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Demetallation of 1,3-diene products obtained from addition of natural products to tricarbonyl(cyclohexadienyl)iron tetrafluoroborate

Timothy I. Odiaka*, Tunmise T. Adebesin, Ibrahim A. Oladosu

Department of Chemistry, University of Ibadan, Ibadan, Nigeria

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ABSTRACT

The demetallation of adducts obtained from the addition of biologically active natural products to [Fe (1-5-η-C_6H_7) $(CO)_3$][BF_4] using the oxidizing agent, trimethylamine-N-oxide, afford new organic compounds which are otherwise inaccessible by conventional organic techniques. The products of demetallation were characterized using NMR (^{1}H, ^{13}C), MS and IR spectroscopic measurements.

1. Introduction

The addition of organic substrates to coordinated π-hydrocarbon of the type [$M(CO)_3$(π-hydrocarbon)][BF_4] e.g [$Fe(CO)_3$(1-5-η-C_6H_7)][BF_4] (**I**) has led to the discovery of novel organometallic compounds such as 1,3-diene substituted products [1–6], 1,3,5-triene-sustituted products [7] or organometallic products [8]. We hereby report the addition of the biologically active natural products, gedunin, khivorin, polyavolensinol and 7-ketokhivorin to the complex [$Fe(CO)_3$(1-5-η-C_6H_7)][BF_4] to afford neutral substituted 1,3-diene products which on demetallation using the oxidizing agent, Me_3NO afforded novel organic compounds of potential medicinal value [9].

Gedunin is a tetranortriterpenoid and an active constituents of *Azadirachta indica A. Juss* and *Melia azedarach* (*L. Meliaceae*) [10], khivorin, and 7-ketokhivorin are isolates from *Khaya ivorensis* [11] and polyavolensinol, all exhibit medicinal characteristics and act as nucleophiles towards the dienylium cation (**I**) to form adducts. Polyavolensinol is obtained from the stem of *Polyathia suaveolens* [12], a medicinal tree grown in western part of Nigeria and used for treating blackwater fever and stomach disorder [13,14]. The adducts formed from the reaction of the dienylium cation (**I**) with the four natural products (Fig. 1) were spectroscopically characterized as well as the novel products obtained from the cleavage of the iron tricarbonyl moiety using Me_3NO.

2. Experimental

[Fe (1-5-η-C_6H_7) $(CO)_3$][BF_4] (**I**) complex was synthesized and purified using published procedure [15]. All the reagents used were obtained in their purest form available (BDH) and used without further purification. The natural products gedunin [10], khivorin [11] were pure, colourless crystalline solids and were isolated as reported in the literature. Polyavolensinol [12,13] is a lilac fluffy solid and 7-ketokhivorin, a light yellow crystal [11]. Infra red spectra were run on a Perkin Elmer Spectrum BX FTIR, and ^{1}H NMR (400 MHz) and ^{13}CNMR (100 MHz) were run on a Bruker AV 400 Spectrometer while the mass spectral measurements were carried out on a Micromass platform II Spectrometer and rotary evaporator for concentration of synthesized compounds.

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* Corresponding author. Tel.: +234 8023209247.
E-mail address: timothy_diaka@yahoo.co.uk (T.I. Odiaka).

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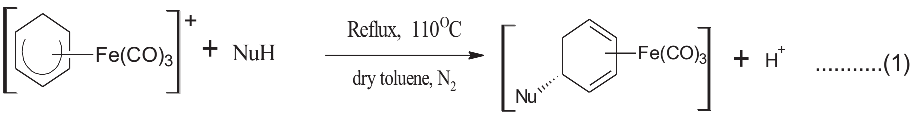
3. Equation for adduct formation



whereNuH=Gedunin/khivorin/7-ketokhivorin/polyavolensinol

where NuH = gedunin/khivorin/7-ketokhivorin/polyavolen sinol

3.1. Products isolation and characterization

This was carried out using the method described by Odiaka et al. [16].

