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METHYLATION OF QUINONES BY METHYLCOBALT(III) COMPLEXES. FACILE CLEAVAGE OF COBALT-CARBON BOND

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Transalkylations, e.g. to Hg(II)$^{1-4)}$ by certain organocobalt complexes have been a subject of considerable interest in connection with the role of the vitamin B_{12} cofactors in biological systems. In this paper, we wish to report a facile C-methylation of quinones which would be considered to be milder cleaving reagents of the Co-C bond by mainly methylcobaloximes$^{5)}$ in the absence or presence of some transition metal salts.

Methylcobaloximes $CH_3Co(DH)_2B$(B=axial bases, e.g. H_2O, imidazole (Im), pyridine (Py) and triphenylphosphine) (I) and methylbis-(diacetylmonoxime-imino)-1,3-propanecobalt perchlorate $[CH_3Co(DO)(DOH)pnB]\ ClO_4$ (B=Im) (II) were employed as methylating agents for 1,4-naphthoquinone(NQ) (III) and 1,4-benzoquinone(BQ) (IV). The methylated products were identified and determined by means of FID gas chromatography.$^{6)}$

I or II(0.5 mmol) reacted with III(1 mmol) in CH_3CN-CH_3OH(10 ml), partly under an aerobic condition, to afford a small amount of 2-methyl-1,4-naphthoquinone, vitamin K_3(VK_3) (V) even after prolonged reaction although it was formed maybe instantaneously by mixing the reactants. In spite of the low yield, its formation bears great significance with regard to the facile cleavage of the Co-C bond by such a milder reagent. However, the reaction of I with IV unexpectedly failed to produce 2-methyl-1,4-benzoquinone, toluquinone (TQ)(VI) possibly due to the differences in electronic density in the quinone rings between III and IV. The other conditions and results are shown in Table 1.

Table 1. Reactions of the Complexes with the Quinones under N_2

Complex	Axial base	Molar ratio $[CH_3(Co) : NQ]$	Temp. (°C)	Time (day)	Yield of VK_3 or TQ (mole %)
I	H_2O	1 : 2	40	1	ca. 1
	Im		40	1	ca. 1
	Im		50	5	ca. 2.5
II	Im		40	1	<1
	Im		50	2	ca. 1
I	Im	$[CH_3(Co) : BQ]$ 1 : 2	40	1-5	0

On the other hand, when some metal salts were added, we have found that a Pd(II) salt[7)] remarkably promoted the formation of V and effected the formation of VI though in low yield. The conditions and results are given in Table 2 showing the effects of several factors on the yield of V.

Table 2. Reactions in the Complexes-Quinones-Pd(II) Systems under N_2

Complex	Axial base	Molar ratio $[CH_3(Co):NQ:Pd(II)]$	Solvent MeCN:MeoH	Temp. (°C)	Time (hr)	Yield of VK_3 or TQ (mole %)$^{a)}$
I	H_2O	1 : 2 : 3	1 : 1	0-40	⩽24	28
	Im					$30^{b)}$
	Py					30
	$P\phi_3$					20
	Im		$[H_2O]$ 10:2:0	40	16	30
	Im		10:2:1			25
	Im	1 : 2 : 6	3 : 1	R.T.	⩽24	$40^{b)}$
II	Im					$43^{b)}$
I	Im	$[CH_3(Co):BQ:Pd(II)]$ 1 : 2 : 3	1 : 1	40	24-72	4
II	Im			40	48	3

a) Yields show approximate values because of either thermal instability of VK_3 or small peak area of TQ.

b) Also run under an aerobic condition.

