possessing common functional groups capable of forming labeled derivatives. Perhaps the greatest advantage of the method lies in the fact that repeated surveys permit continuous quantitative estimation of the development of the column.

Experimental

p-Iodobenzoyl Chloride-I^{131}.—*p*-Iodobenzoic acid-I^{131} was first prepared according to a modification of the method of Meyer.[7] Subsequently Whitmore and Woodward's synthesis[8] was employed at 1/100th scale. The 5 mc. of NaI^{131} in approximately 2 ml. of H_2O was added with the first portion of I_2. The product, carefully dried in a vacuum oven at 60°, was refluxed for 2 hours with 10 ml. of thionyl chloride. The excess thionyl chloride was distilled off under vacuum. The *p*-iodobenzoyl chloride was sublimed under vacuum. The product melted at 65°.

Steryl *p*-Iodobenzoates.—The labeled esters were prepared by dissolving approximately 100 mg. of sterol with a 0.3 molar excess of the labeled acid chloride in sufficient dry pyridine to effect solution. The mixture was kept at 5° for 12 hours and worked up in the usual way. The weight yields of crude esters were 90–96%. The recrystallized esters had the following properties.

Cholestanyl *p*-iodobenzoate: m.p. 186° to a cloudy melt clearing at 230°. *Anal.* Calcd. for $C_{34}H_{51}IO_2$: C, 65.90; H, 8.30; I, 20.48. Found: C, 66.02; H, 8.44; I, 20.58.

Cholesteryl *p*-iodobenzoate: m.p. 184.5° to a brilliantly colored mesomorphic melt clearing at 242°. *Anal.* Calcd. for $C_{34}H_{49}IO_2$: C, 66.11; H, 7.99; I, 20.55. Found: C, 66.00; H, 8.06; I, 20.85.

7-Dehydrocholesteryl *p*-iodobenzoate: m.p. 178.5° (unsharp) to a cloudy melt which decomposes. *Anal.* Calcd. for $C_{34}H_{47}IO_2$: C, 66.33; H, 7.69; I, 20.62. Found: C, 66.54; H, 7.71; I, 20.65.

Two parts of silicic acid, Mallinckrodt, 100 mesh, "specially prepared for chromatographic analysis by the method of Ramsey and Patterson" and one part of Celite 535[9] were mixed in a ball mill and heated for four hours in an oven at 180°. A tube, 14-mm. internal diameter and 80 cm. long, was treated with Silicone Resin Solution[10] as recommended by Idler and Baumann.[11] The adsorbent was poured into a large funnel attached to the upper end of the tube by a rubber sleeve, drawn into the tube and packed by suction, and further settled by gentle tapping. A perforated porcelain disc was placed on top of the column to protect the adsorbent and the column was prewashed with one volume of 10:1 ligroin[12]–benzene. The esters (15 to 75 mg. of each) were applied and washed into the column with the same solvent mixture and the chromatogram was developed with ligroin flowing under suction at the rate of 2 to 3 ml. per minute.

The column was scanned at hourly intervals by a collimated scintillation counter employing a $1^3/_4$ inch diameter by 2 inch high sodium iodide thallium activated crystal and an RCA # 6199 photomultiplier tube. The counter assembly was mounted in a lead shield providing a minimum of 1.5 inches of lead in all directions except for the "viewing" slit. Interchangeable lead plugs with various slit widths were used depending on the level of the activity. The counter and shield were mounted on a vertical steel shaft by means of a counterpoised sliding bracket. The chromatographic column was supported by the same steel shaft. Usually one minute counts were taken at each cm. of length.

