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SUBSTITUTION OF VINYLIC IODIDES BY VARIOUS COPPER(I) AND COPPER(II) DERIVATIVES

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Summary

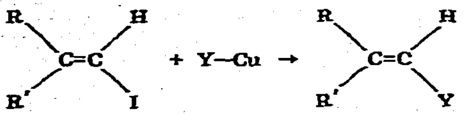
Vinyl iodides have been treated with various copper(I) derivatives (aryl- and alkyl-copper derivatives, copper(I) chloride, cyanide, bromide, thiolate) and found to undergo substitution at carbon with retention of configuration. Copper(II) carboxylates give much better yields of enol esters than the corresponding copper(I) salts. A four centre mechanism accounts best for the results.

The reaction between vinylic halides and copper derivatives has been studied less than the corresponding reactions of halobenzenes. β-Bromostyrene reacts with copper(I) chloride [1], cyanide [2-4] phenylacetylide [5] and phthalimide [7]; 1,2-diiodoethylene with copper(I) phenylacetylide [5, 6] and cyanide [2]; 1-chloro-2-iodoethylene with copper acetylides [5, 8] and 2-bromo-2-butene with copper(I) benzoate [9]. In some cases, the stereochemistry of these substitutions has been studied and shown to involve retention of configuration [1, 8, 6].

Recently, we showed [10] that iodovinyl derivatives are alkylated with complete retention of configuration by primary, secondary or tertiary Grignard reagents in the presence of catalytic amounts of copper(I) salts. However, arylic Grignard reagents failed to react and we were led to study the behavior of aryl-copper compounds toward 1-iodo-1-alkenes.

The desired coupling reaction occurs in almost quantitative yield with complete retention of configuration when more drastic conditions are used, as compared with the catalytic process; solvents such as pyridine or *N*-methyl-pyrolidone (NMP), at 110-135°C, are now necessary. These have already been used in experiments cited above [1, 3]. We have extended this work to various other copper(I) derivatives in order to prepare stereospecifically trisubstituted olefins (Table 1).

TABLE 1



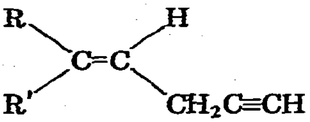
(1)

(Ia) R = n-Bu, R' = Et (II)
(Ib) R = Me, R' = Et

No.	I	Y	T (°C)	Time (h)	Yield of II (%)
1	Ia	C_6H_5	80 [a]	2.5	99.5
2	Ia	$n\text{-}C_4H_9C{\equiv}C$	95 [a]	3	85
3	Ib	$n\text{-}C_4H_9C{\equiv}C$	90 [a]	3	70
4	Ia	$(CH_3)_3SiC{\equiv}CCH_2$	0-5 [a]	2	63
			0-5 [a]	2	80 [d]
5	Ia	$(CH_3)_3CCH_2$	0-5 [a]	2	55
6	Ia	$C_6H_5SCH_2$	90 [a]	1.5	[c]
7	Ia	Cl	110 [a]	8	67
			135 [b]	1.5	88
8	Ia	Br	135 [b]	1.5	91
9	Ia	CN	150 [b]	2	92
10	Ib	CN	130 [b]	1.5	78
11	Ia	C_6H_5S	130 [b]	1.5	90
12	Ia	CH_3COO	110 [a]	6	26
			120 [b]	1.5	21

[a] Pyridine. [b] NMP. [c] 100% of II ($Y = SC_6H_5$) are obtained. [d] With two equivalents of organocopper.

In every case shown in Table 1 complete retention of configuration is observed, and this reaction represents a facile synthesis of bromo- and chloro-alkenes, of β,β-disubstituted acrylonitriles or of styrenes. The thermal stability of the organocopper derivative limits the scope of this reaction, but as shown in Table 1 (entries 4 and 5) even at low temperature a neopentyl- or propargyl-copper compound can react leading, in the latter case, to 1,4-enyne derivatives:



(overall yield 68%)

which could not be obtained from propargyl bromide and an organovinyl copper derivative [11].

It has been reported [12] that copper(I) carboxylates react with haloalkenes in refluxing pyridine, but no yields were stated. In our hands, the reaction of copper(I) acetate, either pure, or in the presence of magnesium salts, gives poor yields of enol ether (Table 1, entry 12). However, dry copper(II) acetate (commercially available) gives, under the conditions stated above, the corresponding enol acetate (in 70% and 60% yield with Ia and Ib respectively) with complete retention of configuration in NMP (2h, 150°C). On the other hand, in boiling pyridine (12 h, 110°C) no selectivity is observed, and a mixture of enol esters ($E/Z = 1/1$) is obtained in 50% yield. With copper(II) chloride Ia gives the corresponding chloride (NMP, 1.5 h, 140°C, yield 61%) with complete retention.

