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A NEW PREPARATION AND SOME REACTIONS OF ORGANOCOPPER(I) ISONITRILE COMPLEXES

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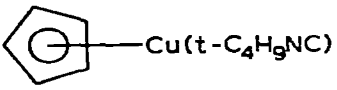
Summary

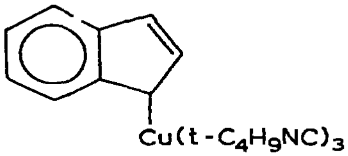
A new preparation and some reactions of organocopper(I) isonitrile complexes are described. In the presence of isonitrile (RNC), some active hydrogen compounds (R'H) react smoothly with Cu_2O and with metallic copper, evolving H_2O and hydrogen, respectively, to produce organocopper(I) isonitrile complexes, $R'Cu(RNC)_2$. The isonitrile insertion and the oxidative coupling by iodine of these complexes are described here.

Introduction

Recently, considerable interest has been shown in the chemistry of organocopper(I) compounds because of their synthetic utility [1]. Several reactions of active hydrogen compounds with a variety of substrates in the presence of Cu_2O/isonitrile or Cu^0/isonitrile were found by us [2], in which we have proposed the intermediacy of organocopper(I) isonitrile complexes. *pentahapto*-Cyclopentadienyl- and *monohapto*-indenyl-copper(I) tert-butyl isocyanide complexes (I and II) were successfully isolated in the reactions of Cu_2O/tert-butyl isocyanide with cyclopentadiene and with indene, respectively [3].



(I)



(II)

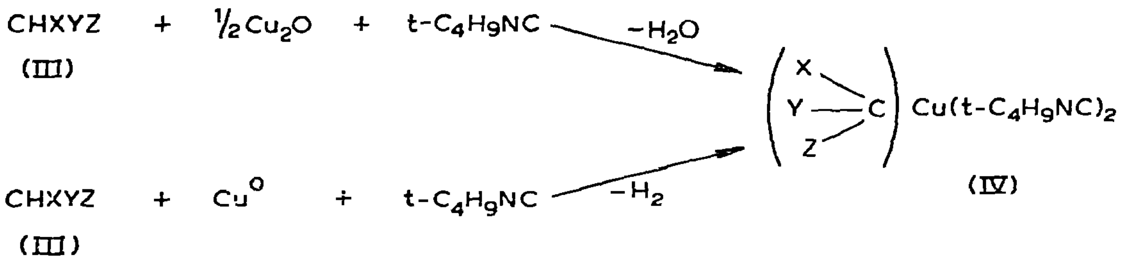
The present paper describes a new synthetic method which gives organocopper(I) isonitrile complexes (IV), in which "active" hydrogen compounds such as acetylacetone, acetoacetate, malonate and cyanoacetate were treated with Cu_2O/isonitrile and with Cu/isonitrile (eqn. 1). These organocopper(I) isonitrile complexes (IV) underwent insertion of isonitriles into the copper—carbon bond and oxidative coupling by iodine.

Results and discussion

Preparation of organocopper(I) isonitrile complexes

On stirring a mixture of acetylacetone (IIIa), tert-butyl isocyanide and Cu_2O for a half hour at room temperature under nitrogen, copper(I) acetylacetonate bis(tert-butyl isocyanide) (IVa) was produced in almost quantitative yield along with water. Complex IVa was reprecipitated from benzene solution with ether or petroleum ether. In a similar way, the corresponding organocopper(I) isonitrile complexes IVb-IVe were prepared from acetoacetate, malonate and cyanoacetate (Scheme 1). All of these complexes are soluble in most organic solvents, and are thermally stable under nitrogen, but they are rapidly oxidized in air.

