Int. J. Chem. Sci.: 12(4), 2014, 1625-1634
ISSN 0972-768X
www.sadgurupublications.com

SYNTHESIS OF SOME 9-ALKENYLANTHRACENES AND ITS CYCLOADDITION: ADDUCTS OF 2-BROMOACRYLALDEHYDE

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ABSTRACT

Anthracene and its derivatives can behave as a diene; therefore, it has ability to undergo cycloaddition reactions with a variety of dienophiles at position 9 and 10, where the lowest benzenoid character exists. This research aims to synthesis some 9-alkenylanthracenes, such as 9-vinylanthracene (9-ethenylanthracne), 9-prop-2-enyl-anthracene (9-allylanthracene), 9-but-3-enyl-anthracene (9-homoallylanthracene), and 9-pent-4-enyl-anthracene and its cycloaddition with 2-bromoacrylaldehyde to give both possible [4+2] cycloadduct (ortho and/or meta). The results showed that ortho is preferred in all of the experimental cases with good yields.

Key words: Anthracene, Grignard reaction, 9-Alkenylanthracenes, Diels-Alder reactions, Dienophiles, Bicyclic.

INTRODUCTION

The progress in the art of organic synthesis has been dependent on chemist ability to construct carbon frameworks through carbon-carbon bond-forming reactions. During the last quarter of the previous century, two processes emerged playing decisive roles in shaping the science of chemical synthesis. These processes are the Grignard reagent and Diels-Alder reactions[1].

The Diels-Alder reactions is one of the most useful synthetic reactions in organic chemistry, and it is a key step for the synthesis of a wide variety of natural products[2]. This reaction is usually called a [4 + 2] cycloaddition reaction as it involves a conjugated

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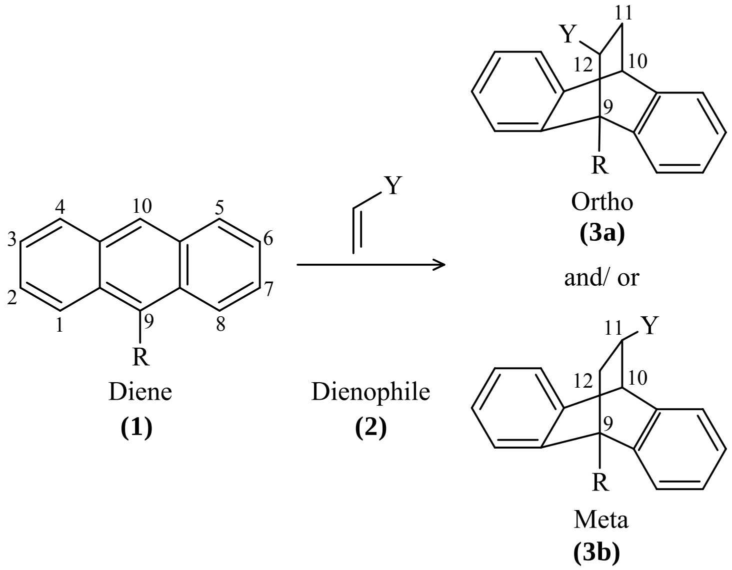
4 π-electron system for the diene and a 2 π-electron system for the dienophile leading to six-membered rings products (carbon-carbon or carbon- and heterocyclic compounds)[3]. For more than 100 years, Diels-Alder reaction is well known to all chemists, and it has been studied intensively by chemists, Though, it is currently under study at most of leading chemical centers in the world due to its importance in organic synthesis[4]. Otto Diels and Kurt Alder were awarded the Nobel Prize in Chemistry in 1950 for their work on this reaction[5]. Nowadays, there are many research papers, books and reviews in the area of this reaction[4,5].

Diels-Alder reactions of anthracene and its derivatives **(1)** with different dienophiles **(2)** have been one of the major synthetic strategies employed to generate bicyclic compounds, which have gained much importance in the recent time, since they constitute the basic structural frame work of several compounds[6,7].

