It is planned to prepare the desired *as*-diphenyl-*o*-tolylglycol and *as*-diphenyldi-α-naphthylglycol by the action of phenylmagnesium bromide on the esters of *o*-tolilic acid and α-naphthilic acid, respectively.

Reaction between Iodomagnesium-diphenyldianisylglycolate and Iodine.—Two grams of *as*-diphenyldianisylglycol was added to a solution of ethylmagnesium iodide in a mixture of ether and benzene; a red color developed but quickly disappeared. The solution absorbed iodine, slowly at room temperature, much more rapidly when heated. The solution was finally warmed with iodine for several hours, then cooled and hydrolyzed. The ether-benzene solution yielded a mixture of benzophenone and 4,4′-dimethoxybenzophenone. The benzophenone was extracted by warming the mixture of ketones with 10 cc. of petroleum ether and filtering the hot mixture. The residual dimethoxybenzophenone after recrystallization from benzene and ligroin melted at 142–144°; yield, 1.0 g. or 87%.

Summary

Three unsymmetrical aromatic pinacols, *as*-diphenyldi-*p*-tolylglycol, *as*-diphenyldi-*m*-tolylglycol and *as*-diphenyldianisylglycol, have been synthesized and rearranged to pinacolins.

These pinacols rearrange to pinacolins with migration of the groups in the following ratios: *p*-tolyl, 49%, phenyl, 51%; *m*-tolyl, 50%, phenyl, 50%; anisyl, 28%, phenyl, 72%.

ANN ARBOR, MICHIGAN

NOTE

Note on the Preparation of Mercury Dibenzyl

BY J. LEWIS MAYNARD

The preparation of this substance in a pure condition and in good yields has heretofore presented certain difficulties. An attempt to prepare it by a reaction of general application to this type of compound failed to yield the desired substance. Benzyl bromide and sodium amalgam do not react to form mercury dibenzyl.[1] It was first prepared by the Grignard reaction between benzylmagnesium chloride and mercuric chloride.[2] The product was slightly impure, as was shown by the melting point of 104°, seven degrees below the true melting point. No yield was given, and the substance was said to possess a characteristic sweet odor. This is not shown by the pure substance.

Other investigators have also used the Grignard reaction to prepare mercury dibenzyl, but the yields either have not been given, or have not

---

[1] Wurtz, *Compt. rend.*, **68**, 1300 (1869); Dreher and Otto, *Ann.*, **154**, 93 (1870). *Cf.* Campisi, *Compt. rend.*, **61**, 861 (1865). The product obtained by the latter melted over 90° higher than pure $(C_6H_5CH_2)_2Hg$.

[2] Pope and Gibson, *J. Chem. Soc.*, **101**, 735 (1912).

exceeded 10%.[3] L. W. Jones reported a yield of 40 g. of mercury dibenzyl by the action of 35 g. of benzylmercuric chloride on benzylmagnesium chloride, but this is obviously an error because the theoretical yield is only 38 g.[4] Apparently the Grignard reaction does not go to completion because it is reported that by means of fractional crystallization it is impossible to separate the mixture of mercury dibenzyl and benzylmercuric chloride formed as a reaction product.[3b] However, treatment of the mixture with copper is said to produce a 75% yield of mercury dibenzyl.[3c] This method has a disadvantage in that it is necessary to carry on the reaction with copper in an inert atmosphere of either nitrogen or carbon dioxide.

A convenient reaction that has been used by the author to prepare mercury diphenyl in excellent yield from phenylmercuric iodide,[5] has been applied successfully to the preparation of mercury dibenzyl. Sodium stannite is one of many reagents used to transform organic mercury compounds of the type RHgX to those of the type R_2Hg.[6] The reaction of the reagent with benzylmercuric iodide is

$$2C_6H_5CH_2HgI + Na_2SnO_2 + H_2O \longrightarrow (C_6H_5CH_2)_2Hg + Hg + 2NaI + Na_2SnO_3$$

