Preparation of 2-Arylthiophenes by Reaction of
2-Thienylcopper with Halogenoarenes

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2-Thienylcopper preparations are obtained by the reaction between 2-thienyllithium and copper(I) iodide or copper(II) bromide. 2-Thienylcopper has been reacted with a number of iodoarenes and some bromoarenes in pyridine or quinoline to give the corresponding 2-arylthiophenes selectively in reasonable yields. The effect of substituents in the halogenoarenes has been studied.

Strongly electron-attracting groups such as nitro- or methoxy-carbonyl ortho to the iodine in the iodobenzenes increase the reaction rate significantly.

A 2-furylcopper preparation on reaction with 4-idoanisole similarly gives some 2-(4-methoxyphenyl)furan.

A preliminary report has been published on the reaction of 2-thienylcopper with iodobenzene in quinoline solution to give 2-phenylthiophene.\(^1\) The thienylcopper was then prepared essentially according to Gilman and Straley\(^2\) from 2-thienylmagnesium iodide and copper(I) iodide in ether. A solvent such as quinoline was found necessary for the unsymmetrical coupling reaction. An analogous coupling could be effected with 4-iodotoluene while attempted couplings with iodomethoxybenzenes were largely unsuccessful and demethylation to phenolic products occurred to a considerable extent. This was suspected to be due to side reactions of Grignard reagent\(^3\) remaining in the thienylcopper preparations. The tendencies of magnesium compounds to be retained in phenylecopper preparations have been discussed by Costa et al.\(^4\)

Arylcopper compounds have been suggested as intermediates in the Ullman reaction\(^5\) and other copper-promoted reactions involving iodoarenes.\(^6,7\) 2-Iodothiophene is known to react readily in the Ullmann reaction\(^5\) giving 2,2'-bithiophenyl as well as polythiencyls.\(^8\) 2-Thenoic acid undergoes decarboxylative coupling with iodoarenes in the presence of copper(I) oxide.\(^9\) The assumed intermediate formation of 2-thienylcopper in this reaction seems analogous to the decarboxylative formation of 2-acetoxymercuri-thiophene from acetoxymercuric thioate.\(^10\)

We have tried to isolate 2-thienylcopper and to investigate its reactions with halogenoarenes. 2-Thienylcopper is soluble in quinoline and pyridine but sparingly soluble in other types of organic solvents. In a series of preliminary experiments 2-thienylcopper preparations obtained from 2-thiennyllithium or 2-thiennymagnesium iodide and copper(I) iodide were reacted with iodo-
benzene, 4-iodotoluene and 2,6-dimethoxyiodobenzene in quinoline solution at ca. 150° to give 2-phenylthiophene, 2(4-methylphenyl)thiophene and 2(2,6-dimethoxyphenyl)thiophene, respectively. Also heating of 2-thienyl-
copper with iodo-benzene and triphenylphosphine gave 2-phenylthiophene.

In a second set of experiments 2-thienylcopper, prepared from 2-thiennyllithium and copper(I) bromide and isolated from the reaction mixture, has been reacted with a number of halogenoarenes (Table 1) in pyridine solution at temperatures between 0 and 115° to give the corresponding 2-aryltiophenes (eqn. 1, Ar = 2-thienyl).

\[
\text{Ar—Cu + Ar'—I} \rightarrow \text{Ar—Ar' + CuI}
\]  

The temperatures were chosen to give reaction times of approximately the same magnitude. For comparison of rates the times corresponding to 50 % of the final yield are given in Table 1. The reaction was followed by GLC analyses of small samples withdrawn from the reaction mixture at short intervals, hydrolysed and extracted with heptane. The reactions were run with internal standards.

RESULTS

So far we have not obtained analytically pure 2-thienylcopper. Ether, copper(I) bromide, and also some lithium bromide are retained.

Attempts were made to estimate the purity of the preparations as we could find no suitable solvent for recrystallisation. Samples were hydrolysed with dilute hydrochloric or sulphuric acids, extracted with hexane and their thiophene content determined by UV spectroscopy. Most thienylcopper preparations gave thiophene corresponding to 50—80 % purity, the average being around 70 %. Attempts were also made to determine the copper content and the impurities. The analysis has confirmed the presence of the impurities mentioned above. The copper content is in agreement with the assumption that the preparations contain ca. 70 % 2-thienylcopper and some additional copper(I) bromide.

