The Bromination of Tris(3-phenyl-2, 4-pentanediono)chromium(III)*

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In connection with the quasiaromatic nature of a chelate ring in the metal acetylacetonates, the electrophilic substitution reactions of these complexes have been systematically investigated.[1] In order to understand further the characteristic properties of a metal-chelate ring formed with β-diketones, the chromium(III) chelate of 3-phenyl-2, 4-pentanedione was prepared in this study.

Into a mixture of tris(3-phenyl-2,4-pentanediono)-chromium(III) and pyridine in carbon tetrachloride, there was added bromine dissolved in the same solvent at around 0°C over a period of 20—25 min. The bromination product was then fractionated into five components by means of liquid-chromatography with a combination of silica gel (60—80 mesh) and benzene. The fraction which came off first from a column was re-crystallized from ligroin as green crystals; m. p. 237—239°C (decomp.).

Found: C, 39.16; H, 3.11; Br, 43.94; Cr, 5.0%. An infrared spectrum of this product is illustrated in Fig. 1, together with that of the starting material.

The absorption peaks characteristic of the starting chromium(III) chelate, i. e., 1452, 1357, 1343, and 928 cm^{-1}, disappeared in the brominated material, while new bands were observed in the latter at 1388 and 1240 cm^{-1}. In addition, absorption bands at 771 and 764 cm^{-1} in the unbrominated chelate spread further to 785 and 758 cm^{-1} in the product. Among these infrared absorption peaks, the 1240 cm^{-1} band in the brominated chelate may be assigned to CH_2 wagging vibration in the CH_2Br group;[2] while the 928 cm^{-1} band in the unsubstituted chelate may be attributed to the coupled stretching vibration of $C-CH_3$ and CO.[3] Therefore, the infrared spectrum of the brominated chelate provides evidence for a substitution reaction through which all the methyl groups in tris(3-phenyl-2, 4-pentanediono)chromium(III) were brominated to the monobromomethyl (CH_2Br).

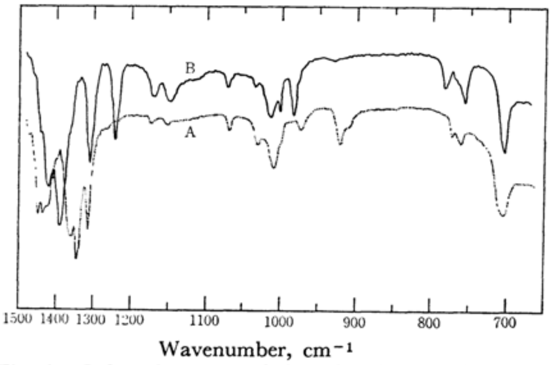

Fig. 1. Infrared spectra of chromium(III) chelates: A, tris(3-phenyl-2, 4-pentanediono)chromium(III); B, a bromination product of tris(3-phenyl-2, 4-pentanediono)chromium(III). (KBr disk method).

Calcd. for $C_{33}H_{27}O_6Br_6Cr$ (hexabromochelate): C, 37.71; H, 2.59; Br, 45.62; Cr, 4.95; and for $C_{33}H_{28}O_6Br_5Cr$ (pentabromochelate): C, 40.77; H, 2.90; Br, 41.17; Cr, 5.35%.

Thus, the possibility of the coexistence of pentabrominated chelate in the first fraction from the column may not be excluded, as its elemental analysis has indicated.

The later fractions from the chromatographic column were identified as less-brominated and unreacted chelates.

An attempt has been made to brominate 3-phenyl-2, 4-pentanedione under similar conditions in the absence of pyridine, but this attempt failed to afford the corresponding bromination product. Thus, the occurrence of the present reaction with the chromium chelate may be said to be due primarily to the chelate ring.

Since the bromination of tris(2, 4-pentanediono)-chromium(III) resulted only in the substitution of the γ-hydrogen,[1,4] the π-electronic interaction of a phenyl ring with the chelate ring in the present chromium chelate[5] seems to activate the methyl groups in the reaction process.

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[1] For a general review, see J. P. Collman, "Reactions of Coordinated Ligands and Homogeneous Catalysis," (Advances in Chemistry Series, 37), American Chemical Society (1963), p. 78; *Angew. Chem., Internat. Edit.*, **4**, 132 (1965).

[2] N. B. Colthup, L. H. Daly and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York (1964), p. 317.

[3] K. Nakamoto, P. J. McCarthy, A. Ruby and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1066 (1961).

[4] J. P. Collman, R. A. Moss, H. Maltz and C. C. Heindel, ibid., **83**, 531 (1961).

[5] Y. Murakami and K. Nakamura, This Bulletin, in press.