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# CERIC AMMONIUM NITRATE AND MANGANESE(III) ACETATE MEDIATED RADICAL OXIDATION AND ADDITION REACTIONS OF ANTHRACENE AND 9-SUBSTITUTED ANTHRACENES

**Mustafa Zengin, Fatih Sonmez, Mustafa Arslan*, Mustafa Kucukislamoglu**

*Sakarya University, Faculty of Arts and Sciences, Department of Chemistry, 54187, Sakarya, Turkey*
mzengin@sakarya.edu.tr, fsonmez@sakarya.edu.tr,
mustafak@sakarya.edu.tr, marslan@sakarya.edu.tr

Radical oxidation and addition reactions of anthracene (**1**), 9-methylanthracene (**2**) and 9-phenylanthracene (**3**) were investigated with dimethyl malonate (4) in the presence of ceric ammonium nitrate (CAN) and manganese(III) acetate ($Mn(OAc)_3$). Although mostly anthraquinone derivatives and bianthrone were obtained with CAN, substituted 9,10-dihydroanthracene and 9,10-substituted anthracene derivatives were obtained with $Mn(OAc)_3$. Dimethylmalonyl addition products (**5a**, 33 % and **5b**, 42 %) were obtained in higher yield than quinones (**5d**, 8 % and **5e**, 3 %) using $Mn(OAc)_3$ as oxidant. **9a** (96 %) and **9b** (84 %) were synthesized in high yield and substitution products (**7a**, 44 % and **8b**, 56 %) were obtained in higher yields than quinones (**5d** and **5e**) using CAN as oxidant. The reactions were carried out in non-acidic medium (dichloromethane and methanol). Based on the structures of the isolated products a mechanism for these transformations was proposed.

**Keywords:** anthracene; oxidation; ceric ammonium nitrate; manganese(III) acetate

## РАДИКАЛСКИ ОКСИДАЦИИ И АДИЦИИ НА АНТРАЦЕН И 9-СУПСТИТУИРАНИ АНТРАЦЕНИ СО ПОМОШ НА ЦЕРИУМ(IV)АМОНИИУМ НИТРАТ И МАНГАН(III) АЦЕТАТ

Испитувани се радикалски оксидациони и адициони реакции на антрацен (**1**), 9-метилантрацен (**2**) и 9-фенилантрацен (**3**) со диметилмалонат (**4**) во присуство на цериум(IV) амониум нитрат (CAN) и манган(III) ацетат ($Mn(OAc)_3$). Притоа со CAN главно се добиени антрахинонски деривати и биантрон, додека пак со $Mn(OAc)_3$ се добиени супституиран 9,10-дихидроантрацен и 9,10-супституирани антраценски деривати. Адициони продукти на диметилмалонил (**5a** 33% и **5b** 42%) се синтетизирани со повисок принос од хиноните (**5d** 8% и **5e** 3%) со употреба на $Mn(OAc)_3$ како оксидационен реагенс. Со реакциите се синтетизирани со висок принос **9a** (96%) и **9b** (84%), како и супституционите продукти (**7a** 44% и **8b** 56%) кои се добиени со повисок принос од хиноните (**5d** и **5e**) со CAN како оксиданс. Реакциите беа изведувани во некисела средина на дихлорометан и метанол. Врз основа на структурите на изолираните продукти е предложен механизам на овие хемиски претворби.

**Клучни зборови:** антрацен; оксидација; цериум(IV) амониум нитрат и манган(III) ацетат

## 1. INTRODUCTION

In recent years, there have been many studies to design and develop catalytic systems for reducing emissions of ecologically harmful compounds in order to protect the environment [1]. Polycyclic aromatic hydrocarbons (PAHs) are pollutants and mainly are produced by natural and anthropogenic sources, generated from incomplete combustion of organic materials in fossil fuels, foods, cigarettes etc. PAHs pose a health risk due to their mutagenic and carcinogenic potential and also they raise the risk of lung cancer deaths because of their presence in air [2, 3].