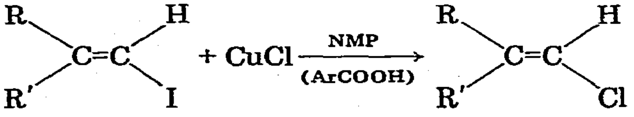
Discussion

Various mechanisms have been suggested for such substitution reactions [7, 9, 12]. Recently, Cohen et al. [13] postulated that vinylic halides behave like arylic halides which supposedly react to form intermediate copper(III) and copper(I) species (eqn. 2). Aryl iodides were converted into arenes in the

$$\mathrm{ArI + CuCl \rightarrow ArCuClI \xrightarrow{3\,CuCl} ArCu + 2\,CuCl_2 + CuI} \qquad (2)$$

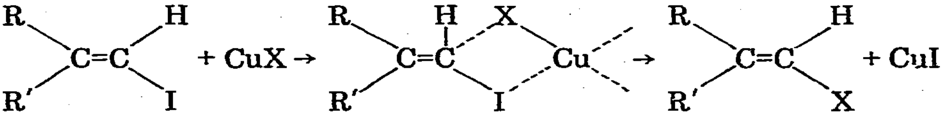
presence of a protonating agent (carboxylic acid) and CuCl.

In our case, we doubt that any vinylcopper(I) species are formed, as they are thermally unstable [14] and immediately decompose to dienes, no trace of which can be detected in our reactions. In the presence or absence of benzoic acid, the exchange (eqn. 3) gives the same yield of chloroalkene and no trace of alkene in either case.

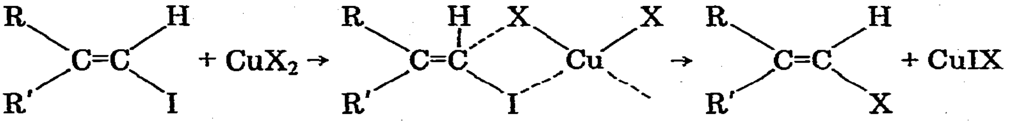


(3)

We assume rather, that in the vinyl case, a four-centre mechanism [7] accounts best for our results, with copper(I) as well as with copper(II) reagents:

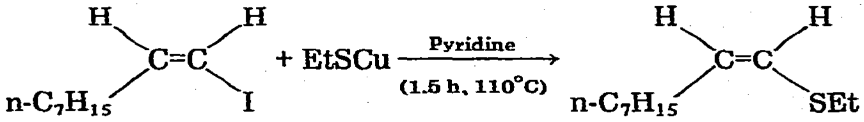


(4)



(5)

No vinylcopper species can be trapped by protonation and a copper(III) intermediate, formed as indicated in eqn. 2, is just as likely when a copper(II) starting material is used. In this case a radical species X, should be liberated, but we have not been able to trap such a species. It has been shown that copper ethylthiolate substituted both bromine atoms of 1,2-dibromoethylene, as did copper phenylthiolate [15]. However, with *cis*-1-iodo-1-hexene we actually observed an elimination reaction when copper ethyl thiolate was used (eqn. 6).



(60%) + $n\text{-}C_7H_{15}C{\equiv}CH$ (6)

(36%)

This β elimination, which does not occur in the absence of a copper reagent, is almost exclusively *trans*, as is shown by the partial reaction of a 9/91 mixture of *cis/trans* β-bromostyrene. This mixture reacted with the same copper reagent to yield β-*trans*-ethylthiostyrene (15%) and pure *trans*-β-bromostyrene (71%) in 6 h in boiling pyridine. We suggest that this is a result of a developing positive centre on the terminal C sp^2 carbon in the four centre mechanism depicted in eqn. 4.

The solvent-dependent behavior of copper(II) carboxylates in such a reaction is the subject of further investigation.