As demonstrated by the preliminary experiments it is not necessary to isolate the thienylcopper before the subsequent coupling reactions. The experiments in the second series were, however, performed with isolated thienyl-
copper. The amounts of reactants were calculated assuming pure thienyl-
copper. The yields given in Table 1 are based on the butyl-lithium used in the preparation of 2-thiennyllithium and can therefore be regarded as practical yields in preparative work.

Reaction between 2-thienylcopper and an iodo- or bromoarene in pyridine solution almost selectively gave the corresponding 2-aryltiophene (eqn. 1) while the only chloro compound tried, methyl 2-chlorobenzoate, failed to react with 2-thienylcopper. The experimental results are summarized in Table 1.
Table 1. Reactions of 2-thienylcopper with halogenoarenes in pyridine. Yields based on the butyl-lithium used to prepare the thienylcopper and generally determined by GLC (internal standards). The starred yields were determined by isolation and weighing of the products.

<table>
<thead>
<tr>
<th>Halogenoarene</th>
<th>Product</th>
<th>Yield %</th>
<th>Temp.</th>
<th>Time for 50 % react., min</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-OCH₃</td>
<td>OCH₃</td>
<td>55*</td>
<td>115°</td>
<td>30—35</td>
</tr>
<tr>
<td>CH₃O</td>
<td></td>
<td>56</td>
<td>110°</td>
<td>5—6</td>
</tr>
<tr>
<td>I</td>
<td></td>
<td>31</td>
<td>75°</td>
<td>70—75</td>
</tr>
<tr>
<td>I</td>
<td></td>
<td>42</td>
<td>75°</td>
<td>35—40</td>
</tr>
<tr>
<td>I-NO₂</td>
<td>NO₂</td>
<td>70</td>
<td>50°</td>
<td>20—22</td>
</tr>
<tr>
<td>I-COOCH₃</td>
<td>COOCH₃</td>
<td>50</td>
<td>50°</td>
<td>11—12</td>
</tr>
<tr>
<td>I-NO₂</td>
<td>NO₂</td>
<td>56</td>
<td>0°</td>
<td>38—40</td>
</tr>
<tr>
<td>I-Br</td>
<td>Br</td>
<td>14*</td>
<td>110°</td>
<td>29—31</td>
</tr>
<tr>
<td>I-COOCH₃</td>
<td>COOCH₃</td>
<td>13</td>
<td>110°</td>
<td>5—10</td>
</tr>
</tbody>
</table>

In most cases the amounts of coupling product and iodoarene, determined by GLC analyses, account for 95 to 100 % of the halogenoarene.

The samples from the reactions were examined for other products as well. Small amounts of biphenyls (ca. 1 %) from dimerisation of iodoarene were observed by GLC in some cases (compare experimental part). However, during the reaction neither the formation of 2-iodothiophene from metal-halogen exchange, eqn. 2, nor 2,2'-bithienyl from "dimerisation" of 2-thienylcopper, eqn. 3, were observed. Some 2,2'-bithienyl is formed during the preparation or storing of 2-thienylcopper (ca. 1 %) and was present during the coupling reactions but the amount was not increased.

The coupling between 2-thienylcopper and activated iodoarenes, such as 2-iodonitrobenzene, seems to be not far from quantitative. The yields from activated iodoarenes are generally around 60%, while the yields from iodo-benzene or bromoarenes are lower.

Nitro- and methoxycarbonyl groups ortho to the halogen in halogenoarenes increase the reaction rate significantly. Similar ortho effects are often observed in the Ullmann reaction and also in copper-catalysed halogen exchange reactions in halogenoarenes. A nitro group in the para position moderately increases the reaction rate, while a methoxy group is slightly deactivating compared to hydrogen.

We were surprised to find that the difference between iodobenzene and 2-iodothiophene was relatively small, as we had expected the "ortho" sulphur atom to exert an activating effect not much less than that of the methoxy-carbonyl group.

