

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°, $\lambda_{\text{infection}}^{95\% \text{ alc.}}$ 226 μ (ϵ 15,500), $\lambda_{\text{max}}^{95\% \text{ alc.}}$ 256 μ (ϵ 17,200). *Anal.* Calcd. for $\text{C}_{20}\text{H}_{22}\text{O}_2$: 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 μ (ϵ 14,030) and 258 μ (ϵ 16,760). *Anal.* Calcd. for $\text{C}_{20}\text{H}_{22}\text{O}_2$: 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 outlined⁸ 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 $\text{C}_{20}\text{H}_{22}\text{O}_4$: C, 73.62; H, 6.75; for $\text{C}_{20}\text{H}_{22}\text{O}_4 \cdot \text{H}_2\text{O}$: 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 $\text{C}_{18}\text{H}_{20}\text{O}_2$: 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).

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An Improved Hydrogenation of Cholesterol to Cholestanol

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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,

(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.

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 test¹ 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

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PROVIDENCE 12, RHODE ISLAND

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-dinitrobenzenesulfonyl chloride, and wish to record some of our observations to date.

The preparation of this reagent by the chlorinolysis of the corresponding disulfide² 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 thiophenol³ was adopted for the preparation, as this method, though giving only a moderate yield of product, was quicker and more reproducible.

(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**, 2746¹ (1943).

The methyl and ethyl esters of 2,4-dinitrobenzenesulfenic acid have not so far been recorded, and were here prepared in somewhat unusual manner. On refluxing a solution of 2,4-dinitrobenzenesulfonyl chloride in absolute ethanol, a procedure similar to that by which Fries⁴ obtained the methyl and ethyl esters derived from anthraquinone-1-sulfonyl chloride, the main product (ca. 80% yield) was the corresponding disulfide, while the ethyl sulfenate was obtained in less than 2% yield. On first warming the reagent in ethylene dibromide solution, however, and then adding excess absolute methanol or ethanol, the corresponding ester crystallized out rapidly and in good yield.

Experimental

2,4-Dinitrobenzenesulfonyl Chloride.—2,4-Dinitrothiophenol was prepared from 3 g. of 2,4-dinitrochlorobenzene according to Willgerodt⁵ and the crude, once-precipitated product filtered and washed twice with water. The precipitate was dissolved in warm benzene, separated from any water, and the benzene removed, finally *in vacuo*. Carbon tetrachloride (40 ml.) was added and the suspension boiled gently under reflux while chlorine gas dried over sulfuric acid was bubbled through for two hours. The yellow precipitate formed was filtered off and the filtrate concentrated to 15 ml. to let the product crystallize; yield directly pure product 1.8 to 1.9 g. (52 to 55%, on dinitrochlorobenzene), m.p. 95–96° (cor.). The insoluble by-product was apparently mainly bis-(2,4-dinitrophenyl)-disulfide which was here not split by chlorinolysis.

Methyl 2,4-Dinitrobenzenesulfenate.—2,4-Dinitrobenzenesulfonyl chloride (500 mg.) dissolved in 2 ml. of ethylene dibromide was heated on the boiling water-bath for 30 minutes, taken off from the water-bath and 10 ml. of absolute methanol added with stirring. The product separated as fine canary-yellow needles within a few minutes; yield 310 mg. (63%), m.p. 124.5–125° not appreciably changed by recrystallization from methanol or acetic acid. Decomposition with evolution of gas set in on heating above the melting point. The crystallized product was sublimed at 100–110° and 0.04 mm. for analysis; m.p. 124.8–125.2° (cor.).

Anal. Calcd. for $C_7H_5O_5N_2S$: C, 36.83; H, 2.63; N, 12.17; S, 13.92. Found: C, 36.63; H, 2.50; N, 12.12; S, 13.62.

Ethyl 2,4-Dinitrobenzenesulfenate.—Prepared as above, the product was obtained as coarse orange-yellow needles, m.p. 124.5–125° (cor.) in 67% yield, and sublimed for analysis as before.

