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# Anodic Oxidation of Aryl Propargyl and Aryl Allyl Ethers at a Platinum Electrode[#]

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*Abstract*: The oxidation reactions of aromatic 3,3-sigmatropic systems have been investigated under different conditions *viz.*, (a) anodic oxidation in amphiprotic and aprotic media, (b) reaction with (diacetoxyiodo)benzene and (c) reaction promoted by ceric ammonium nitrate.

## INTRODUCTION

The aromatic radical cations present a very rich chemistry as they undergo a variety of interesting reactions[1,2]. Hence, there is a continued interest in the studies concerning the reactions of these species and the structural factors which influence their relative importance. In recent years, cation radical induced pericyclic reactions have attracted wide attention[3]. Although cation radical induced cycloaddition reactions are well documented [3-6] there is hardly any report on the corresponding sigmatropic rearrangements, particularly, Claisen rearrangement. In view of the overwhelming interest in these types of reactions[7], we sought to explore the possibility of an electrochemically initiated Claisen rearrangement from aromatic 3,3-sigmatropic systems[8,9]. It is of interest to compare the behaviour of these compounds with that of their alkyl counterparts under electrochemical oxidation conditions.

We have studied the single-electron oxidation of various 3,3-sigmatropic systems which generate the cation radical species, the reaction being mediated by anodic oxidation (in amphiprotic and aprotic media) and also by ceric ammonium nitrate. The effect of other oxidizing agents such as (diacetoxyiodo)benzene on these substrates has also been explored in the present study.

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[#] *Respectfully dedicated to Professor C.N.Pillai of this department on his 60th birthday.*

## RESULTS AND DISCUSSION

*a. Anodic oxidation of aryl ethers in amphiprotic medium.* The cyclic voltammogram of 4-methoxyphenyl prop-2-ynyl ether, **1a** (0.01M) obtained in 60% aqueous methanol on a platinum anode at 0.02Vs$^{-1}$ sweep rate is shown in Fig.1 and the corresponding voltammetric data are summarized in Table 1. The compound **1a** gave a well defined diffusion-limited irreversible anodic peak. The shift in anodic peak potential to more positive values with increase in sweep rate (Table 1) further confirmed the irreversible nature of the electrode process. The current function ($i_{p,a}v^{-1/2}$) values were almost independent of the sweep rate. The micro-scale controlled-potential electrolysis of **1a** in aqueous methanol indicated a transfer of two electrons in the oxidation process.

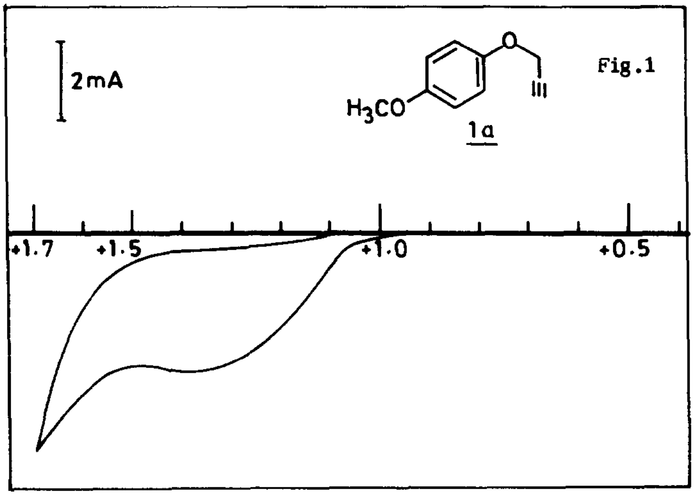
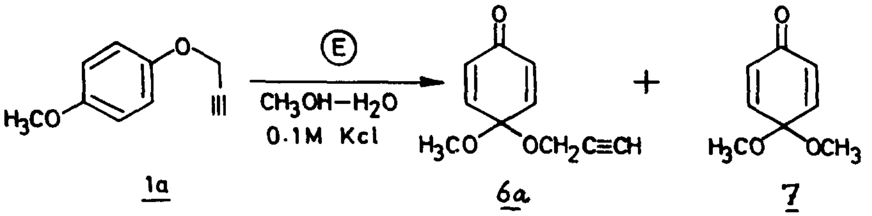


Table 1: CV Data of 4-Methoxyphenyl Prop-2-ynyl Ether (0.01M) in 60% Aqueous Methanol

| Sweep rate, v/V.s$^{-1}$ | Anodic peak current, $i_{p,a}$/mA | Current function $i_{p,a}v^{-1/2}$/ mA. $V^{-1/2}s^{1/2}$ | Anodic peak potential $E_{p,a}$,/V vs SCE |
|---|---|---|---|
| 0.010 | 2.42 | 24.20 | 1.35 |
| 0.020 | 3.49 | 24.68 | 1.41 |
| 0.030 | 4.50 | 25.98 | 1.45 |
| 0.050 | 5.50 | 24.59 | 1.47 |
| 0.070 | 7.83 | 25.50 | 1.54 |
| 0.100 | 8.33 | 26.34 | 1.60 |

Based on the above results, large scale controlled-potential electrolysis of **1a** (2.5 mmol) was performed in 60% aqueous methanol at 1.3V vs. SCE using a platinum electrode. After 3h of electrolysis the anolyte furnished a brown liquid in 90% yield after workup. Analysis of this liquid product by HPLC and NMR indicated it to be a mixture in which the major product was identified as the mixed quinone monoketal, namely, 4-methoxy-4-(prop-2-ynyloxy)-2,5-cyclohexadienone, **6a** while the minor product was found to be 4,4-dimethoxy-2,5-cyclohexadienone,**7**.

