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Reactions of Isocyanides with Carbon Tetrahalogenides in the Presence of Dicobalt Octacarbonyl

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It is well established that isocyanides, analogous to carbon monoxide, coordinate to transition metals to give the complexes of isocyanides. In previous papers we have reported on the catalytic polymerization of isocyanides by $BF_3O(C_2H_5)_2$ or transition metal complexes,[1] and on the reactions of isocyanides with various transition metal complexes.[2]

Bamford and Maltman reported some of the characteristic properties of metal carbonyl-organic halide systems as free radical initiators.[3] In the course of our studies on the polymerization of isocyanides with metal carbonyl-carbon tetrahalogenide systems, we found that isocyanides readily reacted with carbon tetrahalogenides in the presence of $Co_2(CO)_8$ to yield *N*-substituted dihaloacetamides and cobalt(II) complexes of isocyanides, suggesting the formation of carbene as intermediates.

Carbon tetrachloride containing a small amount of water was added to a mixture of cyclohexyl isocyanide and $Co_2(CO)_8$ in benzene at room temperature. The subsequent reaction was initiated with evolution of carbon monoxide and gave *N*-cyclohexyldichloroacetamide and dichlorotetrakis(cyclohexyl isocyanide)cobalt(II).

A similar reaction in methanol gave *N*-cyclohexyldichloroacetimidate and dichlorotetrakis(cyclohexyl isocyanide)cobalt(II). The use of other metal carbonyls or metal carbonyl derivatives, such as $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, $[Co(PPh_3)_2(CO)_3]$-BPh_4 and [Fe(morphorine)][$Fe(CO)_4$] did not promote the reactions. The use of $[Co(PPh_3)_2(CO)_3][Co(CO)_4]$ promoted the reaction to give *N*-cyclohexyldichloroacetamide, $Co(C_6H_{11}NC)_4Cl_2$ and $Co(PPh_3)_2(CO)_2Cl_2$. The results of the reaction are listed in Table 1.

It has been reported by Halleux that *N*-cyclohexyldichloroacetimidate was obtained from the reaction of cyclohexyl isocyanide with dichlorocarbene, prepared from potassium methoxide and chloroform, and it decomposed spontaneously to produce *N*-cyclohexyldichloroacetamide.[4]

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[2] Y. Yamamoto and N. Hagihara, This Bulletin, **38**, 1084 (1966); Y. Yamamoto, H. Yamazaki and N. Hagihara, *ibid.*, **41**, 532 (1968).

[3] C. H. Bamford, *J. Polymer Sci., C*, 1571 (1964); C. H. Bamford and W. R. Maltman, *Trans. Faraday Soc.*, **62**, 2823 (1966).

[4] A. Halleux, *Angew. Chem.*, **76**, 889 (1964).

Table 1. The reactions of isocyanides with carbon tetrahalogenides in the presence of $Co_2(CO)_8$

Isocyanide	CX_4	Product	Yield[a)] (%)	mp[b)] (°C)	Analyses (%)			IR[c)] (cm^{-1})
					C	H	N	
$C_6H_{11}NC$	CCl_4	$C_6H_{11}NHCOCHCl_2$	37	140—141	45.61 (45.73)	6.56 (6.24)	6.24 (6.67)	
		$Co(CNC_6H_{11})_4Cl_2$	93	84—86	59.87 (59.36)	7.86 (7.83)	9.39 (9.35)	2220
	CBr_4	$C_6H_{11}NHCOCHBr_2$	28	172—173	32.65 (32.14)	4.26 (4.38)	4.88 (4.68)	
		$Co(CNC_6H_{11})_4Br_2$	96	116—118	51.27 (50.77)	6.79 (6.78)		2215
$(CH_3)_3CNC$	CCl_4	$(CH_3)_3CNHCOCHCl_2$	48	152—153	39.34 (39.15)	6.03 (6.03)	7.47 (7.61)	
		$Co(CNC(CH_3)_3)_4Cl_2$	94	*ca.* 298	51.59 (51.95)	7.73 (7.85)	11.83 (12.12)	2230
	CBr_4	$(CH_3)_3CNHCOCHBr_2$	25	182—184	27.01 (26.40)	4.38 (4.06)	5.26 (5.13)	
		$Co(CNC(CH_3)_3)_4Br_2$	92		43.91 (43.57)	6.71 (6.58)	10.55 (10.16)	2175
$C_6H_5CH_2NC$	CCl_4	$C_6H_{11}CH_2NHCOCHCl_2$	22	94.5—95.5	49.52 (49.57)	4.20 (4.16)	6.41 (6.42)	
		$Co(CNCH_2C_6H_5)_4Cl_2$	95	106—108	64.17 (64.24)	4.79 (4.79)	9.33 (9.36)	2215
	CBr_4	$C_6H_{11}CH_2NHCOCHBr_2$	23	123—125	35.25 (35.21)	2.89 (2.96)	4.54 (4.56)	
		$Co(CNCH_2C_6H_5)_4Br_2$	95	151—153	55.61 (55.91)	4.17 (4.11)		2215

a) Based on $Co_2(CO)_8$ employed. b) All complexes, $Co(CNR)_4X_2$, decomposed.
c) KBr method, N≡C band.

