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## **SYNTHESIS AND PROPERTIES OF SOME 2-(DIMETHYLAMINO)-METHYL-SUBSTITUTED ARYL COPPER COMPOUNDS\***

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### **Summary**

The synthesis and isolation of 2-[(dimethylamino)methyl]phenylcopper and its 5-methyl, 5-methoxy, 5-chloro and 3-chloro derivatives are described. These hydrocarbon-soluble arylcopper compounds are appreciably more thermally stable than phenylcopper (e.g. 2-[(dimethylamino)methyl]phenylcopper decomposes only at 175-185°). They also show improved hydrolytic and oxidative stability.

Lithiation of 1-methoxy-4-[(dimethylamino)methyl]naphthalene with butyllithium occurs at the 5-position. Metathesis of 1-methoxy-4-[(dimethylamino)methyl]-5-lithionaphthalene with cuprous bromide affords the corresponding organocopper compound.

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### **Introduction**

In recent years efforts in organocopper chemistry have mainly been directed to the exploration of the applicability as intermediates in organic synthesis of organocopper compounds and complexes prepared in situ [2-4]. Among the various organocopper compounds reported, very few have been isolated pure. The general low solubility of organocopper compounds and their tendency to form complexes with metal salts [3, 5] formed as by-products in their preparation (e.g.  $MgX_2$ ,  $LiX$ ) hamper the isolation of pure products. The difficulties are illustrated by the report of Costa et al. [6] on the preparation of phenylcopper, following earlier work by Reich in 1923 [7] and by Gilman in 1936 [8].

In general organocopper compounds have limited thermal stability, aryl-

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\* Part X of the series of papers dealing with Group IB Organometallic chemistry [1].

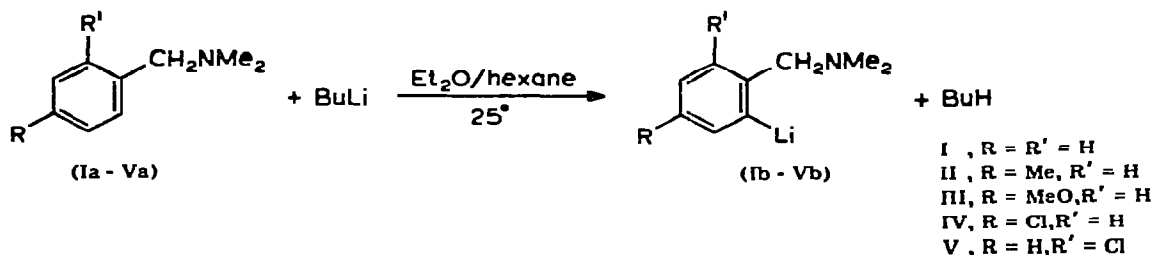
copper compounds (e.g. PhCu stable at room temperature [6]) being more stable than alkylcopper compounds (decomposition above  $-20^{\circ}$  [9]).

In recent years the isolation of new types of arylcopper compounds with improved thermal stability has been described [1a, 1b, 10-12]\*. Introduction of fluorine atoms or of trifluoromethyl substituents in the aryl nucleus of phenylcopper results in greatly increased thermal stability [10], e.g.  $C_6F_5Cu$  m.p.  $210-220^{\circ}$  (dec.). It is noteworthy that Costa and Camus in their extensive research on arylcopper compounds observed that complexation of phenyl-, tolyl- and 2-anisyl-copper [12] with mono- and bi-dentate phosphine ligands does not notably influence the stability of the Cu—C bond [15]. We have attempted to stabilize the Cu—C bond in arylcopper compounds by using an internal (built-in) rather than an external ligand, i.e. by attaching the complexing ligand to the aryl nucleus\*\*, and this paper is concerned with the isolation and properties of stable arylcopper compounds containing the  $Me_2NCH_2$  group as a built-in ligand\*\*\*.

## Results and discussion

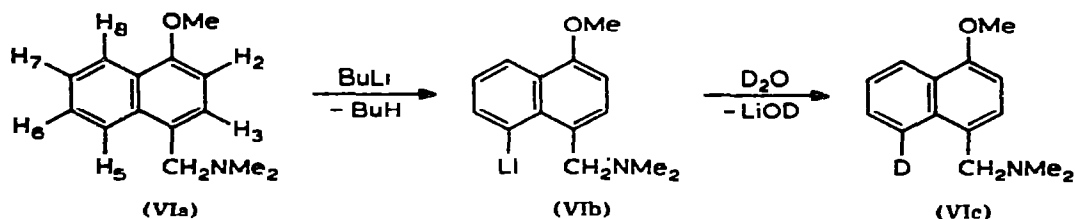
### Preparation of the organolithium starting materials

The  $Me_2NCH_2$ -substituted aryllithium materials Ib-Vb have been prepared via Li—H-exchange reactions of the corresponding arenes with butyllithium [17].



