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COBALOXIME(II)-INITIATED COUPLING OF α,α,α-TRIHALOMETHYLBENZENES

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Summary

Bis(dimethylglyoximato) complexes of cobalt(II), cobaloxime(II), under mild conditions initiate coupling of α,α,α-trihalomethylbenzenes to form $PhCX_2CX_2Ph$ (X = Cl), PhCX=CXPh (X = Cl, Br) and mixtures of halocobaloxime products. Stoichiometry, product distribution, and control experiments suggest that coupling may result from the decomposition of a highly unstable haloalkylcobaloxime intermediate, $Co(dmgH)_2(PhCX_2)(S(CH_3)_2)$. A general mechanism for the formation of this intermediate and its decomposition to the observed products is presented.

Introduction

Metal-initiated coupling reactions of organic halides provide simple and useful routes to many symmetrically substituted alkanes and alkenes. Recent reviews show that coupling occurs for a wide variety of metallic reagents and organic substrates [1]. Aside from their synthetic utility, some of these reactions are of additional interest due to the involvement of directly bonded metal-organic intermediates such as those proposed for certain coupling reactions of tungsten [2], vanadium [3]; palladium and iron [4] complexes. Although cobalt—carbon bonds of varying stability are possible in a great number of complexes, reported examples of cobalt-initiated alkyl halide coupling reactions include no direct evidence for organocobalt intermediates [5]. In one recent example [6] an organocobalt complex was produced along with coupled organic products; however, the intermediacy of that or other organocobalt complexes in the formation of the coupled organic products was not addressed.

Bis(dimethylglyoximato) complexes of cobalt, called cobaloximes, form sta-

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ble sigma bonded complexes with organic ligands *. One technique used for the synthesis of such complexes is the reaction of cobaloxime(II) with an appropriate alkyl halide [8]. In this work we report on the reaction of cobaloxime(II) with α,α,α-trihalomethylbenzenes. In contrast to the corresponding reaction with benzyl halides which produces benzylcobaloxime(III) [9], the α,α,α-trihalomethylbenzene reaction produces coupled organic products in moderate to high yield. These reactions provide indirect evidence for an organocobalt intermediate involved in cobalt-initiated coupling.

Experimental

Materials

α,α,α-Trichloromethylbenzene and α,α-dibromomethylbenzene were obtained commercially and purified by distillation. α,α,α-Tribromomethylbenzene [10] and $Co(dmgH)_2(OH_2)_2$ [11] were prepared by literature methods. All other reagents and solvents were obtained commercially and used without further purification.

Cis- and *trans*-1,2-dibromo-1,2-diphenylethene [12], *cis-* and *trans*-1,2-dichloro-1,2-diphenylethene, 1,2-diphenyl-1,1,2,2-tetrachloroethane [13], $Co(dmgH)_2(Br)(S(CH_3)_2)$, $Co(dmgH)_2(Cl)(S(CH_3)_2)$ [14], $Co(dmgH)(dmgH_2)(Br)_2$, $Co(dmgH)(dmgH_2)(Cl)_2$ [15], $Co(dmgH)_2(PhCHBr)(S(CH_3)_2)$, and $Co(dmgH)_2(PhCHCl)(S(CH_3)_2)$ [8a] were prepared by literature methods to serve as authentic samples for comparison with the products of reactions described in this report. Organohalide purity was confirmed by mass spectrometry. Satisfactory elemental analyses, C, H, N, were obtained for all four halocobaloxime compounds. The authenticity of $Co(dmgH)_2(PhCHBr)(S(CH_3)_2)$ and $Co(dmgH)_2(PhCHCl)(S(CH_3)_2)$ was confirmed by ^1H NMR spectroscopy.

Methods

^1H NMR spectra were obtained using a JEOL MH-100, 100 MHz, spectrometer at ambient temperature with chemical shifts reported in parts per million downfield from internal tetramethylsilane. Gas chromatograms and mass spectra were recorded on a Hewlett-Packard 5990A GC-MS instrument. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona.

All reactions were carried out in a N_2 atmosphere using Schlenk apparatus and deoxygenated solvents and reagents. All organic products were isolated as benzene/hexane solutions and analyzed by combined gas chromatography and mass spectrometry (GC-MS). Product identification and quantitative yields were based on comparison of GC-MS data to that obtained from independently prepared and standardized authentic samples. Although *cis-* and *trans*-1,2-dichloro-1,2-diphenylethene were separable by the gas chromatography techniques used, *cis-* and *trans*-1,2-dibromo-1,2-diphenylethene were not. Therefore, no conclusions are drawn here involving the stereochemistry of the coupled organic reaction products.