There have been a lot of oxidation reactions of PAHs using various methods such as permanganate oxidation [4], vanadium(V), $H_2O_2$, acetic acid systems [5], phthalocyanine based heterogeneous catalyst [6] and sonoelectrochemical oxidations [7] among others.

Anthracene and its derivatives have been extensively studied in many areas, such as material chemistry [8] high fluorescence, thermochromic or photochromic field [9] and applied to optical, electronic devices and switches, and incorporated into polymers, films and crystals [10]. Selective oxidation of aromatic compounds into biaryl or quinone derivativess is an important goal in the synthesis of useful chemicals. Many anthraquinones have been studied for their biological activities especially their anticancer potential since the discovery of anticancer drugs [11]. Anthraquinone derivatives are used or recommended as a laxatives, antiphlogistics and hemostatics in the treatment of obstipation, gastrointestinal indigestion, diarrhea and also exhibit anti tumor activities [12–14].

The field of free radical chemistry has been vastly expanded by generation of radicals with the help of transition metals, especially $Mn^{3+}$, $Co^{3+}$, $Fe^{3+}$, $Ag^{2+}$, and $Ce^{4+}$ and their oxides. These transition metal reagents exhibit regioselectivity and are useful in the preparation of polyfunctional organic compounds [15]. Ceric ammonium nitrate (CAN) and manganese(III) acetate mediated oxidative free radical reactions have been extensively developed due to the prospect for new routes for carbon-carbon bond formation [16]. These two reagents are one of the most important oxidants in organic synthesis and they are commercially available and sufficiently stable in different solvents. The oxidants serve for the generation of radicals from acidic substrates and exhibit similar reactivity pattern [17]. These reagents have been used for many synthetic transformations such as oxidative free radical reactions in green media such as water and ionic liquids [18], carbon-carbon bond formation [19] and one pot synthesis of different heterocycles including dihydrofurans and aminotetralins [20].

In this study, CAN and $Mn(OAc)_3$ mediated oxidation and addition were performed on anthracene in non-acidic media and the obtained oxidation and addition products were isolated and characterized.

## 2. EXPERIMENTAL

*Instruments*: Melting points were obtained on Barnstead Electrothermal 9200 melting point apparatus. $^1$H NMR and $^{13}$C NMR were obtained in $CDCl_3$ with internal standard TMS on Varian 300 MHz FT-NMR spectrophotometer. The mass spectral analyses were carried out on a Micromass Quattro LC-MS/MS spectrometer.

*Reagent*: Ceric ammonium nitrate (Fluka), manganese(III) acetate dihydrate (Fluka), anthracene (Merck), 9-methylanthracene (Merck), 9-phenylanthracene (Merck), dimethyl malonate (Fluka), methanol (Fluka) and dichloromethane (Fluka) were commercial products with highest reagent grade.

*General procedure for ceric ammonium nitrate reactions*: Anthracene compounds (10 mmol) and dimethyl malonate (10 mmol) in 5 ml of dichloromethane were placed in 100 ml round bottom flask in ice bath under nitrogen atmosphere and ceric ammonium nitrate (20 mmol) in 30 ml of methanol was added

dropwise to the reaction mixture at half an hour. The reaction was run for four hours at room temperature. The solvent in the mixture was evaporated and the residue was dissolved with dichloromethane. The solution was washed with water, dried with calcium chloride, filtered and the solvent was evaporated. The products were purified by column chromatography on silica gel with dichloromethane-hexane or crystallization from chloroform-hexane solutions.

*General procedure for $Mn(OAc)_3$ reactions*: The water of manganese(III) acetate dihydrate (15 mmol) was removed by Dean-Stark apparatus in dry benzene. Dried $Mn(OAc)_3$ were placed in 100 ml round bottom flask. Anthracene compounds (**1**–**3**) (10 mmol) and dimethyl malonate (10 mmol) in dichloromethane were added to the reaction flask by dropwise at half an hour. The reaction was carried out under nitrogen atmosphere. The reaction was refluxed for 48 hours. The mixture was washed with water, dried with calcium chloride, filtered and the solvent were evaporated. Then, the products were purified by crystallization from chloroform-hexane solutions.

