

Synthesis and reactivity of 2-(ethylthio)phenylcopper: a stable organocopper compound carrying an intramolecular sulfane ligand

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Abstract

An unusually stable organocopper compound carrying an intramolecular sulfane ligand, 2-(ethylthio)phenylcopper, was synthesized via the reaction of the corresponding organolithium with a copper(I) halide (CuX). This compound was obtained in two forms: one is a salt-free compound which is insoluble in ordinary solvents, the other is a soluble complex of [2-(ethylthio)phenylcopper]₂ · CuX composition. These compounds were either hydrolyzed or underwent a coupling reaction to produce a biphenyl when heated. While these organocoppers are less reactive towards various electrophiles than other known arylcoppers, the soluble complex gives ketones with acyl halides in low yields. The properties as well as the reactivities of the stable organocopper compounds are reported.

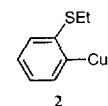
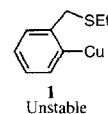
Keywords: Copper; Sulfane ligand

1. Introduction

The stabilities of organocopper compounds are usually enhanced by the introduction of intramolecular ligands and several examples of stable compounds with intramolecular ligands, such as amine-nitrogens and ether-oxygens, have been reported [1–8]. However, little is known about the properties of those carrying intramolecular sulfane–sulfur ligands (for an application of organocopper stabilized by sulfane–sulfur ligands, see Ref. [9]). The lack of information is attributable to the poor stabilizing ability of sulfur ligand(s) towards the reactive organocopper center, as evidenced by the unsuccessful isolation of 2-(ethylthiomethyl)phenylcopper (1) reported recently [10] by the reaction of the corresponding organolithio compound with a copper halide.

The stability of intramolecular organometallic complexes is greatly influenced not only by the kind of ligand atom but also by the relative position(s) of the atom(s) in the molecule. In an attempt to create the isolable sulfur-stabilized organocopper, we tried to change relative positions of the sulfur ligand and prepared 2-(ethylthio)phenylcopper (2), which lacks the benzylic methylene group in 1, by the usual method.

The organocopper compound was found to be isolable in two forms: a less soluble salt-free one and a soluble CuX-containing one. This paper presents the synthesis and properties of the new stable organocopper compounds carrying the sulfane ligand.

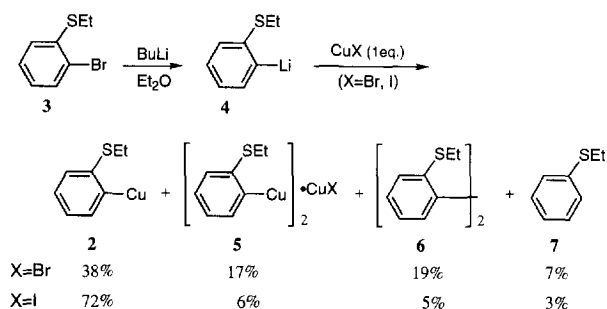


2. Results and discussion

2.1. Synthesis

The organocopper compound was prepared as shown in Scheme 1. 2-(Ethylthio)phenyllithium (4), prepared from 1-bromo-2-(ethylthio)benzene (3) and butyllithium, was treated with 1 equiv. of CuBr or CuI at

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Scheme 1.

–30 °C in diethyl ether. A brown solid was formed during the stirring at room temperature. Two types of stable organocopper compound were isolated from the reaction mixture. The major one is the insoluble brown solid and the minor the orange crystals soluble in ordinary organic solvents, these being identified as 2-(ethylthio)phenylcopper (**2**) and a 2:1 complex of 2-(ethylthio)phenylcopper with CuX (**5**) respectively. The characterization and properties of these organocopper compounds are described in detail in the next section. 2,2'-Bis(ethylthio)biphenyl (**6**) and ethyl phenyl sulfide (**7**) were obtained as by-products, resulting from the coupling of the organocopper compounds and hydrolysis respectively.

The yields of these products are shown in Scheme 1. When CuI was used as copper source, the insoluble organocopper was obtained in a good yield. The reaction with CuBr increased the yield of the soluble organocopper (**5**), although the formation of the decomposition products became significant.

