Preliminary communication

THE STEREOCHEMISTRY OF THE CLEAVAGE OF ORGANOMETALLIC
COMPLEXES WITH COPPER(II)

RICHARD A. BUDNIK and JAY K. KOCHI*

Chemistry Department, Indiana University, Bloomington, Indiana 47401 (U.S.A.)
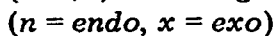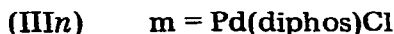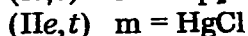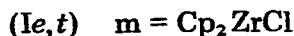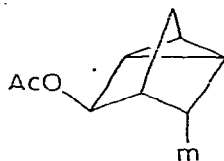
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Summary

The rather unusual loss of stereochemistry resulting from the facile cleavage of 3,3-dimethylbutyl-1,2-d_2 and tricyclo[2.2.1.0^{2,6}]heptyl groups from Pd, Zr and Hg derivatives by copper(II) bromide rules out concerted mechanisms and favors alkyl radicals as intermediates.

Copper(II) complexes play important roles in a variety of catalytic processes, especially those involving oxidation such as the Pd-catalyzed Wacker process. Their function is not known, although it has been generally assumed, largely on presumptive evidence, that copper(II) acts on organometallic intermediates. Indeed, the cleavage of transition metal—carbon bonds by copper(II) halides represented in eq. 1, has been observed for a variety of metals including Pd, Pt,

$$R—m + 2CuBr_2 \rightarrow R—Br + 2CuBr + mBr \qquad (1)$$

Rh, Ir, Tl and Hg [1—5]. The mechanisms of these reactions are a matter of considerable speculation, varying from concerted front-side attack to radical formation to heterolytic cleavage. In order to provide bounds to such mechanisms, we have carried out the stereochemical investigation of the cleavages by copper(II) bromide on four representative alkylmetals* shown below.

$(CH_3)_3C—CHD—CHD—m$

(Ie,t)   m = Cp$_2$ZrCl
(IIe,t) m = HgCl
(e = *erythro*, t = *threo*)

(IIIn)   m = Pd(diphos)Cl
(IVn,x) m = HgCl
(n = *endo*, x = *exo*)

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*In this context, aryl and vinyl analogs are considered separately [6].

The *erythro* (I*e*) and *threo* (I*t*) isomers of $Cp_2 Zr(Cl)CHDCHDC(CH_3)_2$ were prepared in 89 and 92% isomeric purity, respectively, based on the deuterium decoupled PMR spectra ($J(H^1 H^2)$: *erythro* 13 Hz, *threo* 4 Hz) [7]. Treatment of either I*e* or I*t* with a suspension of mercuric chloride in either benzene or chloroform afforded II*e* (81%) or II*t* (83% isomeric purity), both previously prepared by a different route [8]. Bromination of I*e* and I*t* in benzene afforded the bromo derivatives V*e* and V*t*, respectively, with predominant retention of configuration [7, 9]. The *endo*-palladium(II) substituted nortricyclene III*n*, one of the few isolable alkylpalladium complexes [10], was converted to the mercury analog IV*n* with excess mercuric chloride in acetonitrile. The *exo* isomer IV*x* was prepared from norbornadiene with mercuric acetate in acetic acid followed by treatment with aqueous sodium chloride [11]. The epimers IV*n* and IV*x* are readily distinguishable by the chemical shifts of H^3 (*exo* δ 2.67 ppm, *endo* δ 2.37 ppm) and H^5 (*exo* δ 4.67 ppm, *endo* δ 4.83 ppm). *Endo*- and *exo*-bromo-nortricyclenes VI*n* and VI*x* were prepared by brominolysis of IV*n* [12] and bromination of norbornadiene in acetic acid [11], respectively.

Cleavage of both I and II by copper(II) bromide in acetonitrile afforded a mixture of *erythro*- and *threo*-1-bromo-3,3-dimethylbutane-1,2-d_2 as shown in Table 1. In all cases, stereochemical scrambling was essentially complete.