SCHEME 1



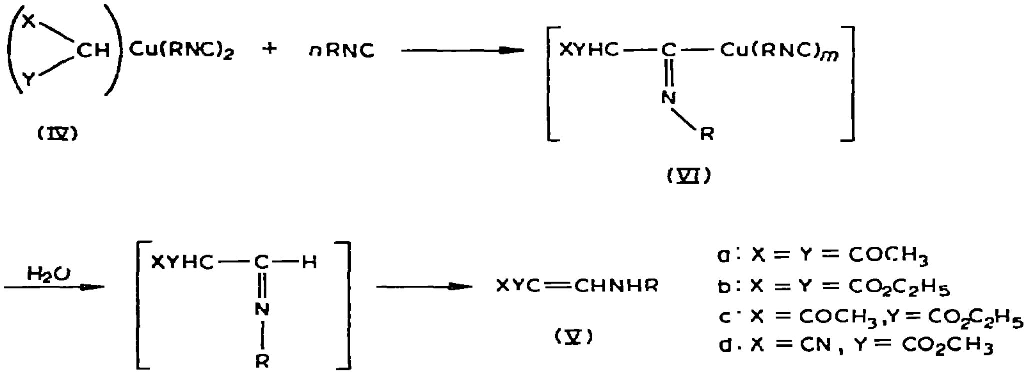
a $X = Y = COCH_3$, $Z = H$
b $X = Y = CO_2C_2H_5$, $Z = H$
c $X = COCH_3$, $Y = CO_2C_2H_5$, $Z = H$
d $X = CN$, $Y = CO_2CH_3$, $Z = H$
e $X = Y = CO_2C_2H_5$, $Z = C_2H_5$

A freshly prepared metallic copper powder also was used effectively in the preparation of organocopper(I) isonitrile complexes IVa-IVe, but with decreased yields. In the case of metallic copper, the evolution of hydrogen gas was observed throughout the reaction. IR and NMR spectral data as well as elemental analyses of IV are summarized in Table 1.

The infrared spectrum of copper(I) acetylacetonate bis(tert-butyl isocyanide) complex IVa showed a strong band at 1610 cm^{-1} which may be taken to indicate a structure of oxygen-bonded copper(I) acetylacetonate [4]. It may be pertinent to mention that a carbon-bonded gold(I) acetylacetonate phosphine complex exhibits two sharp bands at 1660 and 1645 cm^{-1} [5]. As to the detailed structure of other organocopper(I) isonitrile complexes IVb-IVe, no information is now at hand. The structure determination of IVb-IVe will be the subject of future studies.

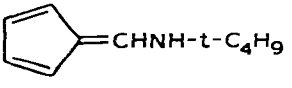
Insertion reactions of the organocopper(I) isonitrile complexes IV

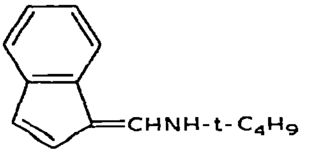
Insertions of carbon monoxide and isonitrile into the carbon—metal bond are reactions characteristic of the transition metal alkyls and constitute a key step in many synthetic reactions catalyzed by transition metal complexes. The insertion of isonitriles was examined with the organocopper(I) isonitrile complexes IV. A benzene solution of IV with excess isonitrile was refluxed under nitrogen, and then the mixture was hydrolyzed to produce an enamine derivative V via the expected insertion product VI. In practice, the product V was obtained simply by heating a mixture of active hydrogen compound III, an excess of isonitrile and Cu_2O or Cu^0 in benzene, without the isolation of complex IV. Products Va-Vd were all identified by comparison of their IR and NMR spectra with those of the authentic samples [6].

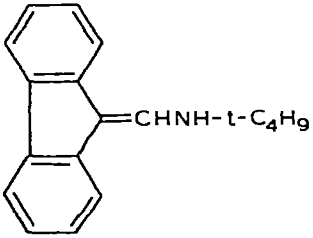


a: $X = Y = COCH_3$
b: $X = Y = CO_2C_2H_5$
c: $X = COCH_3, Y = CO_2C_2H_5$
d. $X = CN, Y = CO_2CH_3$

This type of reaction was also observed in the reaction with *pentahapto*-cyclopentadienylcopper(I) tert-butyl isocyanide (I)[7] and with *monohapto*-indenylcopper(I) tris(tert-butyl isocyanide) (II), producing VII and VIII respectively, in good yields, after hydrolysis. Since both VII and VIII were not sufficiently


(VII)


(VIII)


(IX)

stable, they were hydrogenated by Raney nickel catalyst, and identified as (*N*-tert-butyl)aminomethylcyclopentane and 1-(*N*-tert-butyl)aminomethylindane, respectively. Similarly, IX was obtained in a good yield in the reaction of fluorene with Cu_2O and excess of tert-butyl isocyanide. Results are summarized in Table 2.