Experimental Procedure.—Fifteen grams of benzylmercuric iodide, prepared by the action of mercury on benzyl iodide,[7] was suspended in a solution of 10 ml. of alcohol in 225 ml. of water. A solution containing 25 g. of sodium hydroxide in 125 ml. of water was added to 10 g. of stannous chloride dissolved in 125 ml. of water. This reagent was added to the suspension of benzylmercuric iodide, and the mixture was stirred vigorously with a mechanical stirrer for a period of one hour. At the end of this time the precipitate was filtered off, washed with water, and allowed to dry at room temperature. The mixture was then extracted with acetone. Difficulty was experienced in obtaining a clear filtrate with the extract, so a few grams of powdered zinc was added to amalgamate the finely divided mercury present. After this treatment a clear filtrate was obtained by filtering through an asbestos pad in a Gooch crucible. Water was added to the filtrate until a permanent turbidity was obtained, whereupon cooling to −15° caused the separation of long, needle-like, colorless crystals of mercury dibenzyl, m. p. 111°. The total yield was 64 g. or 93.2% of the theoretical yield.

It has been noted previously in this article[3b,c] that the reaction between

---

[3] (a) Wolff, *Ber.*, **46**, 64 (1913); (b) Banús, *Anales soc. españ. fís. quím.*, **20**, 667 (1922); (c) Hein and Wagler, *Ber.*, **58B**, 1499 (1925).

[4] Jones, This Journal, **40**, 1257 (1918).

[5] Maynard, *ibid.*, **46**, 1510 (1924).

[6] Whitmore, "Organic Compounds of Mercury," American Chemical Society Monograph Series, The Chemical Catalog Co., New York, 1921, p. 40.

[7] Maynard, This Journal, **54**, 2108 (1932).

benzylmagnesium chloride and mercuric chloride leads to a mixture of mercury dibenzyl and benzylmercuric chloride. Since sodium stannite will convert benzylmercuric chloride to mercury dibenzyl, it is suggested that the product of the Grignard reaction be treated with sodium stannite. This procedure would not only eliminate the difficulty of separating the two mercury compounds, but would increase the yield of the desired mercury dibenzyl.

CONTRIBUTION FROM THE
SCHOOL OF CHEMISTRY OF THE
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA

RECEIVED FEBRUARY 12, 1932
PUBLISHED MAY 7, 1932

COMMUNICATIONS TO THE EDITOR

THE RELATION BETWEEN THE ACTIVITY OF THE WATER AND THE POTENTIALS OF THE GLASS ELECTRODE

Sir:

In the differential thermodynamic equation recently used to explain the potentials of the glass electrode [M. Dole, THIS JOURNAL, **53**, 4260 (1931)] the correction for possible transference of solvent [see P. B. Taylor, *J. Phys. Chem.*, **31**, 1480 (1927)] was purposely omitted for two reasons. In the first place it was not certain that water could be carried through the glass by ions on the passage of an electrical current, and in the second place the activity of the water was maintained in the actual experiments nearly the same and constant on both sides of the glass membrane; hence if there had been any transfer of water, there would have been no increase or decrease in the free energy of the water as it passed through the glass from one solution to the other and consequently no contribution to the total e. m. f. due to this effect. MacInnes and Belcher [THIS JOURNAL, **53**, 3315 (1931)] have shown that water may be drawn out of the glass, and there have also been recently published [G. Buchböck, *Z. physik. Chem.*, Abt. A, **156**, 232–236 (1931); D. A. MacInnes and D. Belcher, THIS JOURNAL, **53**, 3315 (1931)] data of experiments performed under conditions in which the activity of the water was not maintained constant, but was reduced by the addition of concentrated acids. The observed potentials did not agree with those of the hydrogen–platinum electrode, the resulting error being negative in sign in contrast to the errors of the glass electrode in alkaline solutions which are positive in sign [Dole, *loc. cit.*]. Considering a possible transfer of water, the equation for the glass electrode in acid solutions (where only hydrogen ions are assumed to carry the current across the boundary) becomes

$$E_1 = \frac{RT}{F} \ln \frac{a'_{\mathrm{H}}}{a''_{\mathrm{H}}} + S\,\frac{RT}{F} \ln \frac{a'_{\mathrm{H_2O}}}{a''_{\mathrm{H_2O}}} \qquad (1)$$