TABLE 1

CLEAVAGE OF 3,3-DIMETHYLBUTYL-1,2-d_2 DERIVATIVES OF ZIRCONIUM AND MERCURY WITH COPPER(II) BROMIDE

Organometal		Isomer purity (%)	Yield (%)[b]	1-Bromo-3,3-butane-1,2-d_2[a]	
				V*e* (*erythro*)	V*t* (*threo*)
I*e*	(*erythro*-Zr)	> 89	67	44	56
I*t*	(*threo*-Zr)	> 92	63	50	50
II*e*	(*erythro*-Hg)	81	55	50[c]	50[c]
II*t*	(*threo*-Hg)	83	44	48[c]	52[c]

[a]Relative accuracy, ±5%. [b]Based on organometal, yields not optimized. [c]Includes 1-chloro-3,3-butane-1,2-d_2 also formed in a 1:1 mixture of *erythro* and *threo* isomers in 17% yield relative to total halides.

Control experiments showed that the products were stable to reaction conditions. Thus, treatment of *threo*-1-bromo-3,3-dimethylbutane-1,2-d_2 (V*t*) with II*t* did not scramble the label. Similarly, treatment of V*t* with $Cp_2 Zr(Cl)Br$, $HgCl_2$ or $CuBr_2$ in acetonitrile effected no change.

The palladium(II) derivative of nortricyclene III*n* with two equivalents of copper(II) bromide in acetonitrile afforded a 1:1 mixture of *exo*- and *endo*-bromides VI*n* and VI*x* in 76% overall yield. The remainder consisted of a mixture of unsaturated bromo acetates which are yet to be fully characterized.

Cleavage of the *endo*-mercurial IV*n* with copper(II) bromide produced a 56:44 mixture of *endo/exo* bromides VI*n* and VI*x*, respectively, together with 17% unsaturated organic material. A similar reaction with the epimer IV*x* gave a 42:58 mixture of the same bromides. In both cases, the starting materials were not epimerized under reaction conditions since IV*n* and IV*x* could be recovered unchanged when less than stoichiometric amounts of copper(II) bromide were employed. The results again clearly show the predominant loss of stereochemistry

when this nortricyclyl skeleton, either as the palladium or the mercury derivative, is cleaved with copper(II) bromide.

Any concerted mechanism for the cleavages by copper(II) bromide is ruled out by the loss of configuration observed in either acyclic or alicyclic, primary or secondary alkyl derivatives of palladium, zirconium and mercury. This includes cyclic, S_E2, or S_N2 types of mechanisms involving the direct cleavages of the carbon—metal bonds by copper(II) bromide. Furthermore, a free carbonium ion is an unlikely intermediate leading to the complete stereochemical equilibration of the 3,3-dimethylbutyl moiety, since the formation of a primary cationic center is improbable. The participation of free carbonium ions can also be eliminated for the secondary nortricyclyl system; their interception should lead to exo-bromide VIx primarily [11, 13].

Our results are most compatible with a two-step process involving the formation of a metastable intermediate, e.g., by alkyl transfer or electron transfer from the organometal to copper(II) [14]. An alkyl radical is a likely intermediate leading to the loss of configuration since inversion is known to be rapid in 3,3-dimethylbutyl as well as nortricyclyl radicals. In the latter case, the facile ring open-

ing of the radical represented in eq. 2, is consistent with the observation of un-saturated bromo acetates in the cleavages of III and IV. Although it is premature to speculate as to how alkyl radicals are generated, suffice it to say that there is evidence, based on related alkyllead compounds [16], for an alkyl exchange followed by spontaneous homolysis of a metastable alkylcopper(II) intermediate, for example:

$$R{-}m + Cu^{II}Br_2 \rightarrow RCu^{II}Br + mBr \qquad (3)$$

$$RCu^{II}Br \xrightarrow{\text{fast}} R^{\cdot} + Cu^{I}Br \qquad (4)$$

$$R^{\cdot} + Cu^{II}Br_2 \xrightarrow{\text{fast}} R{-}Br + Cu^{I}Br \qquad (5)$$

The subsequent scavenging of the alkyl radical by copper(II) bromide in eq. 5 is known to be rapid and to afford alkyl bromide and copper(I) bromide in high yields [17]. The sequence represented in eq. 3—5 leads ultimately to the overall stoichiometry in eq. 1. Electron transfer processes have also been delineated [18]. Finally, epimerization is not necessarily restricted to the homolysis of the intermediate in eq. 4, intramolecular pathways being also conceivable for metastable intermediates [19]. Studies in progress will hopefully delineate such processes in Pd, Zr, Hg and other analogs.

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