The lower reaction rates of the bromo compounds relative to the iodo compounds were expected by comparison with their Ullmann reactions. It should be noted that no products from reactions between 2-thienylcopper and nitro- or methoxycarbonyl groups were observed.

The reaction between 2-thienylcopper and methyl 2-iodobenzoate was also performed in quinoline. It was found that the reaction rate in quinoline is about half of that in pyridine. This result is similar to results with phenylcopper.

In a separate set of experiments 2-thienylcopper was heated neat or in quinoline. No 2,2'-bithienyl was isolated from the experiments with quinoline present. When heated neat or on storing for a few days in a refrigerator or at room temperature 2-thienylcopper forms some 2,2'-bithienyl. When exposed to air it decomposes rapidly.

Analogous to 2-thienoic acid, 2-furoic acid gives 2-aryl furans on decarboxylative coupling with iodoarenes using copper(I) oxide and quinoline. It was of interest to explore the possibilities of using 2-furylcopper for coupling with iodoarenes, especially since arylfurans have apparently not been prepared by the Ullmann reaction. The product obtained after reaction between 2-furyl-lithium and copper(I) iodide, presumably 2-furylcopper, was reacted with 4-iodoanisole in quinoline solution at 150° to give 2-(4-methoxyphenyl)furan and some 4,4'-dimethoxybiphenyl indicating fair prospects for further work in this direction.

**DISCUSSION**

The high selectivity and relatively high yields in the reactions of 2-thienylcopper with iodoarenes make it a valuable synthetic route to 2-aryltiophenones. By modifying the reaction conditions for the preparation of thiencylcopper it might be possible to obtain it in a purer form. Like phenylcopper, 2-thienylcopper is insoluble in most organic solvents with which it does not react, and
can possibly be regarded as a coordination polymer. Solvents which do dissolve 2-thienylcopper are nitrogen-containing aromatics like pyridine and quinoline. As mentioned above iodobenzene also reacts with thienylcopper in triphenylphosphine. Pyridine, quinoline, or tertiary phosphines should reduce the polymer to lower aggregates. Costa et al. have shown that phosphate complexes of phenylcopper are slightly more stable and markedly more soluble than phenylcopper. These findings could possibly open up routes to the purification and characterisation of 2-thienylcopper.

The unsymmetric coupling of thienylcopper seems analogous to the decahydroxylative couplings of 2-thenoic, 2-furoic9 and 2-nitrobenzoic acids6,7 with iodoarenes in the presence of copper(I) oxide with quinoline as solvent. It should also be compared with the coupling of 2-phenylthiophene with iodobenzene to 2,5-diphenylthiophene in quinoline in the presence of copper(I) oxide.1 The unsymmetrical coupling is further reminiscent of the unsymmetrical coupling between iodoarenes and copper(I) arylacetylenes described by Castro et al. (eqn. 4).15,16

\[
\text{Ar} - \text{I} + \text{CuC} \equiv \text{C} - \text{Ar}' \underset{\text{pyridine}}{\longrightarrow} \text{Ar} - \text{C} \equiv \text{C} - \text{Ar}' + \text{CuI} \tag{4}
\]

Furthermore 2-iodothiophene is found to react with copper(I) acetylides to form 2-thienylacetylenes in good yields (eqn. 5, Ar = 2-thienyl).17

\[
\text{Ar} - \text{I} + \text{CuC} \equiv \text{C} - \text{R} \underset{\text{pyridine}}{\longrightarrow} \text{Ar} - \text{C} \equiv \text{C} - \text{R} + \text{CuI} \tag{5}
\]

It seems reasonable to assume that the reaction of copper(I) acetylides and 2-thienylcopper with iodoarenes proceed by similar mechanisms. Stephens and Castro have discussed the possibility that the initial step in reaction 4 is the formation of an aryl radical from the iodoarene followed by interaction of this radical with the copper(I) species to give the coupling product. As discrete aryl radicals formed in this way might be expected to couple to dimeric products and no such “dimers” are found from the reactions 4 and 517 and only very small amounts from the reactions of 2-thienylcopper a radical mechanism does not seem highly probable. Stephens and Castro suggest a concerted path for the coupling reaction involving a four-centre transition state.13

The influence of substituents in the iodoarenes on reaction rates are found to be the same for copper(I) acetylides, phenylcopper, and 2-thienylcopper. The approximate order of increasing reactivity towards 2-thienylcopper is: 4-methoxy-, none (H), 4-nitro, 2-methoxycarbonyl, and 2-nitro.

