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Combination of Transition Metals-(2,4-Pentanedionate) and P_2O_5 as a Regioselective Catalytic System for Nitric Acid Nitration of Ar-Himachalene

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Abstract

A practical system of metals-(2,4-pentanedionate) ($M(acac)_n$ (M= Fe, Zn, Co and V)) and P_2O_5 in the presence of HNO_3 catalyzes regioselective nitration of ar-himachalene **1** to mono-nitro-ar-himachalene **2** in moderate to high yields. Under mild conditions, the selectivity of nitration of **1** to **2** is excellent compared to the classical method using the nitro-sulphuric mixture HNO_3/H_2SO_4, both mono- and di-nitro-ar-himachalene **2** and **3** are obtained. The reaction offers a very good method for the preparation of nitro-aromatic compounds and provides a useful entry to new functionalized terpenic products.

Keywords: Nitration, Sesquiterpene, Ar-Himachalene, $M(acac)_n$, P_2O_5

1. Introduction

The use of renewable feedstock, which may substitute those derived from petroleum, as well as the employment of low or non-toxic substances are currently great challenges in the chemical and pharmaceutical industries. This new trend is known as green chemistry [1,2]. Nitration of ar-himachalene **1**, biodegradable natural sesquiterpene hydrocarbon (obtainable from renewable sources), using an environmentally friendly catalytic method may be useful source of important valuable new green precursors for the manufacture of products with high added value. Nitro aromatic compounds are themselves used as explosives and act as key substrates for the preparation of useful materials such as dyes, pharmaceuticals, per fumes and plastics [3-6]. Extensive and well-documented reviews in this context have been published by Ingold [7], Olah and co-workers [3,8], Schofield and co-workers [9,10], and Ione [11]. The classical nitration method usually requires the use of an excess of nitric acid and assistance of strong acids such as concentrated sulfuric acid. Recent research has been focused on the development of an environmentally friendly nitration process which can avoid excess of acids to minimize waste and offer high regioselectivity. Many catalytic systems have been em- ployed, most of them heterogeneous; such as metal nitrates of iron(III) or copper(II) supported on montmorillonite clay [12-15] have been shown to be efficient nitra- ting agents. Other examples involve the use of lanthanide (III), zirconium(IV) or hafnium(IV) triflate salts as catalysts of nitric acid nitration [16]. Iron (III)2,4pentanedionate [17,18] and zirconium(IV) 2,4-pentanedionate [19] have also been used as catalysts in the presence of dinitrogen pentoxide.

Within this framework, we report here an environmentally friendly one-pot catalytic procedure for the nitric acid nitration of ar-himachalene using $M(acac)_n/P_2O_5$ (M = Fe, Al, Cr, Zn, Co and V) as catalytic system. This procedure would be a versatile method for aromatic nitration.

2. Results and Discussion

Ar-himachalene **1**, sesquiterpene male-produced pheromone component of the flea beetle *Aphthona flava* [20, 21], was isolated with only 0.5% from essential oil of Atlantic Cedar trees (*Cedrus atlantica*). The essential oil is mainly composed of sesquiterpene hydrocarbons α-himachalene, β-himachalene, and γ-himachalene which together can make up almost 70% of the composition [22,

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23]. Several papers describe the synthesis of ar-hymachalene **1** in multistep starting from citronellal or by conversion of ar-turmerone [24,25]. In our laboratory, we have developed a more practical process for the synthesis of ar-hymachalene **1** in good yield by dehydrogenation of the mixture of α-, β- and γ-himachalene [26].

In preliminary studies, we have investigated the nitration of ar-hymachalene with classical method using nitric acid and sulfuric acid as the nitrating mixture at room temperature in free solvent condition. The reaction lead to a mixture of mononitro-ar-himachalene **2** (10% - 85%) and dinitro-ar-himachalene **3** (13% - 80%) with good conversion (75% - 98%) (**Table 1** and **Scheme 1**).

We have also shown that molar ratio of HNO_3:H_2SO_4: ar-hymachalene has a high effect on the selectivity of the nitration. Thus, with a large excess of HNO_3 and H_2SO_4, 90 % of ar-himachalene **1** was converted in to 11 % of mononitro **2** and 89 % of dinitro **3** (**Table 1**, entry 1). On the other hand, a decrease of the amount of HNO_3 and H_2SO_4 act favourably to an increase of selectivity on mononitro **2**. The low selectivity and the problem regarding the waste disposal make this process uneconomic and hazardous in view of environment. That is why the research in avoiding the use of sulfuric acid in the nitration of aromatics is of great interest to minimize the pollution and promote the greater yield of valuable isomer.