Yields given for cobaloxime products were calculated for the unrecrystallized solids, with purity established by ^1H NMR spectroscopy. Methyl sulfide was used as a cobaloxime ligand because of its convenient ^1H NMR spectra in

* Cobaloxime is the common name given to the $Co(dmgH)_2$ moiety [7] where dmgH represents the dimethylglyoximato monoanion $[(CH_3)C(=NOH)C(=NO)(CH_3)]^-$.

the free and complexed form. Relative yields of cobaloxime product obtained as mixtures were calculated from integration of ^1H NMR spectra. Three mole percent of $Co(dmgH)(dmgH_2)(X)_2$ or $Co(dmgH)_2(X)(S(CH_3)_2)$ has been determined as the minimum detectable concentration in cobaloxime product mixtures. ^1H NMR data for cobaloximes used in this study are as follows (resonances are singlets except where noted): $Co(dmgH)_2(Br)(S(CH_3)_2)$, in acetone-$d_6$, δ 2.47 (12 H), 1.60 ppm (6 H); $Co(dmgH)(dmgH_2)(Br)_2$, in acetone-d_6, δ 2.52 ppm; $Co(dmgH)_2(Cl)(S(CH_3)_2)$, in acetone-$d_6$, δ 2.48 (12 H), 1.60 ppm (6 H); $Co(dmgH)(dmgH_2)(Cl)_2$, in acetone-d_6, δ 2.57 ppm; $Co(dmgH)_2(PhCHBr)(S(CH_3)_2)$, in $CDCl_3$, δ 1.71 (6 H), 1.98 (6 H), 2.17 (6 H), 5.54 (1 H), 6.96—7.05 ppm (multiplet, 5 H); $Co(dmgH)_2(PhCHCl)(S(CH_3)_2)$, in $CDCl_3$, δ 1.69 (6 H), 1.99 (6 H), 2.10 (6 H), 5.35 (1 H), 6.96—7.08 ppm (multiplet, 5 H).

Reaction of α,α,α-trihalomethylbenzene with cobaloxime(II)

In a representative reaction, $Co(dmgH)_2(OH_2)_2$, 0.22 g (0.68 mmol), was suspended in 8 ml of acetone in a Schlenk tube. Methyl sulfide, 0.05 ml (0.68 mmol), was added causing the suspended cobaloxime to dissolve. α,α,α-Trichloromethylbenzene, 0.05 ml (0.34 mmol), was then added and the dark brown solution was allowed to stir in the dark at room temperature for 4 h at a slight positive N_2 pressure. At the end of 4 h, the reaction mixture was vacuum distilled at room temperature and the organic products extracted from the residue with benzene and hexane. The remaining powdery brown solid, 0.21 g, was washed with hexane, dried at reduced pressure and characterized by ^1H NMR spectroscopy as $Co(dmgH)_2(Cl)(S(CH_3)_2)$, 85% yield. The organic product solutions were analyzed directly by GC-MS and found to contain $PhCCl_2$-CCl_2Ph, 76% yield, and PhCCl=CClPh, 12% yield. No further products were detected in the vacuum distillate by GC-MS analysis.

Reaction of α,α,α-trihalomethylbenzene with cobaloxime(II) in the presence of 2,3-dimethyl-2-butene or hydroquinone

Reactions of α,α,α-trichloromethylbenzene with two equivalents of cobaloxime(II) were carried out exactly as above except that ten equivalents of 2,3-dimethyl-2-butene or five equivalents of hydroquinone were added just after the addition of the trihalide. Product workup was as previously described. The reaction of α,α,α-trichloromethylbenzene with cobaloxime(II) in the presence of hydroquinone yielded an oxygen sensitive cobaloxime product. Contact with oxygen saturated solvents produced a color change from dark brown to yellow, suggesting the presence of a cobaloxime hydride or unreacted cobalt(II). No further characterization of this cobaloxime was carried out. The reaction of α,α,α-tribromomethylbenzene with two equivalents of cobaloxime(II) was also carried out in the presence of ten equivalents of 2,3-dimethyl-2-butene, as noted above.