A four-centre transition state would account for the influence of ortho substituents and it might also open up routes for metal-halogen exchange as discussed for phenylcopper reactions.13 It should be noted that in reaction 5 a major by-product is the thiophene species where iodine has been replaced by hydrogen.17 This could be an indication of metal-halogen exchange.

It is not yet quite clear why 2-thienylcopper does not take part in reactions 2 and 3. It is possible that interaction between the copper and sulphur atoms raises the activation energy for breaking of the copper-carbon bond. 2-Thienylcopper is slightly more stable to heating than phenylcopper and reacts somewhat slower with halogenoarenes.

The fact that thiencylcopper does not give products from reaction 2 (Ar = 2-thienyl, X = 1) shows that the equilibrium of this reaction is far to the left. Nesmeyanov et al. have described an interesting reaction of bromoferrocene with a mixture of tetra-(2-thienyl)borate and copper(I) bromide giving 2-thienylferrocene. Comparison of this reaction with the reactions of 2-thienylcopper with bromo- and iodoarenes tempts us to suggest that 2-thienylcopper is also an intermediate in this reaction.

**EXPERIMENTAL**

Melting points were determined on a micro hot stage. Infrared spectra were recorded on a Perkin Elmer No. 421 spectrometer, ultraviolet spectra with a Beckman DK 2 instrument, NMR spectra on a Varian A 60 A spectrometer, and gas chromatograms on an Aerograph 204-1B with 5 % SE 30 on Chromosorb W.

All preparations and handling of organometallic compounds were performed under dry oxygen-free nitrogen. Dry reagents and solvents were used, the ether was freshly distilled from lithium aluminium hydride, the pyridine (A.R.) was distilled from phosphorus pentoxide.

The structure of all known compounds were checked by NMR, IR, or UV spectroscopy.

**Preliminary experiments**

2-Phenylthiophene via 2-thienylmagnesium iodide. Magnesium (0.06 mole) was reacted with 2-iodothiophene (0.05 mole) in ether (50 ml) essentially according to Gilman and Straley. The solution was filtered and cooled. Finely powdered copper(I) iodide (0.05 mole) was added in portions with stirring. An oil was formed, which partly solidified after 15–30 min. More ether was added to aid crystallisation. The yellowish solid was allowed to settle. In some experiments the 2-thienylcopper was filtered off, washed with ether and reacted with iodobenzene (0.05 mole) in quinoline (100 ml) at 160 or 240° for 30–60 min. In other experiments the quinoline was added, the mixture stirred and the precipitate — presumably a quinoline complex of 2-thienylcopper — filtered off, washed with ether, dried at room temperature and moderate vacuum and reacted with iodobenzene (0.05 mole) at 160–240°. In still further experiments quinoline and iodobenzene were added directly to the ether suspension of 2-thienylcopper and the mixture heated gradually, with stirring, the ether being distilled off to 160–165° and kept at these temperatures for 30–60 min.

These different methods gave largely the same results. After completed reaction the mixtures were worked up according to the following procedure, which is typical of the work up used for the coupling reaction. Details are excluded from subsequent experimental descriptions.

When the reaction mixture had cooled it was stirred well with excess ether. The yellow complex of copper(I) iodide and quinoline was filtered off, washed with ether and discarded. The filtrate was extracted with hydrochloric acid (2 M) to remove quinoline, washed with water, dried and evaporated. The residue was distilled to give unchanged iodobenzene and 2-phenylthiophene (6 to 8.5 g), b.p. ca. 120°/15 mm, which solidified and was recrystallised from methanol (refrigerator) to give pure material, m.p. 33–35°, lit. m.p. 37°; yield 30–50 %. The IR, UV, and NMR spectra confirmed the structure.

