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Nitrile Addition To Tricarbonylcyclohexadienylium Complexes: The Effect Of Perchlorate Counteranion

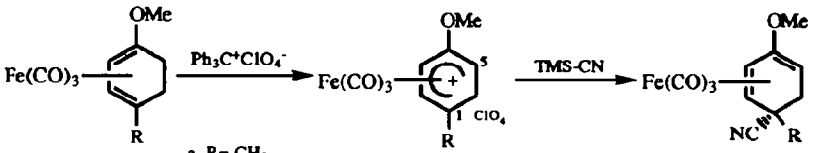
Chi Wi ONG* ,Yen Kai Chao and You An Chang

Department of Chemistry, National Sun Yat Sen University, Kaoshiung, Taiwan 804.

Abstract: A method for the preparation of the tricarbonylcylohexadienyliumiron perchlorate salt and their reactions with TMS-CN were investigated. The nucleophilic addition reactions of TMS-CN were insensitive to the perchlorate counteranion since it cannot dissociate into a nucleophlilic species to release the free cyanide anion. A reductive workup was developed to avoid decompositions.

The ability of cyclohexadienyliumiron complexes to undergo nucleophilic addition reactions have led to their wide application as key intermediates in synthesis. Unfortunately, the cyanide addition reaction has been hampered with severe limitations due to undesirable side reactions and low yield[1]. Stephenson[2] has reported that the use of TMS-CN with the presences of steric hinderance at the C-1 terminus and deactivation by methoxy group also favors the formation of aromatized product. We have recently pinpointed the problem of fluoride ion released from the hexafluorophosphate counterion of the complexes when using TMS-CN[3].It would be of interest to develop a stable counteranion that is insensitive to the TMS-CN for extending the scope of this useful reaction.

The perchlorate salt was chosen for its stability to disproponation and it has been used extensively for this reason in electrochemistry. This counteranion will not react with TMS-CN. The triphenylcarbenium perchlorate was readily prepared as previously described[4] by refluxing triphenylcarbinol with perchloric acid in acetic anhydride. The hydride abstraction of the complexes **1a**, **1b**, **1c** with triphenylcarbenium perchlorate salt occurs with high regioselectivity from the methylene group adjacent to the methoxy substituent, similar to that of triphenylcarbenium hexaflurophosphate salt.[5] The counterion itself does not controlled the regioselection of hydride abstraction. The perchlorate salts **2a**[6], **2b**[7] and **2c**[8] formed were found to be stable for months in the refrigerator before they slowly decomposed. The ^{1}H n.m.r. for the cyclohexadienyliumiron perchlorate complexes showed distinct downfield shifts for the 2-H, 3-H and 5-H protons as compared to the hexafluorophosphate salts. This is in accordance to the more electronegative nature of the perchlorate counteranion.



a. R= CH_3
b. R= $CH(CH_3)_2$
c. R= CH_2COOMe

1 **2** **3**

An investigation of the TMS-CN reactions with the perchlorate salts was conducted. The immediate problem encountered was the spontaneous decomposition of the reaction mixture during standard workup procedure. It was speculated that the aqueous perchlorate formed becomes a powerful oxidizing agents which

causes the decomposition of the complex. This problem was overcomed by pouring the reaction mixture immediately into a cold sodium metabisulfite solution which reduces the perchlorate. The reaction of a large excess of TMS-CN with the perchlorate salt **2a**, **2b**, **2c** were again found to take place regioselectively at the C-1 terminus to give **3a** **3b**, **3c** in high yield. In fact, no side reaction due to deprotonation of the α-acidic proton of the cyclohexadienylium complexes was observed with perchlorate counteranion. The perchlorate counteranion has the advantages of supressing free cyanide anion formation from TMS-CN, and this will allowed a prolong reaction time and a standardized 2.5 equivalents of TMS-CN. The results are shown in Table 1. High yield of nitrile addition at C-1 was obtained with prolong reaction time due to the slow isomerization of TMS-CN to its nucleophilic isocyanide.

Table 1. Reaction of cyclohexadienylium perchlorate salt2 with 2,5 equivalent of TMS-CN with time

Perchlorate salt	Solvent	Reaction condition[4]	yield of 3
2a	CH_3CN	reflux, 3h	40%
	CH_3CN	reflux, 6h	80%
	CH_3CN	reflux, overnight	90%
2b	CH_3CN	reflux, 3h	20%
	CH_3CN	reflux, overnight	80%
2c	CH_3CN	reflux, 3h	18%
	CH_3CN	reflux, overnight	75%

When the reaction were carried out at room temperature, only sluggish reaction was observed. This is due to the requirement of TMS-CN to isocyanide isomerization which takes place at high temperature.

There are several noteworthy features of these results : (i) the new cyclohexadienylium perchorate complexes adds TMS-CN regioselectively at the C-1 terminal in high yield. (ii) a reductive workup to prevents decomposition and (iii) a standardized experimental protocol can be employed. The successful addition of nitrile would serve as a valuable intermediates in organic synthesis.

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6. (**2a**): IR : $\nu_{max.}$ (KBr)2109, 2055 cm^{-1}; ^1H NMR : δ (CD_3CN) 6.90 (1H, dd, 3-H), 5.67 (1H, d, 2-H), 3.99 (1H, m, 5-H), 3.88 (3H, s, OMe), 3.13 (1H, dd, 6-endo-H), 2.25 (1H, dd, 6-exo-H), 1.85 (3H, s, Me). Anal. Calcd for $C_{11}H_{11}O_8Cl_1Fe_1$: C, 36.45; H, 3.06. Found : C, 36.49; H, 3.17.
7. (**2b**): IR : $\nu_{max.}$ (KBr) 2095, 2043 cm^{-1} ; ^1H NMR : δ (CD_3CN) 6.92 (1H, dd, 3-H), 5.68 (1H, d, 2-H), 4.00 (1H, m, 5H), 3.90 (3H, s, OMe), 3.12 (1H, dd, 6-endo-H), 2.45 (2H, m, Me_2CH, 6-exo-H), 1.17 (3H, d, Me), 1.04 (3H, d, Me). Anal. Calcd for $C_{13}H_{15}O_8Cl_1Fe_1$: C, 39.98; H, 3.87. Found: C, 40.07; H, 4.01.
8. (**2c**): IR : $\nu_{max.}$ (KBr) 2115, 2080 (br), 1725 cm^{-1};^1H NMR δ (CD_3CN) 6.97 (1H, dd, 3-H), 5.94 (1H, d, 2-H), 4.01 (1H, m, 5-H), 3.85 (3H, s, COOMe), 3.73 (3H, s, OMe), 3.11 (3H, m, CH_2, 6-endo-H), 2.40 (1H, d, 6-exo-H). Anal Calcd for $C_{13}H_{13}O_{10}Cl_1Fe_1$: C, 37.18; H, 3.10. Found : C, 37.41; H, 3.35.

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