Experimental

(E)-1-Phenyl-2-ethyl-1-hexene

Phenylcopper (32 mmol) was obtained by stirring PhMgCl (32 mmol) and CuBr (4.6 g, 32 mmol) at 0°C and 100 ml THF for 30 min under nitrogen. The solvent was removed in vacuo, and 50 ml of pyridine and (*E*)-1-iodo-2-ethyl-1-hexene [11] (7.14 g, 30 mmol) were added. After 2.5 h at 80°C, the mixture was cooled, diluted with 5*N* HCl, and extracted with pentane. The organic layer was dried and concentrated, and the residue distilled. Yield, 5.62 g (99.5%), b.p. 77°C/0.5 torr, $n_D^{20} = 1.5255$. (Found: C, 89.20; H, 10.57. $C_{14}H_{20}$ calcd.: C, 89.29; H, 10.70%.) IR (NaCl): 1600 (C=C) 700 and 735 (Ph) cm^{-1}. NMR (CCl_4, TMS): δ 6.18 (s, 1H, =CH), 6.90-7.44 (m, 5H, C_6H_5), 2.20 ppm (q, 2H, $CH_3\underline{CH_2}C=$, $J = 8$ Hz).

(E)-1-Thiophenoxy-2-ethyl-1-hexene

Copper(I) thiophenoxide (32 mmol) was obtained from PhSLi (32 mmol) (prepared by the reaction of BuLi and PhSH in ether) and CuI (6.1 g, 32 mmol) in 100 ml ether at 20°C for 40 min. The solvent was removed in vacuo and 50 ml of NMP and (*E*)-1-iodo-2-ethyl-1-hexene [11] (7.14 g, 30 mmol) were added. After it had been stirred for 1.5 h at 130°C, the mixture was cooled, diluted with 5*N* HCl, and extracted with pentane. The organic layer was dried and concentrated, and the residue distilled. Yield 5.95 g (90%), b.p. 100-102°C/0.01 torr, $n_D^{20} = 1.5495$. (Found: C, 76.41; H, 9.23; S, 14.70. $C_{14}H_{20}S$ calcd.: C, 76.30; H, 9.15; S, 14.55%.) IR (NaCl): 1585, 1480, 1440 (C=C); 690, 735 (Ph) cm^{-1}. NMR (CCl_4, TMS): δ 5.78 (s, 1H, =CHS), 6.90-7.40 (m, 5H, C_6H_5), 2.24 ppm (q, 2H, $CH_3\underline{CH_2}C=$, $J = 8$ Hz).

(E)-5-ethyl-5-dodecen-7-yne

Dry copper hexynide (4.63 g, 32 mmol), (*E*)-1-iodo-2-ethyl-1-hexene (7.14 g, 30 mmol), and 50 ml of pyridine were stirred for 3 h at 95°C. The mixture was cooled, diluted with 5*N* HCl, and extracted with pentane, the organic layer dried, and the solvent removed. The residue was distilled. Yield 4.90 g (85%), b.p. 73°C/0.3 torr, $n_D^{20} = 1.4705$. (Found: C, 87.21; H, 12.59. $C_{14}H_{24}$ calcd.: C, 87.42; H, 12.58%.) IR (NaCl): 1630 (C=C) cm^{-1}. NMR (CCl_4, TMS): δ 5.17 (s, 1H, =CHC≡), 2.27 ppm (q, 2H, $CH_3\underline{CH_2}C=$, $J = 8$ Hz).

(Z)-3-methyl-3-decen-5-yne

In the same way, (*Z*)-1-iodo-2-methyl-1-butene (5.88 g, 30 mmol), copper hexynide (4.63 g, 32 mmol), and 50 ml of pyridine, heated at 90°C for 3 h, gave the expected product. Yield 3.15 g (70%), b.p. 81°C/12 torr, $n_D^{20} = 1.4710$.

(Found: C, 87.80; H, 12.12. $C_{11}H_{18}$ calcd.: C, 87.93; H, 12.07%.) IR (NaCl): 1630 (C=C) cm^{-1}. NMR (CCl_4, TMS): δ 5.12 (s, 1H, =CHC≡), 2.25 (q, 2H, $CH_3\underline{CH_2}C=$, $J = 8$ Hz), 1.73 ppm (s, 3H, $CH_3C=$).

(E)-1-chloro-2-ethyl-1-hexene

CuCl (3.17 g, 32 mmol), (*E*)-1-iodo-1-ethyl-1-hexene (7.14 g, 30 mmol), and 50 ml of NMP were stirred 1.5 h at 135°C. The mixture was cooled, diluted with 5*N* HCl and extracted with pentane. The organic layer was dried and concentrated, and the residue distilled. Yield 3.87 g (88%), b.p. 64-65°C/18 torr, $n_D^{20} = 1.4471$. (Found: C, 65.22; H, 10.43; Cl, 23.99. $C_8H_{15}Cl$ calcd.: C, 65.52; H, 10.31; Cl, 24.17%.) IR (NaCl): 1630 (C=C) cm^{-1}. NMR (CCl_4, TMS): δ 5.67 (s, 1H, =CHCl), 2.19 ppm (q, 2H, $CH_3\underline{CH_2}C=$, $J = 8$ Hz).

