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Regioselective Halogenation and Dimerization of Alkoxynaphthalenes with Alumina- or Kieselguhrsupported Copper(II) Halides†

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The reaction of 1-alkoxynaphthalenes 1 with alumina-supported copper(II) bromide or copper(II) chloride gave dimers, 4,4'-dialkoxy-1,1'-binaphthyls 3, as major products, and with Kieselguhr-supported copper(II) bromide afforded 1-bromo-4-alkoxynaphthalenes 2, while the reaction of 2-alkoxynaphthalenes 4 with alumina- or Kieselguhr-supported copper(II) bromide gave preferentially 1-bromo-2-alkoxynaphthalenes 5.

Copper(II) bromide and chloride have been used as halogenating agents under homogeneous conditions for compounds containing active hydrogen atoms such as ketones,¹ and under heterogeneous conditions in non-polar solvents for aromatic hydrocarbons.² In the latter case, the reaction is carried out by heating the reagents in a high-boiling solvent under drastic conditions, when rather complex mixtures of halogenated compounds, are obtained. We have reported that copper(II) halides can be activated remarkably by supporting onto neutral alumina, and that polymethylbenzenes are brominated selectively to give the nuclear-brominated products by use of alumina-supported copper(II) bromide.³ Alkoxybenzenes are regioselectively chlorinated by aluminasupported copper(11) chloride to give 4-chloro-1-alkoxybenzenes in high yield.⁴ In this paper, we describe the halogenation and the dimerization of alkoxynaphthalenes with inorganic-supported copper(11) halides.

The reaction of 1 with copper(II) bromide in refluxing benzene afforded a mixture of 2 and 3. In contrast, similar reaction using Kieselguhr-supported copper(11) bromide proceeded smoothly at 30 °C to give 2 in high yields, and the yield of 3 was negligible. For instance, when 1a was treated with Kieselguhr-supported copper(II) bromide in benzene at 30 °C for 3 h, 2a was obtained in 92% yield. Non-polar solvents such as benzene were better than polar solvents. In polar solvents such as chloroform and tetrahydrofuran, the yield was decreased. The reaction in ethanol did not proceed because of the elution of copper(11) bromide from the Kieselguhr into the solution. These results suggest that the reaction occurs on the surface of the supported reagent and not in solution.5 When alumina-supported copper(11) bromide was employed, bromination did not proceed but dimerization of alkoxynaphthalenes occurred. The reaction of 1a with alumina-supported copper(11) bromide was performed in benzene at 30 °C for 1 h to give 3a in 87% yield and the brominated compounds were formed only in trace quantities. Silica gel and graphite were also effective as supports to give the binaphthyl as a main product along with brominated products. Alumina was most effective and showed the highest selectivity among the supports tested (Table 1).

In the reaction of 1 with copper(π) chloride, both Kieselguhr and alumina gave 3 preferentially, and chlorinated products were formed in low yield (Table 2). The yield of 3 in the reaction using the reagent supported on alumina was slightly higher than that in the reaction using the same reagent supported on Kieselguhr. The reaction of 1a with copper(π) chloride in refluxing benzene gives a mixture of 3a and 4-chloro- and 8-chloro-1-methoxynaphthalene,⁶ whereas a similar reaction with alumina- or Kieselguhr-supported copper(π) chloride proceeded smoothly, even at 30 °C, to



 Table 1
 Reaction of 1-methoxynaphthalene (1a) with CuBr₂-support^e

Support	CuBr₂/ 1a Molar ratio	Time (t/h)	Yield (%)	
			2a ^b	3a ^c
None ^d	2.0	4	47	45
Kieselguhr	1.5	1	40	tr ^e
0	3.0	3	92	tr
Alumina	1.5	1	tr	87
Silica gel	1.5	1	18	69
Graphite	1.5	1	17	76

^aAll reactions were carried out at 30 °C in benzene. ^bBy GLC. ^cIsolated yield. ^dReflux. ^etr indicates a yield of less than 1%.

Table 2Reaction of 1-alkoxynaphthalenes (1) with CuX_2 -support*

1	CuX ₂	Support	Time (t/h)	Yield (%)	
				2 ^b	3 ^c
1b	CuBr ₂	Kieselguhr	3	93	trď
1c	CuBr ₂	Kieselguhr	3	93	tr
1d	CuBr ₂	Kieselguhr	3	95	tr
1b		Kieselguhr	1	15	73
1b	CuBr ₂	alumina	3	15	80
1b		alumina	1	13	80
1d		alumina	1	10	85

^aAll reactions were carried out at 30 °C in benzene. ^bBy GLC. ^cIsolated yield. ^dtr indicates a yield of less than 1%.

give selectively **3a** in high yield, no 8-chloro-1-methoxynaphthalene being formed. For instance, the reaction fo **1a** with alumina-supported copper(π) chloride in benzene at 30 °C for 1 h afforded **3a** in 85% yield and 4-chloro-1-methoxynaphthalene in 8% yield.

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2-Alkoxynaphthalenes 4 were easily brominated under mild conditions by use of Kieselguhr- or alumina-supported copper(11) bromide to give 5 (X = Br) in high yields. Although the reaction with alumina-supported copper(II) bromide proceeded even at 10 °C, dibrominated compounds



Table 3 Reaction of 2-alkoxynaphthalenes (4) with CuX₂-support⁶

4		Support	Yield (%)	
	CuX ₂		5 ^{<i>b</i>}	6 ^{<i>c</i>}
4a	CuBr ₂	Kieselguhr	89	0
4b	CuBr ₂	Kieselguhr	90	0
4c	CuBr₂	Kieselguhr	86	1
4d	CuBr ₂	Kieselguhr	90	0
4a ^d	CuBr ₂	alumina	72	20
4a		alumina	83	10
4b		alumina	84	10
4c	CuCl₂	alumina	85	10
4d		alumina	82	15

^aSolvent: benzene, CuX₂:4 = 3, 50 °C, 2 h. ^bBy GLC. ^clsolated yield. ^d10 °C, 1 h.

and 6 were produced along with 5 (X = Br). In contrast, with Kieselguhr-supported copper(II) bromide, only 5 (X = Br) were obtained in high yields (Table 3).