The literature survey reveals for Diels-Alder reaction of monosubstituted diene such as 9-substituted anthracenes **(1)** with a monosubstituted dienophile **(2)** may lead to the formation of two regioisomeric adducts (ortho and/ or meta) as depicted in the following reaction (**Scheme 1**)[8].



Scheme 1

Meek et al.[9] employed Diels-Alder reactions of some 9-substituted anthracenes such 9-nitroanthracene, 9-cyanoanthracene, 9-anthraldehyde, 9-methoxyanthracene, and 9-anthramide with different dienophiles such as ethylene, acrylic acid, acrylchloride, acrylamide, acrylonitrile, and methylacrylate. The **(3a)** regioisomer has been found as the major isomer in all of the experimental cases except in a few cases, where the meta **(3b)** regioisomer has been preferred in the reaction of 9-substituted anthracene with 2-acetamido acrylate[9-12].

EXPERIMENTAL

Anthrone, alkenyl magnesium bromide and phosphorous pentoxide (P_2O_5) (purchased from Sigma-Aldrich) were used as obtained. THF was freshly dried over sodium. All glassware were dried in the oven before use and all reactions were carried out under nitrogen unless otherwise stated. The synthesis of compounds was ascertained by thin layer chromatography (TLC, silica gel 60 F_{254}). Visualization of the TLC plates was carried by using a U. V. lamp and dipping in iodine or dipping in acidic solution of vanillin in ethanol and then exposure heating by dryer. Melting points were determined on a Mel-Temp (Melting temperature) II apparatus and are uncorrected in Department of Chemistry, Azad College. IR (KBr) spectra were recorded on a Perkin-Elmer 883 spectrophotometer and expressed as ν cm^{-1}. ^1H-NMR and ^{13}C-NMR spectra were measured by using JEOL ECP (400 MHz) in $CDCl_3$. ^1H chemical shifts are expressed as δ ppm and coupling constants *(J)* were given in Hz. MS spectra and HRMS were performed by using EI at 70 eV. The ultrasonic reaction was carried out using Sonerex 200, 50 W power and frequency 35 kHz.

General procedure for the preparation of 9-alkenylanthracenes by Grignard reactions

Anthrone (25 mmol) was slowly added to a solution of alkenyl magnesium bromide prepared from magnesium (50 mmol) and alkenyl bromide (50 mmol) in tetrahydrofuran (100 mL). The mixture was stirred for 8 hr at room temperature. The reaction mixture was subsequently acidified with 10% HCl, the organic layer was separated, and the aqueous layer was extracted with ether (2 × 50 mL).

The combined organic layer was washed with water, dried over $MgSO_4$ anhydrous and the solvent was evaporated. To the crude product, 50 mL benzene and 5 g P_4O_{10} were added and stirred for 6 hr at room temperature. The P_4O_{10} was filtered off and the benzene was removed under vacuum. The crude product was purified by flash column chromatography on silica gel using as solvent mixture (hexane-dichloromethane 1:1) giving pure 9-alkenylanthracene.

9-Vinylanthracene (1a)

Yellow solid; m.p 66-68°C; lit. (4.75 g, 93%); IR (KBr): 3064-2852 cm^{-1} (=CH stretching aroma.), 1620-1445 cm^{-1} (C=C stretching), 729 cm^{-1} (C-H bonding); ^{1}H-NMR ($CDCl_3$/400 MHz, δ): 5.38 (dd, J = 1.48 Hz, J = 10.24 Hz, 1 H, H-2’), 5.84 (dd, J = 1.48 Hz, J = 17.00 Hz, 1H, H-2’), 6.75 (q, J = 11.72 Hz, 1H, H-1’), 7.20-8.39 (m, 9 H, aromatic-H). ^{13}C-NMR ($CDCl_3$/400 MHz, δ): 115.30, 126.75-138.06; MS (EI) m/z (%) = 204; HRMS (EI) Calcd for $C_{16}H_{12}$ [M^+] 204.2669, Found 204.2668.

