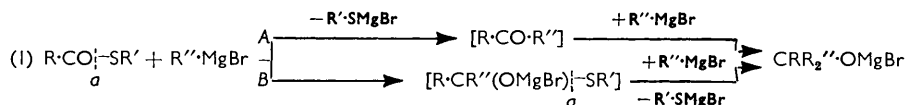


280. *Thioacids. Part II.* Action of Arylmagnesium Halides on Aromatic Thiol-acids.*

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Aromatic thiol-acids with arylmagnesium halides give, through elimination at the carbon-oxygen bond, triarylmethanethiols, in contrast to the triarylmethanols obtained from the same reagent and aromatic thioesters through elimination at the carbon-sulphur bond. A new condensation is described between bromomagnesium salts of aromatic thiol-acids and bromomagnesium derivatives of triaryl-methanols or -methanethiols on decomposition in sulphuric acid, to give triaryl esters or thiol-esters respectively.

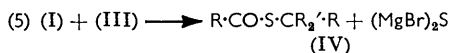
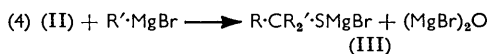
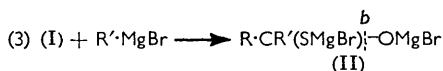
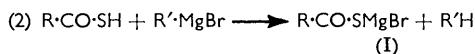
In agreement with Hepworth and Clapham¹ and Gilman *et al.*² we found that 3 mol. of phenylmagnesium bromide react with 1 mol. of phenyl or naphthyl thiolbenzoate to give triphenylmethanol. The course of reaction (*A* or *B*) could not be decided as treatment of



naphthyl thiolbenzoate with 1 equiv. of phenylmagnesium bromide had no effect, but essentially elimination takes place at the carbon-sulphur link (*a*).

Moreover, as Grignard found,³ triphenylmethanol was obtained from 3 mol. of phenylmagnesium bromide and 1 mol. of benzoic acid. The reaction can be represented by the reaction 1, with OMgBr replacing SR'.

Grignard reagents react differently with aromatic thiol-acids; 3 mol. of phenyl- or *p*-tolyl-magnesium bromide and 1 mol. of thiolbenzoic acid afford triphenylmethyl or phenyldi-*p*-tolylmethyl thiolbenzoate respectively on acid decomposition of the magnesium complexes. Decomposition with ammonium chloride followed by ether extraction gave triphenylmethanol (thiol changing to alcohol during decomposition) from the ethereal layer and the starting thiol-acid from the aqueous layer; this eliminates interaction between the products. We thus assume that, on acid decomposition, condensation takes place between the residual bromomagnesium salt of the thiol-acid (I) and the formed bromomagnesium derivative of the triarylmethanethiol (III):



Evidence favouring this mechanism was sought as follows. While the free thiolbenzoic acid and triphenylmethanethiol do not condense, their bromomagnesium derivatives (I) and (III) readily do so to give the triarylmethyl thiolbenzoate (IV) with evolution of

* The paper, *J.*, 1958, 2893, is considered to be Part I.

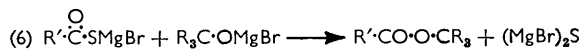
¹ Hepworth and Clapham, *J.*, 1921, **119**, 1188.

² Gilman, Robinson, and Beaber, *J. Amer. Chem. Soc.*, 1926, **48**, 2715.

³ Grignard, *Compt. rend.*, 1904, **138**, 152.

hydrogen sulphide (reaction 5) when poured into dilute sulphuric acid and treated in the usual manner.

This new type of reaction also occurs between the bromomagnesium derivatives of thiolbenzoic acid and triphenylmethanol to give triphenylmethyl benzoate:



but not between the bromomagnesium derivatives of benzoic acid and triphenylmethanol or triphenylmethanethiol. The thiol-acid, necessary to this reaction, loses its sulphur atom: accordingly, the sulphur atom in the S-triarylmethyl esters formed must come from the triarylmethanethiols first formed by an elimination (reaction 4) at the carbon-oxygen link (*b*, reaction 3) in contrast to that at the carbon-sulphur link of thiol-esters.

p-Methoxyphenylmagnesium bromide (3 mol.), with thiolbenzoic acid (1 mol.), however, gives dibenzoyl disulphide on decomposition of the magnesium complex. This reaction cannot be a condensation of two molecules of the bromomagnesium salt of the thiol-acid, as the pure salt gave benzoic acid on the same treatment, even in presence of anisole added to simulate the conditions of the principal reaction. Also, it cannot be due to oxidation as this did not occur in other Grignard reactions under the same conditions. Since we get the same result with either method of decomposition, the disulphide ought to have been formed before decomposition. Therefore, the disulphide is likely to have been formed through the formation of free radicals under the influence of the *p*-methoxyphenylmagnesium bromide. In like manner the action of phenylmagnesium bromide on *p*-chlorothiolbenzoic acid, giving bis-(*p*-chlorobenzoyl) disulphide, can be explained. As the *p*-methoxymagnesium bromide contains an electron-donating group and *p*-chlorothiolbenzoic acid an electron-attracting atom in the *para*-positions, these reactions would be expected to follow the same course.

