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CERIUM CATALYZED PERSULFATE OXIDATION OF POLYCYCLIC AROMATIC HYDROCARBONS TO QUINONES

JACEK SKARŻEWSKI
Institute of Organic and Physical Chemistry, Technical University of Wrocław, 50-370 Wrocław, Poland

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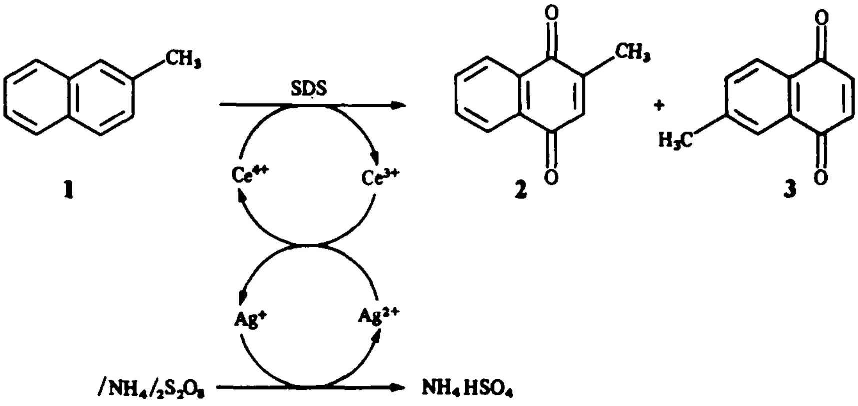
Abstract—A practical synthesis of polycyclic quinones from the parent hydrocarbons is described. The two-phase oxidation of hydrocarbons was accomplished by using ammonium persulfate in the catalytic presence of cerium ammonium sulfate, silver nitrate, and sodium dodecyl sulfate. The reaction conditions and scope have been discussed in detail.

The cerium (IV) salts have been known for a long time to oxidize selectively a variety of organic compounds[1] and proved to be useful in the functionalization of aromatic hydrocarbons.[2] We have previously reported that such reactions can be effectively carried out in the two-phase system,[3a] especially with sodium dodecyl sulfate (SDS) as a micellar catalyst.[3b] On the other hand, the application of Ce-salts to organic synthesis is limited because of the large amounts of the reagent needed. This problem is particularly pronounced in the case of selective oxidation of aromatic hydrocarbons to quinones with cerium (IV) ammonium sulfate (CAS),[4] since as many as six one-electron equivalents of the oxidant are required. However, other oxidants used so far in this important transformation often give unsatisfactory yields.[2b,5]

In order to make these reactions more useful, we have tried to carry out oxidation as a catalytic process with regard to the Ce-salt by taking advantage of the fact that reduced Ce (III) can readily be converted into Ce (IV) state by persulfate with the help of Ag (I) ions as a cocatalyst.[6] The redox reactions anticipated to take place in the catalytic process are shown below.



Scheme 1.

At first, the catalytic system was tested in the oxidation of 2-methylnaphthalene (**1**) and the yields of resulting quinones **2** and **3** were determined. An organic substrate together with ammonium persulfate were gradually added to a stirred aqueous solution of CAS, silver nitrate, SDS, and sulfuric acid. The results given in Table 1 were obtained performing the reaction under the two-phase conditions and using 10% mol of CAS and ammonium persulfate in 20% mol excess. As it can be seen from Table 1, all the components are necessary since: (i) the absence of CAS leads to tarry products only, (ii) the absence of persulfate demands the stoichiometric amounts of CAS, (iii) the absence of Ag-salt slows down a reoxidation of the cerous ions, which thus are eliminated by precipitation, and finally (iv) the absence of SDS makes the two-phase oxidation slow and incomplete. Several concentration conditions were examined in order to get fast reaction, to prevent precipitation of polymeric Ce-salt, and to facilitate the work up by avoiding too much surfactant. Under the optimum concentration conditions, the catalyst solution could be used again giving the same yield of quinones in the second run (Table 1, entry 7). The rate of the reagents addition is also of some importance. When two large portions were applied, poor yield of quinones resulted, probably due to the predominated reaction with ammonium persulfate itself.[7]

Thus, the developed oxidizing system was applied to the synthesis of various quinones. The results are presented in Table 2. The yields reported are given for the pure, isolated products, except of 2-methylnaphthalene where quinones could not be separated by column chromatography and in that case the mixture composition was determined by GLPC and NMR in comparison with the original samples. The syntheses were carried out on the 4 mmol scale using the cyclohexane solutions of organic substrates. Generally,

Table 1. Catalytic activities in oxidation of 2-methylnaphthalene

Entry	Oxidant composition $(NH_4)_2S_2O_8$ g	AgNO$_3$ mM	SDS mM	CAS mM	Yield[a] %	Substrate recovered %
1	—	—	5	100	65[b]	trace
2	3.5	12	5	—	[c]	no
3	3.5	—	5	100	5	58
4	3.5	12	—	100	56	24
5	3.5	12	5	100	67	no
6	3.5	12	1	100	66	no
7	3.5	30	1	100	73, 73[d]	no, no[d]
8	3.5	60	1	100	73	no

[a] 2-Methylnaphthalene (4.16 mmol) was oxidized with an aqueous solution (25 ml) of the given components at 50° for 5 hr. Both quinones **2** and **3** were isolated and determined together.