Scheme 1



1a 6a 7

The anodic oxidation of other aryl ethers, namely, 4-methoxyphenyl allyl (**2a**), 4-methoxyphenyl allenylmethyl (**3a**), 4-methoxyphenyl cinnamyl (**4a**) and 4-methoxyphenyl benzyl (**5a**) ethers was also found to yield the respective mixed quinone monoketals (major product) and dimethoxy quinone monoketal (minor product)(Table 2). On the other hand, the macro scale controlled-potential electrolysis of the symmetrical compound, 1,4-bis(prop-2-ynyl) phenyl ether (**1b**) in 60% aqueous methanol furnished exclusively the mixed quinone monoketal, **6a**.

It is worth mentioning that in all the above experiments there was no evidence for the formation of any products due to sigmatropic rearrangement or intramolecular cyclization as expected. Further, it was observed that 4-methylphenyl, 4-chlorophenyl and 2-naphthyl prop-2-ynyl ethers were electrochemically inactive under the experimental conditions.

Scheme 2

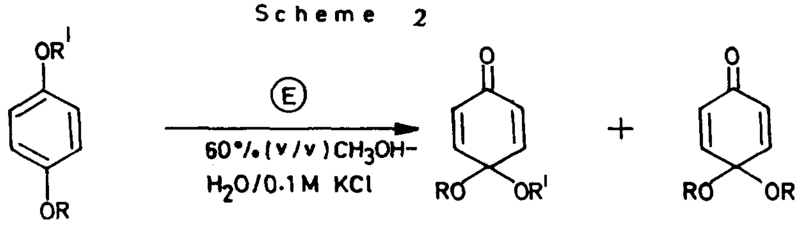


Table 2

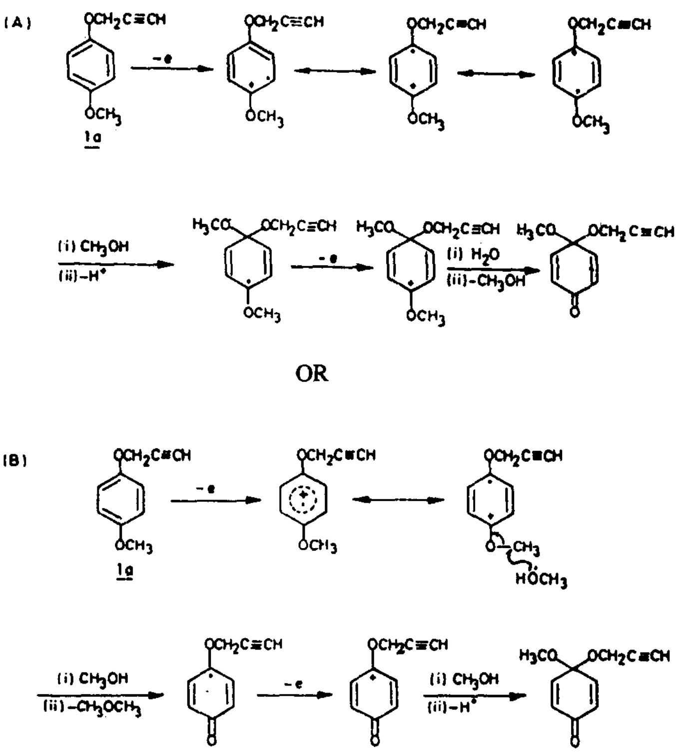
R = $OCH_3$

| compound no.[a] | $R^1$ | % yield[b] of 6 | % yield[b] of 7 |
|---|---|---|---|
| 1a | $CH\equiv C\text{-}CH_2$ | 65 | 28 |
| 2a | $CH_2=CH\text{-}CH_2$ | 70 | 20 |
| 3a | $CH_2=C=CH\text{-}CH_2$ | 72 | 21 |
| 4a | $Ph\text{-}CH=CH\text{-}CH_2$ | 48 | - |
| 5a | $Ph\text{-}CH_2$ | 71 | 19 |

a. Electrolysis was performed at 1.30V vs. SCE for all ethers.
b. Yield based on HPLC analysis of crude material

The formation of these quinone monoketals can be rationalized through an ECEC (electrochemical, chemical, electrochemical, chemical) sequence involving aromatic cation radical intermediates as depicted in scheme 3.