2.2. Properties of organocopper compounds

2.2.1. Salt-free 2-(ethylthio)phenylcopper (**2**)

This compound, red–brown solid, was obtained as a common product by reactions with CuBr or CuI. **2** is quite insoluble in ordinary organic solvents, meaning that the molecules take an oligomeric or polymeric structure in the solid state as other organocopper compounds [1,2]. Purification of the crude material, which usually contains 5–20% inorganic impurities, was attained by centrifugation, whereby the impurity rich part formed the bottom layer and the desired compound the upper layer. The purified sample gave correct analysis data for the composition of 2-(ethylthio)phenylcopper free from solvents and salts. The XPS spectrum of **2** indicated the presence of Cu and S atoms and no bands attributable to halogens were found. The bonding energy of the Cu 2p_{3/2} band at 933.6 eV supports the oxidation state +I for copper atoms in the solid state.

2 is a stable compound in the solid state, showing no significant changes at room temperature in air for at least one month. Thermal decomposition took place in

the range 112–121 °C in a sealed tube. Being suspended in benzene, this phenylcopper survived for several hours at room temperature and decomposed completely to **7** in one to two days, in contrast to the amine-stabilized organocopper compounds that decomposed rather smoothly under the same conditions [4–6].

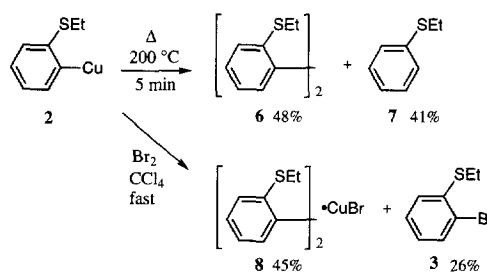
The stability of phenylcopper derivatives is considerably increased by changing the chelating ligand at the 2-position from an ethylthiomethyl to an ethylthio group. The unusual stability, especially against hydrolysis and oxidation, is attributed to a high degree of aggregation in the solid state as well as to the effective steric protection by the fixed sulfane ligand and its electronic effect. The sulfur ligand directly attached to the *ortho*-position allows phenylcopper molecules to take such a structure as to cause the effective Cu–S and Cu–Cu interactions in the solid.

2.2.2. [2-(Ethylthio)phenylcopper]₂ · CuX complexes (**5**)

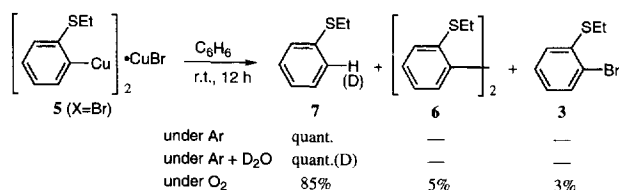
These compounds were purified by recrystallization from benzene to give orange crystals containing solvent molecules. The CuBr and CuI complexes decomposed completely at 130 and 145 °C respectively. In contrast to the salt-free compound, **5** is soluble in the usual organic solvents and the solution has a UV–vis absorption at 390 nm with a shoulder band at around 430 nm. The analysis data show that the soluble phenylcoppers consist of **2** and CuX in a 2:1 ratio. In the XPS spectra, bands attributed to the Br or I atom were observed, in addition to the Cu and S bands.

Compounds **5** are also stable in crystals, but more reactive in solutions than the salt-free organocopper **2**. For example, a significant decomposition was observed after 3 h for solutions in benzene at room temperature. The reactions with various reagents are described in the next section.

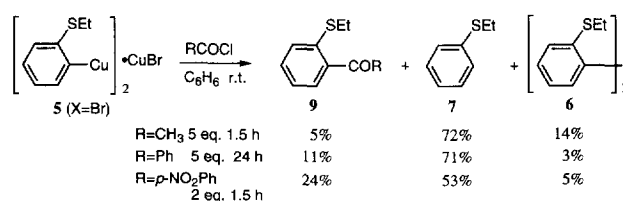
¹H NMR signals due to the ethyl group in **5** were observed as an ABX₃ pattern. The non-equivalence of the methylene protons means that the sulfur ligand coordinates tightly to a copper atom to form the chiral center at the S atom. Another feature is the downfield shift of the signal due to the aromatic proton at the 6-position (δ 8.0). This tendency is generally observed for the aromatic proton *ortho* to the Cu atom in other phenylcopper derivatives [5,6].



Scheme 2.



Scheme 3.