9-Allylanthracene (1b)

Yellow solid; m.p. 46°C; yield (4.79 g, 88 %); IR (KBr): 3047, 2945 cm^{-1} (=CH stretching arom.), 1620, 1444 cm^{-1} (C=C stretching), 729 cm^{-1} (C-H bonding); ^{1}H-NMR ($CDCl_3$ / 400 MHz, δ): 4.37 (d; J = 5.48 Hz, 2 H, H-1'), 4.97 (dd; J =10.24, J = 1.48 Hz, 1H, H-3'), 5.06 (dd; J = 16.84 Hz, J = 1.48 Hz, 1H, H-3'), 6.21-6.28 (m; 1H, H-2'), 7.28-7.60 (m; 9 H, aromatic -H); ^{13}C-NMR ($CDCl_3$/400 MHz, δ): 32.10, 116.00, 124.89, 125.36, 126.25, 128.20, 130.06, 131.56, 131.71, 134.05, 136.50. MS (EI) m/z (%) = 218; HRMS (EI) Calcd. for $C_{17}H_{14}$ [M^+] 218.1096, Found 218.1097.

9-Homoallyanthracene (1c)

Yellow solid; m.p 56-58°C; yield (4.95 g, 85 %); IR (KBr): 3072-2852 cm^{-1} (=CH stretching arom.), 1676-1450 cm^{-1} (C=C stretching), 731 cm^{-1} (C-H bonding); ^{1}H-NMR ($CDCl_3$ / 400 MHz, δ): 2.57-2.60 (m; 2 H, H-2'), 3.73-3.75 (m; 2 H, H-1'), 5.11 (dd; J = 1.48 Hz, J = 10.28 Hz, 1H, H-4'), 5.23 (dd; J = 1.48 Hz, J = 16.88 Hz, 1H, H-4'), 6.05-6.12 (m; 1H, H-3'), 7.47- 8.36 (m; 9 H, Aromatic-H); ^{13}C-NMR ($CDCl_3$ / 400 MHz, δ): 27.53 (C-1'), 35.24 (C-2'), 115.05 (C-4'), 138.38 (C-3'), 124.45, 124.8, 124.93, 125.44, 125.62, 125.92, 126.29, 127.40, 128.20, 129.34, 129.66, 131.73, 134.31, 136.7 (aromatic carbons); MS (m/z) (%) =232; HRMS (EI) Calcd for $C_{18}H_{16}$ [M^+] 232.1251, Found 232.1252.

9-Pent-4-enyl-anthracene (1d)

Yellow solid; m.p. 72°C; yield (5.48 g, 82 %); IR (KBr) 3049 (C-H stretching arom.), 2914-2853 (C-H stretching aliphatic), 1636-1445 (C=C stretching), 733 (C-H bonding); ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 1.92 (qu, J 8.1 Hz, 2 H, H-2’), 2.33 (q, J = 7.36 Hz, 2 H, H-3’), 3.59-3.64 (m, 2 H, H-1'), 5.08-5.16 (m, 1H, H-5'), 5.93-5.97 (m, 1H, H-4'), 7.25-8.43 (m, 9 H, Aromatic-H); ^{13}C-NMR (400 MHz, $CDCl_3$, δ): 27.50 (C-1'), 30.42 (C-2'), 34.35 (C-3'), 115.29 (C-5'), 138.51 (C-4'), 124.53, 124.89, 125.44, 125.50, 125.72, 126.31, 128.26, 129.30,129.64, 131.71, 131.71, 135.11 (aromatic carbons); MS (EI) m/z (%): 246 [M^+]; HRMS (EI) Calcd for $C_{19}H_{18}$ [M^+] 246.1408, Found 246.1410**.**

General experimental procedure for the Diels-Alder reactions of 9-alkenylanthracenes (1a-1d), with 2-bromoacrylaldehyde

A mixture of 2-bromoacrylaldehyde (6.00 mmol) and a solution of 9-alkenylanthracene (3.00 mmol) in toluene (3 mL) was refluxed for 48 hr. The progress of the reaction was monitored on TLC. The reaction mixture was cooled to room temperature. The reaction mixture was concentrated and the residue was purified by column chromatography on silica gel (ethyl acetate-petroleum ether (1:25).

