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SELECTIVITY IN ALLYLIC SUBSTITUTIONS WITH ORGANOMETALLICS THROUGH NEIGHBOURING COORDINATION. SYNTHESIS AND REACTIONS OF COPPER(I) π-COMPLEXES WITH 2-ALLYLOXYBENZOTHIAZOLES *

VINCENZO CALÒ *, LUIGI LOPEZ and GIANNANGELO PESCE
Istituto di Chimica Organica, Università di Bari, Via Amendola, 173 70126 Bari (Italy)

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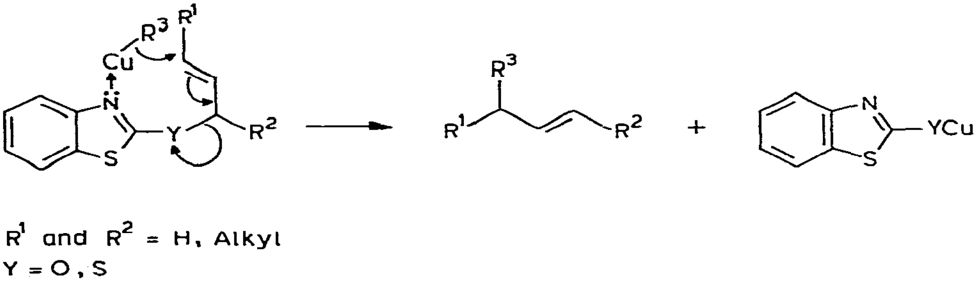
Summary

2-Allyloxybenzothiazoles react with CuBr to give stable Cu^I π-complexes. These complexes undergo nucleophilic attack by organomagnesium compounds to give olefins with very high regio- and stereo-specificity.

Regio- and stereo-chemical control in allylic substitutions with organometallic reagents in order to achieve selective C—C coupling is still a problem for chemists [2]. Utilizing the fact that selectivity in some organometallic reactions can be improved through anchimeric coordination [3—5], we have discovered a number of highly selective organometallic reactions in which preliminary coordination of an allylic benzothiazole derivative at the organometallic reagent, by bringing reacting centers into close proximity, leads to high positional selectivity in a C—C coupling process [6—7] (Scheme 1).



SCHEME 1

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* Part of this work has been reported in preliminary form at the 2nd European Symposium on Organic Chemistry [1].

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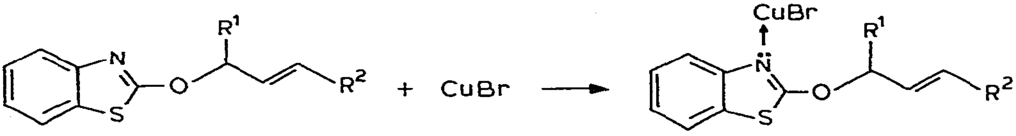
We describe below the synthesis of stable copper(I) π-complexes with 2-allyloxybenzothiazoles and their reactions with organomagnesium compounds.

Results

Addition of a 2-allyloxybenzothiazole, **2a, b**, to a stirred equimolecular suspension of CuBr in THF at room temperature afforded after 3—6 h a precipitate of a stable light-grey powder in high yield. The products, formulated as **3a, b** (Scheme 2), show the well known [8] insolubility exhibited by the copper(I) halides olefin complexes with a copper/ligand ratio 1/1. In contrast, addition of a 2-allylthiobenzothiazole to CuBr does not give any stable, isolable complex.