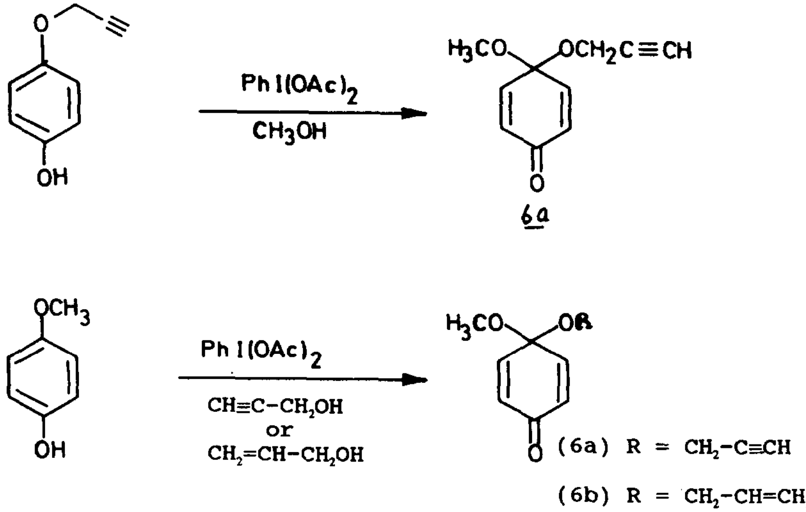
Scheme 3



There are only few examples on the synthesis of mixed quinone monoketals in the literature[10,11] although the synthesis of simple symmetrical quinone monoketals are known[12,13]. Recently Swenton etal[14] had utilized the anodic oxidation of 2-(4-alkylphenoxy)ethanol derivatives in methanol to obtain 4-alkyl-4-methoxycyclohexa-2,5-dienones. In literature, it is reported that the quinone monoketals have been prepared mainly by the electrochemical oxidation of aryl ethers in alkaline medium[13], the first step being the formation of quinone bisketals. Quinone monoketals were then obtained by the regiospecific hydrolysis of bisketals. Interestingly, in the present work the anodic oxidation of aryl ethers in neutral aqueous methanol **directly** furnished the mixed quinone monoketals in good yields.

*b. Reactions Using (Diacetoxyiodo)benzene as Oxidant.* For many electrochemical reactions there also exits a chemical counterpart. It has been recently shown that (diacetoxyiodo)benzene (DAIB) oxidation of phenols gives the same products as those formed in the electrochemical oxidation of phenols and phenol ethers[10,11]. We have investigated the oxidation of 4-(prop-2-ynyloxy)phenol employing DAIB as oxidant. This reaction also yielded the same mixed quinone monoketal **6a** in 62% yield.

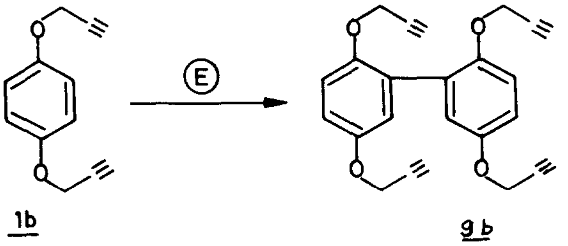
Scheme 4



Further, it was found that the reaction of 4-methoxyphenol with DAIB in propargyl alcohol furnished the same compound **6a** in a comparable yield. Under the same experimental conditions, the above reaction afforded the quinone monoketal **6b** when allyl alcohol was used as the solvent. Thus these reactions highlight the utility of DAIB as a mild and inexpensive oxidant for the preparation of mixed quinone monoketals of unsaturated alcohols.

*c. Anodic Oxidation of Aryl Propargyl Ethers in Aprotic Medium.* We further investigated the electrochemical oxidation of aryl prop-2-ynyl ethers in aprotic medium (dry acetonitrile) with a view to find out whether under these conditions the cation radicals generated would undergo any sigmatropic rearrangement as there is no scope for the formation of quinone monoketals. The controlled-potential electrolysis of 1,4-bis(prop-2-ynyl) phenyl ether (**1b**) when performed on a platinum electrode at 1.6V vs. silver-quasi reference electrode in dry acetonitrile furnished the biphenyl compound, **9b**. It may be pointed out that there is no evidence for the formation of products derived from cation radical mediated sigmatropic rearrangement or radical induced cyclization. Other substituted aryl prop-2-ynyl ethers, **1c-1f** also underwent the same cation radical mediated dimerization reaction to yield the corresponding substituted biphenyl derivatives, **9c-9f** (Table 3). These biphenyl compounds were characterized thoroughly by various spectroscopic and analytical methods.

Scheme 5



In the case of ether **1c**, the product obtained was a biphenyl derivative which could either be a mixture of 5,5'-dimethyl-2,2'-bis(2-propynyloxy)-1,1'-biphenyl and 2,2'-dimethyl-5,5'-bis(2-propynyloxy)-1,1'-biphenyl or 5,2'-dimethyl-2,5'-bis(2-propynyloxy)-1,1'-biphenyl. However, the product was found to be homogeneous in tlc and hplc. In the reported anodic oxidation of 4-isopropylanisole[15], the product identified was also a mixture of biphenyl compounds, namely, 2,2'-dimethoxy-5,5'-diisopropyl-1,1'-biphenyl and 2,5'-dimethoxy-5,2'-diisopropyl-1,1'-biphenyl.

The dimerization reaction in the anodic process leading to the formation of biphenyl compounds occurs mainly through cation radical intermediates. These reactions further reveal that the behavior of cation radicals derived from aryl prop-2-ynyl ethers is quite different from that of neutral free radicals which are reported to yield mainly cyclized products[16].