Although a 1/2 molar ratio of arene to butyllithium has been used by Hauser et al. [17], we have observed that the 1/1 reaction of a series of substituted benzylamines Ia-Va with butyllithium results in almost quantitative lithiation (90-100%) at the *ortho*-position<sup>†</sup>, as shown by deuterolysis experiments (see Experimental).

The metalation of 1-methoxy-4-[(dimethylamino)methyl]naphthalene (VIa) with butyllithium could in principle take place at the 2-, 3-, 5- or 8-position as is shown by separate studies of the metalation of 1-methoxynaphthalene [18]



\* For reports on the synthesis of stable alkylcopper compounds see refs. 1c, 11, 13 and 14.

\*\* This principle was first applied for the stabilization of the Cr—C bond by Bähr et al. [16].

\*\*\* For a preliminary account see ref. 1a.

† The isolation and characterization of several of these 2-[(dimethylamino)methyl]phenyllithium compounds has been reported [5].

and 1-[(dimethylamino)methyl]naphthalene [19] with butyllithium. Actually metalation of VIa occurs at the 5-position.

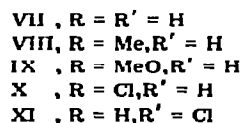
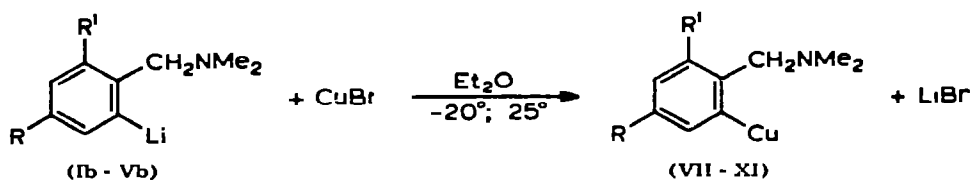
The NMR spectrum of VIa in  $\text{CCl}_4$  shows an aromatic pattern which has been tentatively assigned, on the basis of the results of proton-spin decoupling experiments and by comparison with the patterns found in NMR spectra of other 1,4-disubstituted naphthalene compounds [20], (see Table 1). In this spectrum the low field multiplet belongs to  $\text{H}_5$  and  $\text{H}_8$ , whereas  $\text{H}_2$  and  $\text{H}_3$  appear as a doublet of doublets.

Deuterolysis of the metalated compound gave a naphthalene derivative which contained deuterium (64%) at the 5- or 8-position as deduced from its NMR spectrum in  $\text{CCl}_4$ . In this spectrum the intensity of several peaks in the  $\text{H}_{5,8}$  multiplet was strongly reduced. The approximate peak area ratios appeared to be 1.36 ( $\text{H}_{5,8}$ )/2( $\text{H}_{6,7}$ )/1( $\text{H}_2$ )/1( $\text{H}_3$ )/3( $\text{OCH}_3$ )/2( $\text{NCH}_2$ )/6( $\text{NCH}_3$ ), which excludes metalation at the 2- or 3-position.

The deuterated naphthalene derivative obtained upon deuterolysis of the corresponding organocopper compound, XII\*, with  $\text{CH}_3\text{COOD}$  contained 93% deuterium at the 5- or 8-position. The  $\text{H}_{5,8}$  multiplet was reduced to a doublet of doublets which confirms that metalation had occurred exclusively at only *one* position. Since the  $\text{CH}_2\text{NMe}_2$  group is a better directing group for the metalation than the OMe group [17], it seems plausible to conclude that metalation of VIa with butyllithium gives the 5-lithiated compound VIb as the major product.

#### Synthesis of 2-[(dimethylamino)methyl]phenylcopper compounds

2-[(Dimethylamino)methyl]phenylcopper as well as its 3- or 5-substituted methyl, methoxy and chloro derivatives were synthesized via metathesis of the corresponding organolithium compounds with cuprous bromide\*\*, using diethyl ether as a solvent.