3.1.1. Tricarbonyl [1-4-η-5-(gedunino)cyclohexa-1,3-diene]iron (***II***)

(0.05 g, 0.1634 mmol) of [Fe (1-5-η-C_6H_7)$(CO)_3$][BF_4] and a two-fold molar excess of gedunin (0.157 g, 0.3268 mmol) was refluxed in a three-necked round-bottom flask (50 cm^3) under nitrogen in 30 ml dry toluene at 110 °C for 48 h. The mixture was allowed to cool to room temperature and then concentrated using rotary evaporator under reduced pressure to give a light yellow solid. This solid was shaken with (20/20, v/v) diethylether/water. The aqueous layer was set aside while the organic layer was concentrated using rotary evaporator under reduced pressure to give yellow oil. This was dried in a vacuum line for 3 h to give the same yellow oil (0.04 g, 35% yield). The IR √(CO) bands were observed at 2045 and 1970 cm^{-1}.

3.1.1.1. $C_{37}H_{40}O_{10}Fe$. Yellow oil, IR (film) V_{max} cm^{-1} = 2962 (C–H str of alkanes), 2045 & 1970 (√(CO) bands of coordinated diene of organometallic moiety), 1738 (C=O str of esters), 1667 (αβ-unsaturated ketone), 1495 (C–C band of C_6H_7), 1368 & 1163 (C–O str of esters), 874 (furan band) and 563 (Fe–C band). EMS *m*/*z* (relative intensity%): MS (700.7), 109 (8.125) [M – (2CO) – ($C_{32}H_{39}O_7$)], 150 (1.825) [M – (2CO) – ($C_{25}H_{26}O_7Fe$)], 201 (1.825) [M – (2CO)-($C_{25}H_{31}O_7$)], 257 (6.25) [M – (2CO) – ($C_{23}H_{29}O_5$) – ($2H^+$)], 401 (6.25) [M – (2CO) – ($C_{12}H_{10}O_2Fe$) – (H^+)], 500 (16.25) [M – (2CO) – ($C_3H_3O_3Fe$) – (H^+)], 505 (100) base peak [M – (2CO) – (C_5H_5OFe) – ($2H^+$)], 547 (8.125) [M – (2CO) – (C_2HOFe)], 546 (35) [M – (2CO) – (OHFe) – (H^+)], 604 (3.125) [M – (2CO) – (C_2HO)+(H^+)]. ^1H NMR ($CDCl_3$, 400 MHz δ ppm) see Table 1

3.1.2. Tricarbonyl[1,4-η-5-(khivorino)cyclohexa-1,3-diene]iron (***III***)

(0.025 g, 0.0817 mmol) of [Fe (1-5-η-C_6H_7)$(CO)_3$][BF_4] was weighed into the flask and a two-fold molar excess of khivorin (0.096 g, 0.1634 mmol) was added and refluxed in a three-necked round-bottom flask (50 cm^3) under nitrogen in 30 ml dry toluene at 110 °C for 48 h followed by similar work-up as for gedunin above. This gave yellow oil (0.024 g, 36% yield) which was dried on a vacuum line for 3 h. The IR √(CO) bands were observed at 2050 and 1980 cm^{-1}. The spectroscopic assignments for the products are reported below.