(E)-1-Bromo-2-ethyl-1-hexene

This compound was prepared similarly from CuBr (4.60 g, 32 mmol), (*E*)-1-iodo-2-ethyl-1-hexene (7.14 g, 30 mmol) and 50 ml of NMP at 135°C for 1.5 h. Yield, 5.22 g (91%), b.p. 59-60°C/11 torr, $n_D^{20} = 1.4710$. (Found: C, 50.33; H, 8.02; Br, 40.90. $C_8H_{15}Br$ calcd.: C, 50.28; H, 7.91; Br, 41.81%.) IR (NaCl): 1625 (C=C) cm^{-1}. MNR (CCl_4, TMS): δ 5.80 (s, 1H, =CHBr), 2.19 ppm (q, 2H, $CH_3\underline{CH_2}C=$, $J = 8$ Hz).

(E)-2-Ethyl-1-hexenyl cyanide

This compound was prepared by the same method from CuCN (2.87 g, 32 mmol), (*E*)-1-iodo-2-ethyl-1-hexene (7.14 g, 30 mmol) and 50 ml of NMP at 150°C for 2 h. The mixture was hydrolysed with aqueous NH_4Cl. The final residue was distilled. Yield, 3.78 g (92%), b.p. 46-47°C/0.3 torr, $n_D^{20} = 1.4540$. (Found: C, 78.67; H, 11.05; N, 10.38. $C_9H_{15}N$ calcd.: C, 78.77; H, 11.02; N, 10.21%.) IR (NaCl): 1625 (C=C) 2220 (C≡N) cm^{-1}. NMR (CCl_4, TMS): δ 5.03 (s, 1H, CHC≡N), 2.38 ppm (q, 2H, $CH_3CH_2C=$, $J = 8$ Hz).

(Z)-2-Methyl-1-butenyl cyanide

This compound was obtained by the same method from CuCN (2.87 g, 32 mmol), (*Z*)-1-iodo-2-methyl-1-butene (5.88 g, 30 mmol), and 50 ml of NMP at 130°C for 1.5 h. Yield, 2.22 g (78%) b.p. 50°C/25 torr, $n_D^{20} = 1.4468$. (Found: C, 75.44; H, 9.35; N, 14.52. C_6H_9N calcd.: C, 75.74; H, 9.53; N, 14.72%.) IR (NaCl): 1630 (C=C); 2220 (C≡N) cm^{-1}. NMR (CCl_4, TMS): δ 5.03 (s, =CHC≡N), 2.37 (q, $CH_3\underline{CH_2}C=$, $J = 8$ Hz), 1.91 (s, $CH_3C=$), 1.12 ppm (t, $\underline{CH_3}CH_2C=$).

(E)-1-Trimethylsilyl-5-ethyl-4-nonen-1-yne

Trimethylsilylpropargylcopper, $(CH_3)_3SiC{\equiv}CCH_2Cu$ (32 mmol) was obtained by the reaction of $(CH_3)_3SiC{\equiv}CCH_2Li$ (32 mmol) (prepared [16] from BuLi, $(CH_3)_3SiC{\equiv}CCH_3$ and one equivalent of tetramethylethylenediamine in 100 ml THF) and CuI (6.1 g, 32 mmol). The THF was removed in vacuo, and (*E*)-1-iodo-2-ethyl-1-hexene (7.14 g, 30 mmol), and 50 ml of pyridine were added. The mixture was stirred at 0-5°C for 2 h and was then diluted with 5*N* HCl and extracted with pentane. The organic layer was dried, concentrated, and distilled, to yield 4.17 g (63%) of (*E*)-1-trimethylsilyl-5-ethyl-4-nonen-1-yne (b.p. 62-63°C/0.5 torr) containing a trace of impurity. IR (NaCl): 2180 (C≡C); 1660 (C=C)

cm^{-1}. NMR (CCl_4, TMS): δ 5.02 (t, 1H, $=C\underline{H}CH_2C\equiv$, $J = 7.6$ Hz), 2.82 (d, 2H, $=CHC\underline{H}_2C\equiv$), 1.98 (q, 2H, $CH_3C\underline{H}_2C=$, $J = 8$ Hz), 0.13 ppm (s, 9H, $Si(CH_3)_3$).