Concerning the mechanism of the insertion reaction of complex IV in the present study, it may be plausibly assumed that the oxygen-bonded copper(I) acetylacetonate bis(isonitrile) IVa is converted by excess isonitrile into the carbon-bonded copper(I) acetylacetonate isonitrile complex X, which is the key intermediate responsible for the insertion reaction (Scheme 1). Some attempts to isolate the intermediates X and XI, however, have failed.

(continued on p. 400)

TABLE 1

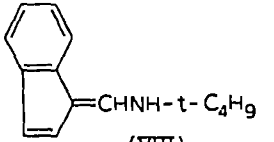
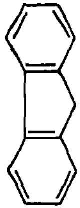
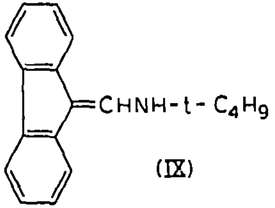
DATA FOR ORGANOCOPPER(I) ISONITRILE COMPLEXES IV

$(XYZC)Cu(t\text{-}C_4H_9NC)_2$[a]		Elemental analysis(%)			IR[b]	NMR(δ)
		C	H	N		
$(CH_3CO)_2CHCu(t\text{-}C_4H_9NC)_2$ (IVa)	Found (calcd.)	54.79 (54.48)	7.66 (7.38)	8.52 (8.18)	2166, 2142 1610, 1525	5.18 (s, 1H)[c] 1.87 (s 6H) 1.42 (s 18H)
$(H_5C_2O_2C)_2CHCu(t\text{-}C_4H_9NC)_2$ (IVb)		52.49 (52.81)	7.51 (7.72)	7.20 (8.16)	2172, 1690 1580	4.19 (q, 4H)[d] 1.47 (s, 18H) 1.25 (t, 6H)
$(H_5C_2O_2C)(CH_3CO)CHCu(t\text{-}C_4H_9NC)_2$ (IVc)		53.54 (53.08)	7.58 (7.25)	7.81 (8.12)	2167, 2144 1690, 1655 1580, 1520	4.06 (q, 2H)[c] 1.87 (s, 3H) 1.43 (s, 18H) 1.21 (t, 3H)
$(CH_3O_2C)(NC)CHCu(t\text{-}C_4H_9NC)_2$ (IVd)		51.48 (52.01)	6.76 (7.10)	12.82 (12.49)	2175, 1640 1620	3180 (s, 3H)[d] 1.20 (s, 18H)
$(H_5C_2O_2C)_2(C_2H_5)CCu(t\text{-}C_4H_9NC)_2$ (IVe)		54.73 (54.44)	7.98 (8.85)		2172, 1690 1585	4.30 (q, 4H)[d] 1.80-1.60 (2H) 1.40 (t, 3H) 1.21 (t, 6H) 0.94 (s, 18H)

[a] All complexes IVa-IVe decomposed at about 150°, depositing metallic copper. [b] Nujol. [c] $CDCl_3$ solution with TMS. [d] C_6D_6 solution with TMS.