*Spectral Data*

Dimethyl 2-((9*r*,10*r*)-9-acetoxy-9,10-dihydroanthracen-10-yl)malonate (**5a**): Colorless crystals; yield: 33 % (conversion: 53 %); mp 121–122 ºC; $^1$H NMR ($CDCl_3$, 300 MHz) δ/ppm: 2.48 (s, 3H, $CH_3$), 3.46 (s, 6H, 2 · $CH_3O$), 3.56–3.60 (d, 1H, CH), 4.86–4.90 (d, 1H, CH), 7.00 (s, 1H, CH), 7.32–7.38 (m, 4H, ArH), 7.45–7.49 (dd, 2H, ArH), 7.55–7.60 (dd, 2H, ArH); 13C NMR ($CDCl_3$, 75 MHz) δ/ppm: 22.1, 45.7, 52.7, 61.8, 73.2, 127.8, 128.9, 129.4, 130.5, 135.3, 140.0, 168.1, 170.9. LC-MS calcd. for $C_{22}H_{18}O_2$, *m/z*: 307.33 [$M^+ - C_2H_4O_2$]; found, *m/z*: 308.10 [$M^+ - C_2H_4O_2$].

Dimethyl 2-((9r,10r)-9-acetoxy-9,10-dihydroanthracen-10-yl)malonate (**5b**): Colorless crystals; yield: 42 % (conversion: 53 %); mp 127–129 ºC; $^1$H NMR ($CDCl_3$, 300 MHz) δ/ppm: 2.05 (s, 3H, $CH_3$), 3.56 (s, 6H, 2 x $CH_3O$), 4.13–4.17 (d, 1H, CH), 4.79–4.83 (d, 1H, CH), 6.84 (s, 1H, CH), 7.27–7.32 (m, 4H, ArH), 7.42–7.46 (dd, 2H, ArH), 7.57–7.60 (dd, 2H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ/ppm: 21.8, 45.8, 52.7, 61.6, 73.2, 127.8, 128.8, 129.4, 130.6, 135.3, 139.9, 168.5, 170.8. LC-MS calcd. for $C_{22}H_{18}O_2$, *m/z*: 307.33 [$M^+ - C_2H_4O_2$]; found, *m/z*: 308.10 [$M^+ - C_2H_4O_2$].

Dimethyl 2-(anthracen-10-yl)malonate (**5c**): White powder; yield: 7 % (conversion: 53 %); mp 178-181 ºC ; $^1$H NMR ($CDCl_3$, 300 MHz) δ/ppm: 3.73 (s, 6H, 2 · $CH_3O$), 6.11 (s, 1H, CH), 7.46–7.58 (m, 4H, ArH), 8.03–8.05 (d, 2H, ArH), 8.24–8.26 (d, 2H, ArH), 8.51 (s, 1H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ/ppm: 51.8, 53.2, 124.4, 125.0, 125.2, 126.9, 129.4, 129.6, 130.9, 131.9, 169.5. LC-MS calcd. for $C_{19}H_{16}O_4$, *m/z*: 331.09 [M+Na]$^+$; found, *m/z*: 331.36 [M+Na]$^+$.

Anthracene-9,10-dione (**5d**): White powder; yield: 8 % (conversion: 53 %); mp 285–286 ºC (lit. [31] mp 283–284 ºC); $^1$H NMR ($CDCl_3$, 300 MHz) δ/ppm: 7.78–7.82 (dd, 4H, ArH), 8.32–8.36 (dd, 4H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ/ppm: 127.3, 133.6, 134.2, 182.9.