Reaction of 1,2-diphenyl-1,1,2,2-tetrachloroethane with cobaloxime(II)

In a typical reaction, $PhCCl_2CCl_2Ph$, 0.43 g (1.4 mmol), was stirred in a N_2 atmosphere with 2.7 mmol of $Co(dmgH)_2(S(CH_3)_2)$, obtained from $Co(dmgH)_2$-$(OH_2)_2$, in 35 ml of acetone for 15 h. The addition of hexane precipitated $Co(dmgH)_2(Cl)(S(CH_3)_2)$ which was isolated by filtration: 0.92 g, 2.4 mmol, 89%

yield. The filtrate was evaporated to dryness to give 1,2-dichloro-1,2-diphenylethene, 0.31 g, 1.3 mmol, 93% yield. The corresponding reaction of $PhCCl_2$-CCl_2Ph with one equivalent of cobaloxime(II) was carried out similarly with a reaction time of 4 h and organic product yields determined by gas chromatography. Differing reaction times are not believed to be significant since equally high yields of chlorocobaloxime indicate complete reaction in both cases, Table 1. No difference in rate of these reactions should be inferred.

Reaction of α,α-dihalomethylbenzene with cobaloxime(II)

In a typical reaction, $Co(dmgH)_2(S(CH_3)_2)$, 2.7 mmol, was generated in situ from $Co(dmgH)_2(OH_2)_2$ and $S(CH_3)_2$ in 15 ml of acetone. $PhCHBr_2$, 0.22 ml (1.4 mmol), was then added. After stirring in the dark for 15 min at −10°C, the reddish-brown solution was poured into 100 ml of hexane. A dark brown precipitate formed (0.62 g) and was isolated by filtration, washed with hexane, dried in a vacuum dessicator and characterized by ^1H NMR as a mixture of $Co(dmgH)_2(PhCHBr)(S(CH_3)_2)$, 4% yield, and $Co(dmgH)_2(Br)(S(CH_3)_2)$, 48% yield. A reddish-orange solid was obtained from the filtrate after concentration and was found to be $Co(dmgH)_2(PhCHBr)(S(CH_3)_2)$, 33% yield; and $Co(dmgH)_2(Br)(S(CH_3)_2)$, 4% yield. The remaining filtrate was analyzed by GC-MS techniques.

Reaction of Br_2 with $Co(dmgH)_2(S(CH_3)_2)$ and $Co(dmgH)_2(Br)(S(CH_3)_2)$

Br_2, 0.037 ml (0.70 mmol), was added to $Co(dmgH)_2(S(CH_3)_2)$ (1.4 mmol) and the mixture was stirred in the dark in a N_2 atmosphere. After 1 h the reaction mixture was poured into 100 ml of hexane to precipitate $Co(dmgH)_2(Br)$-$(S(CH_3)_2)$, which was isolated by filtration, washed with hexane, dried at reduced pressure, and characterized by ^1H NMR: 0.53 g, 87% yield.

Br_2, 0.074 ml (1.4 mmol), was also added to a solution of $Co(dmgH)_2(Br)$-$(S(CH_3)_2)$, 0.61 g (1.4 mmol), in a minimum amount of acetone and the resulting mixture was stirred in the dark in a N_2 atmosphere for 1 h. $Co(dmgH)$-$(dmgH_2)(Br)_2$, 0.63 g, was isolated in quantitative yield and characterized by ^1H NMR.

Reaction of Cl_2 with $Co(dmgH)_2(S(CH_3)_2)$ and $Co(dmgH)_2(Cl)(S(CH_3)_2)$

Cl_2 gas was bubbled through acetone solutions of $Co(dmgH)_2(S(CH_3)_2)$, 1.4 mmol, and $Co(dmgH)_2(Cl)(S(CH_5)_2)$, 0.54 g, (1.4 mmol), respectively, for 15 min. $Co(dmgH)(dmgH_2)(Cl)_2$ was isolated from both reactions and characterized by ^1H NMR.

Reaction of HX with $Co(dmgH)_2(X)(S(CH_3)_2)$, (X = Cl, Br)

HX was bubbled through an acetone solution of $Co(dmgH)_2(X)(S(CH_3)_2)$, 1.0 mmol, for 30 min. Dichloro- and dibromocobaloximes were isolated in 40% and 100% yields, respectively.

Stability of α,α,α-trihalomethylbenzene and 1,2-diphenyl-1,1,2,2-tetrachloroethane

The following control experiments were carried out to demonstrate that cobaloxime(II) is the agent effecting the observed coupling of α,α,α-trihalo-

methylbenzene. A solution of the organic halide in acetone, of the same concentration as in the experiments described above, was stirred in the dark in a N_2 atmosphere at room temperature at least 4 h for α,α,α-trihalomethylbenzenes and 19 h for 1,2-diphenyl-1,1,2,2-tetrachloroethane. The solvent was removed at reduced pressure and the residue characterized as unreacted starting material using ^1H NMR spectroscopy for the α,α,α-trihalomethylbenzenes and GC-MS for 1,2-diphenyl-1,1,2,2-tetrachloroethane.