Scheme 5.

2.3. Reactivity of organocopper compounds

The reactivities of these stable organocopper compounds (**2** and **5**) were examined as a model of reactive organocopper intermediates. The results are shown in Scheme 2 for **2** and Schemes 3–5 for **5**.

2.3.1. 2-(Ethylthio)phenylcopper (**2**)

Because of the insolubility of the salt-free compound, **2** is unreactive under various conditions. As described above, the decomposition in benzene suspension to give ethyl phenyl sulfide required a long time. However, the decomposition is considerably accelerated by the addition of a small amount of Lewis acid, such as BF₃·OEt₂ or nitric acid.

The thermolysis of **2** at 200 °C was completed within 5 min to give 48% of the coupling product (**6**) and 41% of the sulfide (**7**), dimerization and hydrolysis products respectively (Scheme 2). This product distribution is typical for the thermal decomposition of the usual organocoppers [1,3,6,11].

The reaction of **2** with bromine in CCl₄ proceeded rapidly at room temperature to afford the CuBr complex of 2,2'-bis(ethylthio)biphenyl (**8**) (45%) and the bromide (**3**) (26%). The latter product, along with CuBr, is formed by the oxidative addition of Br₂ to copper followed by reductive elimination, and the former by the complex formation of the coupling product **6** with CuBr.

The treatment of **2** with methyl iodide, benzyl bromide, phenyl iodide, acetyl chloride, or benzoyl chloride in benzene afforded no reaction products with the electrophiles but **7** as a sole product even though a large excess of reagent was used. Under similar conditions, the ligand-free phenylcopper reacted with acyl chlorides to give the acylated products in more than 50% yield

[12]. This result is attributed to the insolubility as well as the crowded environment around the metal centers in **2**, which prevents the reagent molecules from approaching the reaction centers. Instead hydrolysis takes place.

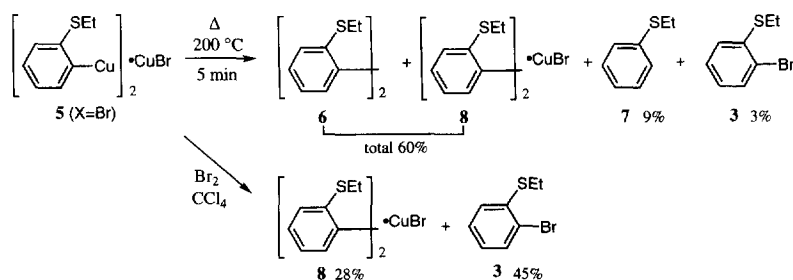
2.3.2. [2-(Ethylthio)phenylcopper]₂ · CuBr (**5** X = Br)

The reactivity of the soluble organocopper was investigated with the use of the CuBr complex (**5** X = Br).

The results of the decomposition of **5** in benzene at room temperature under various conditions are given in Scheme 3. The decomposition under an Ar atmosphere was completed after 12 h to afford the hydrolysis product **7** quantitatively. The addition of D₂O to the reaction mixture allowed the selective deuteration at one of the *ortho*-positions. This indicates that the newly introduced proton in **7** comes from a trace amount of water in the solvent. The decomposition under an oxygen atmosphere gave a small amount of the biphenyl (**6**) and the bromide (**3**) in addition to **7**. The formation of the coupling product as well as **3** means that the radical type coupling is induced by the presence of O₂ to some extent.

The thermolysis at 200 °C afforded mainly the biphenyl (**6**) and its CuBr complex (**8**) together with other minor products (Scheme 4). The ratio of **6** to **8** could not be determined independently because of the fast exchange between the coordinated and uncoordinated biphenyl ligands in solution. The reaction of **5** with Br₂ gave the same products as those of **2**, although the ratio of the two products was different.

The soluble organocopper was also treated with various electrophiles, alkyl halides and acyl chlorides. The reaction with alkyl (aryl) halides never produced the cross-coupling product, but only gave **7**. However, the reaction with acyl halides afforded the acylated prod-



Scheme 4.

ucts, even though the yields were low (Scheme 5), in contrast to the reactions with the salt-free compound. The yield of the coupling product increases in the order acetyl, benzoyl, and *p*-nitrobenzoyl chlorides.