9-(9-oxo-9,10-dihydroanthracen-10-yl)anthracen-10(9H)-one (**5e**): White powder; yield: 3 % (conversion: 53 %); mp 259–261 ºC (lit. [32] mp 262–268 ºC); $^1$H NMR ($CDCl_3$, 300 MHz) δ/ppm: 4.75 (s, 2H, 2 · CH), 6.82–6.86 (dd, 4H, ArH), 7.38–7.46 (m, 8H, ArH), 7.88–7.92 (dd, 4H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ/ppm: 54.5, 126.8, 128.2, 128.8, 132.5, 133.9, 140.1, 183.3. LC-MS calcd. for $C_{28}H_{18}O_2$, *m/z*: 387.13 [M+H]$^+$; found, *m/z*: 387.42 [M+H]$^+$.

Lepidopterene (**6a**): White powder; yield: 43 % (conversion: 57 %); mp 304–306 ºC (lit. [33] mp 298 ºC); $^1$H NMR ($CDCl_3$, 300 MHz) δ/ppm: 2.90–2.91 (d, 4H, 2 · $CH_2$), 4.63–4.65 (t, 2H, 2 · CH), 6.72–6.74 (dd, 4H, ArH), 6.77–6.84 (m, 4H, ArH), 6.98–7.03 (m, 4H, ArH), 7.32–7.35

(dd, 4H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ/ppm: 29.0, 45.5, 54.1, 122.8, 123.5, 125.4, 125.6, 143.4, 143.6. LC-MS calcd. for $C_{30}H_{22}$, *m/z*: 405.16 $[M+Na]^+$; found, *m/z*: 405.50 $[M+Na]^+$.

Anthracen-9-ylmethyl acetate (**6b**): Yellow powder; yield: 15 % (conversion: 57 %); mp 108–110 ºC (lit. [34] mp 110–111 ºC); 1H NMR ($CDCl_3$, 300 MHz) δ/ppm: 2.10 (s, 3H, $CH_3$), 6.16 (s, 2H, $CH_2$), 7.48–7.61 (m, 4H, ArH), 8.03–8.06 (d, 2H, ArH), 8.32–8.35 (d, 2H, ArH), 8.53 (s, 1H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ/ppm: 21.3, 59.1, 124.1, 125.4, 126.9, 128.1, 129.4, 129.6, 131.3, 131.6, 171.6. LC-MS calcd. for $C_{17}H_{14}O_2$, *m/z*: 250.10 $[M]^+$; found, *m/z*: 250.26 $[M]^+$.

9-Methylanthracen-10-yl acetate (**6c**): Yellow powder; yield: 29 % (conversion: 57 %); mp 168-170 ºC (lit. [35] mp 169–172 ºC); $^1$H NMR ($CDCl_3$, 300 MHz) δ/ppm: 2.65 (s, 3H, $CH_3$), 3.10 (s, 3H, $CH_3$), 7.51–7.55 (m, 4H, ArH), 7.95–7.99 (dd, 2H, ArH), 8.30–8.34 (dd, 2H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ/ppm: 14.3, 21.1, 121.0, 122.0, 123.8, 125.3, 125.7, 126.0, 129.2, 130.4, 170.1. LC-MS calcd. for $C_{17}H_{14}O_2$, *m/z*: 289.06 $[M+K]^+$; found, *m/z*: 288.50 $[M+K]^+$.

9-Methoxyanthracene (**7a**): Yellow powder; yield: 44 % (conversion: 100 %); mp 93–95 ºC (lit. [31] mp 95–96 ºC); $^1$H NMR ($CDCl_3$, 300 MHz) δ/ppm: 4.16 (s, 3H, $CH_3O$), 7.46–7.50 (m, 4H, ArH), 7.99–8.03 (dd, 2H, ArH), 8.23 (s, 1H, ArH), 8.29–8.33 (dd, 2H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ/ppm: 63.4, 122.4, 122.5, 124.7, 125.5, 125.7, 128.7, 132.7, 152.4. LC-MS calcd. for $C_{15}H_{12}O$ *m/z*: 209,09 $[M+H]^+$; found, *m/z*: 209,22 $[M+H]^+$.

