Novel Cerium(IV) Ammonium Nitrate Mediated Transformation of Styrenes to α-Methoxy Acetophenones

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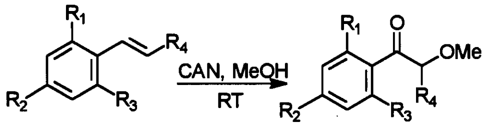
Styrenes when treated with a methanolic solution of CAN underwent a novel transformation to α-methoxy acetophenones presumably via a radical cation

Recently it has been observed that alkoxy styrenes undergo facile cerium(IV) ammonium nitrate (CAN) mediated dimerization resulting in a variety of interesting compounds.[1-3] In this context it was of interest to investigate the reaction of CAN with styrenes devoid of alkoxy groups on the benzene ring. It has been reported by Baciocchi that the reaction of styrene with CAN in acetonitrile led to the exclusive formation of dinitrate.[4] A different reactivity pattern was anticipated in methanol and our preliminary results validating the assumption are presented here.

In a prototype experiment, a methanolic solution of styrene **1a** when treated with CAN afforded α-methoxy acetophenone **2a**.[5] Similar results were obtained with other substituted styrenes (**1b**-**1d**) and these are summarized in Table 1. Interestingly, stilbenes (**1f**, **1g**) also underwent the transformation to afford the corresponding benzoin methyl ethers.[6] Also noteworthy is the reaction of β-methoxystyrene (**1e**) to the dimethyl acetal of phenyl glyoxal in high yield.

Table 1

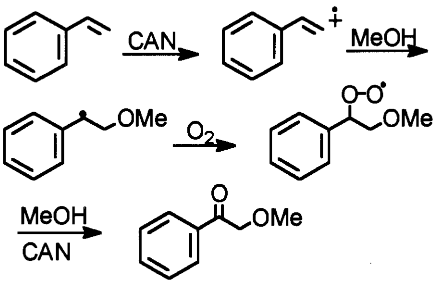


1(a - g) 2(a -g)

Substrate	Yield (%)
1a, $R_1 = R_2 = R_3 = R_4 = H$	44
1b, $R_1 = R_3 = R_4 = H$, $R_2 = Me$	50
1c, $R_1 = R_2 = R_3 = Me$, $R_4 = H$	55
1d, $R_1 = R_2 = R_3 = H$, $R_4 = Me$	61
1e, $R_1 = R_2 = R_3 = H$, $R_4 = OMe$	83
1f, $R_1 = R_2 = R_3 = H$, $R_4 = Ph$	55
1g, $R_1 = R_3 = H$, $R_2 = Me$, $R_4 = Ph$	60

Although the mechanistic details of the reaction are not clear, a tentative rationalization involving a radical cation can be suggested to account for the formation of the product (Scheme 1).[7]

It may be pointed out that the conventional method for the synthesis of α-methoxy acetophenones consists of the $BF_3 \cdot OEt_2$ catalyzed reaction of diazoketones and alcohols,[5,8] in competition with the formation of esters via Wolff rearrangement. Other methods for the synthesis of α-alkoxy and α-hydroxy ketones involve the reaction of alkenes with peracetic acid,[9] catalytic system of OsO_4/Ni(II) complex[10] and permanganate /$CuSO_4$ reagent combination.[11] The reaction reported herein is simple, direct and uses the inexpensive styrene as starting material. The details of the reaction and its mechanistic implications are currently under investigation.



Scheme 1

General Experimental Procedure**:** To a methanolic solution of the styrene (1 mmol) was added a solution of CAN (2.3 mmol) in methanol with stirring. The reaction mixture after the decolorization was diluted with water (20 mL) and then extracted with dichloromethane (5x20 mL). The combined organic extracts were washed with water, brine and dried over sodium sulfate. The solvent was evaporated off. The residue on column chromatography using silica gel (5% ethyl acetate-hexane mixture) afforded the corresponding methoxy acetophenone derivative.

Spectral data for (**2b**) [5] IR (CCl_4): 2940, 2835, 1715, 1625 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.83 (d, 2H, ArH), 7.25 (d, 2H, ArH), 4.68 (s, 1H, CH_2), 3.50 (s, 3H, OCH_3), 2.41 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): 195.80, 144.45, 132.41, 129.40, 127.96, 75.24, 59.42, 21.71.GC-MS m/z (%): 164(M^+)(2) 134(5), 119(65), 91(45), 86 (48), 84(75), 51(35), 49(100).

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