3. Conclusion

The isolation of stable 2-(ethylthio)phenylcopper and its CuX complex indicates that intramolecular sulfane–sulfur ligands are useful for stabilizing unstable species when the ligands are properly arranged in molecules. Although these organocopper compounds are far from reactive, the products from the reactions under some conditions are typical ones for those of the usual organocoppers. The solubility is an important factor in affecting the reactivity, as shown by the fact that the soluble organocopper is more reactive than the salt-free insoluble one. In order to obtain further insight into the stabilizing effect of sulfane ligands, the study of other organocopper compounds carrying intramolecular sulfane ligands at various positions is in progress.

4. Experimental section

4.1. General

Melting points are uncorrected. Elemental analyses were performed by a Perkin–Elmer 240C analyzer. ^1H NMR spectra were measured on a Varian Gemini-300 spectrometer operating at 300.1 MHz. IR spectra were measured on a Hitachi I-2000 spectrometer for chloroform solutions. UV spectra were recorded with a Hitachi U-2000 spectrophotometer for benzene solutions. Mass spectra were measured by a Jeol JMS-DX303 spectrometer. The copper content was determined by flame atomic absorption spectrometry with a Hitachi Z-6100 machine. XPS spectra were collected on a Shimadzu ESCA850 spectrometer with Mg K α radiation and the binding energies were referred to the C 1s signal at 285.0 eV.

1-Bromo-2-(ethylthio)benzene [13] was prepared from sodium 2-bromophenylthiolate and ethyl iodide in an ordinary manner.

1-Bromo-2-(ethylthio)benzene. B.p. 83–85 °C (0.1 mm Hg). ^1H NMR (CDCl_3): δ 1.38 (t, 3H, J 7.4 Hz), 2.96 (q, 2H, J 7.4 Hz), 7.01 (ddd, 1H, J 2.0, 6.9, 8.0 Hz), 7.22 (dd, 1H, J 2.0, 8.0 Hz), 7.27 (ddd, 1H, J 1.3, 6.9, 8.0 Hz), 7.54 (dd, 1H, J 1.3, 8.0 Hz).

4.2. Reaction of 2-(ethylthio)phenyllithium with CuX

4.2.1. Reaction with CuBr

To a solution of 2.00 g (9.21 mmol) of 1-bromo-2-(ethylthio)benzene in 20 ml of dry ether was added

5.9 ml of a 15% butyllithium solution in hexane at -78°C under an argon atmosphere. This solution was allowed to warm to room temperature and stirred for 2 h. To the solution was added 1.32 g (9.21 mmol) of CuBr at -30°C and the whole was stirred for 3 h at room temperature. The resulting brown solid was separated by filtration and washed three times with 10 ml of dry ether. The solvent of the filtrate was evaporated and the residue was extracted with dichloromethane to remove lithium bromide. The extract contained 0.24 g (19%) of 2,2'-bis(ethylthio)biphenyl and 0.09 g (7%) of ethyl phenyl sulfide. The brown solid on the filter was extracted several times with benzene and the combined extracts were evaporated. The residue was immediately recrystallized from benzene–hexane to give 0.45 g (17%) of CuBr-containing 2-(ethylthio)phenylcopper as orange crystals. The insoluble red–brown materials were suspended in benzene and the suspension centrifuged. The upper red–brown layer was collected and the black layer at the bottom removed. The former was practically pure 2-(ethylthio)phenylcopper, 0.70 g (38%). Analytical and physical data of the products are as follows.

[2-(Ethylthio)phenylcopper] $_2$ · CuBr (5 X = Br). Orange crystals containing solvent molecules (benzene). M.P. 121–130 °C (decomp.). ^1H NMR (CDCl_3): δ 1.23 (t, 3H, J 7.4 Hz), 2.94 and 3.39 (AB of ABX $_3$, 2H, J_{AB} 12.6 Hz, $J_{\text{AX}} = J_{\text{BX}}$ 7.4 Hz), 7.17–7.29 (m, 2H), 7.45 (m, 1H), 8.04 (m, 1H). UV (benzene): λ_{max} (log ϵ) 379.5 (3.5), 430 (3.1, sh.) nm. XPS (half-height width and assignment in parentheses): 933.6 (2.1, Cu 2p $_{3/2}$), 164.0 (2.5, S 2p), 69.4 (4.0, Br 3d $_{5/2}$) eV. Anal. Found: C, 37.81; H, 3.58; S, 11.65; Br, 14.57; Cu, 33.8. ($\text{C}_8\text{H}_9\text{CuS}$) $_2$ · CuBr · (C_6H_6) $_{0.30}$. Calc.: C, 37.61; H, 3.51; S, 11.28; Br, 14.06; Cu, 33.53%.