The weight of the 2-thienylcopper preparations filtered off, washed with ether and dried in vacuum were usually higher than should be expected. This is probably due to tenaciously retained magnesium salts and ether (cf. Ref. 4).

2-Phenylthiophene via 2-thienyl-lithium. A solution of 2-thienyl-lithium (ca. 0.1 mole) (prepared from butyl-lithium or phenyl-lithium and thiophene) in ether (ca. 75 ml) was added to an ice-cooled suspension of copper(I) iodide (0.1 mole) in ether and was stirred for 30 min. A yellowish precipitate formed. Iodobenzene (0.1 mole) and quinoline (0.4 mole) were added and the mixture was heated with stirring, the ether being distilled

off, to ca. 240° and kept at this temperature for ca. 15 min. The reaction mixture after the usual work-up procedure gave an oil (14 g) which was distilled to give ca. 4 g unchanged iodobenzene and a solidifying fraction, b.p. 120—140°/15 mm (7 g, crude yield 50%), recrystallised to give essentially pure 2-phenylthiophene, m.p. 32—35° (6.7 g, 41%).

In another type of experiment triphenylphosphine (0.1 mole) was added to 2-thienylcopper (ca. 0.05 mole) in ether. After stirring the greyish precipitate was filtered off and washed with ether. This precipitate was heated with iodobenzene to 160° for 1 h. After cooling the mixture was stirred with ether, the solid filtered off, the filtrate concentrated and distilled to give unchanged iodobenzene and 2-phenylthiophene (ca. 33% yield).

The complex between thienylcopper and triphenylphosphine was fairly easy to handle and was not so sensitive to air as 2-thienylcopper or its quinoline complex.

2-(4-Methylphenyl)thiophene. 2-Thienylcopper prepared via the Grignard reagent (ca. 0.05 mole) was reacted with 4-iodotoluene in quinoline for 1 h at 160°. Distillation and recrystallisation of the crude products gave 2(4-methylphenyl)thiophene (3.1 g, 36%), m.p. 64—66°, lit. 21 m.p. 63—64°, and small amounts of 2,5-bis(4-methylphenyl)thiophene, m.p. 175—177°, lit. 21 m.p. 171°. The NMR spectra were in accordance with the structures.

2(2,6-Dimethoxyphenyl)thiophene. To a suspension of 2-thienylcopper, prepared via 2-thienyl-lithium (ca. 0.02 mole), in ether, quinoline (25 ml) was added followed by solid 2,6-dimethoxyiodobenzene (0.02 mole) at room temperature. The mixture was slowly heated, the ether being distilled off, to ca. 150° (1 h) and kept at 150—170° for ca. 30 min. Chromatography of the crude reaction product (4.3 g) gave: 2,6-dimethoxyiodobenzene (2.84 g, 55%); ca. 1.3 g of a product, m.p. 44—55°, which was recrystallised from methanol and sublimed to give pure 2(2,6-dimethoxyphenyl)thiophene, m.p. 54—55°. (Found: C 65.5; H 5.5; S 14.7. Calc. for C₁₆H₁₂O₂S: C 65.4; H 5.5; S 14.5.) Ultraviolet absorption bands at 285 and 223 nm (ε = 10 500 and 15 000) with shoulders at ca. 292 and 305 nm (ethanol). The NMR spectrum confirmed the structure.

2-(4-Methoxyphenyl)anthracene. 2-Thienylcopper prepared via 2-thienyl-lithium (ca. 0.02 mole) in ether (ca. 30 ml) at 0° with stirring. The mixture was boiled for ca. 5 min. The solution of 2-furyl-lithium was filtered and added to copper(I) iodide (0.02 mole) in ether (20 ml) kept at 0°. 4-Iodoanisole (0.02 mole) and quinoline (25 ml) were added and the mixture heated with stirring and distillation of the ether to 150° and kept at this temperature for 30 min. The crude reaction product (4 g) was chromatographed on silica gel to give: ca. 2.5 g unchanged 4-iodoanisole and ca. 1 g of a mixture which was fractionally crystallised from methanol to give 2(4-methoxyphenyl)anthracene and a small amount of 4,4'-dimethoxybiphenyl. 2-(4-Methoxyphenyl)anthracene was recrystallised from methanol and sublimed to give ca. 0.25 g of reasonably pure material, m.p. 55—58°, which was identical with authentic material.