(E)-5-Ethyl-4-nonen-1-yne

The preceding silyl derivative was obtained in 80% yield when two equivalents (60 mmol) of the copper reagent were used. To this compound (4.2 g, 19 mmol), in 300 ml of CH_3OH at ambient temperature, was added a mixture of 15 g of NaOH and 20 ml of H_2O. After stirring for 15 min, the solution was added to 200 ml of 2*N* HCl at 0°C. The mixture was extracted with pentane. The organic layer was dried, concentrated, and distilled. Yield, 2.42 g (85%), b.p. 72-73°C/11 torr, $n_D^{20} = 1.4532$. (Found: C, 87.90; H, 12.05. $C_{11}H_{18}$ calcd.: C, 87.93; H, 12.07%). IR (NaCl: 1660 (C=C), 2120 ($C\equiv C$), 3310 ($\equiv CH$) cm^{-1}. NMR (CCl_4, TMS): δ 5.31 (t, 1H, $=C\underline{H}CH_2C\equiv$, $J = 8$ Hz), 2.95 (d of d, 2H, $=CHC\underline{H}_2C\equiv CH$), 2.16 (q, 2H, $CH_3C\underline{H}_2C\equiv$, $J = 8$ Hz) 1.86 ppm (t, $CH_2C\equiv C\underline{H}$, $J = 3$ Hz).

(E)-5-Ethyl-2,2-dimethyl-4-nonene

Neopentylcopper (32 mmol) was obtained by stirring $(CH_3)_3CCH_2MgCl$ (32 mmol) and CuBr (4.6 g, 32 mmol) in 50 ml ether at —20°C. The solvent was removed in vacuo, and (*E*)-1-iodo-2-ethyl-1-hexene (7.14 g, 30 mmol) and 50 ml of pyridine were added. After 2 h at 0.5°C, the mixture was diluted with 5*N* HCl and extracted with pentane. The organic layer was dried, concentrated and distilled. Yield, 3.0 g (55%), b.p. 83°C/11 torr, $n_D^{20} = 1.4385$ (Found: C, 85.58; H, 14.30. $C_{13}H_{26}$ calcd.: C, 85.63; H, 14.37%.) IR (NaCl): 1660 (C=C) cm^{-1}. NMR (CCl_4, TMS): δ 5.12 (t, 1H, $=C\underline{H}CH_2C\leqq$, $J = 8$ Hz), 2.01 (q, 2H, $CH_3C\underline{H}_2C=$, $J = 8$ Hz), 1.87 (d, 2H, $=CHC\underline{H}_2C\leqq$), 0.90 ppm (s, 9H, $C(CH_3)_3$).

(E)-2-Ethyl-1-hexenyl acetate

Copper(II) acetate (5.81 g, 32 mmol), (*E*)-1-iodo-2-ethyl-1-hexene (7.14 g, 30 mmol) and 50 ml of NMP were stirred and heated at 150°C for 2 h. The mixture was then cooled, diluted with a slightly acidic aqueous solution to pH = 5 and extracted with pentane. The organic layer was dried, concentrated and distilled. Yield, 3.57 g (70%), b.p. 52-53°C/1 torr, $n_D^{20} = 1.4430$. (Found: C, 70.14; H, 10.69. $C_{10}H_{18}O_2$ calcd.: C, 70.55; H, 10.66; O, 18.79%.) IR (NaCl): 1680 (C=C); 1755 (C=O); 1230 (C—O) cm^{-1}. NMR (CCl_4, TMS): δ 6.84 (s, 1H, =CHO), 2.12 (q, 2H, $CH_3C\underline{H}_2C=$, $J = 8$ Hz), 2.05 ppm (s, 3H, $OOCCH_3$).

(Z)-2-Methyl-1-butenyl acetate

Copper(II) acetate (5.81 g, 32 mmol), (*Z*)-1-iodo-2-methyl-1-butene (5.88 g, 30 mmol), and 50 ml of NMP were stirred and heated at 145°C for 2 h. Workup as above gave 2.3 g (60%) of product, b.p. 72-73°C/50 torr, $n_D^{20} = 1.4300$. (Found: C, 65.25; H, 9.29. $C_7H_{12}O_2$ calcd.: C, 65.60; H, 9.44; O, 24.96%.) IR (NaCl): 1685 (C=C); 1755 (C=O); 1170-1290 (C—O) cm^{-1}. NMR (CCl_4, TMS): δ 6.80 (s, 1H, =CHO), 2.12 (q, 2H, $CH_3C\underline{H}_2C=$, $J = 8$ Hz), 2.04 (s, 1H, $OOCCH_3$), 1.62 (d, 3H, $C\underline{H}_3C=CH$, $J = 2$ Hz), 0.99 ppm (t, 3H, $C\underline{H}_3CH_2C=$).

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