Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

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To cite this article: Praveen K. Tandon, Manish Srivastava, Santosh B. Singh & Nidhi Srivastava (2008) Liquid-Phase and Solventless Oxidation of Cyclohexane, Benzene, and Other Hydrocarbons by Cerium(IV) Catalyzed by Iridium(III) in Acidic Medium, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 38:18, 3183-3192

To link to this article: http://dx.doi.org/10.1080/00397910802109265

Synthetic Communications®, 38: 3183–3192, 2008
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ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910802109265

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Liquid-Phase and Solventless Oxidation of Cyclohexane, Benzene, and Other Hydrocarbons by Cerium(IV) Catalyzed by Iridium(III) in Acidic Medium

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Abstract: Oxidation of some hydrocarbons dissolved in acetic acid by cerium(IV) sulphate at 100 °C in the presence of traces of iridium(III) chloride (catalyst-substrate 1:56818 to 151515) in the solution phase resulted in good to excellent yields of corresponding carbonyl compounds. In the cases of cyclohexane and benzene, 44% and 51.8% yields of corresponding carbonyl compounds were obtained, whereas in other cases, yield ranged from 34.9 to 99.8%. Yield decreased when reactions were performed in a microwave oven by adsorbing reactants (except acetic acid) on alumina. Decrease in the yield was probably due to the high temperature generated during the course of the reaction, resulting in the loss of organics from evaporation. Conditions were optimized for the highest yields under ambient conditions.

Keywords: Cerium(IV), iridium(III) chloride, microwave, oxidation

INTRODUCTION

Cerium(IV) is an unusually strong, one-electron oxidant. Catalysis by iridium(III) chloride in the oxidation of organic compounds has been given little attention because of its sluggish catalytic activity in alkaline medium.[1,2] During kinetic studies, we observed[3–6] that iridium(III) chloride is a more efficient catalyst compared to even ruthenium(III) chloride[7] or osmium teroxide.[8] Surprisingly, when tried from the

Received January 24, 2008.

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synthetic point of view, the system proved to be highly efficient in the oxidation of many hydrocarbons including cyclohexane and benzene also, which otherwise are very difficult to oxidize. Oxidation of cyclohexane has been attempted by many workers with mononuclear iron(III) complexes with H_2O_2 and hydroperoxides,[9] with H_2O_2 in acetonitrile using Bi-VPO catalyst at 60 °C for 12 h with 38% and 36% yields of cyclohexanone and cyclohexanol,[10] and with oxygen in 8 h at 140 °C and pressure of 2.5 Mpa in the presence of iron porphyrin with yield of 21.4%[11] of adipic acid. 1,4-Diketones were prepared by cerium-catalyzed oxidative coupling of styrene with molecular oxygen and 1,3-dicarbonyl compounds.[12] Ceric ammonium nitrate (CAN)-catalyzed oxidation of alkyl aromatics with potassium bromate affords aldehydes, ketones, acids, or alcohols.[13] Aerial and peroxide (30%) oxidation of cyclohexane with Au-MCM 41[14] or mesoporous Ce-MCM-41 catalyst[15] gives a mixture of cyclohexanone and cyclohexanol. To the best of our knowledge, 44% yield of cyclohexanone directly from cyclohexane in a one-pot reaction has not been reported. Here we report the oxidation of cyclohexane, benzene, toluene, ethyl benzene, anthracene, and phenanthrene by cerium(IV) sulphate in an aqueous acetic acid medium catalyzed by iridium(III) chloride (with catalyst–substrate ratio of 1:56818 to 151515) synthetic purposes.

EXPERIMENTAL

Cerium(IV) sulphate, anthracene (Loba Chemie Indaustranal Co.), cyclohexane, benzene, toluene, ethyl benzene, and phenanthrene (E. Merck) were used as such without further purification. Solution of iridium(III) chloride was prepared by dissolving the sample (sodium chloroiridate) (Johnson Matthey & Co.) in a minimum amount of concentrated HCl (analytical reagent [A.R.]), and the final strengths of acid and catalyst were 0.00624 M and 3.35×10^{-3}M, respectively. Cerium(IV) sulphate, prepared by dissolving the sample in 1:1 sulphuric acid, was standardized with a standard solution of ferrous ammonium sulpahate using ferroin (CDH) as an external indicator. All other chemicals used were either A.R. or chemically pure substances. A Kenstar (model OM-20 ESP, 800 W, Aurangabad, India) domestic microwave oven was used for studying the reactions under microwave irradiations, in which control of temperature was not possible. For getting the maximum yield, five to eight sets were performed by changing the concentration or conditions of each component, which can affect the yield, for example in the synthesis of cyclohexanone from cyclohexane (Table 1). For performing the reactions in the solution phase, a calculated amount of hydrocarbon dissolved in a requisite amount of acetic acid was mixed with iridium(III)

