 3-*p*-Methoxyphenylcyclohexanone and the Grignard reagent formed the two cyclohexenes, III and IV, a mixture of which yielded I on hydrogenation. These isomers were separated and shown to be very similar in physical properties. The position of unsaturation in III was demonstrated by oxidizing the compound to the known 1,3-bis-(*p*-methoxybenzoyl)-propane. Ozonization of IV gave a product having aldehydic properties but giving analytical values for a monohydrate of the expected ketoaldehyde.



R = *p*-$CH_3OC_6H_4$



We were interested to observe again that the Grignard reagent reacting with the cyclic ketones gave rise directly to the olefins, II, III and IV instead of the corresponding carbinols. The examples here differ from previous instances in which an adjacent tertiary hydrogen was available for dehydration.[3] However, although only secondary hydrogens were available in this case, the dehydration was still sufficiently facile that any carbinol formed did not survive the relatively mild conditions of hydrolysis.

The acid-catalyzed condensation of anisole with 1,2-dichlorocyclohexane, as well as with cyclohexene oxide and 1,2-dihydroxycyclohexane, was earlier reported to yield the two diastereoisomeric 1,3-bis-(*p*-methoxyphenyl)-cyclohexanes. One of these was an oil and the other melted at 104°. Their relationship was demonstrated through dehydrogenation to the same compound, designated as 4,4″-dimethoxy-*m*-terphenyl by virtue of its non-identity with the *o*- and *p*-isomers and its conversion to a small amount of substance having the properties of *m*-terphenyl.[4] The identity of the crystalline cyclohexane, the dimethoxy-*m*-terphenyl and their derivatives has been confirmed by direct comparison of these compounds, previously obtained, with those resulting from the present syntheses.

## Experimental

**1,3-Bis-(*p*-methoxyphenyl)-cyclohexadiene-1,3.**—To the Grignard reagent prepared from 71 g. (0.38 mole) of *p*-bromoanisole and 10 g. of magnesium in 100 ml. of anhydrous ether was added, dropwise, a solution of 42 g. (0.30 mole) of dihydroresorcinol ethyl ether[1] in 100 ml. of anhydrous ether. The addition required 45 minutes and refluxing was maintained by the heat of reaction. The mixture was poured into ice and dilute sulfuric acid; the ether layer was separated, washed with dilute sodium bicarbonate and water, dried over sodium sulfate and distilled. A fraction was collected, b.p. 183–190° (2 mm.), which crystallized on standing. Upon recrystallization three times from ligroin 19 g. (33%) of 3-*p*-methoxyphenylcyclohexene-2-one, m.p. 80–82°,[2] was obtained. The semicarbazone melted correctly at 215–217°.[5]

A solution of 10 g. (0.05 mole) of the cyclohexenone in 100 ml. of ether was added slowly to *p*-methoxyphenylmagnesium bromide, 0.06 mole prepared in 50 ml. of ether, during 30 minutes. The mixture, which was hydrolyzed as before yielded a solid at the water–ether interface that was collected and dried, m.p. 171–183°. After four recrystallizations from benzene, 6.8 g. of 1,3-bis-(*p*-methoxyphenyl)-cyclohexadiene-1,3 melting at 199–201° was obtained. Treatment of the ether phase as before followed by evaporation and purification of the crystalline residue gave an additional 1.5 g. of product, making the total 8.3 g. or 57%, $\lambda_{\text{max.}}^{95\%\text{ alc.}}$ 265 mμ (ε 28,200).

*Anal.* Calcd. for $C_{20}H_{20}O_2$: C, 82.19; H, 6.85. Found: C, 82.26; H, 6.87.

The cyclohexadiene was dehydrogenated by treating 0.5 g. in 10 ml. of *p*-cymene at reflux for four hours in the presence of 0.1 g. of palladium-on-carbon catalyst.[6] The solvent was removed *in vacuo* and the residue extracted with hot benzene. Recrystallization of the benzene-soluble product resulted in colorless plates, m.p. 197–198°. The melting point in admixture with a sample of 4,4″-dimethoxy-*m*-terphenyl isolated previously[4] was 197–198° while that with the precursory diene was 194–199°. The spectrum of the terphenyl is very similar to that of the cyclohexadiene, showing $\lambda_{\text{max.}}^{95\%\text{ alc.}}$ 262 mμ (ε 38,350).

*Anal.* Calcd. for $C_{20}H_{18}O_2$: C, 82.76; H, 6.21. Found: C, 82.81; H, 6.29.