TABLE 2

INSERTION REACTIONS OF ORGANOCOPPER(I) ISONITRILE COMPLEXES

Active hydrogen compound	Isonitrile	Copper compound	Product (%)
$(CH_3CO)_2CH_2$	$t\text{-}C_4H_9NC$	Cu_2O	$(CH_3CO)_2C{=}CHNH\text{-}t\text{-}C_4H_9$ (34) (Va-i)
$(CH_3CO)_2CH_2$	$t\text{-}C_4H_9NC$	Cu^0	$(CH_3CO)_2C{=}CHNH\text{-}t\text{-}C_4H_9$ (15) (Va-i)
$(CH_3CO)_2CH_2$	$cyclo\text{-}C_6H_{11}NC$	Cu_2O	$(CH_3CO)_2C{=}CHNH\text{-}cyclo\text{-}C_6H_{11}$ (61) (Va-ii)
$(CH_3CO)_2CH_2$	$(CH_3)_3CCH_2(CH_3)_2CNC$	Cu_2O	$(CH_3CO)_2C{=}CHNHC(CH_3)_2CH_2C(CH_3)_3$ (21) (Va-iii)
$(H_5C_2O_2C)_2CH_2$	$t\text{-}C_4H_9NC$	Cu_2O	$(H_5C_2O_2C)_2C{=}CHNH\text{-}t\text{-}C_4H_9$ (44) (Vb)
$(CH_3CO)(H_5C_2O_2C)CH_2$	$t\text{-}C_4H_9NC$	Cu_2O	$(CH_3CO)(H_5C_2O_2C)C{=}CHNH\text{-}t\text{-}C_4H_9$ (50) (Vc)
	$t\text{-}C_4H_9NC$	Cu_2O	 (61)[a] (VIII)
	$t\text{-}C_4H_9NC$	Cu_2O	 (82) (IX)

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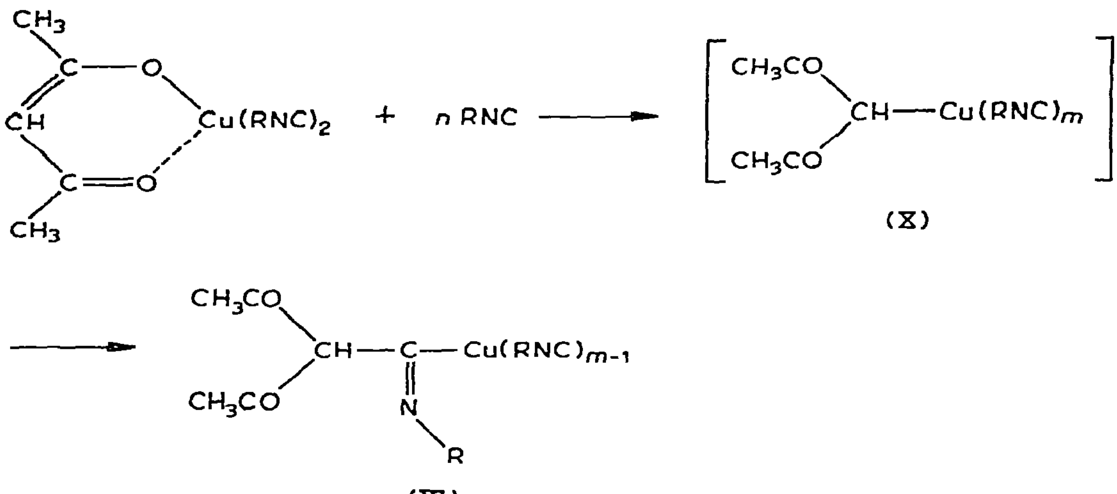
[a] This product was hydrogenated by Raney nickel and identified.



(X)

(XI)

Oxidative coupling of organocopper(I) isonitrile complex IV

The organocopper(I) isonitrile complexes IV are readily oxidized by oxygen, but no definite product has been isolated. However, it was found that iodine as an oxidant successfully caused the oxidative coupling [8] of IV. In the reaction of IVa with one equivalent of iodine, tetraacetylethane [9] was produced in 35% yield along with $CuI(t\text{-}C_4H_9NC)_2$. Similarly, oxidation of IVb by iodine afforded 1,1,2,2-tetracarbethoxyethane [10] in 41% yield.

$$\underset{(IV)}{(X_2CH)Cu(t\text{-}C_4H_9NC)_2} \xrightarrow{I_2} X_2CH{-}CHX_2 + 2\,CuI(t\text{-}C_4H_9NC)_2$$

a: $X = COCH_3$

b: $X = CO_2C_2H_5$

Experimental

Reagents

All reactions were carried out under nitrogen. Cu_2O was a commercial reagent of high purity and used without further purification. Metallic copper was prepared by the reduction of cupric sulfate with zinc powder. Isonitriles were prepared by Ugi's procedure [11]. All reagents and solvents were purified by usual methods under nitrigen prior to use.