9-Methyl-9-nitrateanthracen-10(9H)-one (**8a**): Yellow crystals; yield: 27 % (conversion: 100 %); mp 216–218 ºC; $^1$H NMR ($CDCl_3$, 300 MHz) δ/ppm: 1.34 (s, 3H, $CH_3$), 7.25–7.27 (dd, 2H, ArH), 7.54–7.63 (m, 4H, ArH), 8.37-8.39 (dd, 2H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ/ppm: 32.3, 79.2, 127.2, 127.9, 128.5, 131.1, 133.4, 145.2, 183.5. LC-MS calcd. for $C_{15}H_{11}NO_4$, *m/z*: 287.08 $[M+H_2O]^+$; found, *m/z*: 288.56 $[M+H_2O]^+$.

10-Methoxy-9-methylanthracene (**8b**): Yellow crystals; yield: 56 % (conversion: 100 %); mp 135–137 ºC (lit. [36] mp 138–142 ºC); $^1$H NMR ($CDCl_3$, 300 MHz) δ/ppm: 3.06 (s, 3H, $CH_3$), 4.13 (s, 3H, $CH_3O$), 7.50–7.54 (m, 4H, ArH), 8.28–8.38 (m, 4H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ/ppm: 14.1, 63.5, 123.0, 124.4, 125.0, 125.3, 125.6, 126.3, 130.9, 151.0. LC-MS calcd. for $C_{16}H_{14}O$, *m/z*: 223.10 $[M+H]^+$; found, *m/z*: 223.30 $[M+H]^+$.

9-Methoxy-9-phenylanthracen-10(9H)-one (**9a**): White powder; yield: 96 % (conversion: 90 %); mp 167–168 ºC (lit. [37] mp 169–170 ºC); $^1$H NMR ($CDCl_3$, 300 MHz) δ/ppm: 3.01 (s, 3H, $CH_3O$), 7.14–7.59 (m, 11H, ArH), 8.34–8.36 (d, 2H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ/ppm: 51.9, 78.8, 125.9, 126.6, 127.3, 128.4, 128.5, 128.8, 132.1, 134.4, 145.2, 146.5, 183.9. LC-MS calcd. for $C_{21}H_{16}O_2$, *m/z*: 301.12 $[M+H]^+$; found, *m/z*: 301.38 $[M+H]^+$.

9-Ethoxy-9-phenylanthracen-10(9H)-one (**9b**): White powder; yield: 84 % (conversion: 90 %); mp 158–159 ºC; $^1$H NMR ($CDCl_3$, 300 MHz) δ/ppm: 1.18–1.20 (t, 3H, $CH_3$), 3.09–3.14 (q, 2H, $CH_2$), 7.22–7.56 (m, 11H, ArH), 8.35–8.37 (d, 2H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ/ppm: 15.7, 59.6, 78.2, 125.9, 126.8, 127.2, 128.3, 128.5, 128.8, 131.8, 134.2, 145.9, 146.7, 183.9. LC-MS calcd. for $C_{22}H_{18}O_2$, *m/z*: 337.12 $[M+Na]^+$; found, *m/z*: 337.49 $[M+Na]^+$.

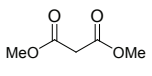
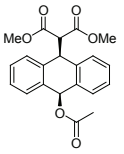
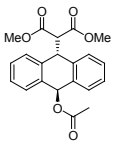
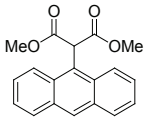
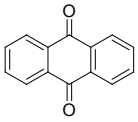
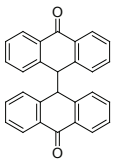
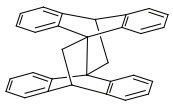
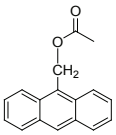
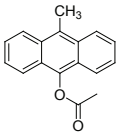
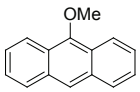
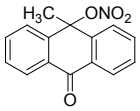
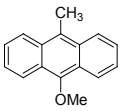
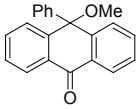
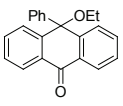
## 3. RESULTS AND DISCUSSION

