

Diazocoupling on Some β -Ketoamino Ti^{IV} Chelates

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ABSTRACT

The electrophilic substitution of p-chlorophenyldiazonium ion on β -ketoamino Ti^{IV} chelates, derived from β -dicarbonyl compounds (acetylacetonate, ethylacetoacetate, benzoylacetone) and 2-aminoethanol, with quasi-aromatic ring, was studied. The coupling products were isolated and characterized by elemental analysis, conductivity and magnetic susceptibility measurement and electronic, IR, 1H NMR spectral studies. The parent chelates had undergone coupling at methine carbon of the chelated ligand. The geometry around the metal ion of the product was octahedral as that of parent chelates.

Key words: Aryldiazonium ion, Metalloaromaticity, β -ketoamino Ti^{IV} chelates, Electrophilic substitution

INTRODUCTION

Metalloaromaticity is the manifestation of aromatic properties in the chelate metallocycle as introduced by Calvin and Wilson in 1945 to explain the stability of $Cu(II)$ -1, 3-diketonate complexes (Masui, 2001). Synthesis and structures of β -diketonates were reviewed when the possibility of creating diverse metal complexes with various modes of coordination of typical chelating ligands was discussed (Skopenko et al., 2004). Acetylacetonatozinc and trifluoroacetylacetonatozinc chelates have been prepared by electrolysis and ligand exchange (Vinokurov et al., 2007). Titanium(IV) β -diketonate complexes with various β -diketones, acetylacetonate, benzoylacetone, ethylacetoacetate were synthesised by the authors (Chowdhury and Uddin, 2000).

The central hydrogen atom on metal β -diketonate chelate C,O,M ring systems can be replaced by several groups under apparently electrophilic conditions such as halogenation, thiocyanogenation, arylsulfenylation, chlorosulfenylation, nitration, acylation, formylation, chloromethylation and dimethylaminomethylation (Collman, 1965). Electrophilic substitution of the phenyldiazonium ions at 2, 4-pentanedionates of aluminum(III), chromium(III), copper(II) and palladium(II) was reported (Krishnantutty and Micheal, 1991, 1993). Electrophilic substitution of the phenyldiazonium ions at titanium(IV) β -diketonates complexes of acetylacetonate, benzoylacetone, ethylacetoacetate was reported by authors (Chowdhury and Uddin, 2000).