[b] The stoichiometric amount of CAS was used.

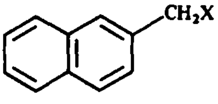
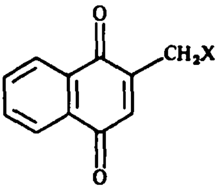
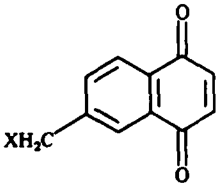
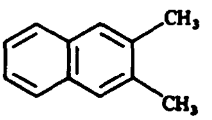
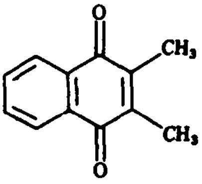
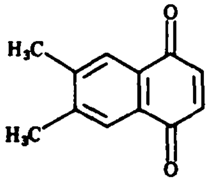
[c] A complex mixture of tarry products was obtained.

[d] The same solution was used in the second run.

the yields were very good, similar to those obtained by the homogeneous CAS oxidation.[4] In the cases when the reaction was scaled up to 0.2 mole, it gave even better yields. It is noteworthy that oxidation of 2-methylnaphthalenes substituted in the side-chain offers a simple route to the important bioalkylating agents.[8] This method presents an essential improvement as compared with the yields obtained in the corresponding CrO$_3$ oxidation of hydrocarbons.[5] However, in the case of 2-chloromethylnaphthalene, the two-phase oxidation with the stoichiometric amount of CAS was the method of choice since in the catalytic system the silver ions were partially removed as AgCl and the homogeneous CAS oxidation gave in this case inferior yield.

In order to establish the scope of the developed method, we examined oxidation of various substrates. Almost all these compounds were effectively oxidized by cerium ammonium nitrate[3,9] or Ce (IV)-NaBrO$_3$.[10] The results shown in Table 3 demonstrate that the

Table 2. Oxidation of polycyclic hydrocarbons

Entry	Substrate	Reaction time, hr	Products Yield, %	
1	Naphthalene	3 (5)	1,4-Naphthoquinone 81 (79)	
2	Anthracene	5	9,10-Anthraquinone 52	
3	Phenanthrene	7	9,10-Phenanthrenequinone 58	
				
4	X : H	5	60	20
5	X : OCOCH$_3$	5	28	31
6	X : OCH$_3$	5	26.5	28.5
7	X : Cl	6	12, 12[a], 27.5[b]	10, 26[a], 47[b]
8	2,6-Dimethylnaphthalene	3 (5)	2,6-Dimethyl-1,4-naphthoquinone 68 (78)	
9	2,7-Dimethylnaphthalene	5	2,7-Dimethyl-1,4-naphthoquinone 89	
10		5	 55	 25

[a] The homogeneous CAS oxidation.

[b] The two-phase CAS oxidation.

Table 3. Oxidation of various compounds

Entry	Substrate	Reaction time, hr	Products Yield, %[a]
1	Durene	5	2,4,5-Trimethylbenzaldehyde 17.5
2	1,2,4-Trimethoxynaphthalene	3	2-Methoxy-1,4-naphthoquinone 27.5
3	3,6-Dimethoxydurene	3	Duroquinone 22.5
4	Benzyl alcohol	5	Benzaldehyde 60
5	α-Methylbenzyl alcohol	5, 7	Acetophenone 67, 62[b]
6	4-t-Butylcyclohexanol, 25% cis	3, 6, 12	4-t-Butylcyclohexanone 30, 55, 40[b]
7	1-Dodecanol	5	None, substrate recovered in 83%
8	6-Dodecanol	5	6-Dodecanone 1.7

[a] The two-phase oxidation was carried out with appropriate amounts of the oxidants (Ce(IV): 10% mol, $/NH_4/_2S_2O_8$: in 20% excess). Yields were determined by GLPC with internal standards. In some cases (entry 1 and 2) the products were isolated.

[b] A consecutive oxidation of product was confirmed in the separate experiments.

catalytic system developed is not suitable for the substrates of higher ionization potential and for the O-containing compounds. Poor yields obtained for 1,4-dimethoxy derivatives and alcohols can be accounted for the well-known complexing of alcohols with Ce (IV),[11] which, in this manner, can be withdrawn from the oxidation system. Thus, attempts to apply our catalytic process to other oxidations failed and the system should be considered as a specific oxidant for polycyclic aromatic hydrocarbons.