3.1.2.1. $C_{41}H_{48}O_{13}Fe$. Yellow oil, IR (film) V_{max} cm^{-1} = 2962 (C–H str of alkanes), 2050 & 1980 (√(CO) bands of coordinated diene of organometallic moiety), 1730 (C=O str ester), 1256, 1083 & 1013 (C–O str ester), 873 (furan band), 563 (Fe–C band). EMS *m*/*z* (relative intensity %): MS (804.8), 173 (2.27) [M – (2CO) – ($C_{31}H_{41}O_{10}$) – ($2H^+$)], 355 (1.135) [M – (2CO) – ($C_{22}H_{34}O_6$) + (H^+)], 541 (5)[M – (2CO) – ($C_9H_{10}O_2Fe$) – (H^+)], 609 (100) base peak [M-(2CO) – (C_5H_5OFe) – ($2H^+$)], 625 (2.27) [M – (2CO) – (C_4H_3OFe)], 687 (1.135) [M – (2CO) – ($C_2H_3O_2$) – ($2H^+$)]. ^1H NMR ($CDCl_3$, 400 MHz δ ppm): 4.55 (1H, m, H^1), 1.41 (2H, dd, $H^{2a\&2b}$), 4.45 (1H, m, H^3), 2.12 (1H, m, H^5), 2.16 (1H, m, H^{6b}), 4.64 (1H, m, H^7), 1.38 (1H, m, H^{11a}), 1.85 (1H, m, H^{11b}), 1.88 (1H, m, H^{12a}), 1.57 (1H, m, H^{12b}), 1.57 (1H, m, H^{12b}), 3.45 (1H, s, H^{15}), 1.17 (3H, s, H^{18}), 0.74 (3H, s, H^{19}), 6.24 (1H, s, H^{21}), 5.54 (1H, s, H^{22}), 0.85 (3H, s, H^{28}), 1.01 (3H, s, H^{29}), 0.94 (3H, s, H^{30}), 2.08 (3H, s, H^{32}), 1.95 (3H, s, H^{33}), 1.49 (3H, s, H^{34}), 7.33 (1H, d, $H^{3'}$), 2.79 (1H, m, $H^{2'}$), 1.60 (1H, m, $H^{6'a}$) and 2.19 (1H, m, $H^{6'b}$).

3.1.3. Tricarbonyl[1,4-η-5-(7-ketokhivorino)cyclohexa-1,3-diene] iron (***IV***)

(0.025 g, 0.0817 mmol) of [Fe (1-5-η-C_6H_7)$(CO)_3$][BF_4] was weighed into the flask followed by the addition of a two-fold excess of 7-ketokhivorin (0.0907 g, 0.1634 mmol). This was refluxed in 25 ml dry toluene for 48 h, followed by a similar work-up as for gedunin above which resulted into a yellow solid after drying on a vacuum line for 4 h. The yield, obtained was (0.028 g (44%)). The IR √(CO) band were observed at 2050 and 1980 cm^{-1}. Spectra data of the products are presented thus.

3.1.3.1. $C_{39}H_{44}O_{12}Fe$. Yellow solid, IR (film) V_{max} cm^{-1} = 2962 (C–H str of alkanes), 2050 & 1980 (√(CO) band of coordinated diene of organometallic moiety), 1728 (C=O str of ester), 1256, 1084 & 1012 (C–O str of ester), 873 (furan band), 565 (Fe–C band). EMS *m*/*z* (relative intensity%): MS (760.73), 191 (1.704) [M – (2CO) – ($C_{29}H_{37}O_8$)], 219 (2.840) [M – (2CO) – ($C_{27}H_{35}$ – O_8) + ($2H^+$)], 541 (3.977) [M – (2CO) – (C_7H_7OFe)], 560 (1.704) [M – (2CO) – ($C_3H_3O_3Fe$)], 593 (3.977) [M – (2CO) – (C_3H_2OFe) – (H^+)], 609 (100) base peak [M – (2CO) – (C_2HOFe) + ($2H^+$)]. ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 4.65 (1H, t, H^1), 1.64 (1H, d, H^{2a}), 1.95 (1H, d, H^{2b}), 4.55 (1H, t, H^3), 2.12 (1H, t, H^5), 1.92 (1H, t, H^{6a}), 1.55 (1H, s, H^{6b}), 4.45 (1H, t, H^9), 1.50 (1H, s, H^{11a}), 1.88 (1H, t, H^{11b}), 2.16 (1H, d, H^{12a}), 1.57 (1H, t, H^{12b}), 3.45 (1H, s, H^{15}), 5.53 (1H, s, H^{17}), 0.94 (3H, s, H^{18}), 0.74 (3H, s, H^{19}), 7.17 (1H, s, H^{21}), 7.12 (1H, s, H^{22}), 2.08 (3H, s, H^{25}), 2.29 (3H, s, H^{26}), 1.01 (3H, s, H^{28}), 0.85 (3H,s, H^{29}), 7.33 (1H, m, $H^{1'}$), 7.34 (1H, t, $H^{2'}$), 6.24 (1H, dd, $H^{3'}$), 2.79 (1H, dd, $H^{5'}$), 1.60 (1H, d, $H^{6'a}$) and 2.19 (1H, d, $H^{6'b}$).