Anal. Calcd. for $C_9H_9O_5N_2S$: C, 39.35; H, 3.30; N, 11.47. Found: C, 39.37, 39.26; H, 3.39, 3.32; N, 11.42.

A mixture of the ethyl and methyl 2,4-dinitrobenzenesulfenates melted at 112–114°.

(4) K. Fries, *Ber.*, **45**, 2966 (1912); K. Fries and G. Schürmann, *ibid.*, **52**, 2173 (1919).

(5) Willgerodt, *ibid.*, **17**, ref., 352 (1884).

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The Heat of Combustion of Biphenyl

BY GEORGE S. PARKS AND LELAND M. VAUGHAN

A new determination of the heat of combustion of biphenyl has seemed desirable in view of its importance in problems of thermodynamics and resonance.

Three samples of this hydrocarbon were burned in the present measurements. The first sample was a high-grade Eastman Kodak Co. material (m.p. 69.1°) which had been dried over anhydrous magnesium perchlorate in an evacuated desiccator

for several weeks. For the second sample some of this material was recrystallized from pure benzene and then likewise dried in vacuum. The third sample was prepared with two recrystallizations from benzene, followed by heating for several hours in an electric oven at 100°. It was then cooled from the molten condition in a vacuum desiccator, where the resulting crystals were subsequently kept over the drying agent for at least a week. Four determinations were carried out on Sample 1 and three each on the other two samples.

These combustion measurements were made with the Parr "illium" bomb and the calorimetric procedures which have been fully described in earlier papers¹ from this Laboratory. They are based on Jessup's recent value of 26,419.4 international joules per gram mass for the standard benzoic acid.² In particular, it should be noted that the temperature changes in our present study were measured by a calibrated platinum resistance thermometer with a precision of better than 0.005%, whereas all earlier investigators on biphenyl utilized mercury-in-glass thermometers with ensuing uncertainties of 0.05% or more.

Our resulting thermochemical data are summarized in Table I. Under the symbols $-\Delta U/m$ and Δ appear the mean values for the combustions on the three biphenyl samples and the mean deviations of the individual combustions from these mean values. These data are expressed in terms of the defined calorie (4.184 absolute joules) and represent the values for the energy evolved in the isothermal bomb process per gram mass at 25°. The final mean for all three samples was then calculated per mole and corrected to the standard constant-volume process where the reactants and products are each at 1 atmosphere by means of the equations of Washburn.³ The energy evolved in this hypothetical process is designated in the table of the symbol $-\Delta U_c$. From this quantity $-\Delta H_c$, the heat evolved in the isobaric process at 1 atm., was obtained by addition of the proper work term. Finally, $-\Delta H_f^0$, the heat of formation of biphenyl from gaseous hydrogen and graphitic carbon, was calculated from $-\Delta U_c$ by use of 68,317.4 kcal. and 94,051.8 kcal.⁴ for the heats of formation of water and carbon dioxide, respectively.

TABLE I

THERMOCHEMICAL DATA FOR BIPHENYL AT 25°
(Mol. Wt., 154.200; Density, 1.17)

$-\Delta U/m$ and Δ , calories per gram	
Mean for Sample 1	9687.4 ± 1.5
Mean for Sample 2	9688.4 ± 0.3
Mean for Sample 3	9687.0 ± 0.6
Final mean	9687.6 ± 1.1
$-\Delta U_c$, kcal. per mole for 1 atm.	1491.82
$-\Delta H_c$, kcal. per mole for 1 atm.	1493.30
$-\Delta H_f^0$, kcal. per mole for 1 atm.	-23.10

(1) J. W. Richardson and G. S. Parks, *THIS JOURNAL*, **61**, 3543 (1939); G. S. Parks, T. J. West, B. F. Naylor, P. S. Fujii and L. A. McClaine, *ibid.*, **68**, 2524 (1946).

(2) R. S. Jessup, *J. Research Natl. Bur. Standards*, **36**, 421 (1946).

(3) E. W. Washburn, *Bur. Standards J. Research*, **10**, 525 (1933).

(4) F. D. Rossini and co-workers, "Selected Values of Properties of Hydrocarbons," United States Government Printing Office, Washington, D. C., 1947, p. 156.