Contributing to this widespread area, we have investigated an environmentally friendly and efficient catalytic system for nitration of ar-hymachalene **1** using metals (2,4-pentanedionate)/P_2O_5 (metal = Fe, Zn, Al, Co, Cr and V) as catalytic system in the presence of nitric acid. The results are summarized in **Table 2**. Nitration of ar-hymachalene **1** was carried out in a solution containing 0.1 mmol of M(acac)$_n$, 14.82 mmol of P_2O_5 and 267 mmol of nitric acid at room temperature. We note here that mononitro-ar-himachalene **2** was the unique obtained product; no di- or tri-nitrated products were observed. In the absence of M(acac)$_n$, ar-hymachalene **1** was not converted (Entry 6). While Al(acac)$_3$ or Cr(acac)$_3$ was not effective (**Table 2**, entries 8, 9), Fe(acac)$_3$, Zn(acac), Co(acac)$_3$ and V(acac)$_2$ were highly effective and selective (**Table 2**, entries 10-13) catalysts. Especially, when Fe(acac)$_3$ was used as the catalyst, the nitration of ar-hymachalene **1** proceeded selectively at room temperature and 93% of mononitro-ar-himachalene **2** was obtained (**Table 2**, entry 10). On the other hand, in the absence of P_2O_5, nitric acid nitration with Fe(acac)$_3$ did not proceed (**Table 2**, entry 7).

It is presumed that a highly reactive nitrating agent is generated in situ by the reaction of P_2O_5 and nitric acid in the presence of M(acac)$_n$ as catalyst. Effectively, it has been reported that N_2O_5 can be prepared from nitric acid in the presence of P_2O_5 [27]. Therefore, N_2O_5 is highly corrosive and liberates toxic nitrogen oxides. Generating it in situ with its decomposition by organometalic catalysts can resolve this problem.

Several reaction conditions were examined; the obtained results are summarized in **Table 3**. This table shows that the yields of the product depend on the nature of the reaction medium. In nitromethane or acetonitrile, the yields were relatively modest with an increase the reaction time (Entries 16, 17).

Table 1. Nitration of ar-himachalene by nitro-sulphuric mixture HNO_3/H_2SO_4.

Entry	Molar ratio HNO_3:H_2SO_4:Ar	Time (h)	Conversion^a (%)	Product distribution^a (%)	
				2	**3**
1	6:9:1	12	90	11	89
2	3:4.5:1	12	82	21	79
3	1.5:2.25:1	12	75	40	60
4	1:1.5:1	12	80	59	41

Conditions: free solvent condition, room temperature. ^{a} Conversion and product distribution were determined by GC.

Table 2. Nitration of Ar-himachalene catalyzed by metal-2,4-pentanedionate/P_2O_5 (metal = Fe, Zn, Al, Co, Cr and V) in the presence of nitric acid.

Entry	Nitrating system	Time (h)	Conversion^a (%)	Isolated yield of **2** (%)
6	P_2O_5	24	0	0
7	Fe(acac)$_3$	24	0	0
8	P_2O_5/Al(acac)$_3$	8	0	0
9	P_2O_5/Cr(acac)	8	0	0
10	P_2O_5/Fe(acac)$_3$	8	100	93
11	P_2O_5/Zn(acac)	12	76	69.5
12	P_2O_5/Co(acac)$_3$	12	82.5	76.5
13	P_2O_5/V(acac)$_2$	12	88.5	83

Condition: S/C=5, P_2O_5/ M(acac)$_n$ = 14.8, 0.267 mol of HNO_3, room temperature, CH_2Cl_2.^{a} the conversion was determined by gaz chromatography.

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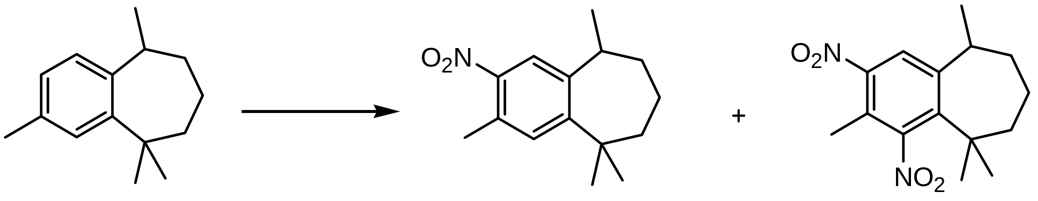
Table 3. Effect of the solvent and the substrate/catalyst ratio (S/C) in the nitration of ar-hymachalene catalysed by Fe(acac)$_3$.

Entry	S/C	Solvent	Time (h)	Isolated yield of 2 (%)
14	5	CH_2Cl_2	8	97
15	5	CCl_4	8	93
16	5	CH_3CN	12	73
17	5	CH_3NO_2	12	52
18	5	MeOH	8	90
19	10	CH_2Cl_2	14	97.5
20	30	CH_2Cl_2	24	91.5
21	50	CH_2Cl_2	24	83

Condition: room temperature, P_2O_5/Fe(acac)$_3$= 14.8, 0.267 mol of HNO_3.