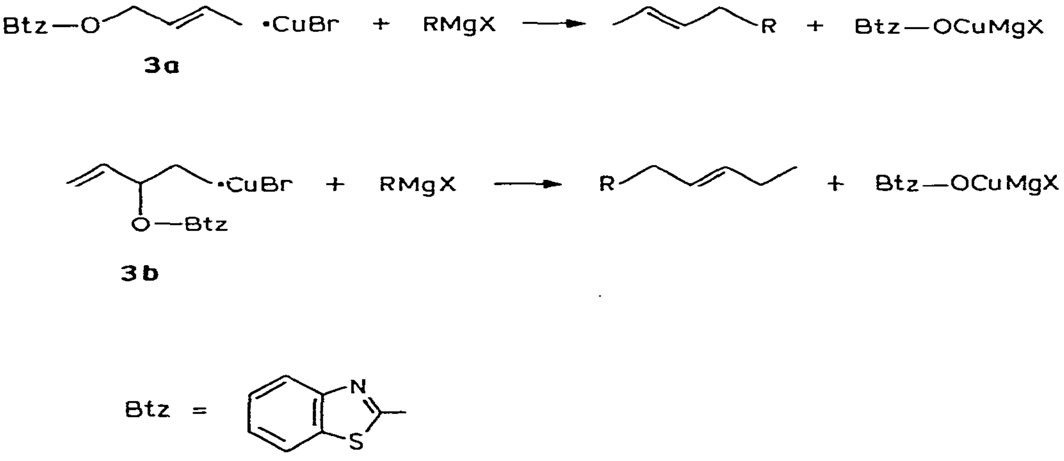
2a.b

3a.b

$2a, R^1 = H; R^2 = CH_3$
$2b, R^1 = C_2H_5; R^2 = H$

SCHEME 2

The complexes **3a, b** react readily at 0°C with equimolecular amounts of various Grignard reagents with very high regio- and stereo-specificity, the positional selectivity of the nucleophile depending on the nature of the substituents on the three allyl carbon atoms. Whereas **3a** suffers only allylic attack, with full preservation of the double bond geometry, **3b** react entirely by an S_N2' process to give exclusively *E*-alkenes:

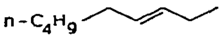
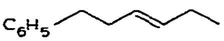
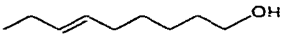
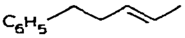


SCHEME 3

The results are shown in Table 1.

TABLE 1

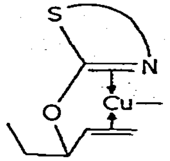
REACTION OF 2-ALLYLOXYBENZOTHIAZOLE-Cu^I π-COMPLEXES WITH GRIGNARD REAGENTS

Complex	Organomagnesium compound	Product b.p. (°C/Torr)	Yield (%) [a]
3b	n-C_4H_9MgBr	 147—148 (lit. [9] 147.4/750)	95 [b]
3b	$C_6H_5CH_2MgCl$	 100—102/15 (lit. [10] 102/15)	70 [c]
3b	$ClMgCH_2(CH_2)_2CH_2OMgBr$ [11]	 80—82/0.2 (lit. [12] 76—84/0.2)	87
3a	$C_6H_5CH_2MgCl$	 77—78/10 (lit. [13] 203—204)	65 [c]
3a	n-$C_8H_{17}MgBr$	 70/2 (lit. [14] 68—75/2)	85

[a] Isolated yield by short column chromatography (silica gel-hexane) unless otherwise indicated. [b] Determined by GLC. [c] Substantial amounts of 1,2-diphenylethane are present in the product.

Discussion

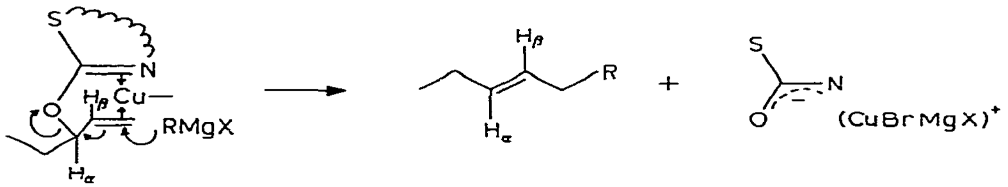
The results indicate the importance of coordination phenomena in the C—C coupling process, and knowledge of the structures of the complexes should be a valuable aid to understanding the regio- and stereo-selectivity observed in the reactions with organomagnesium compounds. Unfortunately, owing to their low solubility, the structures of 3a, b can be elucidated, tentatively, only on the basis of the infrared spectra [8,15]. For example the IR spectrum of 3b shows both a lowering of C=C and C=N stretching frequencies (C=C from 1645 cm^{-1} in the free ligand to 1620 cm^{-1} in the complex and C=N from 1560 and 1530 cm^{-1} to 1540 and 1505 cm^{-1}, respectively). In addition the transverse CH deformation of the terminal vinyl group are shifted from 985 and 900 cm^{-1} to 970 and 885 cm^{-1}, respectively. The data imply that the copper(I) is complexed between the C=N and C=C double bonds, so that 2a, b behave as bidentate ligands. A similar pattern in the frequency shifts is shown by complex 3a. Although IR data do not adequately define the structure of 3a, b, some provisional conclusions can be drawn. It is known [16] that owing to steric effects, particularly stable among copper(I) π-complexes with dienes, are those formed from 1,5-dienes, such as 1,5-cyclooctadiene (COD) in which the boat-shaped COD acts as a bidentate ligand. In our complexes both C=N and C=C



3b

bonds are in a 1,5 relationship, and the metal is probably inserted between these bonds which lie one upon the other. Thus **3b** can be tentatively described as shown.

