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# Bromination of Tris(1,1,1-trifluoro-2,4-Pentanediono)-chromium(III)

TERENCE J. CARDWELL* and TREVOR H. LORMAN

*Department of Chemistry, La Trobe University, Bundoora, Vic. 3083, Australia*

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Electrophilic substitution of metal β-diketonates has been extensively investigated by many workers and reviewed by Collman [1] and Mehrotra *et al.* [2]. Reaction of the metal complexes with a variety of electrophilic reagents leads to substitution on the central carbon of the chelate ring, unless this position is blocked [3].

Although a number of fluoro-substituted metal β-diketonates have been shown to undergo electrophilic substitution [4], Collman claimed that metal chelates of 1,1,1-trifluoro- and 1,1,1,5,5,5-hexafluoro-2,4-pentanediones are exceptions by failing to react with brominating or nitrating agents [5]. More recently, Watkins and Harris measured the rate of bromination of tris-(1,1,1-trifluoro-2,4-pentanediono) aluminium(III) spectrophotometrically and by $^1H$ NMR [6], but reaction products were not isolated. In this paper, we wish to report the preparation and isolation of the bromination products of tris-(1,1,1-trifluoro-2,4-pentanediono)chromium(III).

## Experimental

Tris-(1,1,1-trifluoro-2,4-pentanediono)chromium-(III), $Cr(tfa)_3$, was synthesised by the method of Fay and Piper [7] and purified by chromatography on an alumina column using chloroform as eluant. Bromination of $Cr(tfa)_3$ was performed in chloroform using excess bromine as the reagent at room temperature. Gas chromatography was carried out using a Perkin Elmer F-11 chromatograph with flame ionization detection; operating conditions are given in the text. Mass spectra were recorded on a JEOL JMS D100 Mass Spectrometer in the electron impact mode.

## Results and Discussion

Several procedures for bromination of $Cr(tfa)_3$ were investigated. Use of N-bromosuccinimide in chloroform or glacial acetic acid proved to be unreliable; there was considerable decomposition in the acetic acid medium whereas the reaction in chloroform frequently led to the recovery of unreacted chelate. Bromination using bromine in chloroform proved to be successful only if the temperature of the reaction mixture was maintained below 30 °C, otherwise decomposition took place.

$Cr(tfa)_3$ is readily eluted by gas chromatography and under certain conditions it is possible to resolve the geometrical isomers of the chelate [8]. Gas chromatography was found to be an excellent technique in the present work for monitoring the extent of the electrophilic substitution by bromine. A chromatogram of the reaction mixture which was sampled 1 hr after addition of excess bromine is presented in Fig. 1; it clearly shows three major peaks with retention times ($t_R$) longer than that for unreacted $Cr(tfa)_3$ ($t_R$ = 1.4 min) at a column temperature of 150 °C. Using an effluent splitter, samples of each component in the reaction mixture were collected for analysis by mass spectrometry.

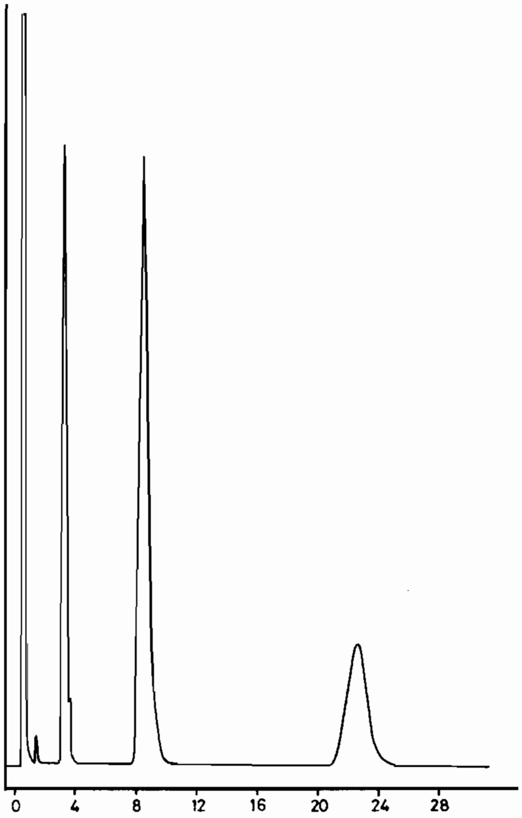

Fig. 1. Gas chromatogram of the reaction mixture from the bromination of $Cr(tfa)_3$ ater 1 hr. Column: glass (1 m × 5 mm i.d.) packed with 2.5% 0V101 on Chromosorb W. Conditions: oven, 150 °C; injector, 200 °C; detector, 190 °C; carrier gas ($N_2$) flow rate, 33 $cm^3$ $min^{-1}$.

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*Present address: Chemistry Dept., University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, U.K.

Parent ions were observed for all three samples and the splitting pattern, based on the isotopic abundance of bromine, gave conclusive evidence for the number of bromine atoms in each species in the reaction mixture. The chromatographic peak at $t_R$ = 3.2 min gave a mass spectrum with parent ions at 591/589 m/e in an intensity ratio 1:1, indicating that this species was the mono-brominated product. The peak at $t_R$ = 8.4 min gave parent ions at 671/669/667 m/e in a ratio 1:2:1, arising from the bi-brominated complex and the peak at 22.6 min had parent ions at 751/749/747/745 m/e in a ratio 1:3:3:1, indicating the tri-brominated complex. The most intense fragments in the mass spectrum of the bi-brominated complex appear as a doublet at 438/436 m/e; as these ions contain only one bromine atom, it implies that the two bromines are on different ligands in the bi-brominated complex. Therefore, the products of the bromination reaction in order of their increasing retention in gas chromatography are $Cr(Brtfa)(tfa)_2$, $Cr(Brtfa)_2(tfa)$ and $Cr(Brtfa)_3$, where Brtfa is the brominated ligand anion.

Bromination of $Cr(tfa)_3$ was essentially complete after 48 hr as determined by gas chromatography. Removal of the solvent and recrystallization from hexane yielded crystals of $Cr(Brtfa)_3$ with 99% purity. A sample of $Cr(Brtfa)_2(tfa)$ could be isolated from a reaction mixture which was allowed to stand for about 2 hr; removal of the solvent and fractional recrystallization from benzene/n-hexane (75/25) resulted in crystals of 99% purity.

Conclusive evidence for the position of substitution on the coordinated ligand has not been obtained in the work described here, but we are currently attempting to isolate sufficient quantities of the corresponding brominated rhodium(III) and cobalt(III) complexes in order to carry out their $C^{13}$-nuclear magnetic resonance spectra and the results will be reported at a later date.

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