**1,3-Bis-(*p*-methoxyphenyl)-cyclohexane.**—A mixture of 1.4 g. of 1,3-bis-(*p*-methoxyphenyl)-cyclohexadiene-1,3, 60 ml. of alcohol and 1 g. of Raney nickel catalyst was shaken for six hours at room temperature and 50 p.s.i. of hydrogen. The filtered solution was concentrated to 30 ml. and on standing in the cold deposited a mixture of two products in the form of needles and plates, respectively. These were separated by hand and the latter proved to be the unreduced diene. The needles on purification from alcohol yielded 70 mg. of crystals, m.p. 103–104°, corresponding to 1,3-bis-(*p*-methoxyphenyl)-cyclohexane.[4] The absorption spectrum of this product showed, $\lambda_{\text{max.}}^{95\%\text{ alc.}}$ 225 mμ (ε 23,330), 277 mμ (ε 5,110) and 284 mμ (ε 4,230).

*Anal.* Calcd. for $C_{20}H_{24}O_2$: C, 81.08; H, 8.11. Found: C, 81.31; H, 8.13.

**1,3- and 2,4-Bis-(*p*-methoxyphenyl)-cyclohexene.**—3-*p*-Methoxyphenylcyclohexanone was prepared from the unsaturated ketone as described by Chandhuri,[2] and 18 g. (0.082 mole) in 200 ml. of ether added dropwise to 0.09 mole

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(1) G. F. Woods and I. W. Tucker, THIS JOURNAL, **70**, 2174 (1948).

(2) P. K. Chandhuri, *J. Ind. Chem. Soc.*, **21**, 341 (1944).

(3) G. P. Mueller, J. G. Fleckenstein and W. H. Tallent, THIS JOURNAL, **73**, in press (1951).

(4) C. C. Price and G. P. Mueller, *ibid.*, **66**, 628 (1944).

(5) All melting points were observed at fifty magnifications in the Kofler apparatus and are corrected.

(6) W. H. Hartung, THIS JOURNAL, **50**, 3370 (1928).

of *p*-methoxyphenylmagnesium bromide in 200 ml. of ether. The addition was complete in 30 minutes and the solution was treated with ice and hydrochloric acid. The ethereal solution was handled as usual, evaporation of which left a crude crystalline product, m.p. 78–87° after one recrystallization from alcohol. Fractional crystallization of 4.4 g. of this mixture from 800 ml. of methanol by slow evaporation at room temperature gave in order, A, 0.7 g., m.p. 93–125°, B, 1.1 g., m.p. 87–91°, C, 0.8 g., m.p. 83–87° and D, 0.5 g., m.p. 92–93.5°. Recrystallization of A gave a fraction, m.p. 91–185°, rich in 4,4′-dimethoxybiphenyl the mother liquor from which was used to recrystallize B, yielding 2,4-bis-(*p*-methoxyphenyl)-cyclohexene, m.p. 93.5–95°, $\lambda_{\text{inflection}}^{95\%\text{ alc.}}$ 226 mμ (ε 15,500), $\lambda_{\text{max.}}^{95\%\text{ alc.}}$ 256 mμ (ε 17,200). *Anal.* Calcd. for $C_{20}H_{22}O_2$: C, 81.63; H, 7.49. Found: C, 81.92; H, 7.46. After further purification C was still a mixture but D proved to be 1,3-bis-(*p*-methoxyphenyl)-cyclohexene, m.p. 92–93.5°, $\lambda_{\text{max.}}^{95\%\text{ alc.}}$ 224 mμ (ε 14,030) and 258 mμ (ε 16,760). *Anal.* Calcd. for $C_{20}H_{22}O_2$: C, 81.63; H, 7.49. Found: C, 81.13; H, 7.35. These were two different compounds as shown by mutual depression of their melting points and the results of oxidation.

1,3-Bis-(*p*-methoxyphenyl)-cyclohexene, 0.2 g. in 30 ml. of acetone, was oxidized overnight at room temperature with 0.3 g. of potassium permanganate. The manganese dioxide was filtered out and the solution diluted with water, decolorized with sodium bisulfite and extracted with ether. Evaporation of the ether left a residue which was crystallized from an alcoholic solution by slow evaporation, first to yield anisic acid followed by a fraction, m.p. 98.8–100°, consisting of 1,3-bis-(*p*-methoxybenzoyl)-propane as shown by its melting point with an authentic sample.[7]

2,4 - Bis - (*p* - methoxyphenyl) - cyclohexene was oxidized similarly but no product could be identified. Ozonization of 100 mg. by the procedure previously outlined[8] yielded from evaporation of the ethyl acetate a product melting at 115–116°, after recrystallization from methanol. This gave positive aldehyde tests with Schiff and Tollens reagents.

*Anal.* Calcd. for $C_{20}H_{22}O_4$: C, 73.62; H, 6.75; for $C_{20}H_{22}O_4 \cdot H_2O$: C, 69.74; H, 7.06. Found: C, 69.72; H, 7.39.