Table 1. Effect of various factors on the yield of cyclohexanone (a′) from cyclohexane (a) (2.0 mmol) by cerium(IV) sulphate catalyzed by iridium(III) chloride in aqueous acetic acid medium in solution phase and in the absence of acetic acid under microwave irradition

Entry	Ce(IV) (mmol)	Acetic acid (for water bath only) (mmol)	$Ir(III) \times 10^6$ (mmol)	Temp. (°C) for water bath	Time in h (for MW in min)	MW power (%)	Yield (%) (yield with MW)
1	4.0	250	—	100	3.0	—	0.0
2	—	250	17.6	100	3.0	—	0.0
3	4.0	250	17.6	Room temp.	48	—	0.0
4	4.0	250	15.4	100	3.0	—	35.9
5	4.0	250	17.6	100	3.0	—	44.0
6	4.0	250	19.8	100	3.0	—	42.0
7	4.0	350	17.6	100	3.0	—	44.0
8	3.0	250	17.6	100	3.0	—	22.4
9	5.0	250	17.6	100	3.0	—	31.0
10	4.0	250	17.6	70	3.0	—	15.2
11	4.0	—	17.6	—	3.0 (min)	40	35.9
12	4.0	—	17.6	—	3.0 (min)	20	19.9
13	4.0	—	17.6	—	3.0 (min)	80	20.6

chloride and cerium(IV) sulphate in a round-bottomed flask. The flask, fitted with a water condenser, was kept in a water bath at a fixed temperature for the desired time. Contents were cooled and extracted with appropriate solvents. The extract was dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressure, and hydrazone of the product was prepared. For performing the reaction in solid phase in a microwave oven, the same amounts of reactants except acetic acid [cerium(IV) sulphate, cyclohexane, and iridium(III) chloride] as in the solution-phase reaction were mixed in 25 g of alumina. The paste was kept in an alumina bath was exposed in the microwave oven at the desired power for the desired time. The workup procedure was the same as given in the solution-phase reactions performed in a water bath. IR (in KBr; Brucker Vector-22 IR spectrophotometer) and ^1H NMR (Xeol 400 MHz in $CdCl_3$ with TMS as internal standard) spectra were recorded, and reactions were monitored with thin-layer chromatography, TLC (Merck GF254 silica-gel-coated plates). Purity and identification of products were confirmed by TLC, mp of the derivatives, and their IR and NMR spectra.

RESULTS

In all the cases, running TLC plates with hydrazone of the authentic sample showed only one spot. In the cases of **a** to **d** and **f**, a mixture was extracted (15 ml × 3) with ether, whereas in the case of **e**, it was extracted with benzene. Reaction conditions in which various experiments were performed are summarized in Table 2, and the general procedures for performing the reactions in solution phase and under microwave irradiation are given in the experimental section. 2,4-Dinitrophenyl hydrazone derivatives of the products were prepared by the standard method.[16] Hydrazone of cyclohexanone (**a′**) from cyclohexane (**a**) was recrystallized with ethyl alcohol. Hydrazone derivative (245 mg) was obtained, corresponding to 44% yield of cyclohexanone; mp of hydrazone was 160 °C (reported as 162 °C). NMR: δ 7.96 to 7.99 (1H, d), δ 8.27 to 8.31 (1H, dd), δ 9.12 to 9.13 (1H, d), δ 1.71 to 2.5 (10H, m). Surprisingly under microwave irradiation (40% power for 3.0 min), the yield decreased to 35.9% (200 mg of hydrazone was obtained). Benzoquinone (**b′**) from benzene (**b**) was prepared as in **a**. Hydrazone (485 mg, 51.8% yield) was obtained, which was recrystallized with ethyl alcohol. Under microwave irradiation (40% power, 3.0 min), yield decreased to 22.4% (210 mg of hydrazone was obtained). Hydrazone mp was 182 °C (reported as 186 °C). IR $\nu_{max}\cdot$1619 nm ($\nu_{C=N}$), 1301 nm$\cdot$($\nu_{Ar\text{-}NO2}$), 1491 nm ($\nu\cdot_{benzene\ ring}$), 3320–3362 (ν_{N-H} str.). NMR: δ 6.8 (4H, s), δ 6.5 (4H, s).

Benzaldehyde (**c′**) from toluene (**c**) prepared as before gave 200 mg of hydrazone (34.9% yield). In the microwave oven (40% power, 3.0 min), yield decreased to 24.4% (140 mg of hydrazone was obtained). Hydrazone mp was 232 °C (reported as 241 °C). NMR: δ 11.2 (1H, s), δ 5.29 (1H, s), δ 9.1 (1H, d), δ 8.1 to 8.3 (2H, m), δ 7.2 to 7.9 (5H, m).