α,α,α-Trihalomethylbenzene, 0.77 mmol, was stirred in the dark at room temperature in a N_2 atmosphere in 15 ml of methanol containing 0.34 g (1.4 mmol) of $Co(OOCH_3)_2 \cdot 4\ H_2O$. After 1 h the solvent was removed at reduced pressure and the residue washed with ethyl ether and carbon tetrachloride. Concentration of the washings at reduced pressure yielded a residue which was characterized by ^1H NMR as unreacted α,α,α-trichloro- or tribromomethylbenzene.

Results

Reaction of α,α,α-trihalomethylbenzene with cobaloxime(II)

The coupling of α,α,α-tribromo- and trichloromethylbenzene was achieved in moderate to high yield by reaction with $Co(dmgH)_2(S(CH_3)_2)$ in acetone. As shown in Table 1, 1,2-dibromo- 1,2-diphenylethene was the only organic coupled product obtained by reaction with the tribromide, whereas a mixture of 1,2-dichloro-1,2-diphenylethene and 1,2-diphenyl-1,1,2,2-tetrachloroethane was obtained from the trichloride. No hydrogenated products, such as $PhCHX_2$ or $PhCH_2X$, were observed in either case. Mixtures of halocobaloximes were identified as the inorganic products (see Table 1). Samples of the α,α,α-trihalomethylbenzenes under identical reaction conditions but without added cobaloxime(II) showed no coupling to form the substituted ethanes or ethenes. In

TABLE 1

REACTIONS OF COBALOXIME(II) WITH $PhCX_3$ (X = Br, Cl) AND $PhCCl_2CCl_2Ph$ [a]

R + n $Co(dmgH)_2(S(CH_3)_2)$		Products (% Yield)			
R	n	$PhCX_2CX_2Ph$	PhCX=CXPh	$Co(dmgH)_2(X)(S(CH_3)_2)$	$Co(dmgH)(dmgH_2)(X)_2$ [b]
$PhCCl_3$	2	71—94	9—13	78—89	≤3
$PhCCl_3$ [c]	2	63	9	85	<3
$PhCCl_3$ [d]	2	18	0	[e]	[e]
$PhCCl_3$	1	20—41	6—7	74—85	<3—7
$PhCCl_2CCl_2Ph$	2	0	93	89	<3
$PhCCl_2CCl_2Ph$	1	56	44	86	<3
$PhCBr_3$	2	0	33—66	78—94	≤3
$PhCBr_3$ [c]	2	0	43	84	<3
$PhCBr_3$	1	0	21—50	74—90	3—19

[a] All reactions carried out in acetone at ambient temperature. Reaction time of 15 h for $PhCCl_2CCl_2Ph$ with 2 $Co(dmgH)_2(S(CH_3)_2)$, all others, 4 h; yield ranges represent data obtained from 2—5 separate experiments. [b] Limit of detection of $Co(dmgH)(dmgH_2)(X_2)$ in the presence of $Co(dmgH)_2(X)(S(CH_3)_2)$ is taken as 3 mole percent. [c] Reaction carried out in the presence of 10 equivalents of 2,3-dimethyl-2-butene. [d] Reaction carried out in the presence of 5 equivalents of hydroquinone. [e] See text.

addition, Co^{2+} ion in the form of $Co(OOCCH_3)_2 \cdot 4\ H_2O$ did not initiate coupling in methanol solution.

Coupling reactions of α,α,α-trichloro- and tribromomethylbenzene were also carried out in the presence of 2,3-dimethyl-2-butene. Coupled organic product yields and cobaloxime yields were not altered by the presence of this carbene trapping agent (see Table 1). No cyclopropyl products corresponding to carbene addition were detected in the reaction distillates or benzene/hexane extracts of the inorganic residues.

Similarly, α,α,α-trichloromethylbenzene was reacted with cobaloxime(II) in the presence of hydroquinone, a hydrogen donor. 1,2-Diphenyl-1,1,2,2-tetrachloroethane, in 18% yield, was the only organic product observed along with unreacted $PhCCl_3$ (see Table 1). No $PhCCl_2H$ was detected by GC-MS analysis in the vacuum distillate of the reaction mixture or in the benzene/hexane extract of the resulting inorganic residue.