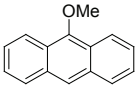
The oxidation of aromatic compounds with $Mn(OAc)_3$ was studied in detail by Dewar *et al.* [21] and Heiba *et al.* [22]. The reaction between aromatic compounds such as substituted naphthalene and benzene derivatives and oxidizing agents such as CAN and $Mn(OAc)_3$ have been

previously reported in acidic medium [23, 24]. The compounds were oxidized in acetic acid to give quinones. These reactions and the obtained products were explained by electron transfer mechanism. It is well known that the radical mechanism involves electron transfer process from $Mn(OAc)_3$-acidic acid systems [22]. In this study, the reactions were carried out in dichloromethane-methanol with CAN and dichloromethane with $Mn(OAc)_3$. As seen in Table 1, the reactions of anthracene compounds with dimethyl malonate and CAN gave quinone derivatives. A plausible reaction mechanism is suggested in scheme 1. As previously reported, the oxidation of anthracene compounds by peroxides leads to the endoperoxide, 9,10-dihydro-9,10-epidioxy anthracene, which is unstable and undergoes further transformations to give anthroquinone as a final product [5] and radical oxidation of anthracene on platinum macro and micro electrodes resulted in quinone derivatives [7, 25].

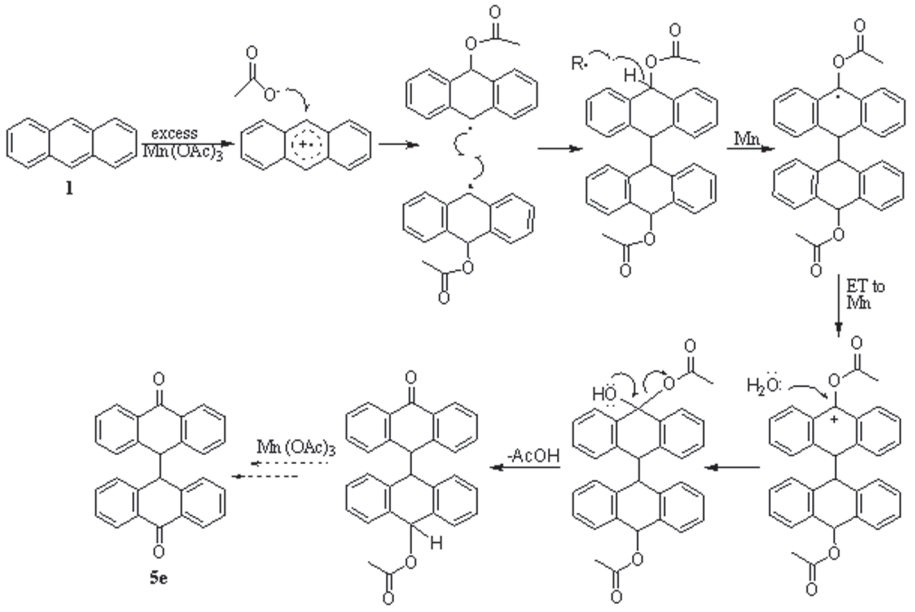
T a b l e 1.

*Isolated products CAN and $Mn(OAc)_3$ mediated radical oxidation and addition reactions*

| E | Oxidant | Diketone | Products | | | | |
|---|---|---|---|---|---|---|---|
| 1 | $Mn(OAc)_3\ 2H_2O$ |  |  |  |  |  |  |
| | | 4 | 5a | 5b | 5c | 5d | 5e |
| 2 | $Mn(OAc)_3\ 2H_2O$ | 4 |  |  |  | – | – |
| | | | 6a | 6b | 6c | | |
| 3 | $Mn(OAc)_3\ 2H_2O$ | 4 | – | – | – | – | – |
| 1 | CAN | 4 |  | 5d | 5e | – | – |
| | | | 7a | | | | |
| 2 | CAN | 4 |  |  | 5d | – | – |
| | | | 8a | 8b | | | |
| 3 | CAN | 4 or none |  |  | – | – | – |
| | | | 9a (in MeOH) | 9b (in EtOH) | | | |