Scheme 6

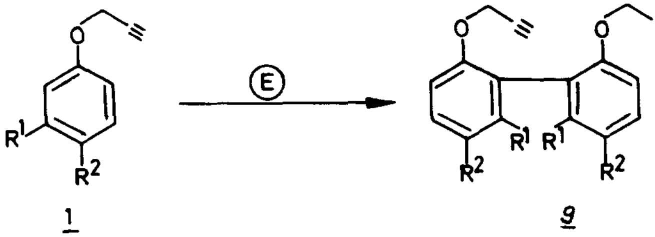


Table 3

| compound no. | $R^1$ | $R^2$ | oxidation potential[a] | % yield of 9[b] |
|---|---|---|---|---|
| 1a[c] | H | $OCH_3$ | 1.60 | 60 |
| 1b | H | $OCH_2C{\equiv}CH$ | 1.60 | 60 |
| 1c | H | $CH_3$ | 1.65 | 55 |
| 1d | H | Cl | 2.00 | 57 |
| 1e | -CH=CH-CH=CH- | | 1.57 | 56 |
| 1f | H | $NO_2$ | 2.38 | 40 |
| 1g | H | H | 1.58 | 58 |

a. Peak potentials versus silver quasi-reference electrode as observed in cyclic voltammetry at a platinum micro electrode at 100 mv/sec sweep rate in acetonitrile.
b. Isolated yield of the product with respect to the reacted starting material.
c. The biphenyl compound formed will be either 5,5'-bis(2-propynyloxy)-2,2'-dimethoxy-1,1'-biphenyl or 5,5'-dimethoxy-2,2'-bis(2-propynyloxy)-1,1'-biphenyl.

*d. Ceric Ammonium Nitrate(CAN) Promoted Reactions.* The mechanism of the oxidation of alkyl aromatics by CAN is well established to involve the formation of radical cations[17]. In the present work, when a solution of CAN in dry acetonitrile was stirred at room temperature with 4-methoxyphenyl prop-2-ynyl ether, **1a** and quenched after 24h, furnished an yellow viscous liquid in 70% yield. The spectral and analytical data of the new product confirmed it to be a nitro derivative. Similar results were obtained when p-methoxyphenyl allyl (**2a**) and p-methoxyphenyl allenylmethyl (**3a**) ethers were treated with CAN (Table 4).

Scheme 7

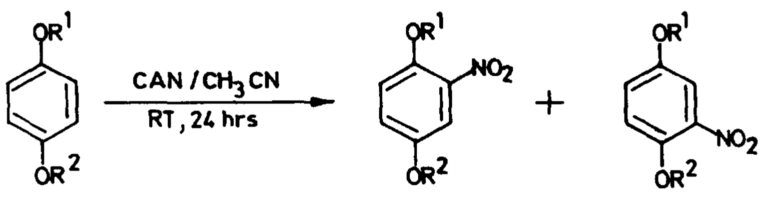


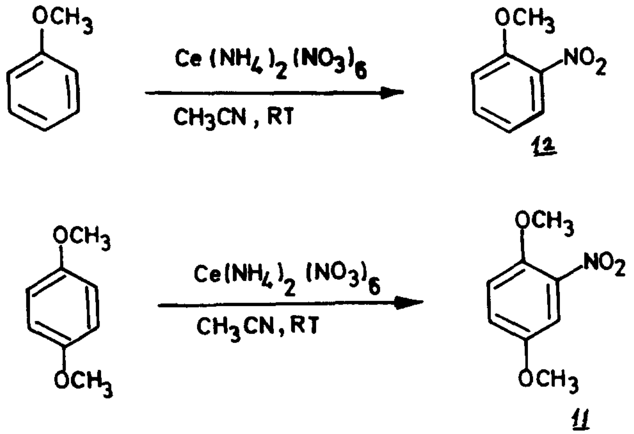
Table 4

| compound no. | $R^1$ | $R^2$ | % yield of 10[a] |
|---|---|---|---|
| 1a | $CH_3$ | $CH{\equiv}C\text{-}CH_2$ | 69 |
| 2a | $CH_3$ | $CH_2{=}CH\text{-}CH_2$ | 70 |
| 3a | $CH_3$ | $CH_2{=}C{=}CH\text{-}CH_2$ | 72 |

a. Isolated yield of the nitro compound.

The reaction of 1,4-dimethoxybenzene with CAN under the same experimental conditions furnished the expected mononitro compound, 11 while anisole yielded surprisingly 2-nitroanisole,12.

Scheme 8



The reaction of CAN with aromatic compounds in aqueous medium is quite different from that in nonaqueous solvents[18,19]. Dincturk and Ridd[20] had investigated the nitration of benzene and a number of alkyl benzenes using CAN in dry acetonitrile and suggested that the nitration reactions of this type occurs through the formation of nitronium ion intermediate from CAN. These authors have observed the formation of both 2-nitro and 4-nitro derivatives with anisole during reaction with CAN in refluxing acetonitrile. However, under our experimental conditions, only 2-nitroanisole was obtained as the major isolable product. Thus, it is evident from these experiments that the product distribution is due to the temperature effect - low temperature directs the nitro group to the ortho position where as higher temperature leads to more of the para substituted product. It is also known that the reaction of polynuclear arenes and hydroxynaphthalenes with CAN adsorbed on silica gel affords mono nitro derivatives whereas the reaction of the same substrates with CAN in solution gave considerable percentage of dinitro derivatives or corresponding quinones[21].