The fact that *N*-substituted dihaloacetamides or *N*-cyclohexyldichloroacetimidate was obtained in our reaction suggested the existence of dihaloketenimine as the intermediates of the reactions. In order to confirm the formation of carbenes, the reaction of $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ with carbon tetrachloride or carbon tetrabromide was carried out in cyclohexene. The reaction gave 7,7-dichloronorcarane and $Co(CO)_2(PPh_3)_2Cl_2$, or 7,7-dibromonorcarane and $Co(CO)_2(PPh_3)_2Br_2$. These results suggest the formation of the carbene intermediates.

The possible pathway for the reaction may be sketched in the following manner:

$$5R\text{-}N{\equiv}C + Co_2(CO)_8 \rightarrow \underset{(I)}{Co(CNR)_5Co(CO)_4} + 4CO \qquad (1)$$

$$I + 2CX_4 + 5RNC \rightarrow 2Co(CNR)_4X_2 + 4CO + 2RN{=}C{=}CX_2 \qquad (2)$$

$$\left.\begin{array}{l} RN{=}C{=}CX_2 + H_2O \rightarrow RNHCOCHX_2 \\ RN{=}C{=}CX_2 + CH_3OH \rightarrow RNC{=}C(OCH_3)CHX_2 \end{array}\right. \qquad (3)$$

When $Co_2(CO)_8$ was added to excess isocyanide, it reacted with isocyanide, as was reported by Sacco,[5)] to yield $Co(CNR)_5Co(CO)_4$ by the evolution of 4 mol of carbon monoxide, according to Eq. (1). In addition, the evolution of 4 mol more of carbon monoxide was observed, when carbon tetrahalogenide was added to the reaction mixture. This fact showed that *N*-substituted dihalokenimine and $Co(CNR)_4X_2$ were formed, according to Eq. (2). *N*-Substituted dihaloketenimine rapidly reacted with water or methanol to produce the corresponding amide or imidate.

Experimental

Materials. Various isocyanides[6)] and transition metal complexes[7)] were prepared according to the prescription given in literature.

The Reaction of Cyclohexyl Isocyanide with Carbon Tetrachloride in the Presence of $Co_2(CO)_8$. To a solution of 1.0 g of $Co_2(CO)_8$ in 25 m*l* of *n*-hexane was added 2.3 g of cyclohexyl isocyanide. After 20 min, into this was added 5.0 g of aqueous carbon tetrachloride (*ca.* 5% H_2O) with constant stirring at room temperature. The reaction was completed within 2 hr to give dark green solution, with the precipitaiton of a green solid. Precipitate was filtered and washed by *n*-hexane. It was found to be $Co(CNC_6H_{11})_4Cl_2$ and was soluble in acetone and chloroform, but was insoluble in petroleum ether. The evaporation of the filtrate gave raw products of *N*-cyclohexyl dichloroacetamide, which was recrystallizad by benzene-acetone mixture. The infrared spectrum and the melting point of this

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5) A. Sacco, *Gazz. Chim. Ital.*, **83**, 632 (1953).

6) I. Ugi and R. Mayr, *Chem. Ber.*, **93**, 239 (1960).

7) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press Inc., New York (1965), p. 98.

product were identical with those of authentic *N*-cyclohexyldichloroacetamide.

By analogous procedure, other *N*-substituted dihaloacetamides and dihalotetrakis(isocyanide)cobalt(II) were obtained. Their melting points, analyses and infrared spectra are summarized in Table 1.

The Reaction of Carbon Tetrachloride with $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ in the Presence of Cyclohexene. Carbon tetrachloride (5.4 g) was added to a mixture of $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ (4.5 g) and cyclohexene (20 m*l*) at room temperature. After the reaction mixture had been kept for 2.5 hr with constant stirring, a pale green precipitate was filtered, and found to be $Co(CO)_2(PPh_3)_2Cl_2$(3.65 g, mp 82—83°C). Glpc analysis of the distillate of the filtrate showed the presence of 7,7-dichloronorcarane, which was identified by comparison of its glpc retention time with that of an authentic sample.

Found: C, 64.52; H, 4.39; Cl, 10.15%. Calcd for $Co(CO)_2(PPh_3)_2Cl_2$: C, 64.24; H, 4.26; Cl, 9.98%.