512. *Thio-acids. Part III.*[1] *Mechanism of the Action of Aryl-metallic Compounds on Diaroyl Disulphides and Aromatic Thio-acids.*

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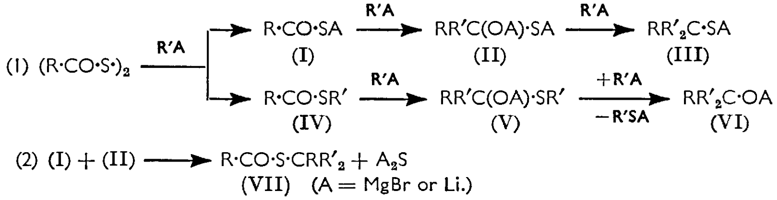
The triarylmethyl thiol-esters previously reported to be formed by the action of arylmagnesium halides on diaroyl disulphides are the result of a series of reactions. Aryl-lithium compounds with diaroyl disulphides or aromatic thio-acids behave, generally, as arylmagnesium halides do with the same compounds.

The action of various Grignard reagents on dibenzoyl disulphide and di-*p*-anisoyl disulphide was reported[2] to give, after decomposition by acid, triarylmethyl thiol-esters or, after decomposition by ammonium chloride, triarylmethanethiol and the thiol-acid from the corresponding disulphide.

We have also shown[1] that with Grignard reagents aromatic thiol-acids give triarylmethanethiols and that their bromomagnesium derivatives condense with the bromomagnesium salts of these thiol-acids to give the triarylmethyl thiol-esters.

In this present paper we report further reactions of diaroyl disulphides and aromatic thiol-acids with other Grignard reagents and with aryl-lithiums. The usual mode of action of aryl-metal compounds may be represented by the following scheme:



Accordingly, heterolysis or dissociation into free radicals (cf. the formation of free radicals from thioaroyl disulphides[3]) of the diaroyl disulphide leading to the formation of a bromomagnesium or lithium salt (I) and an ester (IV) of the thiol-acid must be assumed. The final products of the reaction of the disulphides with the aryl-metallic compounds seem to depend on the facility with which the different steps proceed and on the stability

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[1] Part II, Elkaschef, Nosseir, and Mokhtar, *J.*, 1959, 1438.
[2] Elkaschef and Nosseir, *J.*, 1958, 2893.
[3] Schönberg and Rupp, *Ber.*, 1933, **66**, 1932.

of the different products and intermediates, as well as on which of the products present in the reaction mixture are more liable to react with the aryl-metal compounds used.

Di-*p*-chlorobenzoyl disulphide with phenyl-lithium gave *p*-chlorothiobenzoic acid (I; $R = C_6H_4Cl$, $A = H$) together with some *p*-chlorobenzoic acid formed by decomposition of this acid; *p*-chlorobenzoic acid was also obtained when phenylmagnesium bromide was used. Similarly, *p*-anisic acid was isolated by acidic decomposition of the product of the reaction of di-*p*-anisoyl disulphide with *p*-methoxyphenyl- or *p*-tolyl-lithium. These experiments confirm the fission of such disulphides, further evidence for which, by the isolation of esters (IV) from similar reactions, was reported earlier.[2]

According to the above scheme, an excess of Grignard reagent leads to the formation of both triphenylmethanol (VI; $R = R' = Ph$, $A = H$) and triarylmethanethiol (III; $A = H$). On use of 6 mols. of phenylmagnesium bromide, only triphenylmethanol was isolated. The presence of triphenylmethanethiol was, however, now proved by benzoylation of the reaction mixture before decomposition, whereby the benzoate (VII; $R = R' = Ph$) was isolated along with the triphenylmethanol. On the other hand, using only 3 mols. of the Grignard reagent restricts the reaction almost completely to one route. Thus 1 mol. of dibenzoyl disulphide with 3 mols. of phenylmagnesium bromide or phenyl-lithium afforded triphenylmethyl thiolbenzoate after decomposition by acid. Similar results were obtained with *p*-tolyl-lithium or magnesium bromide. Decomposition with ammonium chloride in case of the magnesium compounds and with water in case of lithium compounds gave, as expected, the triarylmethanols. Indeed, the easily crystallisable triphenylmethanol was isolated after reaction between phenylmagnesium bromide and dibenzoyl disulphide. In other cases, where some of the products do not crystallise easily, these could not be isolated. Thus, when the reaction mixture from phenylmagnesium bromide (3 mols.) and di-*p*-anisoyl disulphide (1 mol.) was treated with ammonium chloride, phenyl *p*-thiolanisate (IV) was the only product isolated.[1]