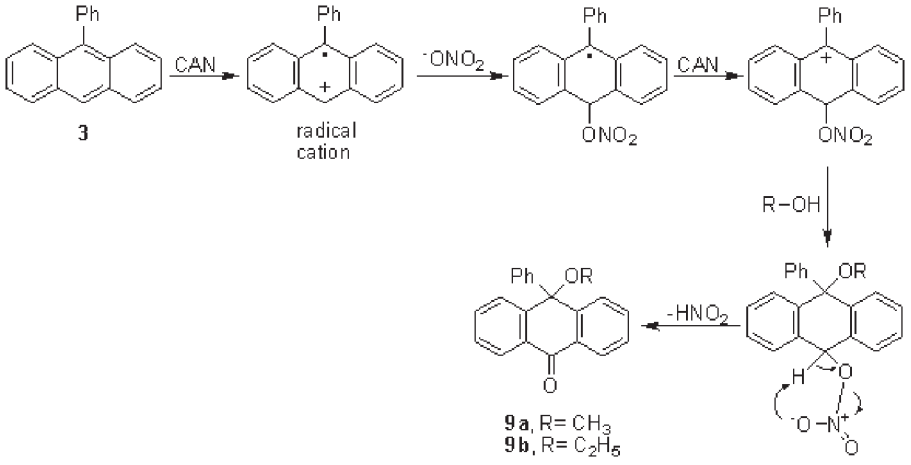


1: R = H; 2: R = Me; 3: R= Ph



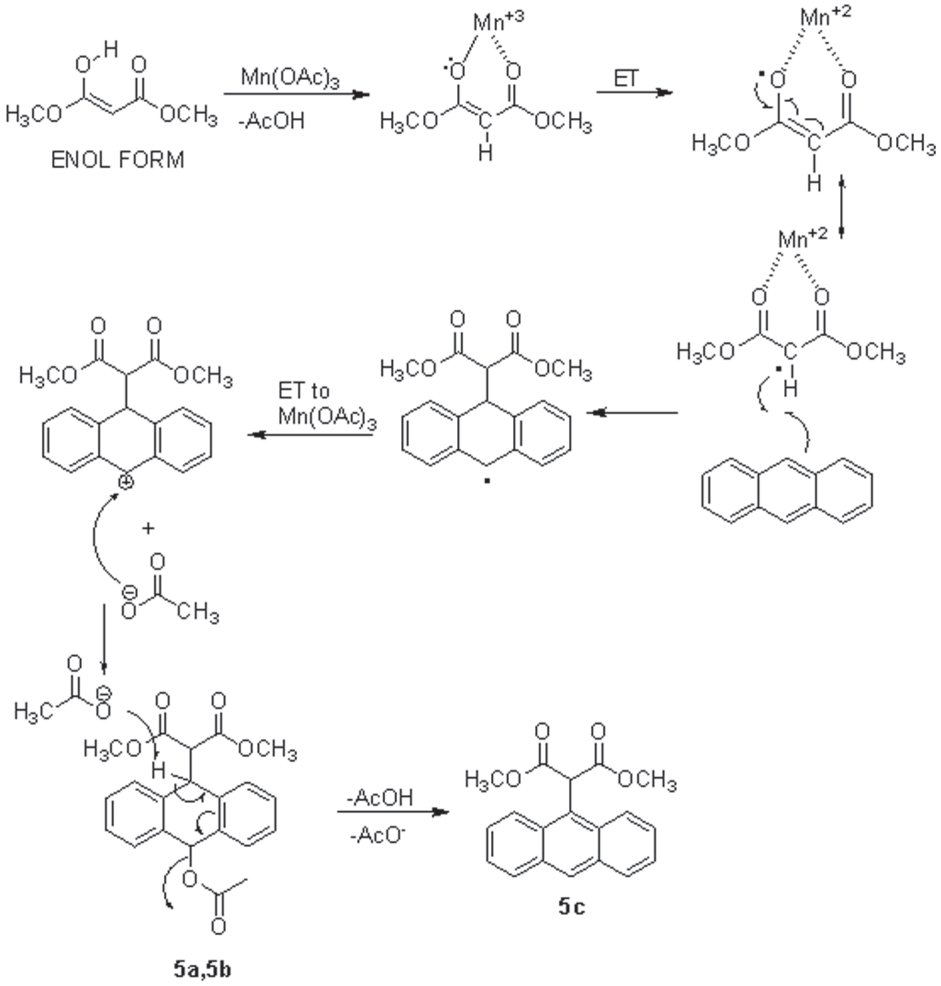

**Scheme 1**. Proposed reaction mechanism of the oxidation reaction

The oxidation of anthracene (**1**) and 9-methylanthracene (**2**) by CAN gave anthraquinone, bianthrone, 9-methyl-10-methoxyanthracene and 9-nitrate-9-methylanthrone. 9-Phenylanthracene (**3**) gives only one product, 9-methoxy-9-phenylanthrone, in methanol. When ethanol is used as a solvent, 9-ethoxy-9-phenylanthrone was obtained as a single product and a plausible mechanism is shown in scheme 2. There is no effect of dimethyl malonate during the oxidation of substituted anthracenes due to the formation of more stable triphenylmethine radicals than the malonyl radical. However, Kurz *et al*. [24] mentioned that acetonylated substituted aromatic compounds were obtained by CAN and $Mn(OAc)_3$ in acetic acid media. 9,10-anthraquinone (**5d**) was observed from 9-methylanthracene. Turner *et al*. [26] and Clough *et al*. [27] obtained 9,10-anthraquinone (**5d**) from 9-methylanthracene (**2**) by the radical reactions with *endo*-peroxide and the mechanism of demethylation has not been explained.




**Scheme 2.** Proposed reaction mechanism of the CAN promoted oxidation reaction in methanol/ethanol solution

The reaction of anthracene with dimethyl malonate and $Mn(OAc)_3$ gave anthraquinone and cis/trans-9-malonyl-10-acetoxy-9,10-dihydroanthracene compounds. A plausible reaction mechanism for the formation of **5a**, **5b** and **5c** is suggested in scheme 3. According to the mechanism shown in scheme 3, $Mn(OAc)_3$ and the dimethyl