12-Bromo-9,10-dihydro-9.10-ethanoanthracene-9-ethene-12-carbaldehyde (3a)

White solid m.p. 133°C; yield (1.05 g, 89%); IR (KBr, cm^{-1}): 1719 (H-C=O); ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 2.27 (dd, J = 2.20 Hz, J = 11.72 Hz, 1H, H-11), 3.05 (dd, J = 2.96 Hz, J = 11.72 Hz, 1H, H-11), 4.36 (t, J = 2.92 Hz, 1H, H-10), 5.61 (d, J = 18.36 Hz, 1H, H-2'), 6.22 (d, J = 11.76 Hz, 1H, H-2'), 6.71 (q, J = 11.72 Hz, 1H, H-1'), 7.24-7.53 (m, 8H, aromatic-H), 9.31 (s, H-C=O); ^{13}C-NMR (400 MHz, $CDCl_3$, δ ppm): 190.55 (C=O); MS (m/z): 338. HRMS (EI) Calcd for $C_{19}H_{15}BrO$ [M^+] 338.0276, Found 338.0278.

12-Bromo-9,10-dihydro-9.10-ethanoanthracene-9-(pro-2-en-1-yl)-12-carbaldehyde (3b)

White solid; m.p. 145°C; yield (0.86, 81%); IR (KBr, cm^{-1}): 1716 (H-C=O); ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 2.27 (dd, J = 14 Hz, J = 2.92 Hz, 1H, H-11), 3.01 (dd, J = 14 Hz, J = 2.92 Hz, 1H, H-11), 3.43-3.86 (m, 2 H, H-1'), 4.33 (t, J = 2.92 Hz, 1H, H-10), 5.27-5.31 (m, 1H, H-3'), 5.44-5.49 (m, 1H, H-3'), 5.95–6.05 (m, 1H, H-2'), 7.12-7.53 (m, 8H, aromatic-H), 9.35 (s, H-C=O); ^{13}C-NMR (400 MHz, $CDCl_3$, δ ppm): 191.04 (C=O); MS (m/z): 352. HRMS (EI) Calcd for $C_{20}H_{17}BrO$ [M^+] 352.0465, Found 352.0463.

12-Bromo-9,10-dihydro-9.10-ethanoanthracene-9-(but-3-en-1-yl)-12-carbaldehyde (3c)

White solid; m.p. 157°C; yield (0.86, 78%); IR (KBr, cm^{-1}): 1717 (H-C=O); ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 2.10 (d, J = 2.92 Hz, 1H, 1H-11), 2.13 (d, J = 2.20 Hz, 1H, 1H-11), 2.52-2.68 (m, 2 H, H-2'), 2.95-3.10 (m, 2 H, H-1'), 4.32 (t, J = 2.92 Hz, 1H, H-10), 5.16-5.29 (m, 2 H, H-4'), 6.08-6.12 (m, 1H, H-3'), 7.20-7.52 (m, 8H, aromatic-H), 9.35 (s, H-C=O); ^{13}C-NMR (400 MHz, $CDCl_3$, δ ppm): 191.15 (C=O); MS (m/z): 366; HRMS (EI) Calcd for $C_{21}H_{19}BrO$ [M^+] 366. 0667, Found 366.0665.

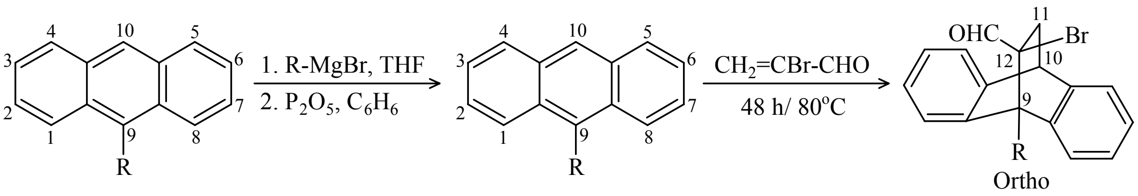
12-Bromo-9,10-dihydro-9.10-ethanoanthracene-9-(pent-4-en-1-yl)-12-carbaldehyde (3d)