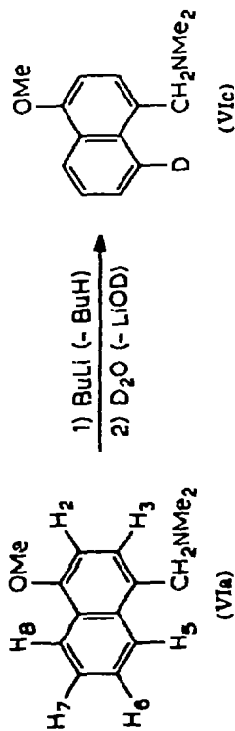
These benzene-soluble organocopper compounds were isolated as yellow- to green-coloured crystalline solids in 25-66% yield after recrystallization from benzene or ethers.

The 4-(dimethylamino)methyl-substituted naphthylcopper compound (XII) was synthesized analogously:

\* Obtained from the reaction of the metalated reaction mixture (VIa + BuLi) with cuprous bromide.

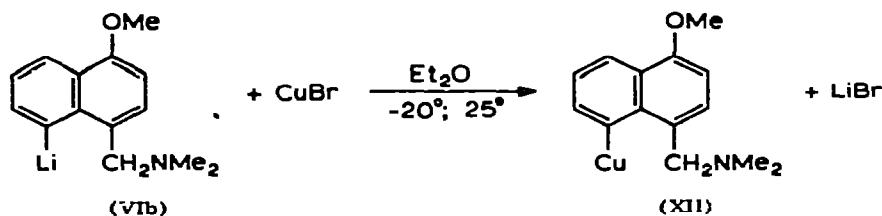
\*\* From the 2/1 reaction of the organolithium compound Ib with cupric bromide pure VII was isolated in 47% yield (calculated on the amount of  $\text{CuBr}_2$  used). For a discussion of the relative merits of the use of cuprous or cupric bromide as starting material see ref. 5.

TABLE 1

NMR SPECTRA (IN  $CCl_4$ ) OF NON-DEUTERATED AND DEUTERATED 1-METHOXY-4-[(DIMETHYLAMINO)METHYL]NAPHTHALENE (VI)

Compound	$\delta$ (ppm; TMS internal)						$D^c$ (%)
	$NCH_3$	$NCH_2$	$OCH_3$	$H_2^d$	$H_3^d$	$H_{6,7}^b$	
VIa	2.14 (s, 6)	3.60 (s, 2)	3.78 (s, 3)	6.47 (d, 1)	7.00 (d, 1) <sup>d</sup>	7.38 (m, 2)	8.16 (m, 2)
Irradiation at $H_{5,8}$						7.38 (2 x d) <sup>e, f</sup>	
Irradiation at $H_{6,7}$							8.16 <sup>g</sup>
Vic h	2.16 (s, 6)	3.61 (s, 2)	3.81 (s, 3)	6.49 (d, 1)	7.11 (d, 1) <sup>d</sup>	7.38 (m, 2)	8.15 (m, 1.36)
Vic h, i	2.16 (s, 6)	3.60 (s, 2)	3.80 (s, 3)	6.48 (d, 1)	7.10 (d, 1) <sup>d</sup>	7.38 (m, 2)	8.18 (m, 1.07) <sup>j</sup>

<sup>a</sup> Tentatively assigned as  $H_2$  and  $H_3$ , respectively. <sup>b</sup> Position of the centre of the multiplet. <sup>c</sup> Calcd. for substitution of 1 D for 1 H. The peak areas of the  $OCH_3$ ,  $NCH_2$  and  $NCH_3$  protons are used as internal standards. <sup>d</sup>  $J_{2,3}$  7.9 Hz. <sup>e</sup>  $J_{6,7}$  7.6 Hz. <sup>f</sup> AB pattern with a very small  $\Delta\delta$ . <sup>g</sup> It has been possible to observe separate singlets for  $H_5$  and  $H_8$  but  $\Delta[\delta(H_5)-\delta(H_8)]$  is very small. <sup>h</sup> Tentatively assigned to the 5-D derivative. <sup>i</sup> Obtained upon deuteration of the organocopper compound (XII). <sup>j</sup>  $J_{7,8}$  6.9;  $J_{6,8}$  3.0 Hz.



This yellow compound, which is almost insoluble in hydrocarbon and ether solvents, was isolated in 50% yield.