## CONCLUSION

The behaviour of cation radicals of aromatic 3,3-sigmatropic systems have been studied during anodic oxidation in amphiprotic medium. The oxidation provides a generalised route for the direct preparation of mixed quinone monoketals. Further it is observed that the cation radicals of aryl propargyl ethers undergo mainly dimerization on the electrode surface to yield the biphenyl derivatives. The reactions of other oxidizing agents such as (diacetoxyiodo)benzene and ceric ammonium nitrate are also explored in the present work.

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## EXPERIMENTAL

General methods: Solvents were purified and dried according to standard procedures. Column chromatography was performed on silica gel using hexane and then increasing the amounts of ethyl acetate. The melting points of compounds reported are all uncorrected.

The aryl allyl[22], aryl propargyl[23] and aryl allenylmethyl[24] ethers were prepared according to literature procedure.

The basic cyclic voltammetric studies were carried out in a Metrohm cell with a three electrode assembly using BAS-100A Electrochemical analyser. A platinum wire electrode was used as the working electrode and a platinum sheet (area 1 cm$^2$) served as the counter electrode. The reference electrode was saturated calomel electrode (SCE) in amphiprotic medium and silver wire in acetonitrile (aprotic medium). Potassium chloride (0.1M) and tetraethylammonium perchlorate (0.1M) were used as the supporting electrolytes in aqueous methanol and acetonitrile, respectively.

$^1$H nmr and $^{13}$C nmr spectra were recorded in deuterated chloroform containing tetramethylsilane as the internal standard on a JEOL JNM - GSX 400MHz instrument. Chemical shifts are reported in $\delta$(ppm). IR spectra were recorded on Shimadzu 470 spectrophotometer. Low-resolution as well as high-resolution mass spectra were obtained on a Finnigan MAT 8230 model. Analytical high performance liquid chromatography was performed on a Shimadzu LC-5A chromatograph using zorbax ODS column with a UV detector. Elemental analyses were carried out on Heraeus CHN–O–RAPID analyzer.

*Macro scale controlled-potential electrolysis procedure:* The electrolysis was performed in an undivided Metrohm cell in amphiprotic medium at room temperature. The experimental solution (50 mL) containing the substrate (2.5 mmol) and the supporting electrolyte (0.1M) was stirred using a magnetic stirrer. A platinum foil (1 cm$^2$) was used as the working electrode, another platinum sheet served as the counter electrode and SCE as the reference electrode. The course of the oxidation reaction during electrolysis was monitored by TLC and HPLC and was stopped when the initial current reached a minimum value. It is observed that in the oxidation of various ethers, the time of electrolysis is generally 2-3h, during which period the initial current attains a constant minimum value. The solvent was removed under reduced pressure after electrolysis and the residue was then extracted with dichloromethane. The organic extracts were washed twice with water and dried over anhydrous sodium sulfate. Products were isolated by column chromatography using hexane-ethylacetate as eluent.

The electrolysis in aprotic medium was carried out in an H-shaped divided cell following the above procedure.

*Experimental procedure for the chemical oxidation using DAIB:* To a stirred solution of phenol substrate (1 mmol) in the desired alcohol (20 mL) was added DAIB (1.2 mmol) all at once at room temperature. The reaction was monitored by TLC and deemed complete after an hour. The reaction mixture was then poured into an equal volume of saturated sodium bicarbonate solution to neutralise the residual acid. The solvent was then removed in a rotary evaporator under reduced pressure and the residue was extracted with dichloromethane, washed with brine and dried over anhydrous sodium sulphate. The pure products were isolated by column chromatography.

**(i) 4-methoxy-4-(prop-2-ynyloxy)-2,5-cyclohexadienone (6a)**: Yield-65% IR($CCl_4$) $cm^{-1}$ : 3300, 2880, 1675, 1620, 1500, 1420, 1300, 1205, 1120, 1045. $^1H$ NMR($CDCl_3$/TMS): $\delta$(ppm) 2.55(t, J = 1.5Hz, 1H), 3.4(s, 3H), 4.3(d, J = 1.5Hz, 2H), 6.26(d, J = 10Hz, 2H), 6.89(d, J = 10Hz, 2H). $^{13}C$ NMR($CDCl_3$): $\delta$(ppm) 50.698(q), 63.910(t), 75.030(d), 79.857(d), 92.759(s), 129.735(d), 142.577(d), 184.896(s). HRMS: m/z 178.06131 calculated for $C_{10}H_{10}O_3$(178.06299).

**(ii) 4-methoxy-4-(prop-2-enyloxy)-2,5-cyclohexadienone (6b)**: Yield- 70%. IR($CCl_4$) $cm^{-1}$ 2900, 1675, 1615, 1490, 1410, 1305, 1200, 1180, 1045. $^1H$ NMR($CDCl_3$/TMS): $\delta$(ppm) 3.38(s, 3H), 4.15(d, 2H), 5.18(d, J = 10.9Hz, 1H), 5.31(d, J = 17.5Hz, 1H), 5.86-5.95(m, 1H), 6.27(d, J = 10.2Hz, 2H), 6.86(d, J = 10.2Hz, 2H). $^{13}C$ NMR($CDCl_3$): $\delta$(ppm) 50.334(q), 63.706(t), 92.425(s), 117.076(t), 129.872(d), 134.107(d), 143.366(d), 185.124(s). HRMS: m/z 180.08026 calculated for $C_{10}H_{12}O_3$(180.07864)