White solid; m.p. 169°C; yield (0.88 g, 77%); IR (KBr, cm^{-1}): 1717; ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.16-1.21 (m, 2 H, H-3'), 1.57-1.61 (m, 2 H, H-2'), 1,86-1.97 (m, 2 H, H-1'), 2.39 (dd, J = 14.00 Hz, J = 3.00 Hz, 1H, H-11), 2,86 (dd, J = 14.00 Hz, J = 3.00 Hz, 1H, H-11), 4.28 (t, J = 4.40 Hz, 1H, H-10), 5.04-5.29 (m, 2 H, H-5'), 5.91-5.92 (m, 1H, H-4'), 7.24-7.41 (m, 8H, aromatic-H), 9.57 (s, H-C=O); ^{13}C-NMR (400 MHz, $CDCl_3$, δ ppm): 191.14 (C=O); MS (m/z): 380; HRMS (EI) Calcd for $C_{22}H_{21}BrO$ [M^+] 380. 0775, Found 380.0778.

RESULTS AND DISCUSSION

In this article, we describe the Grignard reactions as a classical method for synthesizing some 9-alkenyl anthracenes by treatment of anthrone as carbonyl compound with Grignard reagent, which was prepared from magnesium metal and alkenyl bromide in tetrahydrofuran followed by dehydration using P_4O_{10} to gave 9-alkenylanthracene with change the hydrocarbon chain (**1a-d**) [13-15].

9-Alkenylanthracenes main substrates in [4 + 2] cycloaddition reactions. Treatment of these compounds with 2-bromoacrylaldehyde yielded the corresponding olefins (**3a-d**) under suitable conditions (reflux under nitrogen in suitable solvent), see (**Scheme 2**).



(4) **(5)** **(1a-1d)** **(2)** **(3a-3d)**

R = (1a): CH = CH_2, (1b): CH_2 = CH-CH_2, (1c): CH_2=CH-CH_2-CH_2, (1d): CH_2=CH-CH_2-CH_2-CH_2; (3a): CH=CH_2, (3b): CH_2=CH-CH_2, (3c): CH_2=CH-CH_2-CH_2, (3d): CH_2=CH-CH_2-CH_2-CH_2

Scheme 2

Structures of all 9-alkenylanthracenes, and [4 + 2] cycloadduct were confirmed using spectroscopy data such as IR, ^{1}H-NMR, ^{13}C-NMR, and MS spectroscopy.

The IR spectrum for compound **(1a)**, shows absorption band in the range of 3064-2852 cm^{-1} for (C-H stretching aroma) and shows peaks in the range of 1620-1445 cm^{-1} for (C=C stretching) and the absorption band at 729 cm^{-1} for (C-H bonding). The ^{1}H-NMR spectrum exhibit a characteristic doublet of doublet at δ 5.38 ppm for (one proton, H-2') and exhibit doublet of doublet at δ 5.84 ppm for (one proton, H-2'), and shows quartet at δ 6.75 ppm for (one proton, H-1'), and multiple in the range of 7.21-8.40 for (9 proton aromatic). The ^{13}C-NMR shows one peak at δ 115.33 ppm for (carbon C-1'), and peaks in the range of δ 134.38-138.06 ppm for (carbons C-2' and C aromatic).The mass spectrum showed the molecular ion peak at m/z 204. HRMS (*EI*) Calcd for $C_{16}H_{12}$ [M^+] 204.2669, Found 204.2668.