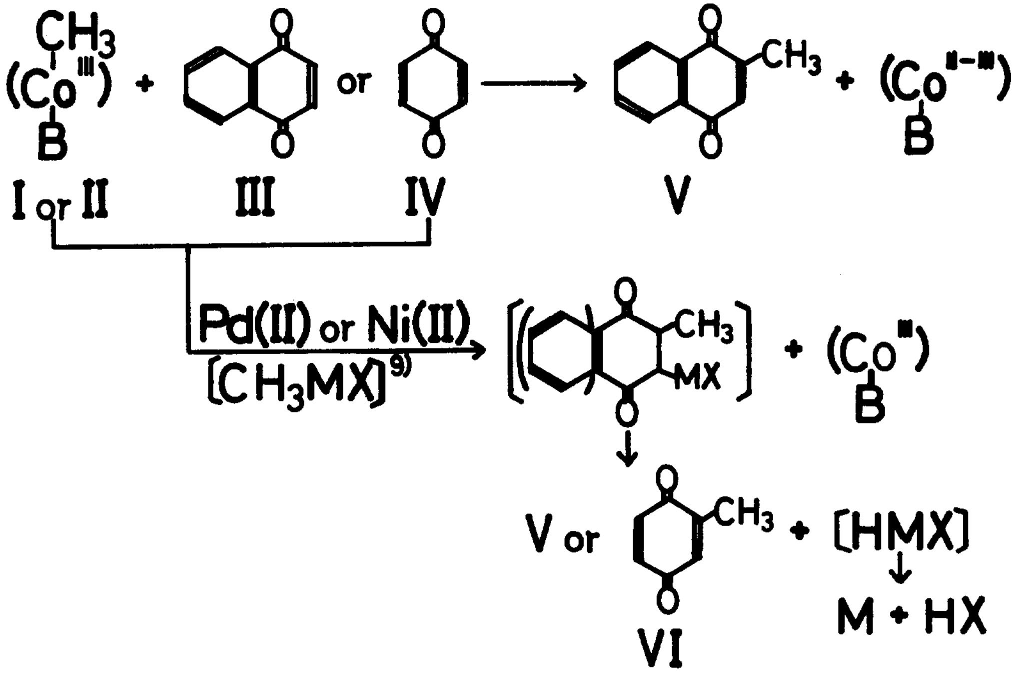
The reactions are hardly influenced by the difference in the axial bases of I, insensitive to O_2 while depressed by the presence of a considerable amount of H_2O, more promoted by higher Pd(II) concentrations, and in particular completed instantaneously even at 0°.

A Ni(II) salt also promoted the formation of V to some extent which was much lower than that by Pd(II) under similar conditions, but Fe(III), Cu(II), and Ag(I) as Ag_2O were ineffective.

It was also observed that higher concentrations of the quinones considerably increased the products only when Pd(II) was added demonstrating again its being the best among the additives used.

For comparison's sake, when common methylating agents such as CH_3I and $(CH_3)_2SO_4$ were used instead of the complexes with or without Pd(II) added, neither of the products were formed.

The possible pathways of the reactions are considered as follows:



The Pd(II) salt was first employed by Heck[8)] followed by Vol'pin et al.[10)] to alkylate or arylate aliphatic olefins with some organometallic compounds. By this work, however, its application has been shown to be extensible at least to the alkylation of quinones, pseudoaromatic olefins and to provide a new and convenient method for the synthesis of their methyl substituents.

Further work is now in progress including the use of methylcobalamin to induce biochemical implication of the reactions.

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References and Notes

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4) N. Imura, E. Sukegawa, S. K. Pan, K. Nagao, J. Y. Kim, T. Kwan and T. Ukita, Science, **172** 1248 (1971).

5) Cobaloxime is a trivial name of bis(dimethylglyoximato)cobalt(III).

6) Analyzed on Apiezon Grease L (for VK_3), Silicone DC 550 (for TQ), Silicone XF 1105, and Silicone DC 11 (for both).

7) $PdCl_2$ was used as either $LiPdCl_3$ in CH_3CN or Li_2PdCl_4 in CH_3OH after Heck.[8)]

8) R. F. Heck, J. Amer. Chem. Soc., **90**, 5518 (1968).

9) Such active species as are plausible were assumed in ref. 8 in the case of some transition metals and the case would be similar in Ni also.

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