**(iii) 4-mehtoxy-4-(buta-2,3-dienyloxy)-2,5-cyclohexadienone (6c)**: Yield-72%. IR($CCl_4$) $cm^{-1}$ 2940, 1955, 1680, 1635, 1445, 1370, 1300, 1175, 1100, 1060, 1038. $^1H$ NMR($CDCl_3$/TMS): $\delta$(ppm) 3.4(s, 3H), 4.14-4.18(td, J = 2.5, 6.5Hz, 2H), 4.78-4.82(td, J = 2.5, 6.5Hz, 2H), 5.23-5.30(quintet, J = 6.5Hz, 1H), 6.27(d, J = 10.7Hz, 2H), 6.84(d, J = 10.7Hz, 2H). $^{13}C$ NMR($CDCl_3$): $\delta$(ppm) 50.379(q), 61.020(t), 76.487(d), 88.008(t), 92.577(s), 129.690(d), 143.320(d), 185.139(s), 209.213(s). HRMS: m/z 192.07578 calculated for $C_{11}H_{12}O_3$(192.07864).

**(iv) 4-methoxy-4-(3-phenyl-prop-2-enyloxy)-2,5-cyclohexadienone (6d)**: Yield-48%. IR($CCl_4$): $cm^{-1}$ 2900, 1670, 1615, 1475, 1430, 1360, 1263, 1097, 1051, 955. $^1H$ NMR($CDCl_3$/TMS): $\delta$(ppm) 3.42(s, 3H), 4.31(d, J = 6Hz, 2H), 6.23-6.28(m, 1H), 6.30(d, J = 10Hz, 2H), 6.54(d, J = 15.4Hz, 2H), 6.89(d, J = 10Hz, 2H), 723-7.38(m, 5H). $^{13}C$ NMR($CDCl_3$): $\delta$(ppm) 50.592(q), 63.631(t), 92.622(s), 125.182(d), 126.517(d), 127.914(d), 128.597(d), 129.826(d), 132.710(d), 136.399(s), 143.412(d), 185.184(s). HRMS: molecular ion not observed

**(v) 4-methoxy-4-benzyloxy-2,5-cyclohexadienone (6e)**: Yield-71%. IR($CCl_4$):$cm^{-1}$ 2898, 1688, 1615, 1480, 1426, 1362, 1270, 1060, 1026. $^1H$ NMR($CDCl_3$/TMS): $\delta$(ppm) 3.4(s, 3H), 4.65(s, 2H), 6.25(d, J = 10.5Hz, 2H), 6.87(d, J = 10.5Hz, 2H), 7.32(s, 5H). $^{13}C$ NMR($CDCl_3$): $\delta$(ppm) 50.561(q), 64.890(t), 92.683(s), 127.534(d), 127.853(d), 128.430(d), 129.705(d), 137.522(s), 143.427(d), 185.139(s). HRMS: m/z 230.09399 calculated for $C_{14}H_{14}O_3$(230.0943). Spectral data are in accordance with an authentic sample prepared[10]

**(vi) 4,4-dimethoxy-2,5-cyclohexadienone (7)**: Yield:19-28%. IR($CCl_4$): $cm^{-1}$ 2890, 1675, 1625, 1485, 1420, 1290, 1205, 1180, 1115, 1062, 1036. $^1H$ NMR ($CDCl_3$/TMS): $\delta$(ppm) 3.35(s, 3H), 6.28(d, J = 10.3Hz, 2H), 6.82(d, J = 10.3Hz, 2H). $^{13}C$ NMR($CDCl_3$): $\delta$(ppm) 50.394(q), 92.501(s), 129.705(d), 143.336(d), 185.169(s). Spectral data are in accordance with an authentic sample[10]

**(vii) The biphenyl compound from 1a (9a)**: Yield-60%. m.p.118-119°C. IR($CCl_4$): cm$^{-1}$ 3300, 2927, 2130, 1480, 1456, 1377, 1270, 1040, 915, 900. $^{1}$H NMR ($CDCl_3$/TMS): $\delta$(ppm) 2.5(t, J=2Hz, 2H), 3.75(s, 6H), 4.62(d, J=2Hz, 4H), 6.8-6.91(m, 6H). $^{13}$C NMR($CDCl_3$): $\delta$(ppm) 56.345(q), 56.527(q), 75.303(d), 78.946(wd), 112.219(d), 114.754(d), 118.548(d), 128.308(s), 151.259(s), 151.927(s). HRMS: m/z 322.12228 calculated for $C_{20}H_{18}O_4$(322.12051). Anal. Calcd. for $C_{20}H_{18}O_4$: C,74.22; H,6.00 % Found: C,74.25; H,5.96%

**(viii) 2,2',5,5'-tetra(prop-2-ynyloxy)-1,1'-biphenyl (9b)**: Yield-60% m.p.126°C IR($CCl_4$): cm$^{-1}$ 3313, 2900, 2100, 1592, 1494, 1371, 1272, 1100. $^{1}$H NMR($CDCl_3$/TMS): $\delta$(ppm) 2.44(t, J=2.2Hz, 2H), 2.52(t, J=2.4Hz, 2H), 4.58(d, J=2.2Hz, 4H), 4.66(d, J=2.4Hz, 4H), 6.93-7.10(m, 6H). $^{13}$C NMR($CDCl_3$/TMS): $\delta$(ppm) 56.466(q), 57.164(q), 75.182(d), 75.455(d), 78.825(s), 79.235(s), 114.890(d), 116.029(d), 118.366(d), 129.007(s), ,149.908(s), 152.120(s). HRMS: m/z 370.12036 calculated for $C_{24}H_{18}O_4$(370.12051). Anal. Calcd. for $C_{24}H_{18}O_4$: C,77.55; H,5.23 % Found: C,77.68; H,5.30 %