1 **2** **3**

Scheme 1

Therefore, in dichloromethane, tetrachlomethane and methanol (Entries 14, 15 and 18), the reaction mixture was homogeneous and the yields were very high (≥90%). We note here that the corresponding product was then obtained in 100% selectivity. This table also shows the effect of the amount of catalyst. With molar ratio S/C = 10 in dichloromethane after 14 h, the nitration product was obtained in 97.5% yield (Entry 19). Moreover, when we increased the molar ratio (S/C) from 30 to 50, no appreciable loss in activity was observed (Entries 20, 21).

On the other hand, using the reported procedure [26], HNO_3 in the presence of P_2O_5/silica gel, only 51% of ar-hymachalene **1** were converted to mono-nitro **2** (68%) and di-nitro **3** (32%) after 17 h.

This study reveals that the use of Fe(acac)$_3$, Zn(acac), Co(acac)$_3$ and V(acac)$_2$ in the presence of P_2O_5 gives excellent results in nitric acid nitration of ar-hymachalene **1**.

3. Conclusions

Regioselective nitration of ar-hymachalene **1** to 3,5,5,9-Tetramethyl-2-nitro-6,7,8,9-tetrahydro-5H-benzocycloheptene **2** was achieved using series of metals-2,4- pentanedionate/P_2O_5 as catalysts with high conversion and selectivity. Nitric acid was used as nitrating agent without use of sulphuric acid, which makes this process environmentally benign. High yields of nitrated products were obtained with catalyst loadings of 5 - 50 mol%.

4. Experimental Section

Chemicals were purchased from the Fluka, Merck and Aldrich chemical companies and used as received. Arylhimachalene is prepared according to our previews work [24]. NMR studies were performed on a Bruker Avance 300 spectrometer in $CDCl_3$, chemicals shifts are given in ppm relative to external TMS and coupling constant (J) in Hz. Mass spectra were recorded on a GC-MS Thermofinnigan Polaris-Q mass spectrometer.

5. Procedure of Catalytic Studies

Addition of 30 ml CH_2Cl_2 and Fe(acac)$_3$ (1 mmol) to a stirred solution of P_2O_5 (14,8 mmol) and HNO_3 (0,267 mol) (63% w/w) at 0˚C results in the formation of the nitrating complex as a light pink solid. When the solution becomes yellow, 5 mmol of substrate was added to the reaction, which is stirred at room temperature for appropriate time. The solution was then quenched with 5 ml of HCl 10%. The reaction was extracted with ethyl acetate and washed with aqueous Na_2CO_3 and brine. Removal of solvent and purification by column chromatography over silica gel afforded the pure nitrated compounds in near quantitative yields.

3,5,5,9-Tetramethyl-2-nitro-6,7,8,9-tetrahydro-5H-benzocycloheptene 2, yellow oil, ^1H NMR δ: 1,2 (3H, m, CH_3), 1.24 (2H, m, CH_2), 1.25- 1,35 (6H, s, CH_3), 1.46 (3H, d, J 6.9, $CHCH_3$), 1.70 - 1.85 (4H, m, CHH), 2.45 (3H, s, CH_3), 3,2 (1H, m, $CHCH_3$), 2,48 (2H, s,$ArCH_2$),

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7.71 (1H, s, ArH), 7,75 (1H, s, ArH); ^{13}C NMR δ: 20.79, 21.09, 24.18, 30, 34.14, 34.78, 36.42, 40.29, 40.97, 122.21, 130.93, 131.48, 143.86, 147. 25, 154.03. EIMS, *m/z* 247.1 (M^{+}, 100), 232.1 (68.5), 230.1 (28), 144.1 (18), 41.1 (19). HRMS, 247.0288.

2,5,9,9-Tetramethyl-1,3-dinitro-6,7,8,9-tetrahydro-5H-benzocycloheptene 3, yellow oil, ^{1}H NMR δ: 1,2 (3H, m, CH3), 1.24 (2H, m, CH_2), 1.25 - 1,35 (6H, s, CH_3), 1.46 (3H, d, J 6.9, $CHCH_3$), 1.70 - 1.85 (4H, m, CHH), 2.45 (3H, s, CH_3), 3,2 (1H, m, $CHCH_3$), 2,48 (2H, s,ArCH2), 7,8 (1H, s, ArH); ^{13}C NMR δ: 14.34, 20.4, 22.9, 30.34, 31.63, 34.48, 35.49, 42.51, 44.61, 122.43, 123.62, 132, 143.22, 146.38, 149. EIMS, *m/z* 292.1 (M^{+}, 100), 248.1 (86), 232.1 (61.5), 230.1 (32), 144 (21), 41.1 (19). HRMS, 292.1090.

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