2-(Ethylthio)phenylcopper (2). Red–brown powder. M.P. 112–121 °C (decomp.). XPS 933.6 (2.3, Cu 2p $_{3/2}$), 163.6 (163.5, S 2p). Anal. Found: C, 47.48; H, 4.39; S, 15.57; Cu, 31.0. $\text{C}_8\text{H}_9\text{CuS}$ Calc.: C, 47.86; H, 4.52; S, 15.97; Cu, 31.65.

2,2'-Bis(ethylthio)biphenyl (6). Colorless crystals. M.p. 53.0–54.0 °C (lit., m.p. 54–55 °C) [14]. ^1H NMR (CDCl_3): δ 1.24 (t, 6H, J 7.4 Hz), 2.84 (q, 4H, J 7.4 Hz), 7.17 (dd, 2H, J 1.6, 7.3 Hz), 7.22 (dt, 2H, J 1.7, 6.6 Hz), 7.34 (dt, 2H, J 1.7, 6.6 Hz), 7.37 (m, 2H).

4.2.2. Reaction with CuI

The reaction was similarly carried out as the reaction with CuBr. The products were 2-(ethylthio)phenylcopper (72%), [2-(ethylthio)phenylcopper] $_2$ · CuI (6%), 2,2'-bis(ethylthio)biphenyl (5%), and ethyl phenyl sulfide (3%).

[2-(Ethylthio)phenylcopper] $_2$ · CuI (5 X = I). Recrystallization from benzene gave orange crystals containing solvent molecules. M.p. 135–145 °C (decomp.). ^1H NMR (CDCl_3): δ 1.23 (t, 3H, J 7.4 Hz), 2.94 and 3.39 (AB of ABX $_3$, 2H, J_{AB} 12.6 Hz, $J_{\text{AX}} = J_{\text{BX}}$ 7.4 Hz).

7.17–7.29 (2H, m), 7.45 (1H, m), 8.04 (1H, m). UV (benzene): $\lambda_{\max}$ (log ϵ) 390.0 (3.5) nm. XPS: 933.6 (2.1, Cu 2p_{3/2}), 631.8 (2.0, I 3d_{3/2}), 620.3 (2.0, I 3d_{5/2}), 163.5 (2.4, S 2p). Anal. Found: C, 38.48; H, 3.51; S, 10.19; I, 19.22; Cu, 29.5. (C₈H₉CuS)₂ · CuI · (C₆H₆)_{0.80}. Calc.: C, 38.17; H, 3.51; S, 9.80; I, 19.39; Cu, 29.13%.

4.3. Reactivity of [2-(ethylthio)phenylcopper]₂ · CuBr (5 X = Br)

4.3.1. Decomposition in benzene

The compound (100 mg, 0.35 mmol based on the phenylcopper unit) was dissolved in 2 ml of dry benzene under an argon atmosphere. This solution was stirred at room temperature for 12 h until the orange color of the solution disappeared. After the removal of the insoluble materials by filtration, the filtrate was evaporated. The residue was submitted to preparative TLC and the product, ethyl phenyl sulfide, was identified by NMR spectroscopy. The decomposition in the presence of a trace amount of D₂O gave ethyl phenyl-2*d* sulfide, whose isotopic purity (> 97%) was established by ¹H NMR and mass spectroscopy. ¹H NMR (CDCl₃): δ 1.31 (t, 3H, *J* 7.4 Hz), 2.95 (q, 2H, *J* 7.4 Hz), 7.16 (dt, 1H, *J* 1.6, 7.3 Hz), 7.25–7.37 (m, 3H). Mass (EI) Found: M⁺ 139. C₈H₉DS Calc.: M 139. The decomposition under an oxygen atmosphere was similarly carried out, with 1-bromo-2-(ethylthio)benzene and 2,2'-bis(ethylthio)biphenyl obtained in small amounts together with ethyl phenyl sulfide.