Hydrogenation of a mixture of 1,3- and 2,4-bis-(*p*-methoxyphenyl)-cyclohexenes, 1.3 g. in 50 ml. of absolute ethanol, with 0.1 g. of palladium-carbon catalyst at 50 p.s.i. for 72 hours yielded 0.8 g. of purified 1,3-bis-(*p*-methoxyphenyl)-cyclohexane, m.p. 103–105°, identical with that obtained from the cyclohexadiene.

A solution of 0.75 g. of the dimethyl ether in 15 ml. of alcohol with 1.85 g. of potassium hydroxide was heated at 200° for 24 hours and the product isolated as usual. This was recrystallized twice from dilute methanol to give 0.52 g. of the phenol, m.p. 233–236°, corresponding with that reported previously.

*Anal.* Calcd. for $C_{18}H_{20}O_2$: C, 80.60; H, 7.47. Found: C, 80.42; H, 7.76.

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

[8] G. P. Mueller and D. Pickens, THIS JOURNAL, **72**, 3626 (1950).

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## An Improved Hydrogenation of Cholesterol to Cholestanol

BY HAROLD R. NACE

The hydrogenation of cholesterol in glacial acetic acid at 65–75° to produce cholestanol has been described by Bruce.[1a] Attempts to repeat the procedure in This Laboratory invariably led to incomplete hydrogenation. The products, cholestanol and its acetate, began to crystallize from the solvent as the reduction approached 75% of completion, coating the catalyst and rendering it ineffective. An alternate procedure[1b] utilizing cholesteryl acetate eliminates this difficulty but requires the acetylation of cholesterol.

The procedure reported here has been found to be more satisfactory than either of the above methods. By employing a solvent consisting of cyclohexane and glacial acetic acid, a higher yield of cholestanol has been obtained directly from cholesterol in a shorter time, the inconvenience of having to heat the reduction mixture has been eliminated, and crystallization of the product does not occur during the reduction.

### Experimental

A solution of 12.0 g. (0.031 mole) of cholesterol (Eastman Kodak Co. White Label grade was used without further purification) in 120 ml. of cyclohexane and 60 ml. of glacial acetic acid was added to a suspension of Adams platinum catalyst prepared by prereducing 0.30 g. of platinum oxide (Baker and Co., Inc.) in 30 ml. of glacial acetic acid. The resulting mixture was shaken with hydrogen at room temperature and pressures of 1–2 atmospheres. The hydrogen uptake ceased in one to two hours at 110–120% of the theoretical value.[2] The solution, after removal of the catalyst, was concentrated to dryness under reduced pressure, 250 ml. of 95% ethanol, 5.0 g. of sodium hydroxide, and 30 ml. of water were added, the resulting mixture was heated under reflux for four hours, and then cooled at 5–10° for several hours. The yield of crystals after air drying was 11.1–12.0 g. and an additional 1.0–0.6 g. was obtained by dilution of the filtrate with water. The combined crops were recrystallized from 165 ml. of 95% ethanol, and the crystals dried four hours at 100° (2 mm.) to give 10.5–10.7 g. (86.5–88%) of cholestanol, m.p. 141.5–142° (cor.). The product gave a faint Liebermann-Burchard test[1] after several minutes.

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[1] (a) W. F. Bruce, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 191; (b) J. O. Ralls, *ibid.*, p. 191.

[2] The excess hydrogen consumption was probably due to the presence of more highly unsaturated compounds in the cholesterol.

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## Derivatives of Sulfenic Acids

BY G. W. PEROLD AND H. L. F. SNYMAN

A research program currently being carried out in this Laboratory involves frequent characterization of volatile unsaturated compounds as solid derivatives. In this connection we are studying the application of the elegant reagent described by Kharasch and co-workers,[1] *viz.*, 2,4-dinitrobenzenesulfenyl chloride, and wish to record some of our observations to date.

The preparation of this reagent by the chlorinolysis of the corresponding disulfide[2] led to uncertain results in our hands, apparently due to variability in the quality of the disulfide when prepared from normally available reagents. The action of chlorine gas on a solution of the corresponding thiophenol[3] was adopted for the preparation, as this method, though giving only a moderate yield of product, was quicker and more reproducible.

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[1] N. Kharasch, H. L. Wehrmeister and H. Tigerman, THIS JOURNAL, **69**, 1612 (1947); N. Kharasch and C. M. Buess, *ibid.*, **71**, 2724 (1949).

[2] N. Kharasch, G. I. Gleason and C. M. Buess, *ibid.*, **72**, 1796 (1950).

[3] T. Zincke and K. Eismayer, *Ber.*, **51**, 756 (1918); K. Fries and G. Schürmann, *ibid.*, **52**, 2174 (1919); H. Lecher and F. Holschneider, *ibid.*, **57**, 757 (1924); W. H. Ebelke, U. S. Patent 2,304,557, *C. A.*, **37**, $2746^5$ (1943).