**(ix) The biphenyl compound from 1c (9c)**: Yield-55%. IR($CCl_4$): cm$^{-1}$ 3302, 2895, 2098, 1602, 1479, 1365, 1258, 1098. $^{1}$H NMR($CDCl_3$/TMS): $\delta$(ppm) 2.1(s, 3H), 2.32(s, 3H), 2.42(t, J=2.65Hz, 1H), 2.50(t, J=2.7Hz, 1H), 4.58(d, J=2.65Hz, 2H), 4.67(d, J=2.7Hz, 1H), 6.8-7.2(m, 6H). $^{13}$C NMR($CDCl_3$): $\delta$(ppm) 19.095(q), 20.507(q), 55.920(t), 56.011(t), 75.227(d), 75.288(d), 78.872(s), 78.931(s), 113.008(d), 113.843(d), 116.484(d), 128.794(d), 129.917(s), 130.418(d), 131.147(s), 131.845(d), 132.194(s), 139.889(s), 152.246(s), 155.282(s). HRMS: m/z 290.12965 calculated for $C_{20}H_{18}O_2$(290.13068). Homogeneous in tlc, $R_f$ = 0.70 (hexane-ethyl acetate mixture 9:1) and apparently a single peak in hplc with $R_t$ = 6.8 min. ($CH_3OH$ - $H_2O$ 80:20)

**(x) 5,5'-chloro-2,2'-bis(prop-2-ynyloxy)-1,1'-biphenyl (9d)**: Yield-57%. m.p.148°C. IR($CCl_4$): cm$^{-1}$ 3315, 2928, 1600, 1550, 1390, 1220, 1060. $^{1}$H NMR($CDCl_3$/TMS): $\delta$(ppm) 2.48(t, J=2.3Hz, 2H), 4.61(d, J=2.3Hz, 4H), 7.04-7.32(m, 6H). $^{13}$C NMR($CDCl_3$): $\delta$(ppm) 56.557(t), 75.698(d), 78.415(wd), 114.222(d), 126.381(s), 128.551(s), 128.688(d), 131.192(d), 153.612(s). HRMS: m/z 330.02244 calculated for $C_{18}H_{12}Cl_2O_2$(330.02143). Anal. Calcd. for $C_{18}H_{12}Cl_2O_2$: C,65.28; H,3.91 % Found: C,65.36; H,3.98 %

**(xi) 2,2'-bis(prop-2-ynyloxy)-1,1'-binaphthyl (9e)**: Yield-56%. m.p.100-101°C. IR($CCl_4$): cm$^{-1}$ 3320, 1603, 1504, 1340, 1252, 1020. $^{1}$H NMR($CDCl_3$/TMS): $\delta$(ppm) 2.48(t, J=2Hz, 2H), 4.59(d, J=2Hz, 4H), 7.12-8.0(m, 12H). $^{13}$C NMR($CDCl_3$): $\delta$(ppm) 57.271(t), 75.212(d), 79.295(wd), 116.029(d), 124.073(d), 125.591(d), 129.411(d), 127.914(d), 129.401(d), 129.766(s), 133.940(s), 153.156(s). HRMS: m/z 362.13018 calculated for $C_{26}H_{18}O_2$(362.13068). Anal. Calcd. for $C_{26}H_{18}O_2$: C,85.85; H,5.34 % Found: C,85.94; H,5.41%

**(xii) 5,5'-dinitro-2,2'-bis(prop-2-ynyloxy)-1,1'-biphenyl (9f)**: Yield-40% m.p.120-122°C IR($CCl_4$): cm$^{-1}$ 3322, 1605, 1540, 1350, 1280, 1100. $^{1}$H NMR ($CDCl_3$/TMS): $\delta$(ppm) 2.69(t, J=2.4Hz, 2H), 4.99(d, J=2.4Hz, 4H), 7.4-8.8(m, 6H). $^{13}$C NMR($CDCl_3$): $\delta$(ppm) 57.862(t), 75.698(d), 78.582(wd), 115.300(d), 121.903(s), 121.948(d), 128.855(d), 140.801(s), 155.099(s). HRMS: m/z 352.06745 calculated for

**$C_{18}H_{12}N_2O_6$(352.06954). Anal. Calcd. for $C_{18}H_{12}N_2O_6$: C,61.22; H,3.67; N,7.93 % Found: C,61.30; H,3.75; N,7.98 %**

*Experimental procedure for CAN promoted reactions:* A solution of ceric ammonium nitrate (1 mmol) in dry acetonitrile (20 mL) was stirred at room temperature with 1 mmol of the substrate. A change of colour of the solution from red to yellow was observed during the course of the reaction. After 24h the reaction was quenched with an equal volume of water and the aqueous mixture was thoroughly extracted with dichloromethane. The organic layer was then dried over anhydrous sodium sulfate. The product was purified by column chromatography.

