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Silver(I)-promoted Oxidation and Ring-enlargement Reactions of Unstrained Hydrocarbons, Polyphenyl-cyclopentadiene

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Abstract: A unique sliver(I)-promoted oxidation reaction of polyphenyl-cyclopentadiene is described, in which an oxygen is inserted into the cyclopentadiene-ring, forming a six-membered pyrylium cation.

Keywords: Oxidation, pyrylium, bond activity, polyphenyl-cyclopentadiene.

The activation of carbon-carbon bonds by soluble transitional metal complexes has been one of the most prominent challenges in recent years[1-3]. Despite the inertness of carbon-carbon bonds, some possible ways to cleave carbon-carbon bonds have been devised, such as relieving ring energy[4], inducing aromatic stabilization[5], forming stable metallocyclic complexes[6], *etc*.

Silver salts, such as silver perchlorate and silver trifluoroacetate, play an important role in carbon-carbon bond activation, especially in strained hydrocarbons[7]. It has been found by Koser and his coworkers[8] that strained hydrocarbons can be oxidized by Ag(I) salts, with the formation of silver metal and protic acid. However, the reactions for unstrained substrates, to the best of our knowledge, have not yet been reported. We present herein an unprecedented example of oxidation and ring-enlargement reaction of unstrained five-membered cyclopentadiene-ring promoted by silver(I) ions, shown in **Scheme 1**.

It was found in the synthesis of coordination compounds between silver perchlorate and aromatic hydrocarbons that oxidation and oxygen-inserted reactions occur when polyphenylcyclopentadiene, such as 1,2,3,4,5-pentaphenyl-cyclopentadiene (PPCP) and 1,2,3,4-tetraphenyl-cyclopentadiene (TPCP), was treated with $AgClO_4 \bullet H_2O$ in mixed solvent(CH_2Cl_2/toluene)[9], forming a pyrylium salt other than the expected simple silver-coordinated complex[10-12]. In order to investigate the source of the oxidant, 1,2,4-triphenyl-cyclopentadiene (TPD), owing to its availability, was selected. The reaction was carried out at room temperature. To a solution of TPD (0.1mmol) in a mixed solvent (benzene/ CH_2Cl_2) was added $AgClO_4 \bullet H_2O$ (0.1mmol). After 8 days' stirring, a precipitate of gray-white powder and a dark-green solution was obtained.

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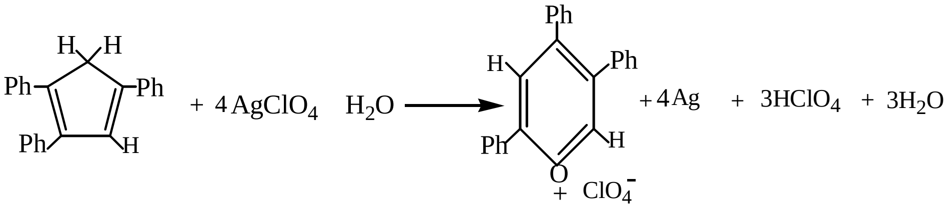
The precipitate was proved to be silver metal by powder XRD[13]. Green crystals were crystallized out of the dark-green solution by solvent diffraction method[10-11]. MS[13](*m/z* 309; M^+ 100%) and ^{1}HNMR[13]($CDCl_3$, 400MHZ, δ in ppm, 8.45 s, 9.17 s)[14] data of the crystals proved the structure of the pyrylium in **Scheme 1**. It was also found that the pH value of the reaction solution decreased during the reaction, indicating the generation of protic acid. The pyrylium structure was further supported by single crystal X-ray analysis[13]. Thus we postulate that Ag(I) is the oxidant of the reaction.

Scheme 1



TPD

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