Reaction of 1,2-diphenyl-1,1,2,2-tetrachloroethane with cobaloxime(II)

The reaction of 1,2-diphenyl-1,1,2,2-tetrachloroethane with two equivalents of cobaloxime(II) in acetone resulted in high yields of 1,2-dichloro-1,2-diphenylethene and $Co(dmgH)_2(Cl)(S(CH_3)_2)$. In the presence of one equivalent of cobaloxime(II), only one-half of the organic substrate was dehalogenated to the dichloride. 1,2-Diphenyl-1,1,2,2-tetrachloroethane at identical reaction conditions, but with no added cobaloxime(II), showed no tendency to form 1,2-dichloro-1,2-diphenylethene.

Reaction of α,α-dihalomethylbenzene with cobaloxime(II)

The reaction of α,α-dibromo- or dichloromethylbenzene with one and two equivalents of $Co(dmgH)_2(S(CH_3)_2)$ resulted in the formation of mixtures of $Co(dmgH)_2(PhCHX)(S(CH_3)_2)$ and $Co(dmgH)_2(X)(S(CH_3)_2)$ in moderately high yield. In a total of eight separate reactions no coupled products such as PhCHXCHXPh or PhCH=CHPh were detected by GC-MS analysis.

Reaction of X_2 and HX with $Co(dmgH)_2(S(CH_3)_2)$ and $Co(dmgH)_2(X)(S(CH_3)_2)$ (X = Br, Cl)

High yields of halocobaloximes were obtained from the reaction of bromine with cobaloxime(II) in acetone. As shown in Table 2, a cobaloxime to bromine ratio of 2 : 1 gave $Co(dmgH)_2(Br)(S(CH_3)_2)$ as the only cobaloxime product, while a 1 : 1 ratio resulted in a mixture of $Co(dmgH)_2(Br)(S(CH_3)_2)$ and $Co(dmgH)(dmgH_2)(Br)_2$. Finally, bromine in acetone was found to quantitatively convert $Co(dmgH)_2(Br)(S(CH_3)_2)$ to $Co(dmgH)(dmgH_2)(Br)_2$. Likewise, reaction of excess Cl_2 in acetone with $Co(dmgH)_2(Cl)(S(CH_3)_2)$ gave the protonated dichlorocobaloxime, $Co(dmgH)(dmgH_2)(Cl)_2$, in 70% yield. Reaction of Cl_2 with cobaloxime(II) also produced the dichlorocobaloxime but in lesser yield (see Table 2).

Treatment of $Co(dmgH)_2(Br)(S(CH_3)_2)$ with HBr in acetone resulted in the quantitative conversion of the complex to $Co(dmgH)(dmgH_2)(Br)_2$. Forty percent conversion to $Co(dmgH)(dmgH_2)(Cl)_2$ was effected by treatment of $Co(dmgH)_2(Cl)(S(CH_3)_2)$ with HCl (see Table 2).

TABLE 2

REACTIONS OF COBALOXIME(II) AND $Co(dmgH)_2(X)(S(CH_3)_2)$ WITH X_2 AND HX (X = Cl, Br) [a]

Reaction	Products (% Yield)	
	$Co(dmgH)_2(X)(S(CH_3)_2)$ [b]	$Co(dmgH)(dmgH_2)(X)_2$ [b]
Br_2 + 2 $Co(dmgH)_2(S(CH_3)_2)$	87	<3
Br_2 + $Co(dmgH)_2(S(CH_3)_2)$	36	43
Br_2 + $Co(dmgH)_2(Br)(S(CH_3)_2)$	0	100
excess Cl_2 + $Co(dmgH)_2(S(CH_3)_2)$	<3	31
excess Cl_2 + $Co(dmgH)_2(Cl)(S(CH_3)_2)$	<3	70
HBr + $Co(dmgH)_2(Br)(S(CH_3)_2)$	0	100
HCl + $Co(dmgH)_2(Cl)(S(CH_3)_2)$	58	40

[a] All reactions carried out in acetone at ambient temperature. Reaction times for reactions with Br_2, 1 h; with Cl_2, 15 min; with HX, 30 min. [b] Limit of detection of each cobaloxime product in the presence of the other is taken as 3 mole percent.

Discussion

The data in Table 1 show that $PhCCl_3$ is converted quantitatively to coupled products, 1,2-diphenyl-1,1,2,2-tetrachloroethane and 1,2-dichloro-1,2-diphenylethene, by the action of two equivalents of cobaloxime(II). However, one equivalent of cobaloxime(II) initiates coupling of less than one-half the organic substrate. The same general trend in product yield is observed for the reactions of cobaloxime(II) with $PhCBr_3$, although 1,2-dibromo-1,2-diphenylethene is the only coupled organic product formed. In these reactions the amount of substrate coupled exceeds 50% only in the presence of two equivalents of cobalt(II) (see Table 1). These results suggest that the reaction by which coupling occurs must be of overall 2 : 1 (cobaloxime(II) : $PhCX_3$) stoichiometry. The constant high yields of halocobaloxime products shown in Table 1 are also consistent with this interpretation of reaction stoichiometry.