We thus consider that reaction proceeds by the path (I $\longrightarrow$ III) in preference to the path (IV $\longrightarrow$ VI). Any arylmetallic compound that remains is incapable of reacting with the thiol-ester.[1] The residual bromomagnesium or lithium salt of the thiol-acid (I) condenses with the bromomagnesium or lithium derivative of the thiol (III) to give the triaryl thiol-ester (VII).

With aromatic thiol-acids, aryl-lithium compounds reacted in rather the same way as arylmagnesium halides. Phenyl-lithium (3 mols.) or phenylmagnesium bromide [1] (3 mols.) with thiolbenzoic acid gave triphenylmethyl thiolbenzoate and triphenylmethanol (initially triphenylmethanethiol). However, *p*-methoxyphenyl- and *p*-tolyl-lithium (3 mols.) reacted with thiolbenzoic acid (1 mol.) to give dibenzoyl disulphide. This reaction might have proceeded through free radicals:

$$(3)\quad 2R{\cdot}CO{\cdot}SA \longrightarrow 2R{\cdot}CO{\cdot}S{\cdot} + 2A{\cdot}$$

$$(4)\quad 2R{\cdot}CO{\cdot}S{\cdot} \longrightarrow (R{\cdot}CO{\cdot}S{\cdot})_2$$

$$(A = MgBr \text{ or } Li)$$

Moreover the free radical R·CO·S· can dissociate further:

$$(5)\quad R{\cdot}CO{\cdot}S{\cdot} \longrightarrow R{\cdot} + COS \text{ (cf. dissociation of } R{\cdot}CO_2{\cdot}\,^4)$$

This dissociation could be the reason for production of *p*-thiolanisic acid (decomposed to anisic acid) along with dibenzoyl disulphide on reaction of *p*-methoxyphenyl-lithium with thiolbenzoic acid (reactions 3 and 4). The production of the thiolanisic acid may be represented by:

$$(6)\quad RLi + COS \longrightarrow R{\cdot}CO{\cdot}SLi$$

This is in support of our previous speculation about the formation of dibenzoyl and di-*p*-chlorobenzoyl disulphide from the corresponding thio-acids by the action of Grignard reagents.[1]

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[4] Hey and Waters, *Chem. Rev.*, 1937, **21**, 185.

The appearance of sulphur in some reactions may be due to decomposition of intermediate products.

EXPERIMENTAL

Light petroleum had b. p. 70—80° except where otherwise stated.

p-*Tolylmagnesium Bromide* (3 *Mols.*) *and Dibenzoyl Disulphide* (1 *Mol.*).—Dibenzoyl disulphide (2·74 g.) in dry benzene was added to *p*-tolylmagnesium bromide (from 3·8 ml. of *p*-bromotoluene) in ether. The mixture was left overnight and then refluxed for 4 hr. After decomposition with dilute hydrochloric acid and ice, the ethereal layer and ethereal extract were united, washed with water, dried (Na_2SO_4), and evaporated. The residual oil solidified (1·1 g.) under methanol. Recrystallisation from ethanol gave αα-di-*p*-tolylbenzyl thiolbenzoate,[1] m. p. and mixed m. p. 136°.

Phenylmagnesium Bromide (3 *Mols.*) *and Di*-p-*chlorobenzoyl Disulphide* (1 *Mol.*).—To a Grignard reagent [from bromobenzene (1·6 ml.) in ether] di-*p*-chlorobenzoyl disulphide [1] (1·7 g.) in dry benzene was added. After treatment as above, the oil, isolated from the ethereal layer, crystallised from light petroleum, to give *p*-chlorobenzoic acid (0·3 g.), m. p. and mixed m. p. 239°. The mother-liquor, on further concentration gave sulphur and resins.