Preparation of copper(I) acetylacetonate bis(tert-butyl isocyanide) (IVa)

A mixture of 10 mmol of Cu_2O, 40 mmol of tert-butyl isocyanide and 20 mmol of acetylacetone was vigorously stirred under nitrogen at room temperature. After about a half hour, the mixture solidified. The solid was dissolved in 20 ml of benzene and heated at 50° for an additional hour to complete the reaction, and the mixture was filtered. On the addition of 60 ml of ether to the filtrate, copper(I) acetylacetonate bis(tert-butyl isocyanide) precipitated in almost quantitative yield as a white crystalline solid. Other complexes IVb-IVe could be prepared in a similar way. IR and NMR spectral data as well as the data of elemental analyses of IV are summarized in Table 1.

Insertion reaction of isonitrile with IV

A mixture of 5 mmol of Cu_2O, 40 mmol of cyclohexyl isocyanide and 10 mmol of acetylacetone in 10 ml of benzene was refluxed for several hours under nitrogen. The reaction mixture was extracted with ether, and the ether solution was distilled under reduced pressure. The residue was examined by GLPC. The product, 1,1-diacetyl-2-cyclohexylaminoethylene (61% yield) (Va-ii), was identified by the comparison of its IR spectrum with that of the authentic sample which was prepared by the reaction of 1-(*N*-cyclohexyliminoformyl)imidazole with acetylacetone [6].

For other combinations in Table 2, the reactions were carried out according to the above procedure. Identification of Va-i, Va-iii, Vb, and Vc were performed by the comparison with the authentic samples. 9-(*N*-tert-butyl)aminomethylenefluorene (IX) (m.p. 141°) was identified by elemental analysis and spectral data. (Found: C, 86.66; H, 7.32; N, 5.25. $C_{18}H_{19}N$ calcd.: C, 86.70; H, 7.68; N, 5.62%.) IR (KBr): 3405, 3050, 1640, 1315 and 1210 cm^{-1}. NMR ($CDCl_3$): δ 8.10-7.11 (m, 9H), 5.25 (broad, 1H), 1.36 (s, 9H). 1-(*N*-tert-butyl)-aminomethyleneindene (VIII) was hydrogenated as follows. Crude 1-(*N*-tert-butyl)aminomethyleneindene (VIII) (a fraction of 100-200°/3 mm) was dissolved in ethanol and the solution was put under 100 atm. of hydrogen in the presence of a catalyst of Raney nickel at room temperature for 24 h. The product of 1-(*N*-tert-butyl)aminomethylindane was isolated by distillation (b.p. 140°/1 mm) and identified by elemental analysis and spectral data. (Found: C, 70.12; H, 10.61; N, 5.76. $C_{14}H_{21}N$ calcd.: C, 70.25; H, 10.53; N, 5.85%.) IR(neat): 3060, 3030, 3020, 1230 cm^{-1}. NMR ($CDCl_3$): δ 7.2-6.9 (m, 4H), 3.1-2.4 (m, 5H), 2.3-1.8 (m, 2H), 1.03 (s, 9H).

Oxidative coupling of IV by iodine

To a solution of 10 mmol of copper(I) (diethyl malonate) bis(tert-butyl isocyanide) (IVb) in 20 ml of benzene was added dropwise 5 mmol of iodine in 20 ml of ether, and the mixture was stirred for 3 h at room temperature. The reaction mixture was extracted with ether. 1,1,2,2-Tetracarbethoxyethane was obtained by distillation (32%) and identified by comparison with the authentic sample [10].

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