2,2'-Bithienyl. 2-Thienylcopper prepared via 2-thienyl-lithium (ca. 0.09 mole) was heated to 150° and kept at this temperature for 3 h under nitrogen. After cooling, ether and dilute hydrochloric acid were added. The ether solution gave 0.88 g organic material (excluding thiophene) of which 0.43 g could be sublimed onto a cold finger condenser at 150°/0.5 mm. Chromatography on silica gel gave 0.25 g 2,2'-bithienyl, m.p. 28—31°. Recrystallisation raised the m.p. to 31—32°, lit. 4 m.p. 32—33.5°. The identity was proved by the UV spectrum.

**General procedure for the preparation of 2-thienylcopper**

Butyl-lithium (30 mmole) in ether (ca. 50 ml) was added to thiophene (60 mmole) in ether (ca. 50 ml) at room temperature. After stirring for 30—40 min the 2-thienyl-lithium was transferred to a dropping funnel. Some nitrogen-swept, dry ether was added bringing the volume up to ca. 150 ml. Copper(I) bromide (30 mmole) was suspended in ether (ca. 75 ml) in a reaction flask. The thienyl-lithium was added over ca. 50 min at room temperature with magnetic stirring. During the addition a characteristic colour change took place from pale yellow to bright yellow to orange and after 25% addition to brownish red. Then the colour faded and after complete addition the suspension had an olive colour. The copper(I) bromide did not dissolve. The suspension was stirred for 1 h at room temperature. The solid was filtered off under nitrogen (in a glove bag) and washed several times with dry ether. The yellowish solid was collected and dried under

vacuum. Thiénylcoopper can be stored under nitrogen or in a vacuum until the next day. No proper solvent has been found for recrystallisation or purification of the thiénylcoopper which was contaminated by LiBr, CuBr, and ether. The purity varied for the preparations with a maximum around 80%. It was rather difficult to estimate the yield as the weight of the isolated solid was often higher than that corresponding to a 100% yield of pure product.

The copper(I) bromide used was prepared according to Vogel and stored at 110°C. It was important to have the copper(I) bromide finely powdered before use to improve the purity of the thiénylcoopper. In the preparation of 2-thienyl-lithium a 100% excess of thiophene was used to avoid contamination of butyl-lithium in the subsequent step in which the presence of butyl-lithium seemed to cause the formation of metallic copper and a black oil which was not further investigated. The butyl-lithium used is a commercial product, 20% in hexane (Fluka or Merck). It is important to add the thiényl-lithium slowly to the copper bromide. Attempts to add the copper bromide to thiényl-lithium gave a black mess which was not further investigated (cf. Ref. 4).

General procedure for the coupling reactions

A reaction flask (100 ml) was fitted with a gas inlet tube, a magnetic stirrer and occasionally a reflux condenser. In a glove bag swept with nitrogen the reaction flask was charged with thiénylcoopper, halogenoaorene, internal standard, and pyridine. For simplicity the thiénylcoopper was considered to be pure and an equimolar amount of halogenoaorene was used. Thus the halogenoaorene was always present in excess.

Nitrogen was passed through the apparatus and the flask placed in an oil bath or a cooling bath, respectively, and kept at constant temperature. Small samples (0.08 ml) were withdrawn from the reaction mixture at short intervals, hydrolysed with 2 M hydrochloric acid, extracted with heptane and analysed by gas chromatography.

When the reaction was complete the mixture (when cool) was diluted with ca. 200 ml ether and solid copper(I) halide complex filtered off. The filtrate was extracted with 2 M hydrochloric acid and after washing with water and drying, the ether was removed at reduced pressure. The crude reaction product was investigated by GLC. The amounts of halogenoaorene left and coupling product were determined using internal standards and standard solutions for calibration. In most cases the products were isolated by chromatography on silica gel for identification and weighing. The yields determined by weighing were usually 5-10% lower than the yields determined by GLC. This difference probably is partly due to the loss of material during isolation and partly to the uncertainty in the GLC determinations.