The formation of 2-(dimethylamino)methyl-substituted arylcopper compounds VII-XII in these reactions was established by elemental analysis (correct C, H, N, Cu and O analyses, see Table 2), by IR spectroscopy (correct aromatic substitution pattern) and by NMR spectroscopy (correct resonance patterns). As an additional check for the site and degree of metalation of the aromatic ring, the organocopper compounds were treated with D<sub>2</sub>O. The deuterolysis products formed were compared with those obtained upon deuterolysis of the corresponding organolithium compounds. The same *ortho*-deuterated benzyl-dimethylamines were isolated (see Table 3). The naphthylcopper compound XII showed a surprisingly low reactivity towards deuterolysis. After three weeks almost no reaction had occurred. However, when XII was treated with CH<sub>3</sub>COOD rapid deuterolysis took place, to give the deuterated product VIc (93% D; see Table 1) which was isolated in 76% yield.

#### Properties of the arylcopper compounds VII-XII

Decomposition temperatures of the solid compounds VII-XII were determined by heating samples in capillary tubes in a N<sub>2</sub> atmosphere at a rate of 5°/min\*. The compounds decompose into black tars at 110-210° without melting (see Table 2).

It appears that as compared with phenylcopper\*\* (slow decomposition at 25° [6]), introduction of the (dimethylamino)methyl group increases the thermal stability considerably. Introduction of other substituents may increase or decrease thermal stability. Heating of VII at 131-133° during 5 h caused almost no decomposition. This was concluded from the isolation of (2-deuteriobenzyl)dimethylamine in about 90% yield after deuterolysis of the heated sample.

With the exception of the 3-chloro and 5-chloro derivatives the organocopper compounds are stable in boiling benzene. No decomposition products were detected in the NMR spectrum of a benzene-*d*<sub>6</sub> solution of VII which had been heated at 80° for 4 h.

The unsubstituted (VII) and 3-chloro substituted (XI) derivatives are very soluble in benzene and show a moderate solubility in ether and pentane. These

\* TGA analysis of 5-methyl-2-[(dimethylamino)methyl]phenylcopper (5-MeRCu): conditions: 2.372 mg as a powder, platinum pan used, flow rate of N<sub>2</sub> gas 32 ml/min, heating rate 5°/min; results, weight loss starts at 170°, at 215° 50% loss of weight and at 240° 100% loss of weight (calculated on the amount of 5-MeR).

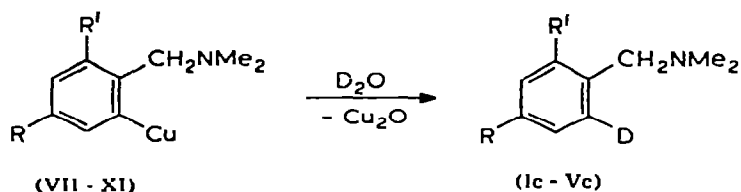
\*\* The decomposition temperature of phenylcopper depends very much on the purity of the sample. Very pure phenylcopper decomposes at about 100° [6].

TABLE 2  
 PHYSICAL AND ANALYTICAL DATA FOR THE 2-[(DIMETHYLAMINO)METHYL]PHENYL COPPER COMPOUNDS VII-XII

Compound	Yield (%)	Colour	Dec. temp. <sup>a</sup> (°C)	Analysis, found (calcd) (%)				Mol. wt. <sup>b</sup> found (calcd.) <sup>c</sup>
				C	H	Cu	N	
VII RCu	44	Yellow	175-185	54.9 (54.66)	6.3 (6.12)	31.6 (32.13)	7.0 (7.08)	792, n = 4.0; A (197.5)
VIII (5-MeR)Cu	56	Yellow	170-210	56.5 (56.72)	6.7 (6.66)	29.8 (30.00)	6.4 (6.81)	863, n = 4.1; B (211.5)
IX (5-MeOR)Cu	38	Yellow-green	140-145 (fast 170)	52.6 (52.73)	6.3 (6.20)	27.8 (27.00)	6.0 (6.15)	921, n = 4.0; A (227.8)
X (5-CIR)Cu	41	Green	140-142	46.6 (46.56)	4.9 (4.78)	27.5 (27.37)	5.9 (6.03)	15.2 (15.27)
XI (3-CIR)Cu	25	Yellow	108-109	46.5 (46.56)	4.6 (4.78)	27.2 (27.37)	5.0 (6.03)	15.3 (15.27)
XII (Naphth)Cu	50	Yellow	162-165	55.8 (50.52)	5.7 (5.80)	21.7 (22.88)	5.2 (5.04)	e f

<sup>a</sup> Determined in a capillary under N<sub>2</sub> atm. <sup>b</sup> In benzene; A by cryometry (1.5°); B by ebulliometry (≈ 80°). <sup>c</sup> Calcd. for the monomer (n = 1). <sup>d</sup> No reliable results were obtained by method B, most probably as a result of slow decomposition of the solution. <sup>e</sup> See ref. 22. <sup>f</sup> Very insoluble.

