

Preparation of, and Problems in the Assignment of Configuration of, Some Optically Active Alkyl-transition Metal Compounds

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Summary Optically active (1-methylheptyl)bis(dimethylglyoximinato)pyridine-cobalt(III) and -rhodium(III) have been prepared from (–)-1-methylheptyl bromide; cleavage of the organocobalt compound with bromine regenerates (–)-1-methylheptyl bromide of greater than 50% optical purity.

MUCH information about the mechanism of reaction of organic halides and of organic compounds of the non-transition metals has been obtained from a study of the stereochemical transformations that take place at the α -carbon atom.¹ Recently, the same approach has been applied to alkyl derivatives of the transition metals, and organic compounds of iron,² manganese,² and iridium,^{3,4} in which the α -carbon is asymmetric, have been prepared. We now report the isolation of the first such compounds of cobalt and rhodium, but at the same time cast some doubt on one of the methods frequently used for the assignment of configuration.

Thus, (–)-1-methylheptyl bromide, $[\alpha]_D - 29^\circ$, reacts with the bis(dimethylglyoximinato)pyridinecobalt(I) nucleophile within 10 min in methanolic solution at 50° , to give orange (1-methylheptyl)bis(dimethylglyoximinato)pyridinecobalt(III), $[\alpha]_D (\text{CHCl}_3) + 50 \pm 8^\circ$ and with the bis(dimethylglyoximinato)pyridinerhodium(I) nucleophile in 1 h at 60° to give yellow (1-methylheptyl)bis(dimethylglyoximinato)pyridinerhodium(III), $[\alpha]_D (\text{CHCl}_3) + 15 \pm 2^\circ$. However, the assignment of configuration to these two compounds is not as simple as has generally been supposed.

Jensen⁵ has shown that the bis(dimethylglyoximinato)pyridinecobalt(I) nucleophile reacts with cyclohexyl halides, and with other cyclohexyl derivatives, with inversion of configuration at the α -carbon. The close similarity between the reaction of this nucleophile with cyclohexyl and with 1-methylheptyl halides indicates that the (1-methylheptyl)bis(dimethylglyoximinato)pyridinecobalt(III) prepared in this work should have the opposite configuration to that of the starting halide. Since cleavage of non-transition metal alkyls by electrophiles is generally presumed to take place with retention of configuration at the α -carbon, and this has been verified in a few cases,¹ we expected to obtain (+)-1-methylheptyl bromide from the reaction of the optically active (1-methylheptyl)bis(dimethylglyoximinato)pyridinecobalt(III) with bromine in acetic acid. Since the product is substantially (–)-1-methylheptyl bromide of $[\alpha]_D - 20 \pm 5^\circ$, one of our assumptions must be incorrect. Either the reaction of the cobalt(I) nucleophile with the alkyl halide proceeds with retention of configuration, or the reaction of the alkylcobalt with bromine involves predominant inversion of configuration.

A decision between these possibilities is not possible at this time, but the probability that halogenation of the d^6 alkylcobalt compound proceeds by a different mechanism from that observed for the halogenation of non-transition metal alkyls is high. Indeed, the isolation of some oct-1-ene and oct-2-ene dibromides, but not of 1-methylheptyl acetate, along with the 1-methylheptyl bromide suggests either that there are competing mechanisms or that the predominant mechanism of halogenation is unusual.

Two communications have recently appeared in which very similar iridium(I) derivatives have been shown to react with optically active alkyl halides. In one case it was deduced that the reaction occurred with inversion,³ and in the other case with retention,⁴ at the α -carbon atom. Both

of these deductions may be correct, but it is notable that the assignment of configuration in one case rests on the assumption that cleavage of the carbon-iridium bond with bromine involves retention of configuration at the α -carbon.⁴

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¹ C. K. Ingold, 'Structure and Mechanism in Organic Chemistry', 2nd edition, Cornell University Press, 1970, ch. VII.

² R. W. Johnson and R. G. Pearson, *Chem. Comm.*, 1970, 986.

³ J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *Chem. Comm.*, 1970, 612.

⁴ R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, 1970, **92**, 5520.

⁵ F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Amer. Chem. Soc.*, 1970, **92**, 1414.