

## Quinolinium Bromochromate as a New Brominating Agent for the Bromination of Metal $\beta$ -Diketonates

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Reactions of metal(II) and metal(III)  $\beta$ -diketonates with quinolinium bromochromate (QBC) in glacial acetic acid medium at room temperature produce electrophilic  $\gamma$ -substituted bromo products. The products have been characterised by elemental analyses, IR and  $^1\text{H}$  NMR spectral studies. Based on the experimental evidences, the reagent QBC can act as a brominating agent for the bromination of metal  $\beta$ -diketonates.

### INTRODUCTION

Although in recent years a number of studies on oxidation reactions involving quinolinium halochromates<sup>1</sup> and some organic compounds have been published, none of these deals with the bromination of metal  $\beta$ -diketonates by this type of quinolinium halochromates. Quinolinium bromochromate (QBC) has been very recently used as a reagent to oxidise some organic compounds<sup>2</sup>. The present work represents an attempt to search for newer and if possible better halogenating agents for  $\beta$ -diketonate chelates. QBC is here introduced for the first time as a brominating agent for the bromination of metal  $\beta$ -diketonates of many transition metals in glacial acetic acid medium.

### EXPERIMENTAL

The metal acetylacetonates of Cu(II), Co(II), Ni(II), Cr(III), Co(III) and Mn(III) were prepared as reported<sup>3</sup>. QBC was prepared by the same procedure used for the preparation of quinolinium fluorochromate. The brominated products were identified by comparison with authentic bromoproducts prepared using reagents like N-bromosuccinimide,<sup>4,5</sup> pyridinium bromochromate<sup>6</sup> etc. The IR spectra of all the complexes were recorded on a Perkin-Elmer model 577 spectrophotometer using KBr discs. The  $^1\text{H}$  NMR spectra were recorded on a Perkin-Elmer R32 Spectrophotometer operating at 90 MHz using TMS as internal standard.

#### Bromination of metal $\beta$ -diketonates using QBC

To a solution of QBC in glacial acetic acid was added to the  $\beta$ -diketonate chelate dissolved in acetic acid in stoichiometric amount. The reaction mixture was heated on a water bath for about 1 h with occasional stirring and the completion of the reaction was evidenced by the supernatant solution turning green colour. Then the contents were cooled for 2 h. The solid bromoproduct was filtered, washed with chloroform and dried *in vacuo*. In the case of Cr(III), Co(III)

and Mn(III) chelates, the green solution was treated with petroleum ether and chloroform. The solid bromoproduct was filtered and dried *in vacuo*.

## RESULTS AND DISCUSSION

The reaction products obtained in the bromination of metal  $\beta$ -diketonates employing QBC in glacial acetic acid as a brominating agent are listed in Table-1. An examination of the products listed in Table-1 reveals that a simple electrophilic substitution reaction takes place at the  $\gamma$ -carbon of the coordinated  $\beta$ -diketone ring to give  $\gamma$ -bromoproducts without the rupture of the metal diketone bonding, that is to say the chelate rings remain intact. Major part of the reaction is over within 1 h. The yield of the solid bromoproduct is around 40–50%.

TABLE-1  
ANALYTICAL DATA OF THE ELECTROPHILIC  $\gamma$ -SUBSTITUTED  
BROMO COMPLEXES

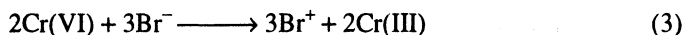
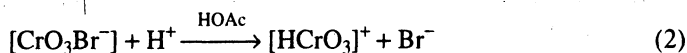
S.No.	Complex	Analysis-Found (Calcd) %				Colour	Yield (%)
		M	C	H	Br		
1.	Cu(Bracac) <sub>2</sub>	15.0 (15.2)	28.9 (28.6)	2.8 (2.9)	37.8 (38.1)	Green	52
2.	Co(Bracac) <sub>2</sub>	14.3 (14.2)	28.7 (28.9)	2.7 (2.9)	38.1 (38.6)	Blue	42
3.	Ni(Bracac) <sub>2</sub>	14.0 (14.2)	29.4 (28.9)	2.8 (2.9)	38.0 (38.5)	Brownish green	33
4.	Cr(Bracac) <sub>3</sub>	8.7 (8.9)	31.4 (30.8)	3.2 (3.1)	39.8 (40.9)	Brown	53
5.	Co(Bracac) <sub>3</sub>	9.8 (9.9)	30.8 (30.4)	3.0 (3.1)	40.0 (40.5)	Green	40
6.	Mn(Bracac) <sub>3</sub>	9.0 (9.3)	30.8 (30.5)	3.1 (3.1)	39.2 (40.7)	Pale yellow	30

\*acac = acetylacetonone.

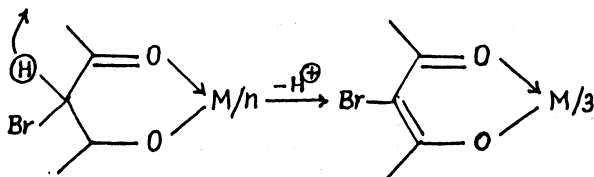
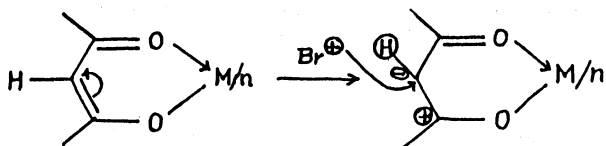
Comparison of the IR spectrum of the substrate chelate with that of the electrophilic bromo- $\beta$ -diketonate product reveals that because of the C—H bond becoming C—Br, the absorption bands corresponding to pure C—H vibration or their combined vibrations wherein C—H is a part would be most affected. Thus, the weak band at 1195  $\text{cm}^{-1}$  and the medium intensity band at 795  $\text{cm}^{-1}$  corresponding to the in-plane bending ( $\delta_{\text{C-H}}$ ) and out-of-plane bending ( $\pi_{\text{C-H}}$ ) respectively disappear in the spectrum of the  $\gamma$ -substituted product. Bands at 1520, 1195 and 795  $\text{cm}^{-1}$  present in the unsubstituted complexes are totally absent in the substituted complexes. The absence of these bands confirms that substitution has occurred at the 3-position in the chelate ring.<sup>7</sup> The absence of bands in the 1750–1700  $\text{cm}^{-1}$  range indicates that no ring flipping has occurred and that the diketones have coordinated through their carbonyl group.<sup>4,5</sup> In <sup>1</sup>H NMR, the proton resonance occurring at 5.3  $\delta$  corresponding the methine proton dramatically disappears in the spectrum of the bromoproduct confirming  $\gamma$ -substitution.<sup>7</sup>

The formation of the electrophilic  $\gamma$ -substituted bromochelate suggests an involvement of  $\text{Br}^+$  cationic species. This can be accounted for by the probable *in situ* oxidation of  $\text{Br}^-$  to  $\text{Br}^+$  by  $[\text{HCrO}_3]^+$  species of the QBC reagent in acid medium.<sup>6</sup> A propable mechanism as shown in Scheme 1 can be visualised.

### Scheme 1. Formation of Electrophilic Substituted Product



where  $\text{M} = \text{Cu(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cr(II)}, \text{Co(III)}, \text{Mn(III)}$ ,  $n = 2$  or  $3$  as the case may be



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