In a typical run with a mixture of 25 mg. of each of the esters, the 7-dehydrocholesteryl ester zone was apparent after one-half hour and was completely separated in 7 hours. The cholesteryl–cholestanyl ester zone began to resolve in 5 hours and the two were virtually separate in 16 hours. At this time the column was allowed to run dry and a careful survey taken. A plot of net counts per minute against distance from the top of the column showed bell-shaped curves, with some tailing, corresponding to the zones. The maxima of the three esters appeared at the following distances: cholestanol, 46.5 cm.; cholesterol, 34 cm.; 7-dehydrocholesterol, 16 cm. Appropriate zones were cut from the column and the esters eluted and identified by melting points and mixed melting points. The area under the curve for each zone was proportional to the millimoles of unrecrystallized ester recovered with an average deviation of 9.6%.

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Oxidation of Aromatic Alcohols with Manganese Dioxide

BY D. L. TURNER

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Manganese dioxide has been used to oxidize polyene alcohols[1] and allyl alcohols[2,3] to the corresponding carbonyl compounds. Benzyl alcohol resisted oxidation.[1] A naturally occurring alcohol, lymphokentric acid,[4] has been found to be oxidized by manganese dioxide at room temperature as detected by the biological test used for examining the oxidation products of reference 4. Because this material appeared to have no reducible double bonds, we have re-examined the effect of aromatic rings in activating the oxidation of alcohols with manganese dioxide.

The following alcohols showed no oxidation: furfuryl alcohol, benzyl alcohol, *p*-anisyl alcohol, ethyl β-phenyl-β-hydroxypropionate and methyl mandelate. Oxidation to the corresponding ketones was successful with secondary alcohols, as shown in Table I.

Experimental

Oxidation Method.—The alcohols, in 2-g. samples, were treated with equal weights of manganese dioxide (prepared according to reference 2) at room temperature for twelve days (method A), or by refluxing for one hour (method B). The solvent was dry benzene (20 ml.), except in the case of furoin, where 1:1 chloroform–benzene (40 ml.), was used.

γ-(5,6,7,8-Tetrahydro-1-naphthyl)-butyric Acid.—β-(1-Naphthoyl)-propionic acid, prepared by the method of Lontz,[5] was reduced to γ-(1-naphthyl)-butyric acid by the method of Huang-Minlon[6,7] in 80% yield. This product was then reduced by the Raney alloy procedure,[8] which

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TABLE I

Alcohol	Yield of ketone, % Meth. A	Meth. B	Source of alcohol	Identification of ketone
Benzohydrol	33	33	[a]	[b]
Xanthhydrol	70	100	[a]	[b]
Furoin	88	66	[a]	[b]
Phenylmethylcarbinol	34		[a]	[c]
α-Naphthylmethylcarbinol	45		[d,g]	[e]
1,3-Diphenylpropanol-1	50		[e]	[b]
3-Furyl-1-(2-naphthyl)-propanol-1	59		[f]	[b]
1-Hydroxy-1,2,3,4-tetrahydrophenanthrene	50		[d,h]	[b,c]
1-Hydroxy-1,2,3,4,5,6,7,8-octahydrophenanthrene	50		[f]	[b,c,f]
1-Hydroxy-1,2,3,4,5,6,7,8-octahydroanthracene	50		[d,i]	[b,c,f]

[a] Commercial preparation (Distillation Products Inc.). [b] By melting point of mixture with authentic sample. [c] By conversion to semicarbazone and comparison with authentic sample. [d] By reduction of ketone with sodium borohydride in methanol. The alcohols were free of ketone as indicated by treatment with semicarbazide. [e] By reduction of benzalacetophenone using a method described in the Experimental section for a furfuryl ketone. [f] Preparation described in Experimental section. [g] M.p. 64–65°; reported m.p. 66° by Pickard and Kenyon, *J. Chem. Soc.*, **105**, 1126 (1914). [h] M.p. 100–101°; reported m.p. 100–101° by Cook, *Proc. Roy. Soc. (London)*, **B121**, 133 (1936). [i] M.p. 92–94°; reported m.p. 94–95° by Schroeter.[11]

has been used for the preparation of the corresponding 5,6,7,8-tetrahydro-2-naphthylbutyric acid. The product crystallized from cyclohexane, m.p. 95–97° (reported[9] 94–95°), yield 40%. The preliminary Huang-Minlon reduction facilitated the purification of the product.[8]

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.04; H, 8.31. Found: C, 77.11; H, 8.08.