TABLE 3

DEUTEROLYSIS OF THE ARYL COPPER COMPOUNDS VII-XI AT ROOM TEMPERATURE<sup>a</sup>

Compound	Reaction time (h)	Solvent	Yield of RD (%) <sup>b</sup>
VII, R = R' = H	66	Ether	90
VIII, R = Me, R' = H	140	Benzene	63
IX, R = MeO, R' = H	140	Ether	45
X, R = Cl, R' = H	264	Benzene	74
XI, R = H, R' = Cl	30	Benzene	80

<sup>a</sup> For a discussion of the deuteration of the naphthylcopper compound XII see text. <sup>b</sup> The % D in deuterated amines, isolated from these deuteration reactions, was at least 95%. The yield of RD has been determined by GLC using decane as an internal standard.

compounds are also soluble in pyridine, acetonitrile and dioxane without forming complexes with these solvents. The 5-substituted derivatives are less soluble, while the naphthylcopper compound XII is very insoluble in the solvents mentioned.

In contrast to the high sensitivity towards hydrolysis and oxidation of phenylcopper [6], *ortho*-, *meta*- and *para*-tolylcopper [12], perhalogenated phenylcopper [10] and 4-(dimethylamino)phenylcopper [5], the solid organo-copper compounds VII-XII appeared to be surprisingly stable in air. This allows their handling in the atmosphere for a limited period of time. The unchanged IR spectrum and decomposition point of a sample of the 5-methyl derivative, after 48 h exposure to the atmosphere, as well as the isolation of (4-methyl-2-deuteriobenzyl)dimethylamine as the single product from subsequent deuteration of the exposed sample, support this view. However, in solution the oxidative stability of the arylcopper compounds VII-XII is comparable with that of the other arylcopper compounds mentioned above.

## Experimental (with Mr C.A. Schaap)

### General

All reactions were carried out in an atmosphere of dry oxygen-free nitrogen. Solvents were carefully purified, dried, and distilled under nitrogen before use.

<sup>1</sup>H NMR spectra, which were run by Mrs. L. van der Grift-Veldstra, were recorded on a Varian Associates HA-100 NMR spectrometer. IR spectra, which were run by Mrs. H. de Ridder-Alberda and Mrs. G.M. Bijlsma-Kreuger, were recorded on a Grubb-Parsons Spectromaster. Elemental analyses were carried out under the supervision of Mr. W.J. Buis in the Analytical Department of this Institute.

*Metalation of the tertiary benzylamines Ia-Va*

The following standard procedure was used. Tertiary benzylamine (10 mmol) was added at room temperature to a solution of 10 mmol of butyllithium (2M solution in hexane) in ether/hexane (50 ml). The reaction mixture was stirred at room temperature until Gilman test II [21] for the presence of butyllithium was negative.

*Reaction of the 2-[(dimethylamino)methyl]phenyllithium compounds Ib-Vd with D<sub>2</sub>O*

The solution or suspension of the lithiated benzyldimethylamine was added in portions with stirring to a cold (0°) mixture of 50 ml of diethyl ether and 2 ml of deuterium oxide (D<sub>2</sub>O). This mixture was stirred for 2 h and then filtered. The filtrate was dried over MgSO<sub>4</sub>, filtered and analyzed by GLC [% yield of (2-deuteriobenzyl)dimethylamine]. The ether solution was extracted with 2N HCl. The water layer was extracted with ether and then made alkaline with solid sodium hydroxide. The resulting solution was extracted with ether. The ether layer was dried over MgSO<sub>4</sub>, filtered and concentrated, yielding the pure (2-deuteriobenzyl)dimethylamine. NMR spectroscopy (in CCl<sub>4</sub>) gave the amount of D (see below), while IR spectroscopy revealed that exclusively 2-deuterated benzylamines were present (substitution pattern of the aromatic ring in the 830-690 cm<sup>-1</sup> region). Reaction time for the metalation, yield of RH/RD, % D; Ia: 24, 90, 100; IIa: 66, 86, 80; IIIa: 66, 90, 96; IVa: 24, 75, 97; Va: 24, 80, 90.