**(xiii) Mononitro-4-methoxyphenyl prop-2-ynyl ether (10a)**: Yield-68%. IR($CHCl_3$): cm$^{-1}$ 3300, 2980, 1499, 1444, 1354, 1298, 1000. $^1$H NMR ($CDCl_3$/TMS): $\delta$(ppm) 2.49(t, J=2.3Hz, 2H), 3.7(s, 3H), 3.81(s, 3H), 4.63(d, J=2.3Hz, 2H), 4.71(d, J=2.3Hz, 2H), 6.96-7.44(m, 6H). $^{13}$C NMR($CDCl_3$): $\delta$(ppm) 56.721(q), 57.389(q), 68.526(t), 69.730(t), 75.710(d), 76.681(d), 77.531(s), 77.744(s), 111.198(d), 112.398(d), 114.295(d), 115.479(d), 121.186(d), 122.370(d), 139.361(s), 139.730(s), 147.019(s), 147.977(s), 150.527(s), 150.982(s). MS: m/z 207(p$^+$), 169, 107, 79. HRMS: m/z 207.05298 calculated for $C_{10}H_9NO_4$(207.05316). Homogeneous in tlc, $R_f$ = 0.65 (Hexane-ethyl acetate mixture 9:1)

**(xiv) Mononitro-4-methoxyphenyl prop-2-enyl ether (10b)**: Yield-70% IR($CHCl_3$): cm$^{-1}$ 2948, 1500, 1450, 1400, 1352, 1280, 1022, 930. $^1$H NMR($CDCl_3$/TMS): $\delta$(ppm) 3.35(s, 3H), 3.42(s, 3H), 4.04(d, J=5Hz, 2H), 4.14(d, J=5Hz, 2H), 4.8-5.02(m, 4H), 5.5-5.6(m, 2H), 6.52-6.95(m, 6H). $^{13}$C NMR($CDCl_3$): $\delta$(ppm) 55.886(q), 56.889(q), 69.547(t), 70.777(t), 109.726(d), 111.047(d), 114.902(d), 116.860(d), 118.029(t), 118.105(t), 120.533(d), 121.475(d), 132.054(d), 132.358(d), 139.264(s), 139.947(s), 146.034(s), 147.324(s), 151.605(s), 152.917(s). MS: m/z 209(p$^+$), 168, 107, 79. HRMS: m/z 209.06981 calculated for $C_{10}H_{11}NO_4$(209.06881). Homogeneous in tlc, $R_f$ = 0.70(Hexane-ethyl acetate mixture 9:1)

**(xv) Mononitro-4-mehtoxyphenyl buta-2,3-dienyl ether (10c)**: Yield-72% IR($CHCl_3$): cm$^{-1}$ 2944, 1955, 1500, 1484, 1444, 1350, 1283, 1036. $^1$H NMR($CDCl_3$/TMS): $\delta$(ppm) 3.72(s, 3H), 3.83(s, 3H), 4.47(td, J=6.5, 2.4Hz, 2H), 4.57(td, J=6.5, 2.4Hz, 2H), 4.75-4.82(m, 4H), 5.22-5.32(m, 2H), 6.74-7.34(m, 6H). $^{13}$C NMR($CDCl_3$): $\delta$(ppm) 56.249(q), 57.266(q), 67.057(t), 68.635(t), 77.060(d), 77.135(d), 86.683(t), 86.774(t), 110.044(d), 111.698(d), 115.250(d), 117.891(d), 120.821(d), 122.157(d), 139.612(s), 140.739(s), 146.079(s), 147.794(s), 151.680(s). MS: m/z 221(p$^+$), 169, 124, 123, 109. HRMS: m/z 221.06878 calculated for $C_{11}H_{11}NO_4$(221.06881). Homogeneous in tlc, $R_f$ = 0.65 (Hexane-ethyl acetate mixture 9:1).

**(xvi) 2-nitro-1,4-dimethoxybenzene (11)**: Yield-70%. m.p. 70-72$^0$C(lit[25] m.p.72-73$^0$C) IR($CHCl_3$): cm$^{-1}$ 2964, 1496, 1462, 1436, 1350, 1283, 1040, 900. $^1$H NMR($CDCl_3$/TMS): $\delta$(ppm) 3.8(s, 3H), 3.9(s, 3H), 7.0-7.38(m, 3H). $^{13}$C NMR($CDCl_3$): $\delta$(ppm) 55.840(q), 56.857(q), 109.847(d), 114.887(d), 120.640(d), 139.249(s), 147.142(s), 152.652(s). MS: m/z 183(p$^+$), 123, 107, 92.

**(xvii) 2-nitroanisole (12)**: Yield-65%. IR($CHCl_3$): cm$^{-1}$ 2980, 1500, 1451, 1400, 1352, 1284, 1023. $^1$H NMR($CDCl_3$/TMS): $\delta$(ppm) 3.96(s, 3H), 7.03(t, J=7.5Hz, 1H), 7.10(d, J=8.5Hz, 1H), 7.55(t, J=7.5Hz, 1H), 7.85(d, J=8.5Hz, 1H). $^{13}C$ NMR ($CDCl_3$): $\delta$(ppm) 56.420(q), 113.430(d), 120.215(d), 125.618(d), 134.210(d), 139.910(s), 152.910(s). MS: m/z 153($p^+$), 123, 106, 92, 77. Spectral data are in accordance with an authentic sample prepared[25].

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