4.3.2. Thermolysis

The compound (100 mg) was heated in a sealed flask under a diminished pressure at 200 °C for 5 min. After cooling, the content was treated with 5 ml of benzene and the insoluble material was removed by filtration. The products were similarly analyzed. The yield of each product is shown in Scheme 4.

4.3.3. Reaction with Br₂

To a suspension of 100 mg of the organocopper compound in 2 ml of CCl₄ was added a CCl₄ solution of Br₂ (62 mg, 0.38 mmol). The whole was stirred for 1 min at room temperature and the black solid was removed by filtration. The filtrate was evaporated and the treatment of the residue with hexane gave [2,2'-bis(ethylthio)biphenyl]bromocopper(I) as a white powder in 28% yield. 1-Bromo-2-(ethylthio)benzene was obtained from the hexane solution in 45% yield.

[2,2'-Bis(ethylthio)biphenyl]bromocopper(I) (**8**). M.p. 109.0–110.5 °C. ¹H NMR (CDCl₃): δ 1.29 (t, 6H, *J* 7.4 Hz), 2.90 and 2.96 (AB of ABX₃, 4H, *J*_{AB} 12.1, *J*_{AX} = *J*_{BX} 7.4 Hz), 7.17 (d, 2H, *J* 7.4 Hz), 7.25–7.34 (m, 2H), 7.36–7.41 (m, 4H). Anal. Found: C, 45.75; H, 4.22. C₁₆H₁₈BrCuS₂: C, 45.99; H, 4.34%. This com-

plex was also obtained by treatment of the biphenyl and CuBr in CH₂Cl₂.

4.3.4. Reaction with an acyl halide

To a solution of 100 mg of the organocopper compound in 2 ml of dry benzene was added an amount of an acyl chloride as follows: acetyl chloride (5 equiv.), benzoyl chloride (5 equiv.), and *p*-nitrobenzoyl chloride (2 equiv.). The solution was stirred for 24 h at room temperature under an argon atmosphere. The products were analyzed similarly.

2-(Ethylthio)acetophenone (**9** R = CH₃). The authentic specimen of this compound was prepared by reaction of 2-(ethylthio)benzoic acid and 2 equiv. of methyl-lithium in THF according to the method described in Ref. [15]. The desired compound was obtained in moderate yield as a colorless oil. ¹H NMR (CDCl₃): δ 1.37 (t, 3H, *J* 7.4 Hz), 2.63 (s, 3H), 2.94 (q, 2H, *J* 7.4 Hz), 7.19 (dt, 1H, *J* 1.6, 7.3 Hz), 7.37 (dd, 1H, *J* 8.1, 1.2 Hz), 7.44 (dt, 1H, *J* 1.6, 7.6 Hz), 7.80 (dd, 1H, *J* 7.8, 1.5 Hz). IR (neat): 1672 cm⁻¹ (C=O). HRMS Found: MH⁺ (FAB) 181.0719. C₁₀H₁₃OS Calc.: MH 181.0687.

2-(Ethylthio)benzophenone (**9** R = Ph). The authentic sample was synthesized by the Friedel–Crafts reaction of 2-(ethylthio)benzoyl chloride in benzene in the presence of AlCl₃ [16]. After the purification the desired compound was obtained as a colorless oil, which crystallized upon standing. M.p. 39.0–41.0 °C. ¹H NMR (CDCl₃): δ 1.24 (t, 3H, *J* 7.4 Hz), 2.88 (q, 2H, *J* 7.4 Hz), 7.26 (dt, 1H, *J* 7.6, 1.0 Hz), 7.36 (dd, 1H, *J* 7.6, 1.0 Hz), 7.40–7.51 (m, 4H), 7.57 (dt, 1H, *J* 7.4, 1.0 Hz), 7.79 (dd, 2H, *J* 8.3, 1.4 Hz). IR (neat): 1666 cm⁻¹ (C=O). HRMS Found: MH⁺ (FAB) 243.0831. C₁₅H₁₅OS Calc.: 181.0844.

