and by recrystallization from ethanol (solution in excess of hot ethanol as rapidly as possible and evaporation of part of the solvent under reduced pressure to avoid decomposition by heat). M. p. 149° (decomp.). (Found: C 59.8; H 6.2; N 7.8; O 26.3; equiv.wt. by titration using thymolphthalein as indicator: 181. Calc. for $C_9H_{11}NO_3$: C 59.7; H 6.1; N 7.7; O 26.5; equiv.wt. 181.) The IR curve shows amino and carboxyl bands. UV absorption: $\lambda_{max.}$ = 235, 284 and 350 mμ.

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o-Methoxybenzhydrol

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o-Methoxybenzhydrol has been prepared by Stoermer and Friderici [1] by reacting *o*-methoxybenzaldehyde with phenylmagnesium iodide. Kahil and Nierenstein [2], who verified the results of Stoermer and Friderici, obtained the compound also by reduction of *o*-methoxybenzophenone. In both cases the melting point was reported to be 141°. Martynoff [3], who synthesized *o*-methoxybenzhydrol from *o*-methoxybenzaldehyde and phenylmagnesium iodide, did not report any melting point but used the crude product for the preparation of bis-*o*-methoxybenzhydryl ether.

When the experiment of Stoermer and Friderici was repeated in this laboratory with *o*-methoxybenzaldehyde and phenylmagnesium bromide the statements as to the melting point of *o*-methoxybenzhydrol could not be verified. Instead of a solid substance, an oil, b.p. 181—182°/8 mm, was obtained. The same substance was formed when *o*-methoxybenzophenone was reduced with zinc in alkaline ethanol. The identity of the oil with *o*-methoxybenzhydrol was established by preparing its 3,5-dinitrobenzoic acid by oxidizing it to *o*-methoxybenzophenone.

o-Methoxybenzhydrol can be heated in boiling xylene for several hours without any change. However, if a minute quantity of an acid is added to the solution, the substance is rapidly and quantitatively converted into bis-*o*-methoxybenzhydryl ether, m. p. 137—137.5°. This property seems to be the reason for the incorrect melting points reported previously.

When the products of the reaction between *o*-methoxybenzaldehyde and phenylmagnesium bromide were decomposed with ice and hydrochloric acid, a small quantity of bis-*o*-methoxybenzhydryl ether was isolated in spite of the fact that the reaction products were almost immediately treated with a potassium carbonate solution. If the decomposition was effected by adding ammonium chloride solution, the yield of the alcohol was slightly greater and no ether could be isolated. These observations demonstrate the instability of the alcohol towards acids.

Considering the difference in stability in the presence and absence of acids, it seems probable that the crude *o*-methoxybenzhydrol that Martynoff used in his synthesis of bis-*o*-methoxybenzhydryl ether contained a small quantity of acid.

Experimental. To a cooled Grignard reagent prepared from magnesium (3.60 g) and bromobenzene (23.55 g) in dry ether (60 ml), *o*-methoxybenzaldehyde (13.60 g) in dry ether (50 ml) was gradually added. After the mixture had been warmed in a water bath for 15 min, the products were decomposed by pouring them into a mixture of ice and dilute hydrochloric acid. The ether phase was thoroughly washed with water and a dilute potassium carbonate solution. After drying with sodium sulphate, the ether was evaporated and the residue distilled under reduced pressure. The yield of *o*-methoxybenzhydrol, b. p. 181—182°/8 mm, was 77.5 % (16.61 g). (Found: C 78.37; H 6.45. Calc. for $C_{14}H_{14}O_2$: C 78.48; H 6.59.)

The residue in the distillation flask was dissolved in a small quantity of ethanol. After a while bis-*o*-methoxybenzhydryl ether (1.26 g) crystallized. It melted after recrystallization from ethanol at 137—137.5°.

When the decomposition of the reaction products was effected with ammonium chloride solution, the yield of the alcohol was almost 80 % (17.04 g) and no bis-*o*-methoxybenzhydryl ether could be isolated. In this case the washing with potassium carbonate solution was omitted.