The steric requirements of these complexes strongly influence the positional selectivity of the nucleophile in the C—C coupling. Moreover the stereoselectivity observed in the S_N2' substitutions suggests a lack of conformational mobility in the transition state so that a highly ordered reaction pathway is followed. As an explanation for the exclusive formation of *E* isomers from the homoallylic reaction of **3b** with Grignard reagents we suggest that in the complex **3b** the pro-olefinic hydrogens H_α and H_β are in an anti relationship, and consequently the nucleophilic attack of RMgX gives only the *E* olefin, as depicted in Scheme 4.



SCHEME 4

We are preparing more-soluble copper(I) complexes and studying the behavior of the ligands toward other transition metals. However the ready availability of the starting ligands and the simplicity of the experimental procedures render this method attractive for regio- and stereo-controlled olefin syntheses.

Experimental

The 2-allyloxybenzothiazoles **2a, b** were synthesized by reaction of potassium allyloxide with 2-chlorobenzothiazole in dry ethyl ether, as previously described [7]. The stereochemical purity of the reaction products was checked by capillary GCL (3% SP 2100 on 100/120 Supelcoport, 50 mt.). The boiling points of the olefins were determined with a Kugelrohr apparatus.

2(1-Penten-3-yloxy)benzothiazole-CuBr complex (3b)

To CuBr (0.28 g, 0.2 mol) suspended in 10 ml of dry THF was added 2(1-penten-3-yloxy)benzothiazole (0.45 g, 0.2 mol). After 6 h stirring at room temperature, the light grey precipitate (0.64 g, 86% yield) was filtered off and dried under vacuum: m.p. 118—122°C (dec.). Analysis, Found: C, 39.20; H, 3.60; N, 3.78; Br, 23.0; Cu, 18.2. $C_{12}H_{13}BrCuNOS$ (362.72) calcd.: C, 39.73; H, 3.61; N, 3.87; Br, 22.03; Cu, 17.5%.IR (KBr pellet) 1620 (C=C); 1540 and 1505 (C=N); 970 and 885 cm^{-1} ($CH=CH_2$). The free ligand **2b** shows bands at 1645 (C=C); 1560 and 1530 (C=N); 985 and 900 cm^{-1} ($CH=CH_2$). The complex is stable for months if stored in a well-stoppered bottle, and is insoluble in organic solvents.

2(2-Buten-1-yloxy)benzothiazole-CuBr complex (3a)

This complex was obtained by the same procedure starting from 2a. Yield 85%, m.p. 123—125°C (dec.). Analysis. Found: C, 37.40; H, 3.20; N, 3.92; Br, 23.82; Cu, 18.9. $C_{11}H_{11}BrCuNOS$ (348.71) calcd.: C, 37.88; H, 3.18; N, 4.01; Br, 22.91; Cu, 18.2%. IR (KBr pellet): 1540 and 1505 (C=N); 930 cm^{-1} (CH=CH). Free ligand. IR: 1670, 1560, 1530 and 965 cm^{-1}. ^1H NMR (CCl_4) δ: 1.77—1.83 (m, 3 H); 4.97—5.03 (m, 2 H); 5.77—5.94 (m, 2 H); 7.14—7.78 ppm (m, 4 H Ar).

General procedure for reactions of copper complexes with organomagnesium compounds

To 30 mmol of the complex suspended in 30 ml of dry THF the Grignard reagent (30 mmol) in 30 ml of dry THF was added with stirring at 0°C. After 30 min, the suspension was evaporated to small volume and chromatographed on a short column of silica gel, with hexane, as eluant, to give the pure olefin. The ^1H NMR and IR data were in accord with the proposed structures.

Acknowledgement

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