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°, $\lambda^{95\%\text{ alc.}}_{\text{inflection}}$ 226 mμ (ε 15,500), $\lambda^{95\%\text{ alc.}}_{\text{max.}}$ 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°, $\lambda^{95\%\text{ alc.}}_{\text{max.}}$ 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.

(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).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TENNESSEE
KNOXVILLE, TENN. RECEIVED DECEMBER 6, 1950

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.

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

METCALF LABORATORIES
BROWN UNIVERSITY
PROVIDENCE 12, RHODE ISLAND RECEIVED DECEMBER 21, 1950

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.

(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.

(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[8] (1943).