

## The Preparation of a Complex Containing a Secondary Carbon-Chromium Bond and of Air-Stable Complexes Containing Primary Carbon-Chromium Bonds

By R. G. COOMBES, M. D. JOHNSON, M. L. TOBE, N. WINTERTON, and LAI-YONG WONG  
(*William Ramsay and Ralph Forster Laboratories, University College, Gower Street, London, W.C.1*)

IN view of the increasing activity<sup>1,2</sup> in the field of  $\sigma$ -bonded organochromium complexes we now report the preparation of the first air-stable  $\sigma$ -bonded organochromium complexes and of the first complex containing a secondary carbon-chromium bond.

On addition of chromous ion to solutions of 2-, 3-, or 4-bromomethylpyridinium bromide or to 2-bromomethyl-1-methylpyridinium bromide, red solutions are immediately obtained. The cationic species present in these solutions can be separated on ion-exchange resins, whereby the complex

<sup>1</sup> J. K. Kochi and D. Buchanan, *J. Amer. Chem. Soc.*, 1965, **87**, 853.

<sup>2</sup> J. K. Kochi and D. D. Davis, *J. Amer. Chem. Soc.*, 1964, **86**, 5264.

organochromium ions, penta-aquo-(2-, 3-, or 4-pyridiomethyl)chromium(III) or penta-aquo-(1-methyl-2-pyridiomethyl)chromium(III) ions (I, II, III, or IV), respectively, are obtained in perchloric acid solution. We have been unable to isolate solid salts, but analyses of the material in solution show that the ratio of chromium:substituted pyridine is 1:1 in all cases.

The ions (I), (II), and (III) are decomposed quantitatively to the corresponding 2-, 3- or 4-methylpyridines and to the corresponding 2-, 3- or 4-(deuteromethyl)pyridine on addition of alkali in water and  $D_2O$ , respectively. Solutions of the ions, unlike solutions of the corresponding

penta-aquobenzylchromium(III) complex<sup>3</sup> are stable for several weeks at room temperature in the presence of air. The ready solubility of these ions and of their solvolysis products in water, together with their air stability, has made them ideally suitable for studies on the character of carbon-chromium bonds in aqueous solution.

The addition of chromous ion to an aqueous solution of 2-(1-bromoethyl)pyridinium bromide likewise gives a red solution from which can be obtained an aqueous solution of the perchlorate (V). This ion has similar characteristics to those described above, in that it gives 2-ethylpyridine and 2-(1-deuteroethyl)pyridine on alkaline decomposition in water and  $D_2O$  respectively, but it is considerably more labile and, like the penta-aquobenzylchromium(III) ion, is unstable in air.

This, the first organochromium complex containing a secondary carbon-chromium bond, despite its instability, should provide useful information as to the stereochemistry of the formation and reactions of carbon-chromium ions.

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