2-(Ethylthio)-4'-nitrobenzophenone (**9** R = *p*-NO₂Ph). This compound was separated from the reaction mixture by preparative TLC and recrystallization from hexane–dichloromethane gave the pure material as pale yellow crystals. M.p. 84.0–87.0 °C. ¹H NMR (CDCl₃): δ 1.25 (t, 3H, *J* 7.4 Hz), 2.89 (q, 2H, *J* 7.4 Hz), 7.30 (m, 1H), 7.39 (d, 1H, *J* 7.9 Hz), 7.51 (m, 2H), 7.92 (d, 2H, *J* 8.9 Hz), 8.30 (d, 2H, *J* 8.9 Hz). IR (CHCl₃): 1674 (C=O), 1528 and 1348 (NO₂) cm⁻¹. Anal. Found: C, 62.45; H, 4.48; N, 4.80. C₁₅H₁₃NO₃S Calc.: C, 62.70; H, 4.56; N, 4.87%.

4.3.5. Reaction with other alkyl or aryl halides

The organocopper compound was similarly treated with methyl iodide (5 equiv.) benzyl bromide (5 equiv.), or phenyl iodide (3 equiv.) in benzene. The only product was ethyl phenyl sulfide in each reaction.

4.4. Reactivity of 2-(ethylthio)phenylcopper (**2**)

The decomposition and the reaction with Br₂ of the salt-free organocopper were similarly performed. The products and their yields are shown in Scheme 2.

Acknowledgements

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References

- [1] G. van Koten, in E.W. Abel, F.A. Stone and G. Wilkinson (eds.), *Comprehensive Organometallic Chemistry II*, Vol. 3, Pergamon, Oxford, 1995; G. van Koten and J.G. Noltes, in G. Wilkinson, F.A. Stone and E.W. Abel, *Comprehensive Organometallic Chemistry*, Vol. 2, Pergamon, Oxford, 1984, Chap. 14.
- [2] J.K. Taylor, *Organocopper Reagents*, Oxford University Press, New York, 1994.
- [3] A.E. Jukes, *Adv. Organomet. Chem.*, **12** (1974) 215.
- [4] G. van Koten, A.J. Leusink and J.G. Noltes, *J. Chem. Soc., Chem. Commun.*, (1970) 1107; G. van Koten, A.J. Leusink and J.G. Noltes, *Inorg. Nucl. Chem. Lett.*, **7** (1971) 227.
- [5] G. van Koten, A.J. Leusink and J.G. Noltes, *J. Organomet. Chem.*, **84** (1975) 117; G. van Koten and J.G. Noltes, *J. Organomet. Chem.*, **84** (1975) 129.
- [6] E. Wehman, G. van Koten, M. Knotter, H. Spelten, D. Heijdenrijk, A.N.S. Mak and C.H. Stam, *J. Organomet. Chem.*, **325** (1987) 293.
- [7] G. van Koten and J.T.B.H. Jastrzebski, *Tetrahedron*, **45** (1989) 569.
- [8] A. Camus, N. Marsich, G. Nardin and L. Randaccio, *J. Organomet. Chem.*, **174** (1979) 121; A. Camus and N. Marsich, *J. Organomet. Chem.*, **14** (1968) 441.
- [9] F.E. Ziegler, I. Chliwner, K.W. Fowler, S.J. Kanfer, S.J. Kuo and N.D. Sinha, *J. Am. Chem. Soc.*, **102** (1982) 790.
- [10] S. Toyota, Y. Matsuda, M. Ki and H. Akashi, *Chem. Lett.*, (1995) 31; S. Toyota, Y. Matsuda, S. Nagaoka, M. Ōki and H. Akashi, *Bull. Chem. Soc. Jpn.*, **69** (1996) 3115.
- [11] H. Hashimoto and T. Nakano, *J. Org. Chem.*, **31** (1966) 891.
- [12] H. Gilman and J.M. Straley, *Recl. Trav. Chim. Pays-Bas*, **55** (1936) 821.
- [13] T. Watanabe, A. Hiratsuka, T. Sone and T. Ishihara, *J. Chem. Soc., Chem. Commun.*, (1983) 585.
- [14] D.W. Allen, P.N. Braunton, I.T. Millar and J.C. Tebby, *J. Chem. Soc. C*, (1971) 3454.
- [15] M.J. Jorgenson, *Org. React.*, **18** (1970) 1.
- [16] D.M. McKinnon and K.R. Lee, *Can. J. Chem.*, **66** (1988) 1405.