*Reaction of the 2-[(dimethylamino)methyl]phenylcopper compounds VII-XI with D<sub>2</sub>O*

1 to 5 Mmol of the appropriate organocopper compound VII-XI, dissolved or suspended in Et<sub>2</sub>O or benzene (10 ml) and 1 ml of D<sub>2</sub>O, was stirred at room temperature until no further change was observed. The cuprous oxide formed was filtered off and the filtrate was analyzed by GLC [% of (2-deuteriobenzyl)-dimethylamine, see Table 3]. The isolation and purification of the benzylamines was carried out as described above. The resulting (2-deuteriobenzyl)dimethylamines were identical with the corresponding samples obtained from the benzylamine/BuLi/D<sub>2</sub>O route (by NMR and by IR spectroscopy).

*Synthesis of 2-[(dimethylamino)methyl]phenylcopper (VII)*

*Addition of CuBr to RLi (Ib).* Solid CuBr (60 mmol) was slowly added (in about 1½ h) at -20° to a freshly prepared suspension of 2-[(dimethylamino)-methyl]phenyllithium\* (Ib) (60 mmol) in ether (160 ml). Initially a black solid was formed, followed by the precipitation of a white solid (R<sub>2</sub>CuLi), the colour of which slowly turned yellow (RCu) when the RLi/CuBr ratio decreased from 2 to 1. The mixture was stirred at -20° for 1 h, warmed to room temperature, then stirred for another 2 h. The yellow-green solid was filtered off and extracted with cold ether until a test for the presence of Br<sup>-</sup> (from LiBr) in the filtrate (vide infra) was negative.

The yellow-green solid was dried in vacuo and subsequently extracted

\* Stirring during the reaction of Ia with BuLi is essential.



with ether (4 × 80 ml; removal of Cu<sup>0</sup>). Concentration of this ether extract by low temperature distillation at diminished pressure (LTD) afforded yellow crystalline VII which was filtered off, washed with pentane and then dried in vacuo. Physical data, see Table 2; IR spectrum, see Fig. 1; NMR and mass spectrum, see ref. 22.

*Addition of CuBr<sub>2</sub> to RLi (Ib).* Solid CuBr<sub>2</sub> (15 mmol) was added at -40° in about 3 h to a solution of 30 mmol of (Ib) in Et<sub>2</sub>O (125 ml). The resulting mixture was stirred at -40° for 2 h and at 0° for 1½ h. During the reaction the organocopper compound VII precipitated. For the isolation and purification of VII (47% yield), vide supra, (Found: Cu, 31.8. C<sub>9</sub>H<sub>12</sub>CuN calcd.: Cu, 32.13%.)