malonate form manganase(III)-enolate complex and then $Mn^{3+}$ is reduced to $Mn^{2+}$. A radical intermediate product which is stable is obtained and the carbon-centered radical is added to central ring of the anthracene. The intermediate product is oxidized to the carbocation with the equivalent of $Mn(OAc)_3$ and acetoxy group from the reactive is added. Generally, central ring of anthracene is considered more reactive than the other two rings and α-complex at the C9-position of anthracene could be stabilized by two benzene rings which might prevent rearomatization [28]. During the radical addition reaction to anthracene compounds such as photochemical nitration by tetranitromethane showed that anthracene is transformed to 9,10-substituted 9,10-dihydroanthracenes [29, 30].




**Scheme 3**. Proposed reaction mechanism of the $Mn(OAc)_3$ promoted addition reaction with dimethyl malonate

## 4. CONCLUSION

Carbon-centered radicals can be generated from the $Mn(OAc)_3$ and CAN oxidation of 1,3-dicarbonyl compounds and they can engage in addition reactions with aromatic compounds. These reagents can be used as one electron oxidants in non-acidic media, which is of significance because many organic compounds are acid-sensitive. Oxidation and addition products were obtained. The applicability of this one-step oxidation method is attractive for organic

synthesis. Dimethyl malonate addition products to 9-methylanthracene or 9-phenylanthracene were not observed and that could be explained by the increased stability of the generated radicals and also due to the steric effects.

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