Phenylmagnesium Bromide (6 *Mols.*), *Dibenzoyl Disulphide* (1 *Mol.*), *and Benzoyl Chloride* (1 *Mol.*).—To phenylmagnesium bromide (from 12·6 ml. of bromobenzene) in ether, dibenzoyl disulphide (5·5 g.) in dry benzene was added. The mixture was refluxed for 2 hr. and left overnight, then cooled, treated with benzoyl chloride (4·6 ml.), refluxed for 4 hr., and poured in dilute sulphuric acid and ice. The ethereal layer and the ethereal extract were united, washed with water, dried (Na_2SO_4), and evaporated. The remaining oil solidified under light petroleum. The solid, recrystallised from the same solvent, afforded triphenylmethanol (3·8 g.), m. p. and mixed m. p.[2] 163°, and, on further concentration of the mother-liquor, triphenylmethyl thiolbenzoate (0·35 g.) was obtained (m. p. and mixed m. p.[2] 188°).

Phenyl-lithium (3 *Mols.*) *and Dibenzoyl Disulphide* (1 *Mol.*).—To phenyl-lithium [prepared from lithium metal (0·83 g.), and bromobenzene (6·3 ml.) in dry ether] dibenzoyl disulphide (5·5 g.) in dry benzene was added. The mixture was left overnight, refluxed for 4 hr., and poured into dilute sulphuric acid and ice. The ethereal layer and the ethereal extract were united, washed with water, dried (Na_2SO_4), and evaporated. The remaining triphenylmethyl thiolbenzoate solidified under light petroleum and, recrystallised (2·8 g.) from the same solvent, had m. p. and mixed m. p.[2] 188°. The mother-liquor, on concentration and cooling, gave triphenylmethanol, m. p. and mixed m. p.[2] 163° [from light petroleum (b. p. 110—120°)]. The ethereal layer gave a positive test for thiophenol.[6]

p-*Methoxyphenyl-lithium* (3 *Mols.*) *and Dibenzoyl Disulphide* (1 *Mol.*).—Dibenzoyl disulphide (2·75 g.) in dry benzene was added to *p*-methoxyphenyl-lithium [prepared as above from *p*-bromoanisole (3·7 ml.)] in dry ether. The mixture was treated as above. The ethereal layer gave an oil that solidified under light petroleum. The solid (0·8 g.) was boiled with methanol and sulphur (0·25 g.), m. p. and mixed m. p. 120°, was separated by filtration while hot. The solution, on cooling, gave benzoic acid (0·53 g.), m. p. and mixed m. p. 122° (from water).

p-*Tolyl-lithium and Dibenzoyl Disulphide.*—(*a*) Dibenzoyl disulphide (2·74 g.) and *p*-tolyl-lithium (from 3·8 ml. of *p*-bromotoluene) in a reaction as above gave, from the ethereal layer, an oil that solidified under ethanol. The solid (1·1 g.) was dissolved in methanol and filtered from the insoluble sulphur (0·1 g.). On cooling, the solution gave dibenzoyl disulphide (0·98 g.), m. p. and mixed m. p.[6] 132°. In a similar reaction but with decomposition by water and ice, sulphur (0·7 g.) was obtained from the ethereal and thiolbenzoic acid from the aqueous layer.

(*b*) Reaction as above, with 6·3 g. of *p*-bromotoluene and decomposition with dilute sulphuric acid and ice, gave from the ethereal layer an oil that solidified under ethanol containing a little ether on cooling. The solid (1·0 g.), recrystallised from ethanol, proved to be αα-di-*p*-tolylbenzyl thiolbenzoate, m. p. and mixed m. p. 136°. In a similar reaction decomposition with water afforded an unidentified oil from the ethereal layer and benzoic acid (1·6 g.; m. p. 122°) from the aqueous layer.