In the IR spectrum for compound **(1b)** a band was observed in the range of 3047-2945 cm^{-1} indicating the presence of (=C-H stretching aroma) and a peak in the range of 1620-1444 cm^{-1} for (C=C stretching), and the absorption band at 729 cm^{-1} for (C-H bonding). ^{1}H-NMR spectrum exhibits a characteristic doublet at δ 4.37 ppm for (two proton, H-1') and doublet of doublet at δ 4.97 ppm for (one proton, H-3'), doublet of doublet at δ 5.06 ppm for (one proton, H-3'), and multiplet in the range of 6.21-6.28 for (one proton, H-2') and also in the range of 7.28-7.60 for (9 proton aromatic). The ^{13}C-NMR shows one peak at δ 32.10 ppm for (carbon C-1'), and at δ 116.00 ppm for (carbon C-3'), and at δ 136.50 ppm for (carbon C-2'). It also and shows fourteen peaks in the range of δ 124.89-134.05 ppm for (aromatic carbons). The mass spectrum showed the molecular ion peak at m/z 218. The HRMS (EI) Calcd for $C_{17}H_{14}$ [M^+] 218.1096, Found 218.1097.

In the IR spectrum for compound **(1c)**, absorptions were observed in the range of 3072-2852 cm^{-1} indicating the presence of (=C-H stretching aroma), a peak in the range of 1676-1450 cm^{-1} for (C=C stretching), and the absorption band at 731 cm^{-1} for (C-H bonding). ^{1}H-NMR spectrum exhibits a characteristic multiplet in the range of 2.57-2.60 ppm for (two protons, H-2'), and also in the range of 3.73-3.75 ppm for (two protons, H-1'). It exhibits doublet of doublet at 5.11 ppm for (one proton, H-4'), and also at 5.23 ppm for (one proton, H-4'), and a multiplet in the range of 6.05-6.12 ppm for (one proton, H-3'), and and in the range of 7.47-8.36 ppm for (9 proton aromatic). The ^{13}C-NMR shows one peak at δ 27.53 ppm for (carbon C-1'), a peak at δ 35.24 ppm for (carbon C-2'), at δ 115.05 ppm for (carbon C-4'), and at δ 138.38 ppm for (carbon C-3'). It shows fourteen peaks in the range of δ 124.45-136.70 ppm for (aromatic carbons). The mass spectrum showed the molecular ion peak at m/z 232. The HRMS (EI) Calcd for $C_{18}H_{16}$ [M^+] 232.1251, Found 232.1252.

The IR spectrum for compound **(1d)** shows absorptions in the range of 3049-2852 cm^{-1} indicating the presence of (C-H stretching aroma), a peak in the range of 1636-1445 cm^{-1} for (C=C stretching), and an absorption band at 733 cm^{-1} for (C-H bonding). ^{1}H-NMR spectrum exhibits a characteristic quintet at 1.92 ppm for (two protons, H-2'), a quartet at 2.33 ppm for (two protons, H-3'), and multiplets in the range of 3.59-3.64 ppm for (two protons, H-1'), at 5.08-5.16 ppm for (two protons, H-5'), at 5.93-5.97 ppm for (two protons, H-4'), and also in the range of 7.25-8.43 ppm for (9 proton aromatic). The ^{13}C-NMR shows a peak at δ 27.50 ppm for (carbon C-1'), at δ 30.42 ppm for (carbon C-2'), at δ 34.35 ppm for (carbon C-3'), at δ 115.29 ppm for (carbon C-5'), and also at δ 138.51 ppm for (carbon

C-4’). It shows peaks in the range of δ 124.53-135.11 ppm for (aromatic carbons). The mass spectrum showed the molecular ion peak at m/z 246. The HRMS (EI) Calcd for $C_{19}H_{18}$ [M^+] 246.1408, Found 246.1410.

The IR spectrum for compound (**3a**), shows a strong peak at 1719 cm^{-1} (C=O). The ^{1}H-NMR exhibits a characteristic doublet of doublet at δ 2.27 ppm for (one proton, H-11), also at δ 3.05 ppm for (one proton, H-11), triplet at δ 4.36 ppm for (one proton, H-10), doublet at *δ* 5.61 ppm (one proton, H-2’), at *δ* 6.22 ppm (one proton, H-2’), doublet of doublet at *δ* 6.71 ppm (one proton, H-1’) and showed a characteristic singlet at *δ* 9.31 ppm for (CHO). ^{13}C-NMR spectrum came consistent with the structural formula of the compound through the emergence of eighteen lines spectrum representing the number of carbon atoms in the compound and showed one peak at *δ* 190.55 ppm for carbon (CHO). The mass spectrum of compound **(3a)** reveals the molecular ion peak at *m/z* 338. The HRMS (EI) Calcd for $C_{19}H_{15}BrO$ [M^+] 338.0276, Found 338.0278.