1-Hydroxy-1,2,3,4,5,6,7,8-octahydrophenanthrene.—The preceding acid was cyclized by a standard method[10] to 1-keto-1,2,3,4,5,6,7,8-octahydrophenanthrene, m.p. 80–81° (reported[9] 80.5–81°).

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.06; H, 7.96.

The ketone (5 g.) was dissolved in 50 ml. of methanol, and treated with 1 g. of sodium borohydride. After standing overnight, the solution was diluted with water, the product was filtered and recrystallized from ether–pentane; yield 3.0 g., m.p. 104–105° (reported[11] 94°). It showed no reaction with semicarbazide, and formed a phenylurethan, m.p. 192–194° (reported[11] 194°).

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.04; H, 9.01.

1-Hydroxy-1,2,3,4,5,6,7,8-octahydroanthracene.—The cyclization of γ-(5,6,7,8-tetrahydro-2-naphthyl)-butyric acid was effected by the use of stannic chloride[10,12] on the acid chloride prepared with phosphorus pentachloride. The yield of crude product, b.p. 140–160° (4 mm.), was 95%. On crystallization from pentane, material of m.p. 47.5–48° was obtained in a yield of 65% (reported[13] m.p. 47°). This is the 1-keto-1,2,3,4,5,6,7,8-octahydroanthracene. The alternative cyclization product[11,12] may have been present in the mother liquor. The ketone was reduced to the alcohol with sodium borohydride. It had m.p. 92–93°; phenylurethan, m.p. 151–153° (reported[11] 94–95°, 153°). A sample of the alcohol was dehydrogenated with palladium to anthracene to make sure that it was indeed the linearly cyclized product.

3-Furyl-1-(2-naphthyl)-propanone-1.—This was prepared from furfurylidene-2-acetylnaphthalene by hydrogenation in methanol at 40° in the presence of palladium–strontium carbonate catalyst. Crystallized from methanol, it had m.p. 64–65°.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.52; H, 5.70.

3-Furyl-1-(2-naphthyl)-propanol-1.—The preceding ketone was hydrogenated in acetone and hydrochloric acid, in the presence of palladium chloride-on-carbon (Wilkens–Anderson Co., 5% palladium), following a procedure developed for a different purpose by Londergan, Hause and Schmitz.[14] The resulting alcohol was crystallized from ether–pentane, and melted at 65°. Unlike the ketone, it was very soluble in methanol. A mixture with the ketone melted at 41–46°. It was purified before oxidation by treatment with Girard reagent.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.83, 80.88; H, 6.25, 6.26.

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Oxidation of Semicarbazide

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Linch[1] has reported that oxidation of semicarbazide with sodium hypobromite forms tetrahydro-3,6-*sym*-tetrazinedione (I).[2] Stollé[3] in a short article containing no experimental results stated that the reaction product was biurea (II) rather than I.

$$O{=}C(NHNH)_2C{=}O \longleftarrow NH_2CONHNH_2 \longrightarrow$$

I

$$NH_2CONHNHCONH_2$$

II

The latter interpretation seems more likely in view of D'Arcangelo's[4] oxidation of semicarbazide to biurea using iodine and cyanogen iodide. These oxidations are similar to the one using hypobromite in that the oxidizing agent is also positive halogen. Biurea was obtained in 66% yield using the procedure of Linch[1] which involves the use of 1.5 moles of bromine per mole of semicarbazide hydrochloride. The biurea was identified by comparison of physical properties with those of an authentic sample and by analysis. When equimolecular amounts of bromine and semicarbazide hydrochloride were used in the reaction, the yield of biurea was 91%. The probable sequence of reactions involved is

$$NH_2CONHNH_2 \xrightarrow{NaOBr} NH_2CONHNHBr \xrightarrow{NaOH} NH_2CONHN{=}NNHCONH_2 \longrightarrow II + N_2$$

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