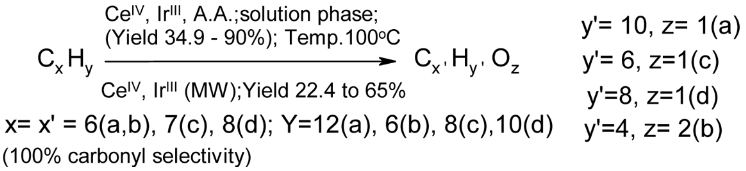
Acetophenone (**d′**) from ethyl benzene (**d**) prepared as before gave 540 mg of hydrazone (90% yield). On conducting the reaction in microwave oven (60% power, 3.0 min), yield decreased to 65% (390 mg of hydrazone). Hydrazone mp was 244 °C (reported as 250 °C). NMR: δ 7.26 (1H, s), δ 4.0 (1H, s), δ 1.55 (3H, s), δ 8.77 to 8.76 (1H, d), δ 8.42 to 8.41 (2H, d), δ 8.39 to 8.38 (1H, d), δ 7.88 to 7.82 (2H, d), δ 7.48 to 7.46 (1H, t).

Anthraquinone (**e′**) from anthracene (**e**) prepared as before gave 207 mg (99.8% yield). On conducting the reaction in a microwave oven (60% power, 2.0 min), the yield decreased to 79.8% (166 mg of anthraquinone). Anthraquinone mp was 284 °C (reported as 286 °C). IR ν_{max} 1673 cm^{-1} ($\nu_{C=O}$), 935–809 cm^{-1} ($\nu_{subs.benzene\ ring}$), NMR: δ 7.049 to 8.12 (8 Hm). Phenanthraquinone (**f′**) from phenanthrene (**f**) gave 200 mg, (96.1% yield). In a microwave oven (60% power, 2.0 min), the

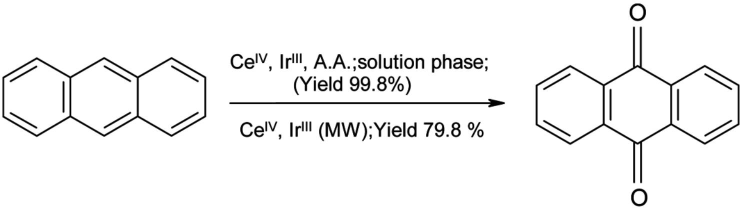
Table 2. Oxidation of hydrocarbons (dissolved in acetic acid) by cerium(IV) sulphate in presence of iridium(III) chloride in solution phase and under microwave irradiation in the absence of acetic acid

Organic substrate	Product	Ce(IV) (mmol)	Acetic acid (for water bath only) mmol	Ir(III) × 10^6 (mmol)	Temp. (°C) for water bath	Time in h (for MW in min)	Yield (%) (yield with MW)
Cyclohexane (**a**)	Cyclohexanone (**a′**)	4.0	250	17.6	100	3.0 (3.0)	44 (35.9)
Benzene (**b**)	Benzoquinone (**b′**)	4.0	250	11.0	100	3.0 (3.0)	51.8 (22.4)
Toluene (**c**)	Benzaldehyde (**c′**)	4.0	250	8.8	100	3.0 (3.0)	34.9 (24.4)
Ethyl benzene (**d**)	Acetophenone (**d′**)	4.0	250	6.6	100	3.0 (3.0)	90 (65)
Anthracene (**e**)	Anthraquinone (**e′**)	2.3	250	15.4	100	2.0 (2.0)	99.8 (79.8)
Phenanthrene (**f**)	Phenanthraquinone (**f′**)	2.5	250	11.0	100	2.0 (2.0)	96.1 (72.1)

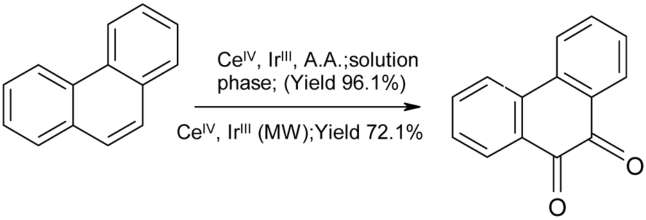
Note: Amount of organic substrate **a** to **d** (2.0 mmol); **e** and **f** (1.0 mmol).



Scheme 1. Oxidation of hydrocarbons (**a–d**).



Scheme 2. Oxidation of anthracene (**e**).



Scheme 3. Oxidation of phenanthrene (**f**).

yield decreased to 72.1% (150 mg of phenanthraquinone). Phenanthraquinone mp was 206 °C (reported as 208 °C). IR $\nu_{\mathrm{max}}\cdot$3053 cm^{-1} ($\nu_{\mathrm{Ar\cdot C-H}}$), 1674 cm^{-1} ($\nu_{\mathrm{C=O}}$), and 732 cm^{-1} ($\nu_{\mathrm{subs.benzene\ ring}}$).