Phenyl-lithium (3 *Mols.*) *and Di*-p-*chlorobenzoyl Disulphide* (1 *Mol.*).—Di-*p*-chlorobenzoyl disulphide (1·7 g.) and phenyl-lithium (from bromobenzene, 1·6 c.c.) on a similar treatment gave, from the ethereal layer, an oil that solidified under light petroleum; recrystallised from methanol it gave *p*-chlorobenzoic acid (1·1 g.), m. p. and mixed m. p. 239°. Concentration of the mother-liquor gave *p*-chlorothiolbenzoic acid (0·4 g.), m. p. and mixed m. p.[1] 187° (from light petroleum).

Phenyl-lithium (3 *Mols.*) *and Di*-p-*anisoyl Disulphide* (1 *Mol.*).—Phenyl-lithium (from 3·1 ml. of bromobenzene) and di-*p*-anisoyl disulphide (3·4 g.) gave, from the ethereal layer, an oil that solidified (1·1 g.) under light petroleum on long cooling. It recrystallised from light petroleum and had m. p. and mixed m. p. 178° with 4-methoxy-αα-diphenylbenzyl *p*-thiolanisate.[1]

p-*Methoxyphenyl-lithium* (3 *Mols.*) *and Di*-p-*anisoyl Disulphide* (1 *Mol.*).—Di-*p*-anisoyl disulphide (3·4 g.) and *p*-methoxyphenyl-lithium (from 3·8 ml. of *p*-bromoanisole) in a reaction as above, with 4 hours' refluxing and acid decomposition, afforded, from the ethereal layer, oily anisic acid that solidified (1·7 g.) on long cooling under light petroleum. Recrystallised from the same solvent it had m. p. and mixed m. p. 182°.

p-*Tolyl-lithium and Di*-p-*anisoyl Disulphide.*—Di-*p*-anisoyl disulphide (3·34 g.) with *p*-tolyl-lithium from *p*-bromotoluene (4 ml., 3 mol.; or 6·3 ml., 5 mol.) in a reaction as above afforded anisic acid (*ca.* 1·3 g.), m. p. 182° on decomposition by acid or water.

Phenyl-lithium (3 *Mols.*) *and Thiobenzoic Acid* (1 *Mol.*).—(*a*) In a similar reaction with decomposition by acid, phenyl-lithium (from 6·3 ml. of bromobenzene) and thiobenzoic acid (2·76 g.) gave, from the ethereal layer, an oil that solidified under light petroleum. Recrystallised from light petroleum (b. p. 110—120°) this gave triphenylmethanol (2·4 g.), m. p. and mixed m. p. 163°. The mother-liquor on concentration and cooling afforded triphenylmethyl thiolbenzoate (0·2 g.), m. p. and mixed m. p.[2] 188°. (*b*) Decomposition with water gave triphenylmethanol (2·6 g.) from the ethereal and thiobenzoic acid (2·3 g.) from the aqueous layer on acidification.

p-*Methoxyphenyl-lithium* (3 *Mols.*) *and Thiobenzoic Acid* (1 *Mol.*).—From a reaction as above with acid-decomposition *p*-methoxyphenyl-lithium (from 7·5 ml. of *p*-bromoanisole) and thiobenzoic acid (2·76 g.) an oil was isolated with ether. It solidified on cooling under ethanol. Recrystallisation from light petroleum gave anisic acid (2·0 g.), m. p. and mixed m. p. 182°. Concentration of the mother-liquor and cooling gave dibenzoyl disulphide (0·2 g.), m. p. and mixed m. p.[5] 132°.

p-*Tolyl-lithium* (3 *Mols.*) *and Thiobenzoic Acid* (1 *Mol.*).—As before *p*-tolyl-lithium (from 11·3 ml. of *p*-bromotoluene) and thiobenzoic acid afforded an oil that solidified under light petroleum and recrystallised therefrom (1·1 g.). It had m. p. 132° alone or mixed with dibenzoyl disulphide.[5]

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[5] Schelton and Rider, *J. Amer. Chem. Soc.*, 1936, **58**, 1282.
[6] Rheinbolt's test for thiophenol, *Ber.*, 1927, **60**, 184.