For example, while the reaction of 4c with copper(II) bromide in benzene at 50 °C for 2 h produced only a 6% yield of 5c (X = Br), a similar reaction with Kieselguhr-supported copper(11) bromide gave an 86% yield of $5c(\bar{X} = Br)$. On the other hand, with alumina-supported copper(11) bromide, the reaction proceeded completely at 10 °C in 1 h to give, in addition to 5c (X = Br) (77%), the dibromide (21%) and 6c (2%). In contrast to the bromination, chlorination of 4 with alumina-supported copper(11) chloride proceeded at 50 °C to give 5 (X = Cl) in high yields. When the reagent supported on Kieselguhr was employed, a mixture of 5 (X = Cl) and 6was obtained. 4a was chlorinated with alumina-supported copper(11) chloride in benzene at 50 °C for 2 h to give 5 (C = Cl) in 83% yield, whereas a similar reaction with copper(II) chloride under the same conditions did not take place. These reactions are postulated to proceed by electron trans-



fer to give the radical cation of the alkoxynaphthalene, which either undergoes reaction with the copper(II) halide or dimerizes.

1- and 2-methylsulfanylnaphthalene 7 reacted with alumina-supported copper(II) halides to give the halogenated compounds 8 in high yields, and dimerization of 7 did not occur. The reaction of 7b with copper(II) bromide in benzene at 50 °C yielded no detectable products after 5 h. In contrast, with alumina-supported copper(11) bromide, 8b (X = Br) was obtained in 92% yield from a reaction run at 50 °C for 1 h. These results are shown in Table 4. Copper(11) chloride was less reactive than copper(11) bromide towards 7. Chlorination required a higher temperature than bromination.

Table 4 Halogenation of methylsulfanylnaphthalenes (7) with CuX₂-Al₂O^a₃

7	CuX ₂	Conditions		Yield (%) ^b	
		<i>T/</i> °C	<i>t/</i> h	8a	8b
7a 7b 7a 7b	CuBr ₂ CuBr ₂ CuCl ₂ CuCl ₂	50 50 80 80	2 2 1 1	80 81	92 90

^aSolvent: benzene, CuX₂/7 = 5. ^bBy GLC.

Experimental

Preparation of Supported Copper(11) Halides.—The reagents were prepared by a method previously reported.34 Kieselguhr-supported copper(11) halides were also prepared by similar method. Reagents

having 9% (w/w) copper(II) halide on a support were used. 1-Bromo-4-methoxynaphthalene **2a**: General Procedure for Bromi-nation of 1-Alkoxynaphthalenes.—A mixture of **1a** (1.90 g, 12 mmol) and Kieselguhr-supported copper(II) bromide (24 g, 36 mmol) in benzene (150 ml) was stirred at 30 °C for 3 h. The mixture was filtered and the grant reason two unsold with homoron. The was filtered, and the spent reagent was washed with benzene. The combined filtrates were evaporated, and the residue was distilled under vacuum to give 2.3 g (85%) of 1-bromo-4-methoxynaphtha-lene 2a bp 155–157 °C at 5 Torr (lit., 6 159–160 °C at 4 Torr). 4,4'-Dimethoxy-1,1'-binaphthyl 3a.—A mixture of 1a (0.95 g, 6

mmol) and alumina-supported copper(n) chloride (5.56 g, 12 mmol) in benzene was stirred at 30 °C for 1 h. The mixture was filtered and the spent reagent was washed several times with hot benzene. Hexane was added to the combined filtrates, which were concentrated, to precipitate 4,4'-dimethoxy-1,1'-binaphthyl **3a** (0.8 g, 85%) mp 254–255 °C (from hexane-benzene) (lit.,⁶ 252–254 °C). GLC analysis of the filtrate after removal of the material showed the presence of 1-chloro-4-methoxynaphthalene.

1-Chloro-2-methoxynaphthalene 5a: General Procedure for Chlorination of 2-Alkoxynaphthalenes.—A mixture of **4a** (0.95 g, 6 mmol) and alumina-supported copper(II) chloride (8.34 g, 18 mmol) in benzene (30 ml) was stirred at 50 °C for 2 h. The mixture was worked up as above and 2,2'-dimethoxy-1,1'-binaphthyl **6a** (0.09 g, 10%), mp 193–195 °C (lit.,⁷ 190–195 °C), separated out from the old filtrate. The filtrate offer remember of curves above my CLC to cold filtrate. The filtrate after removal of 6a was shown by GLC to contain 4a (3%) and 1-chloro-2-methoxynaphthalene 5a (83%). This filtrate was evaporated and the residue was chromatographed on silica gel. Elution with hexane gave 5a (X = Cl), mp 66-67 °C (lit.,⁸ 68 °C).

1-Chloro-2-methylsulfanylnaphthalene 8b.-The reaction was carried out as above using 2-methoxysulfanylnaphthalene (0.52 g, 3 mmol) and alumina-supported copper(π) chloride (6.95 g, 15 mmol) in benzene (30 ml) at 80 °C for 1.5 h. The mixture was filtered and the spent reagent was washed with benzene. The combined filtrates were evaporated and the residue was recrystallized from ethanol to give **8b** (X = Cl) (0.58 g, 93%), mp 77–78 °C.

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