EXPERIMENTAL

Yields are mostly of pure products; low yields are due to losses in reaction and to the inefficiency of the method of separation.

Action of Phenylmagnesium Bromide (3 Mols.) on Phenyl Thiolbenzoate (1 Mol.).—A cold solution of phenylmagnesium bromide [from bromobenzene (3.2 c.c.)] in ether (40 c.c.) was added to a cold solution of phenyl thiolbenzoate (2.1 g.) in benzene (20 c.c.). Next day the mixture was refluxed for 2 hr., then poured into water (250 c.c.), concentrated sulphuric acid (2.5 c.c.), and crushed ice (30 g.). The organic layer and the ethereal extract were united, washed, and dried (Na₂SO₄), and on evaporation of the solvents gave a solid (1 g.), which (from light petroleum, b. p. 60–90°) afforded triphenylmethanol, m. p. and mixed m. p. (cf. ref. 4) 163°.

Action of Phenylmagnesium Bromide (3 Mol.) on Naphthyl Thiolbenzoate (1 Mol.).—As above, naphthyl thiolbenzoate (cf. ref. 5) (2.6 g.) gave triphenylmethanol (0.8 g.), m. p. and mixed m. p. 163°. Using only 1 mol. of phenylmagnesium bromide, we recovered the starting materials.

Phenylmagnesium Bromide (3 Mol.) and Benzoic Acid (1 Mol.).—Benzoic acid (1.2 g.) in a reaction as above afforded a solid from the ethereal layer. This, on fractional crystallisation from light petroleum (b. p. 60–90°), gave triphenylmethanol (0.25 g.), m. p. and mixed m. p. 163°, and benzoic acid, m. p. 121° (from water).

Phenylmagnesium Bromide (3 Mol.) and Thiolbenzoic Acid (1 Mol.).—(i) In a reaction as before, with thiolbenzoic acid (cf. ref. 6) (1.5 g.) in ether and phenylmagnesium bromide [from bromobenzene (3.2 c.c.)], the residue, isolated with ether, on fractional crystallisation from light petroleum (b. p. 70–80°) afforded triphenylmethanol (0.3 g.), m. p. and mixed m. p. 163°, and triphenylmethyl thiolbenzoate (0.7 g.), m. p. and mixed m. p. (cf. ref. 7) 188°.

(ii) Reaction as above, but decomposition with ammonium chloride and ice, gave triphenylmethanol from the ethereal layer and thiolbenzoic acid from the aqueous layer.

⁴ Acree, *Ber.*, 1904, **37**, 2755.

⁵ Taboury, *Compt. rend.*, 1904, **138**, 983.

⁶ Kym, *Ber.*, 1899, **32**, 3533.

⁷ Elkaschew and Nosseir, *J.*, 1958, 2893.

Triphenylmethanethiol treated with phenylmagnesium bromide and decomposed with ammonium chloride gave triphenylmethanol.

p-Tolylmagnesium Bromide (3 Mol.) and Thiolbenzoic Acid (1 Mol.).—Thiolbenzoic acid (4.2 g.) and *p*-tolylmagnesium bromide [from *p*-bromotoluene (11.4 g.)], as above, with 4 hours' reflux and decomposition with sulphuric acid, afforded *phenyl di-p-tolylmethyl thiolbenzoate* from the ethereal layer as an oil that solidified under methanol. It gave colourless crystals (2.0 g.) m. p. 136°, from ethanol, giving yellowish-brown colours with concentrated sulphuric acid (Found: C, 82.3; H, 5.8; S, 7.9. $C_{28}H_{24}OS$ requires C, 82.3; H, 5.9; S, 7.8%). To this ester (0.3 g.) in boiling acetic acid (20 c.c.) containing 1 c.c. of concentrated hydrochloric acid, zinc powder (activated with copper sulphate) (0.7 g.) was added, and the mixture poured into water. Isolation with ether afforded phenyldi-*p*-tolylmethane, m. p. and mixed m. p. (cf. ref. 8) 54°.

Condensations.—(a) *Bromomagnesium thiolbenzoate and triphenylmethanethiol bromomagnesium derivative*. Bromomagnesium thiolbenzoate [from phenylmagnesium bromide (from 1.1 c.c. of bromobenzene) and thiolbenzoic acid (1.4 g.) refluxed in dry ether for 2 hr.] and the bromomagnesium derivative of triphenylmethanethiol [from phenylmagnesium bromide as before and triphenylmethanethiol (cf. ref. 9) (2.7 g.) refluxed in ether for 2 hr.] were mixed, left overnight, and refluxed for 1 hr. After decomposition with dilute sulphuric acid, the oil isolated with ether solidified under light petroleum (b. p. 60–90°) on cooling. Recrystallised from light petroleum (b. p. 100–120°), triphenylmethyl thiolbenzoate (1.2 g.) had m. p. and mixed m. p. (cf. ref. 7) 188°.