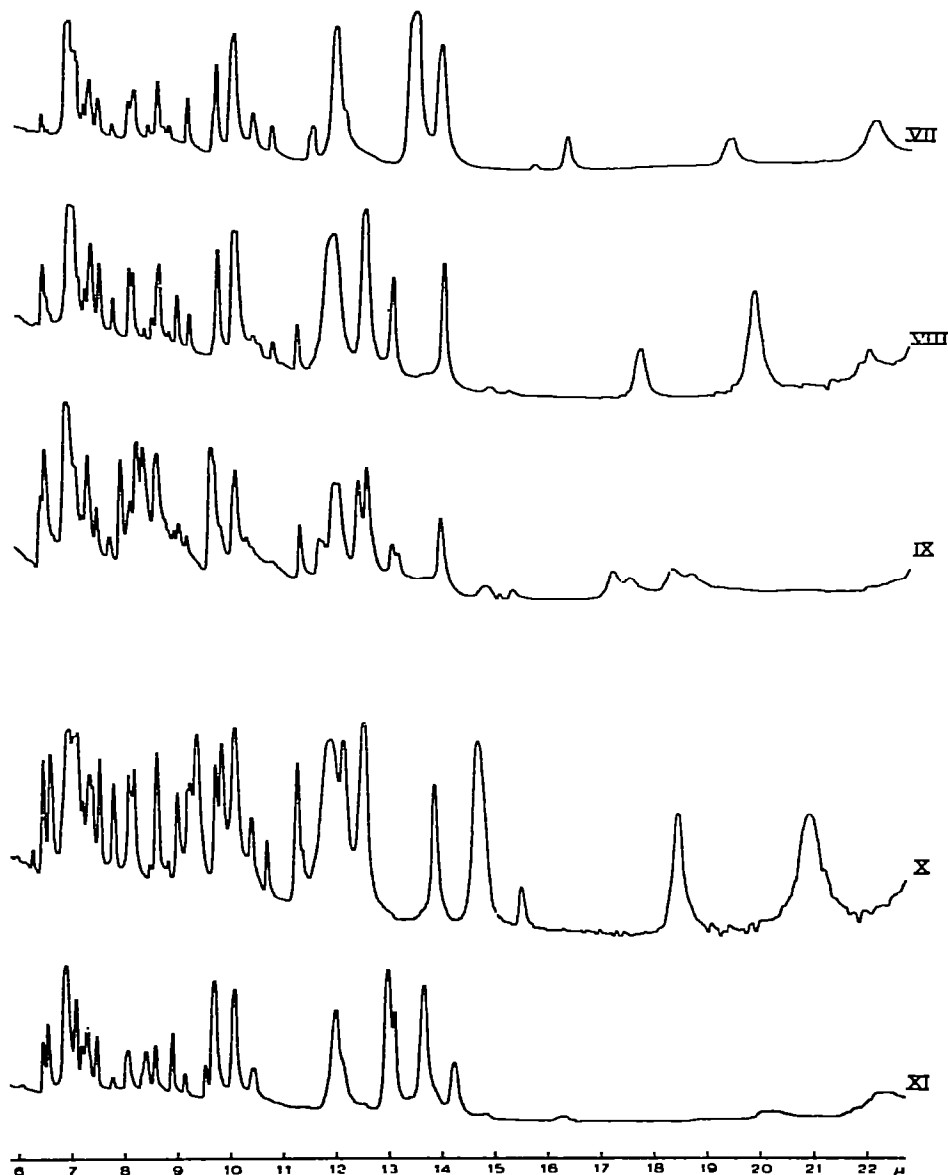


Fig. 1. IR spectra (nujol) of the 2-[(dimethylamino)methyl]phenylcopper compounds VII-XI.

IR spectrum, identical to that of a sample of VII, obtained via the CuBr/RLi route.

*Synthesis of 3-chloro-2-[(dimethylamino)methyl]phenylcopper (XI)*

Solid cuprous bromide (20 mmol) was added at  $-20^{\circ}$  to a red solution of Vb. During the reaction a black solid separated. After stirring for an additional hour yellow XI precipitated. The solids were filtered off and washed with cold ether (removal of LiBr). The residue was extracted with benzene. The benzene extract upon concentration yielded a yellow solid XI which was recrystallized from benzene/pentane. Physical data, see Table 2; IR spectrum, see Fig. 1; NMR spectrum, see ref. 22.

*Synthesis of the 5-substituted 2-[(dimethylamino)methyl]phenylcopper compounds VIII-X*

Solid cuprous bromide was added at  $-20^{\circ}$  to a solution of the appropriate organolithium compound (1/1 molar ratio). The mixture was stirred at  $-20^{\circ}$  for 2 h, warmed to room temperature (1 h), and stirred at room temperature for an additional 2 h. The precipitate was filtered off and extracted with Et<sub>2</sub>O (removal of LiBr). The remaining solid was recrystallized from benzene.

Physical data of VIII-X, see Table 2; IR spectra, see Fig. 1; NMR (of VIII-X) and mass spectra (of VIII), see ref. 22.

*Synthesis of 1-methoxy-4-[(dimethylamino)methyl]-5-cuprionaphthalene (XII)*

A mixture of 20 mmol of butyllithium and 20 mmol of 1-methoxy-4-[(dimethylamino)methyl]naphthalene (VIa) was stirred at room temperature for 24 h.

The resulting purple suspension of VIb in ether was cooled to  $-20^{\circ}$  and 20 mmol of solid cuprous bromide were slowly added. The yellow suspension was stirred at  $-20^{\circ}$  for 2 h, warmed to room temperature, then stirred for another 1 h. The precipitate was filtered off and extracted with ether. The residue was suspended in benzene and stirred during 2 h. Filtration afforded yellow XII. The filtrate contained a small amount of a very finely divided black solid. Physical data, see Table 2.

*Reaction of XII with CH<sub>3</sub>COOD.* Solid XII (2.7 mmol) was added to a mixture of benzene (15 ml) and CH<sub>3</sub>COOD (2 ml 10 N in D<sub>2</sub>O) and stirred for 24 h. The resulting mixture was made alkaline with 6N NH<sub>4</sub>OH solution, stirred for 1 h, and filtered. The precipitate was extracted with benzene and with 6N NH<sub>4</sub>OH (2 × 5 ml). The water layer was extracted with benzene. The combined benzene extracts were dried. GLC analysis indicated the presence of 2.07 mmol (67%) of the amine. The amine was purified by an acid/base work-up procedure (see above) using ether as a solvent. The resulting oil appeared to be pure 1-methoxy-4-[(dimethylamino)methyl]-5-deuterionaphthalene (VIc) (see Table 1).