DISCUSSION

The study was performed mainly to determine the efficiency and economy of the novel, simple, one-pot cerium(IV)–iridium(III) reaction on to oxidize various organic compounds. Five to seven sets were performed to obtain the maximum yield by changing concentration or conditions of each component. Change in the concentration of acetic acid did affect the yield (Table 1, entries 5 and 7), indicating that it acts as a solvent to dissolve the hydrocarbons. Yields in all the cases reached a maximum and then started to decrease with further increase in catalyst (entries 4 to 6, Table 1) and oxidant concentrations (Table 1, entries 5, 8, and 9), indicating that optimum conditions are required to get the highest yield or that some nonreactive complex is formed at higher concentrations of the catalyst and oxidant. Lack of formation of the desired products, after prolonged heating in the absence of oxidant (Table 1, entry 2) or leaving the mixture for 48 h at room temperature (Table 2, entry 3), indicates that aerial oxidation was not taking place at higher temperatures and also that temperature control was essential for getting the product with the desired yield. It was also observed that the system was incapable of to oxidizeing cyclohexane in the absence of catalyst (Table 2, entry 1), indicating that it is the catalyst that is responsible for the oxidation, at least in the case of cyclohexane. Probably the catalyst facilitates the decomposition of the complex formed between oxidant and the organic substrate. During the kinetic study of the oxidation of cyclic alcohols and aromatic aldehydes, we observed[4–6] that it is not the catalyst but cerium(IV) that forms the complex with the organic substrate in the first step, and iridium(III) facilitates the decomposition of the complex formed between cerium(IV) and organic substrate. It is known that $IrCl_3$ in HCl medium gives $IrCl_6^{3-}$ species.[17] It has also been reported that Ir^{III} and Ir^{I} ions are the stable species of iridium.[18] Further, the aquation of $[IrCl_6]^{3-}$ gives $[IrCl_5H_2O]^{2-}$, $[IrCl_4(H_2O)_2]^{1-}$ and $[IrCl_3(H_2O)_3]$ species.[19,20] In the present case, also for preparing the catalyst, sodium hexachloroiridate(III) was dissolved in aqueous hydrochloric acid, and the concentration of acetic acid did not affect the yield, indicating that acetic acid probably does not change the species of catalyst in the medium. Therefore, an active species of iridium taking part in the solution-phase reaction may well be considered to be $IrCl_5(H_2O)^{2-}$, which has been considered previously also.[1–6] Cerium(IV) is a typical one-equivalent oxidant that removes one electron at a time from the substrate. In this regard, it shares certain similarities in reaction patterns with Mn(III), Co(III), and V(V). In one-equivalent oxidation of neutral or anionic organic species, cation radicals or free radicals are generated.[21] Normally, these intermediates undergo rapid oxidation to afford neutral products by electron transfer (outer-sphere reaction) or by ligand transfer (inner-sphere reaction). As Ce(IV) oxidations deal most frequently with neutral organic compounds, radical intermediates are encountered most of the time. The fates of these intermediates, to undergo C–H, C–C bond cleavage or hydrogen transfer, depend on their structure. In the oxidation of alcohols[22] and aromatic aldehydes[23] with cerium(IV) in aqueous acetic acid, involvement of both 1:1 and 2:1 inner-sphere complexes has been reported. In the present study the presence of Ir(III) probably facilitates the removal of hydrogen from the complex formed in the first step between the oxidant and the organic substrate by forming another complex.[3–6] Homolysis of the C–H bond may give rise to H■, which may transfer its electron to Ir(III), giving rise to [$HIrCl_6^{2-}$], which in turn may dissociate back into the original Ir(III) species, although homolysis of water may provide OH■, giving rise to alcohol, which is further oxidized to a carbonyl compound. The presence of alcohol in the system could not be detected, but its formation as an intermediate cannot be ruled out.

The reported novel one-pot system is highly efficient, easy, and also can be used to oxidize a variety of other functional groups, for which studies are being done. Above all, it oxidizes cyclohexane and benzene, which are otherwise difficult to oxidize. High yield of the carbonyl group makes the system very attractive from a synthetic point of view. Solventless synthesis under MW irradiation is also important from an environmental point of view.

ACKNOWLEDGMENT

The authors are grateful to University Grants Commission [32–240/2006 (S.R.)] and Council of Scientific and Industrial Research [01(2150)/07/ EMR-II], New Delhi, India, for financial assistance. Help from Central Drug Research Institute, Lucknow, India, is acknowledged for spectral studies.

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