2-Thiénylcoopper and 4-iodoanisole. Reaction temperature 115°C. 2-Thiénylcoopper (1.56 g, 10 mmole) was reacted with 4-iodoanisole (10 mmole) in 25 ml pyridine with 0.18 g 2-methoxyanaphthalene as internal standard. Within 130 min more than 90% of the reaction was completed and after 160 min the reaction was interrupted. Chromatography of the crude reaction product gave: 4-iodoanisole (0.66 g); 2-methoxyanaphthalene (0.07 g); 2-[4-methoxyphenyl]thiophene (1.11 g) recrystallised from methanol, m.p. 104-107°C, lit. m.p. 107-108°C, UV spectrum in accordance with literature data.9 No other products were isolated although GLC indicated that small amounts of products of higher molecular weight were present.

2-Thiénylcoopper and 2,6-dimethoxyiodobenzene. Reaction temperature 110°C. 2-Thiénylcoopper (2.00 g, 13.6 mmole) was reacted with 2,6-dimethoxyiodobenzene (13.5 mmole) in 35 ml pyridine with 0.20 g 4-methoxybiphenyl as internal standard. After 16 min more than 90% of the reaction was completed and after 60 min the reaction was interrupted. Chromatography of the crude reaction product gave: 4-methoxybiphenyl (0.22 g, containing some stopcock grease); 2,6-dimethoxyiodobenzene (0.84 g); 2-[2,6-dimethoxyphenyl]thiophene (1.35 g) recrystallised from methanol twice, m.p. 53-55°C. UV in accordance with that of an authentic sample.

2-Thiénylcoopper and iodobenzene. Reaction temperature 75°C. 2-Thiénylcoopper (0.84 g, 5.7 mmole) was reacted with iodobenzene (5.1 mmole) in 30 ml pyridine with 0.13 g naphthalene as internal standard. After 180 min more than 90% of the reaction was completed and after 195 min the reaction was interrupted. Chromatography of the crude product indicated that no products of higher molecular weight were present.

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reaction product gave: iodobenzene (0.23 g); naphthalene (0.09 g); 2-phenylthiophene (0.28 g), recrystallised from methanol, m.p. 30—35°.

2-Thienylcopper and 2-iodothiophene. Reaction temperature 75°. 2-Thienylcopper (0.99 g, 6.7 mmole) was reacted with 2-iodothiophene (6.0 mmole) in 30 ml pyridine with 0.16 g naphthalene as internal standard. The reaction was interrupted after 90 min. Chromatography of the crude reaction product gave: 2-iodothiophene (0.28 g); naphthalene (0.09 g); 2,2'-bithienyl (0.37 g) m.p. 25—30°, lit.² m.p. 32—33.5°. Identification was made by IR.

2-Thienylcopper and 4-iodonitrobenzene. Reaction temperature 50°. 2-Thienylcopper (2.20 g, 15 mmole) was reacted with 4-iodonitrobenzene (15 mmole) in 30 ml pyridine with 0.15 g 4-methoxybiphenyl as internal standard. After 45 min more than 90 % of the reaction was completed and after 120 min the reaction was interrupted. Chromatography of the crude reaction product gave: 0.03 g of a substance, m.p. 25—50°, retention time and melting point indicated 2,2'-bithienyl; 4-iodonitrobenzene (1.46 g); 4-methoxybiphenyl (0.15 g); 2(4-nitrophenyl)thiophene (1.96 g) m.p. 137—140°, recrystallised from toluene, to give 1.21 g, m.p. 138—139.5°, lit.¹⁴ m.p. 137—138°, the UV spectrum agreed with that previously reported;¹⁹ 2,5-bis(4-nitrophenyl)thiophene (ca. 10 mg) m.p. 258—264°, lit.²³ m.p. 253—254°, UV spectrum in agreement with that reported.²²