**Acknowledgement**

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## References

- 1 a. Part I: G. van Koten, A.J. Leusink and J.G. Noltes, *Chem. Commun.*, (1970) 1107;
- b. Part II: G. van Koten, A.J. Leusink and J.G. Noltes, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 227;
- c. Part III: G. van Koten and J.G. Noltes, *J. Chem. Soc., Chem. Commun.*, (1972) 59;
- d. Part IV: G. van Koten and J.G. Noltes, *ibid.*, (1972) 452;
- e. Part V: J.M. Guss, R. Mason, J. Sofofte, G. van Koten and J.G. Noltes, *ibid.*, (1972) 446;
- f. Part VI: J.M. Guss, R. Mason, K.M. Thomas, G. van Koten and J.G. Noltes, *J. Organometal. Chem.*, 40 (1972) C79;
- g. Part VII: G. van Koten and J.G. Noltes, *J. Chem. Soc., Chem. Commun.*, (1972) 940;
- h. Part VIII: A.J. Leusink, G. van Koten and J.G. Noltes, *J. Organometal. Chem.*, 56 (1973) 379;
- i. Part IX: A.J. Leusink, G. van Koten, J.W. Marsman and J.G. Noltes, *J. Organometal. Chem.*, 55 (1973) 419.
- 2 G.H. Posner, *Organic Reactions*, Vol. 19, Wiley, New York, 1972, p. 2; 1974, to be published
- 3 J.F. Normant, *Syn.*, (1972) 63.
- 4 G. Bähr and P. Burba, in Houben-Weyl (Eds.), *Organo-Kupfer Verbindungen, Methoden der Organischen Chemie*, Vol. 13/1, 1970, p. 747.
- 5 G. van Koten and J.G. Noltes, *J. Organometal. Chem.*, to be published.
- 6 G. Costa, A. Camus, L. Gatti and N. Marsich, *J. Organometal. Chem.*, 5 (1966) 568.
- 7 R. Reich, *C. R. Acad. Sci.*, 177 (1923) 322.
- 8 H. Gilman and J.M. Straley, *Rec. Trav. Chim. Pays-Bas.* (1936) 821.
- 9 K.H. Thiele and J. Kohler, *J. Organometal. Chem.*, 12 (1968) 225.
- 10 A. Cairncross and W.A. Sheppard, *J. Amer. Chem. Soc.*, 93 (1971) 247; A. Cairncross, H. Omura and W.A. Sheppard, 93 (1971) 248.
- 11 A. Cairncross and W.A. Sheppard, *J. Amer. Chem. Soc.*, 90 (1968) 2186.
- 12 A. Camus and N. Marsich, *J. Organometal. Chem.*, 14 (1968) 441.
- 13 M.F. Lappert and R. Pearce, *J. Chem. Soc., Chem. Commun.* (1973) 24.
- 14 H. Schmidbauer, J. Adlkofer and W. Buchner, *Angew. Chem.*, 85 (1973) 448.
- 15 G. Costa, A. Camus, N. Marsich and L. Gatti, *J. Organometal. Chem.*, 8 (1967) 339; A. Camus and N. Marsich, *J. Organometal. Chem.*, 21 (1970) 249.
- 16 G. Bähr and H. Zohm, *Angew. Chem.*, 75 (1963) 94.
- 17 E.g., F.N. Jones and C.R. Hauser, *J. Org. Chem.*, (1962) 4389; K.P. Klein and C.R. Hauser, *J. Org. Chem.*, 32 (1967) 1479.
- 18 D.A. Shirley and C. Fong Cheng, *J. Organometal. Chem.*, 20 (1969) 251.
- 19 R.L. Gay and C.R. Hauser, *J. Amer. Chem. Soc.*, 89 (1967) 2297.
- 20 E.g., W. Brügel, *Nuclear Magnetic Resonance Spectra and Chemical Structure*, Vol. 1, Academic Press, New York, 1967.
- 21 G.E. Coates and K. Wade, *Organometallic Compounds*, Vol. 1, The Main Group Elements, 3rd ed., Methuen, London, 1967, p. 31.
- 22 G. van Koten and J.G. Noltes, *J. Organometal. Chem.*, 84 (1975) 129.