394. *Tribenzylmethanethiol—A By-product from a Grignard Reaction.*

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During the preparation of phenyl(dithioacetic) acid [1] by the action of benzylmagnesium chloride on carbon disulphide, a neutral by-product, $C_{22}H_{22}S$, is formed. It crystallises from ethyl acetate in very large, colourless prisms, m. p. 166—167°. It is very stable and can be distilled unchanged at atmospheric pressure. It gives an emerald-green colour with sodium nitrite in acetic acid, thereby showing the presence of a thiol group attached to a tertiary carbon atom or to an aromatic ring (Rheinboldt's test [2]).

It is known [3] that the carbonation of Grignard reagents sometimes yields ketones or

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[1] Houben, *Ber.*, 1906, **39**, 3227.

[2] Rheinboldt, *Ber.*, 1927, **60**, 184.

[3] Grignard, *Bull. Soc. chim. France*, 1904, **31**, 751.

tertiary alcohols as by-products and it is probable that similar side-reactions can occur when carbon disulphide is used in place of carbon dioxide. The most likely structure for the by-product, therefore, seemed to be the previously unknown compound, tribenzylmethanethiol. In agreement with this, the compound gave tribenzylmethane[4] when heated with Raney nickel. In addition, the ultraviolet spectrum of the by-product in ethanol ($\lambda_{\text{max.}}$ 248, 253, 259, 265, and 268; $\log_{10} \varepsilon$ 2·46, 2·74, 2·85, 2·76, and 2·67) was closely similar to that of tribenzylmethanol ($\lambda_{\text{max.}}$ 249, 253, 260, 265, and 258; $\log_{10} \varepsilon$ 2·53, 2·71, 2·83, 2·72, and 2·56).

The structure was confirmed by its synthesis from methyl phenyl(dithioacetate) and benzylmagnesium chloride. Attempts to prepare the thiol by the action of thiourea on tribenzylmethyl chloride[5] or by the addition of thioacetic acid to 1,1-dibenzyl-2-phenylethylene[6] were unsuccessful.

Only one previous example of a Grignard reaction involving a dithio-ester has been recorded. Gilman, Robinson, and Beaber[7] treated ethyl dithiobenzoate with phenylmagnesium bromide, followed by benzoyl chloride. The product, m. p. 184—185° (obtained in "small amount"), was not analysed, but was thought to be the benzoate of triphenylmethanethiol.

Experimental.—Reaction of benzylmagnesium chloride with carbon disulphide. Carbon disulphide (96 g.) was added to an ice-cooled solution of benzylmagnesium chloride (from 30·8 g. of magnesium and 160 g. of benzyl chloride) in ether (400 ml.). Next day, the gelatinous orange-red mixture was treated with water (300 ml.) and then with concentrated hydrochloric acid (160 ml.), with ice-cooling. Ether (100 ml.) was added and the ethereal layer collected. The phenyl(dithioacetic) acid was extracted from the ether by shaking it with successive portions of 2N-sodium hydroxide until the extracts were alkaline to Bromothymol Blue (*ca.* 190 ml.; this corresponds to *ca.* 30% yield). After being washed with water, the ethereal solution was dried and concentrated, thereby giving *tribenzylmethanethiol* (1,1-*dibenzyl*-2-*phenylethanethiol*) (13·6 g., 10%) as prisms, m. p. 165—167°, which after recrystallisation from ethyl acetate had m. p. 166—167° [Found: C, 83·0; H, 7·0; S, 9·9; *M* (Rast), 310. $C_{22}H_{22}S$ requires C, 83·0; H, 6·9; S, 10·05%; *M*, 318]. Oxidation of this product with boiling aqueous potassium permanganate gave benzoic acid (46%) but no phthalic acid.

Desulphurisation. Raney nickel sludge[8] (2 teaspoonfuls) was added to the thiol (2·0 g.) in benzene (75 ml.), and the mixture was boiled under reflux for 2·5 hr. The hot solution was filtered and the nickel was washed twice with boiling ethanol. The combined filtrates were distilled, leaving tribenzylmethane (1·5 g., 83%), m. p. 79—80°. After sublimation at 115—120°/17 mm. the compound had m. p. 79·5—80° alone or admixed with an authentic specimen[4] (Found: C, 92·2; H, 7·9. Calc. for $C_{22}H_{22}$: C, 92·3; H, 7·7%).

Alternative synthesis. Methyl phenyl(dithioacetate), b. p. 148—160°/20 mm., was prepared by shaking an aqueous solution of sodium phenyl(dithioacetate), obtained in the Grignard reaction above, with dimethyl sulphate (36 ml.). The dithio-ester (20 g.) in ether (25 ml.) was added dropwise to benzylmagnesium chloride (made from 55·6 g. of benzyl chloride and 10·5 g. of magnesium) in ether (150 ml.), and the mixture was boiled under reflux for 6·5 hr. Next day a mixture of concentrated hydrochloric acid (30 ml.) and water (50 ml.) was added to the ice-cooled Grignard mixture. The ethereal layer was collected and the aqueous layer was extracted with more ether (2 × 100 ml.). Ethyl acetate (50 ml.) was added to the combined ether extracts, and the mixture, after being dried, was concentrated, thereby yielding crystals (6·2 g., 18%), m. p. 164—165°. Recrystallisation from ethanol–ethyl acetate gave the thiol, m. p. and mixed m. p. 167° (Found: C, 83·1; H, 6·8; S, 10·2%).

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[4] Hill, Little, Wray, and Trimbey, *J. Amer. Chem. Soc.*, 1934, **56**, 911.
[5] Jones and Scott, *J. Amer. Chem. Soc.*, 1922, **44**, 419.
[6] Bergmann and Weiss, *Annalen*, 1930, **480**, 64.
[7] Gilman, Robinson, and Beaber, *J. Amer. Chem. Soc.*, 1926, **48**, 2715.
[8] Mozingo, Wolf, Harris, and Folkers, *J. Amer. Chem. Soc.*, 1943, **65**, 1013.