Ethereal thiolbenzoic acid and triphenylmethanethiol, in equimolecular quantities, when heated for 1 hr., poured into cold dilute sulphuric acid, and treated as above, afforded the starting substances.

(b) *Bromomagnesium thiolbenzoate and triphenylmethanol bromomagnesium derivative*. Similarly, triphenylmethanol (2.6 g.) gave a solid from the ethereal layer. After being boiled with light petroleum (b. p. 60–90°), the part that dissolved gave on cooling and recrystallisation from benzene triphenylmethyl benzoate (0.1 g.), m. p. and mixed m. p. (cf. ref. 10) 166°; the insoluble part, recrystallised from the same light petroleum, afforded triphenylmethanol (0.4 g.), m. p. 163°.

(c) *Bromomagnesium benzoate and triphenylmethanethiol bromomagnesium derivative*. Using triphenylmethanethiol (13.8 g.) and benzoic acid (6.1 g.) as in (a), we got back the starting materials.

Action of p-Methoxyphenylmagnesium Bromide (3 Mol.) on Thiolbenzoic Acid.—Thiolbenzoic acid (4.2 g.) and a Grignard reagent (from 11.4 c.c. of *p*-bromoanisole) in a reaction as before with 4 hours' boiling and decomposition with either sulphuric acid or ammonium chloride, gave dibenzoyl disulphide (1.0 g.), m. p. and mixed m. p. (cf. ref. 11) 132°.

Bromomagnesium thiolbenzoate prepared from equimolar amounts of thiolbenzoic acid and methylmagnesium iodide gave, after the usual treatment, benzoic acid, m. p. 121°, together with much resin.

A similar bromomagnesium salt of thiolbenzoic acid (from ethylmagnesium bromide) in ether was refluxed for 4 hr. in presence of 1 equiv. of anisole. After treatment as before benzoic acid was obtained together with much resin.

Action of Phenylmagnesium Bromide (3 Mol.) on p-Chlorothiolbenzoic acid (1 Mol.).—Reaction of *p*-chlorothiolbenzoic acid (1 g.) in dry benzene and a Grignard reagent [from bromobenzene (1.8 c.c.)] with 4 hours' boiling and decomposition with sulphuric acid, gave bis-(*p*-chlorobenzoyl) disulphide as an oil from the ethereal layer. It solidified under ethanol and, crystallised therefrom (0.25 g.) had m. p. and mixed m. p. (cf. below) 127°.

Preparation of p-Chlorothiolbenzoic Acid.—*p*-Chlorobenzoyl chloride¹² (13.0 g.) was added in portions to a solution of potassium hydrogen sulphide in ethanol (from 13 g. of potassium hydroxide in ethanol saturated with hydrogen sulphide) with cooling and passage of hydrogen sulphide. Most of the alcohol was distilled off. The solution was acidified with hydrochloric acid, filtered, diluted with water, and extracted with ether. The ethereal extract, washed, dried (Na_2SO_4), and evaporated, gave *p-chlorothiolbenzoic acid* (13.0 g.) Crystallised from dry

⁸ Kliegl, *Ber.*, 1905, **38**, 84.

⁹ Vörländer and Mittag, *Ber.*, 1913, **46**, 3453.

¹⁰ Wieland, Ploetz, and Indest, *Annalen*, 1937, **532**, 186.

¹¹ Schelton and Rider, *J. Amer. Chem. Soc.*, 1936, **58**, 1282.

¹² Meyer, *Monatsh.*, 1901, **22**, 778.

light petroleum (b. p. 70—80°), it had m. p. 187—188° (Found: C, 48.7; H, 2.3. C_7H_5OSCl requires C, 48.7; H, 2.8%).

Preparation of Bis-(p-chlorobenzoyl) Disulphide.—Crystalline sodium disulphide (5 g.) was added to a solution of *p*-chlorobenzoyl chloride (5 g.) in acetone (20 c.c.), containing anhydrous sodium sulphate (3 g.) The mixture was refluxed for 1 hr., allowed to cool, then diluted with water and made alkaline with sodium hydroxide. The precipitate was filtered off, and washed with water. *Bis-(p-chlorobenzoyl) disulphide* (5 g.) thus obtained crystallised from methanol or light petroleum (b. p. 100—110°) in crystals, m. p. 127°; it becomes red at 190° (Found: C, 48.9; H, 2.5; S, 19.4; Cl, 20.4. $C_{14}H_8O_2S_2Cl_2$ requires C, 49.0; H, 2.3; S, 18.7; Cl, 20.7%).

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