The results given in Tables 1 and 2 and the 2 : 1 stoichiometry deduced above may be incorporated into a general mechanism for cobaloxime(II)-initiated $PhCX_3$ coupling as shown in Scheme 1. In this scheme the coupled products $PhCX_2CX_2Ph$ and PhCX=CXPh are produced from a single, perhaps highly transient, intermediate, I, by one or all of three possible paths, a, b and c. Intermediate I is produced from the starting reagents by a reaction of the required 2 : 1 stoichiometry.

$$PhCX_3 + Co(dmgH)_2(S(CH_3)_2) \rightarrow Ph\dot{C}X_2 + Co(dmgH)_2(X)(S(CH_3)_2) \quad (1)$$

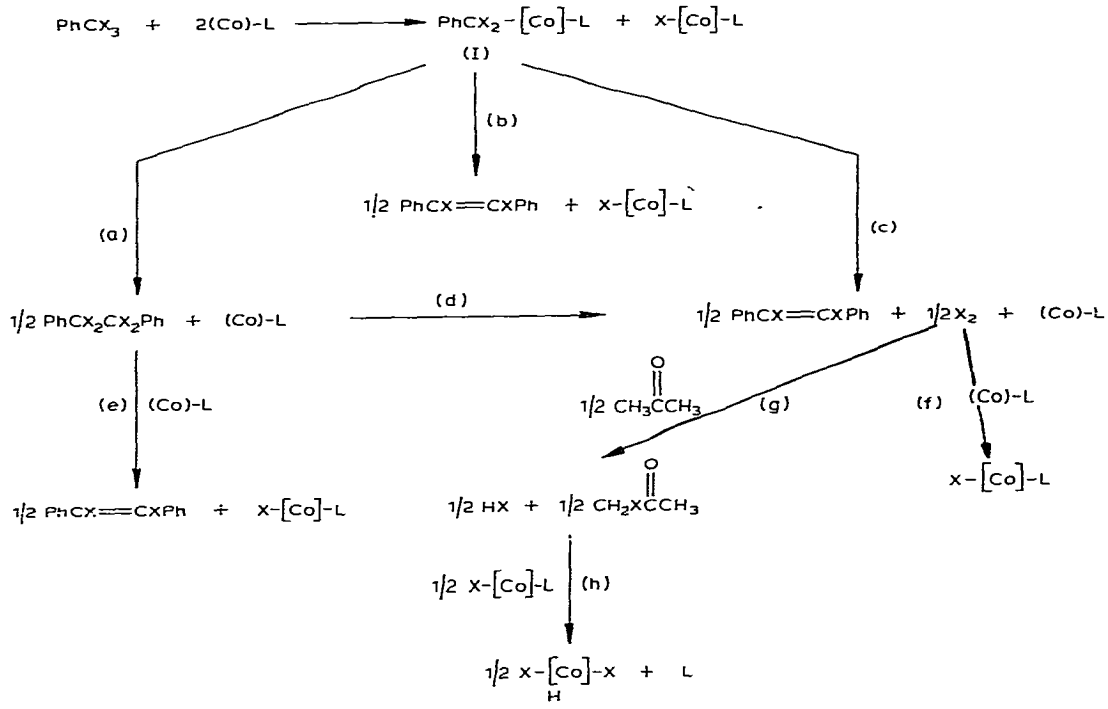
$$Ph\dot{C}X_2 + Co(dmgH)_2(S(CH_3)_2) \rightarrow Co(dmgH)_2(PhCX_2)(S(CH_3)_2) \quad (2)$$

(I)

The formation of I and $Co(dmgH)_2(X)(S(CH_3)_2)$ most probably occurs by a two-step process, eqs. 1 and 2. The production of intermediate I in this way is analogous to other reports of cobaloxime(II) reactions with alkyl halides [8,16], some of which have been shown to occur in two steps [8d,9]. Although eqs. 1 and 2 are shown as free radical reactions, no $PhCHX_2$, the abstraction product of $Ph\dot{C}X_2$ with acetone, was detected. Hydroquinone, an even better