The IR spectrum for compound (**3b**) exhibited a strong peak at 1716 cm^{-1} (C=O). ^{1}H-NMR exhibited a doublet of doublet at δ 2.27 ppm (one proton H-11), doublet of doublet at δ 3.01 ppm (one proton H-11), a multiplet in the range of δ 3.43-3.86 ppm (two proton H-1’), a doublet of triplet at δ 3.85 ppm (one proton H-1’), a triplet at δ 4.33 ppm (one proton, H-10), a multiplet in the range of δ 5.27-5.31 ppm (one proton, H-3’), a doublet of doublet at δ 5.44-5.49 ppm (one proton, H-2’), a multiplet in the range of δ 5.95-6.05 ppm (one proton, H-2’) and a singlet at δ 9.35 ppm for (CHO).The ^{13}C-NMR spectrum was consistent with the structural formula of the compound through the emergence of nineteen lines in the spectrum, which represents the number of carbon atoms in the compound and shows one peak at δ 191.04 ppm for carbon (CHO). The mass spectrums of this compound reveals the molecular ion peak at m/z 352. The HRMS (EI) Calcd for $C_{20}H_{17}BrO$ [M^+] 352.0465, Found 352.0463.

The IR spectrum for compound **(3c**) exhibited a strong peak at 1717 cm^{-1} (C=O). ^{1}H-NMR exhibited a doublet at δ 2.10 ppm (one proton H-11), a doublet at δ 2.13 ppm (one proton H-11), a multiplet in the range of δ 2.52-2.68 ppm (two proton H-2’), a multiplet in the range of δ 2.95-3.10 ppm (two proton H-1’), a triplet at δ 4.32 ppm for (one proton, H-10), a multiplet in the range of δ 5.16-5.29 ppm (two proton H-4’), a multiplet in the range of δ 6.08-6.12 ppm for (two proton H-3’) and also exhibited a characteristic singlet at δ 9.35 ppm for (CHO). The ^{13}C-NMR spectrum was consistent with the structural formula of the compound through the emergence of twenty lines spectrum representing the number of carbon atoms in the compound and shows one peak in δ 191.15 ppm for carbon (CHO); The mass spectrums of compound (**3c**) reveals the molecular ion peak at m/z 366; The HRMS (EI) Calcd for $C_{21}H_{19}BrO$ [M^+] 366. 0667, Found 366.0665.

The IR spectrum for compound (**3d**) exhibited a strong peak at 1717 cm^{-1} (C=O). ^1H-NMR exhibited a multiplet in the range of δ 1.16-1.21 ppm (two proton H-3'), a multiplet in the range of δ 1.57-1.61 ppm (two proton H-2'), a doublet of doublet at δ 2.39 ppm (one proton, H-11), a doublet of doublet at δ 2.86 ppm (one proton, H-11), a triplet at δ 4.28 ppm (one proton, H-10), a multiplet in the range of δ 5.04-5.29 ppm for (two proton H-5'), a multiplet in the range of δ 5.91-5.92 ppm (two proton H-4') and also exhibited a characteristic singlet at δ 9.57 ppm for (CHO). The ^{13}C-NMR spectrum was consistent with the structural formula of the compound through the emergence of twenty one lines spectrum, which represents the number of carbon atoms in the compound and shows one peak in δ 191.14 ppm for carbon (CHO). The mass spectrums of compound **(3d)** reveals the molecular ion peak at m/z 380; The HRMS (EI) Calcd for $C_{22}H_{21}BrO$ [M^+] 380.0775, Found 380.0778.

CONCLUSION

Diels-Alder reaction of 9-alkenylanthracene with 2-bromo acrylaldehyde gives ortho isomer in all experiments. The steric factors appear to play a dominant role in directing to ortho adduct.

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Accepted : 31.08.2014