2-Thienylcopper and methyl 2-iodobenzoate. Reaction temperature 50°. 2-Thienylcopper (1.34 g, 9 mmole) was reacted with methyl 2-iodobenzoate (9 mmole) in 25 ml pyridine with 0.16 g naphthalene as internal standard. After 30 min more than 90 % of the reaction was completed and after 115 min it was interrupted. Chromatography of the crude reaction product gave: naphthalene; methyl 2-iodobenzoate; methyl 2-(2-thienyl)benzoate, b.p. 145—147°/1 mm, lit.¹⁴ b.p. 95—110°/0.3 mm. GLC showed small amounts of substances with longer retention times. One of these seemed to be dimethyl diphenate (retention time in agreement with authentic sample). Methyl 2(2-thienyl)benzoate was hydrolysed in NaOH—H₂O ethanol for 24 h. The mixture was neutralised and the 2(2-thienyl)benzoic acid collected, m.p. after recrystallisation and sublimation 91.5—94°, lit.¹⁴ m.p. 92—94°.

2-Thienylcopper and 2-iodonitrobenzene. Reaction temperature —1 to +4°. 2-Thienylcopper (1.18 g, 8 mmole) was reacted with 2-iodonitrobenzene (8 mmole) in 25 ml pyridine with 0.20 g naphthalene as internal standard. After 100 min more than 90 % of the reaction was completed and it was interrupted after 195 min. Chromatography of the crude reaction product gave: naphthalene (0.14 g); 2-iodonitrobenzene (0.76 g); 1.5 g an oil which was distilled at 98—100°/0.05 mm to give 2(2-nitrophenyl)thiophene (1.15 g), m.p. 46—50°, recrystallisation from methanol gave m.p. 49—51.5°, lit.²³ m.p. 51—52°, UV spectrum λ=251 nm, ε=11 400; 2,2'-dimethoxybiphenyl (ca. 10 mg), recrystallisation from methanol and sublimation gave m.p. 100—124°, lit.²³ m.p. 124°, UV spectrum in agreement with that previously reported.²⁴

2-Thienylcopper and 3-bromothiophene. Reaction temperature 110°. 2-Thienylcopper (1.86 g, 12.7 mmole) was reacted with 3-bromothiophene (12.7 mmole) in 25 ml pyridine with 0.20 g naphthalene as internal standard. After 65 min more than 90 % of the reaction was completed and after 220 min it was interrupted. Chromatography of the crude reaction product gave: 3-bromothiophene; naphthalene (0.10 g); 0.31 g crude material m.p. 51—54°, recrystallised from methanol to give 2,3'-bithienyl (0.10 g), m.p. 50—56°, after sublimation m.p. 53—59°, lit.²⁷ m.p. 68°. UV spectrum in agreement with that previously reported;²⁷ a yellow substance (a few mg), not further investigated; a blue substance, relatively stable in solution but decomposing on evaporation, not further investigated.

2-Thienylcopper and methyl 2-bromobenzoate. Reaction temperature 110°. 0.66 g Thienylcopper (4.5 mmole) was reacted with methyl 2-bromobenzoate (4.5 mmole) in 20 ml pyridine with 0.15 g naphthalene as internal standard. After 50 min more than 90 % of the reaction was completed and after 413 min it was interrupted. The product, methyl 2(2-thienyl)benzoate, was identified by GLC and TLC, comparison with an authentic sample.

2-Thienylcopper and methyl 2-chlorobenzoate. Reaction temperature 110°. 0.76 g 2-thienylcopper (5.2 mmole) was reacted with methyl 2-chlorobenzoate (5.2 mmole) in 20 ml pyridine with 0.16 g naphthalene as internal standard. No reaction between 2-thienylcopper and methyl 2-chlorobenzoate could be observed. The disappearance of

2-thienylocopper could be followed by GLC as the hydrolysis product but the formation of 2,2'-bithienyl could not be observed. After 200 min at 110° no 2-thienylocopper was left.

2-Thienylocopper in pyridine. 0.62 g 2-Thienylocopper was heated in pyridine with 0.15 g naphthalene as internal standard. After 5 h at 60° 2,2'-bithienyl had been formed. The temperature was raised to 114° and left for another 3 h. No 2,2'-bithienyl was isolated.

2-Thienylocopper in quinoline. 0.15 g 2-Thienylocopper and 0.10 g naphthalene as internal standard in 15 ml quinoline was heated to 150° for 90 min. No 2,2'-bithienyl was isolated.

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