SCHEME 1

PROPOSED MECHANISM FOR COUPLING OF $PhCX_3$ BY $Co(dmgH)_2(S(CH_3)_2)$



$H^{\bullet}$ donor than acetone also failed to produce a detectable amount of $PhCHX_2$. The low yield of 1,2-diphenyl-1,1,2,2-tetrachloroethane (Table 1) and the oxygen-sensitive cobaloxime product formed in the presence of hydroquinone are believed to result from the reaction of some cobaloxime(II) with that reagent, perhaps to form a hydrido complex such as $Co(dmgH)_2(H)(S(CH_3)_2)$ *. These observations are not necessarily inconsistent with the formation of $Ph\dot{C}X_2$ radicals, but may instead reflect the high radical scavenging ability of cobaloxime(II), which is itself a free radical [17]. Alternatively, a scheme may be proposed whereby cobaloxime(II) undergoes disproportionation to produce cobaloxime(III) and cobaloxime(I), the latter of which may then undergo nucleophilic attack on α,α,α-trihalomethylbenzene to produce the intermediate species I without the generation of $Ph\dot{C}X_2$ radicals. This alternate scheme is unlikely, however, in view of recent work [18].

* A minor factor may also be that hydroquinone does trap some $Ph\dot{C}X_2$ radicals to produce $PhCHX_2$, and that this species reacts further with cobaloxime(II) to form $Co(dmgH)_2(PhCHX)(S(CH_3)_2)$, which is susceptible to decomposition. While none of these species were detected in our experiments, trace amounts below our detection limits could contribute to the low yield of $PhCCl_2CCl_2Ph$ in the presence of hydroquinone.

Equations 1 and 2 are then proposed as initial steps in the overall coupling scheme based on stoichiometry, the isolation of $Co(dmgH)_2(X)(S(CH_3)_2)$ as the major cobaloxime product, and analogy to the reactions for benzyl halides [8d] and carbon tetrachloride [16]. Support for intermediate species I is also found in the reaction of cobaloxime(II) with $PhCHX_2$ (X = Cl, Br), a similar substrate which reacts as proposed for $PhCX_3$ to give $Co(dmgH)_2(X)(S(CH_3)_2)$ and an alkylcobaloxime analogous to I, $Co(dmgH)_2(PhCHX)(S(CH_3)_2)$. Furthermore, $Co(dmgH)_2(PhCHBr)(S(CH_3)_2)$ and $Co(dmgH)_2(PhCHCl)(S(CH_3)_2)$ are both unstable and decompose to give $Co(dmgH)_2(X)(S(CH_3)_2)$ in organic solvents [19].

The instability of I is most likely due to steric factors, although an electronic influence cannot be ignored. The steric bulk of the α-chloro or -bromo substituents has been postulated to influence *trans* ligand substitution rates of α-haloalkylcobaloximes [20]. Previous studies of halomethylcobaloximes (chloro, bromo, and iodo) also suggest that increased halogenation of the α-carbon leads to increased instability of the cobalt—carbon bond [16,20,21]. Therefore, steric effects may explain why $Co(dmgH)_2(PhCX_2)(S(CH_3)_2)$, I, in Scheme 1 cannot be directly observed, while $Co(dmgH)_2(PhCHX)(S(CH_3)_2)$ is sufficiently stable to be isolated and $Co(dmgH)_2(PhCH_2)L$ has been studied without reported decomposition [9]. Consequently, the proposed formation of I from $PhCX_3$ and cobaloxime(II), its instability, and its decomposition to $Co(dmgH)_2(X)(S(CH_3)_2)$ is supported not only by the observed reactions of $PhCHX_2$ with cobaloxime(II) and the instability of $Co(dmgH)_2(PhCHX)(S(CH_3)_2)$, but also by the general instability of α-haloalkylcobaloximes.

As shown in Scheme 1 the decomposition of intermediate I is proposed to yield the observed coupled organic products. Paths a—e represent all probable routes by which these products may be formed. Their relative importance for X = Cl and X = Br is discussed below and is based on product distributions and independently verified reactions. Paths f, g and h are confirmed by independent reactions of X_2 and HX with $Co(dmgH)_2(X)(S(CH_3)_2)$ and X_2 with $Co(dmgH)_2(S(CH_3)_2)$, Table 2.