A sample of *o*-methoxybenzhydrol was treated with the equivalent quantity of 3,5-dinitrobenzoyl chloride in benzene and pyridine. After the solution had stood for several hours, the precipitate was filtered off and the filtrate washed with water, dilute hydrochloric acid,

and dilute potassium carbonate solution. After drying with sodium sulphate, most of the benzene was distilled off and the residue dissolved in ether. The solution was kept for some hours in a refrigerator and the pure crystals of 3,5-nitrobenzoic *o*-methoxybenzhydryl ester, m. p. 129—130°, that separated were isolated by filtration. (Found: N 6.71. Calc. for $C_{21}H_{16}N_2O_7$: 6.86.)

o-Methoxybenzophenone (10.36 g) was reduced with zinc (9.00 g) in a solution of potassium hydroxide (12.30 g) in water (6.4 ml) and ethanol (85 ml) according to the method previously used for the preparation of di-*o*-tolylcarbinol [4]. After the mixture had been boiled for 4 h, the excess of zinc was filtered off and the filtrate poured into a cold dilute sulphuric acid solution (4 l). The crude product was taken up in ether and the ether solution washed with dilute potassium carbonate solution. After drying with sodium sulphate, the ether was evaporated and the residue distilled under reduced pressure. The yield of *o*-methoxybenzhydrol, b. p. 181—182°/8 mm, was 82 % (8.50 g). The identity of the substance was established by preparing its 3,5-dinitrobenzoic ester, which was identical with the above *o*-methoxybenzhydryl compound.

o-Methoxybenzhydrol (11.22 g) and a minute quantity of *p*-toluenesulphonic acid (0.02 g) were dissolved in xylene (100 ml). When the solution was heated in an apparatus for the determination of water, an almost quantitative amount of water distilled within 10 min. After cooling, the solution was washed with a dilute sodium hydroxide solution and the solvent was distilled off. The residue consisting of colourless crystals of crude bis-*o*-methoxybenzhydryl ether was treated with ethanol and filtered. After recrystallization from ethanol, the substance (10.14 g) melted at 137—137.5°.

When the experiment was repeated without adding *p*-toluenesulphonic acid, no water distilled within 6 h.

o-Methoxybenzhydrol (13.96 g) was stirred with a cold solution of potassium bichromate (17.7 g) and concentrated sulphuric acid (15 ml) in water (85 ml). When the exothermic reaction was over and the mixture had cooled, it was extracted with ether. The ether solution was washed twice with water, twice with dilute potassium hydroxide, and finally twice with water. After drying with sodium sulphate, the ether was evaporated and the residue distilled under reduced pressure. The yield of *o*-methoxybenzophenone, b.p. 177—178°/12 mm, was 73 % (10.12 g). Its 2,4-dinitrophenylhydrazone, prepared according to Wild [5], melted at 173—174° or at the same temperature at which a previously obtained sample melted. By mistake the melting point of this substance was incorrectly reported previously [6].

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The Estimation of Iodine in Urine

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Recently Rodger and Poole [1] have published an investigation on the determination of small amounts of iodine in urine and other biological materials. In order to get acceptable recoveries of iodine, they find it necessary to rely on a distillation method. With a dry ashing technique, slightly modified from that of Barker, Humphrey and Soley [2] for serum, we have obtained a recovery of 96 % of iodine in urine. Our modifications are founded on the experience that the losses of iodine will be smaller when K_2CO_3 is substituted for Na_2CO_3 in the incineration mixture [3], which must have a sufficient content of carboniferous material [4].

Technique: 1 ml 30 % $Zn(Ac)_2$ + 1 ml 0.5 N NaOH are mixed in the tubes used for incineration. The precipitates are allowed to stand about 30 min and centrifuged, the centrifugate is decanted, 1 or 2 ml of the urine and 2 ml of 4 N K_2CO_3 are added and thoroughly mixed with the precipitate.

The tubes are brought in an oven at 90°C in a declined position and their content is dry after 18—20 h. They are then incinerated in a furnace at 600°C for 3 h in a horizontal position. After cooling