The reaction of Br_2 with two equivalents of cobaloxime(II) is readily understood in terms of path f, giving the predicted high yield of $Co(dmgH)_2(Br)(S(CH_3)_2)$, Table 2. The reaction of Br_2 with one equivalent of cobaloxime(II) produces an approximately equal mixture of mono- and dibromocobaloximes. This mixture presumably results from reaction of one-half equivalent of Br_2 with cobaloxime(II) by path f. The remaining Br_2 may then react with acetone, path g, to produce one-half equivalent of HBr, which can then convert half of the $Co(dmgH)_2(Br)(S(CH_3)_2)$, formed previously, into $Co(dmgH)(dmgH_2)(Br)_2$, reaction h. The reactions of Cl_2 with $Co(dmgH)_2(Cl)(S(CH_3)_2)$ and $Co(dmgH)_2(S(CH_3)_2)$, Table 2, are assumed to occur in the same way. However, because an excess of Cl_2 was used, $Co(dmgH)(dmgH_2)(Cl)_2$ was the only cobaloxime product of both reactions. The low yield of the dichlorocobaloxime from $Co(dmgH)_2(S(CH_3)_2)$ relative to the yield from $Co(dmgH)_2(Cl)(S(CH_3)_2)$ is probably due to the greater number of steps, reactions f, g, and h, involved in its formation.

When X = Cl, path a of Scheme 1 is proposed as the primary path for the decomposition of I based on the observation that 1,2-diphenyl-1,1,2,2-tetra-

chloroethane is the major product. 1,2-Dichloro-1,2-diphenylethene is also produced as a minor product. Control experiments show that cobaloxime(II) can dehalogenate 1,2-diphenyl-1,1,2,2-tetrachloroethane as shown in path e. However, most of the PhCCl=CClPh produced must arise directly from the decomposition of species I by path b rather than e, since the product ratio ($PhCCl_2CCl_2Ph$: PhCCl=CClPh) is unaffected by the ratio of reactants (cobaloxime(II) : $PhCCl_3$). Path c, followed by g and h, is also operative to a small extent as evidenced by the observation of $Co(dmgH)(dmgH_2)(Cl)_2$ as a minor product and the independent verification of paths g and h.

When X = Br, 1,2-dibromo-1,2-diphenylethene is the only coupled organic product observed. Due to its simplicity, path b in the Scheme is favored as its mode of production. However paths a and d, or a and e, with $PhCBr_2CBr_2Ph$ as a transient species, and paths c and f give equivalent organic and cobaloxime products and cannot be ignored since their feasibility has been independently established. Path d, the spontaneous decomposition of transient $PhCBr_2CBr_2Ph$ is believed to be reasonable since the tetrabromoalkane is unreported, presumably because steric hindrance makes it highly unstable. Thus, if formed, $PhCBr_2CBr_2Ph$ would be expected to decompose readily to the observed dibromide by path d. Path c may also produce significant amounts of 1,2-dibromo-1,2-diphenylethene. Finally, relative yields of $Co(dmgH)(dmgH_2)(X)_2$ show that paths c (or d), g and h are more important for X = Br than X = Cl.

Although the overall scheme by which the observed products are formed has been well verified experimentally, less is known about the intimate mechanism by which the proposed paths occur. Paths e and f, involving cobaloxime(II), may be reasonably assumed to be free radical in character because of the radical nature of that cobaloxime. Path g has been well studied [22], and h involves ligand substitution at cobalt(III). Least is known, however, about paths a, b, and c; those which involve the decomposition of the proposed haloalkylcobaloxime intermediate. Paths a and c are most probably free radical in character since the production of cobaloxime(II) implies homolytic cobalt—carbon bond cleavage. Although a free radical mechanism for paths a, b or c might seem to require the observation of $H^{\bullet}$ abstraction products, at least in the presence of hydroquinone, all three paths occur in the presence of relatively high concentrations of cobaloxime(II), an excellent radical scavenger. Finally, mechanisms for these decomposition paths which involve free carbenes may be ruled out by the observation that organic product yields for the reaction of $PhCX_3$ with two equivalents of cobaloxime(II) were unaffected by 2,3-dimethyl-2-butene and that no cyclopropyl addition products were detected in the presence of that carbene trap.

In conclusion, the coupling observed for reactions of $PhCX_3$ with cobaloxime(II) is consistent with the scheme shown, which accounts for all the observed products and variations in product distribution for $PhCBr_3$ and $PhCCl_3$. The coupled products may arise from $Co(dmgH)_2(PhCX_2)(S(CH_3)_2)$, I, by reasonable and in most cases experimentally verified routes. The formation of $Co(dmgH)_2(PhCHX)(S(CH_3)_2)$ in the reaction of $PhCHX_2$ with cobaloxime(II) is consistent with the proposed initial step in the coupling of $PhCX_3$. The failure to observe coupled products from $PhCHX_2$ shows that the coupling observed for $PhCX_3$ with cobaloxime(II) is not a general reaction applicable to all α-halo-

methylbenzenes. The observation of coupled products may, instead, depend on the initial alkylcobaloxime formed, its relative stability, and favored mechanism of decomposition.

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