Resuming, we conclude that the developed procedure presents a convenient way for a practical preparation of polycyclic quinones from the parent hydrocarbons.

EXPERIMENTAL

M.ps were determined on a Kofler block. The IR spectra were recorded on a Perkin–Elmer 621 spectrophotometer in KBr. The ^1H-NMR spectra were recorded on a Tesla 100 MHz instrument in $CDCl_3$ with TMS as internal standard. Analytical TLC were performed on E. Merck precoated plates (Kieselgel 60, F 254), the chromatograms being revealed by UV light. Kieselgel 60 (Merck) was used for flash chromatography. Eluent: petroleum ether–ethyl ether–CH_2Cl_2. The GLPC analyses were recorded on a Perkin–Elmer F 11 apparatus using a 10% XE-60 on Chromosorb G column. n-Decane of ne-hexadecane were applied as internal standards. The catalysts used were the highest available purity materials. Organic substrates and ammonium persulfate were reagent grade commercial products. Distilled water was used.

General oxidation procedure—An aqueous soln of CAS (0.1 M), $AgNO_3$ (0.03 M), SDS (1×10^{-3} M), H_2SO_4 (0.55 M) (25 ml) was magnetically stirred at 50°. To this soln, the organic substrate (4.16 mmol) in *ca* 15 ml of cyclohexane and ammonium persulfate (3.5 g) were added portionwise at the same temp. After an appropriate period of time (Table), the mixture was cooled to room temp and extracted with ethyl ether (3 × 15 ml). The combined extracts were washed with water, brine, and dried over Na_2SO_4. Evaporated crude product was subjected to flash chromatography to give analytically pure samples.

In the case of 2-methylnaphthalene, 2-methyl- and 6-methyl-1,4-naphthoquinone could not be separated. 2-Methyl-isomer was obtained from the mixture by crystallization from MeOH, m.p. 105–106°, lit.[12] 104–105°. 6-Methyl-isomer was prepared from *p*-benzoquinone and isoprene,[13] m.p. 91°, lit.[13] 91° and compared with the mixture by means of GLPC and NMR. The ratio of isomers [2]/[3] was found being 3.0/1.0.

The other products obtained were as follows: 1,4-naphthoquinone, m.p. 123–125°, lit.[12] 124–125°; 9,10-anthraquinone, m.p. 284–285°, lit.[14] 285.5–286°; 9,10-phenanthrenequinone, m.p. 208–211°, lit.[14] 209–210°; 2-chloromethyl-1,4-naphthoquinone, m.p. 90–92°, lit.[8] 92°; 6-chloromethyl-1,4-naphthoquinone, m.p. 109–110.5°, lit.[8] 107–108°; 2-acetoxymethyl-1,4-naphthoquinone, m.p. 109.5–110°, lit.[8] not given; 6-acetoxymethyl-1,4-naphthoquinone, m.p. 86–87°, lit.[8] 87–88°; 2-methoxymethyl-1,4-naphthoquinone, m.p. 104–105.5°, lit.[8] 104–105°; 2,6-dimethyl-1,4-naphthoquinone, m.p. 134–135°, lit.[15] 136–137°; 2,3-dimethyl-1,4-naphthoquinone, m.p. 126–127°, lit.[12] 127°; 6,7-dimethyl-1,4-naphthoquinone, m.p. 117–119°, lit.[16] 116–117°; 2,7-dimethyl-1,4-naphthoquinone, m.p. 113–114°, lit.[17] 114°; 2-methoxy-1,4-naphthoquinone, m.p. 145–146°, lit.[18] 144–144.5°; 2,4,5-trimethylbenzaldehyde, oxime, m.p. 109–109.5, lit.[19] 112°. Spectral characteristics of the compounds obtained were in agreement with their structures. The IR spectra of symmetrically disubstituted or unsubstituted 2,3-$(X)_2$-1,4-naphthoquinones showed single $\nu_{C=O}$ band at 1660 cm^{-1}. In the spectra of monosubstituted 2-X-1,4-naphthoquinones double $\nu_{C=O}$ band at 1630 and 1660 cm^{-1} appeared. The NMR spectra of 2-X-1,4-naphthoquinones revealed a coupling between 3-H and the protons of X-substituent, J ~ 1.5–2.0 Hz.

6-Methoxymethyl-1,4-naphthoquinone, m.p. 81–83°; IR ν_{C-H} 3070, 3030, 2930, 2890, 2840, $\nu_{C=O}$ 1660, $\nu_{C=C}$ 1595, ν_{C-O} 1092; NMR (δ, ppm), 3.45 (3H, s, $-CH_3$), 4.60 (2H, s, $-CH_2-$), 7.00 (2H, s, 2-H, 3-H), 7.68–8.28 (3H, m, aromatic). (Found: C, 71.60; H, 5.05. Calc for $C_{12}H_{10}O_3$: C, 71.27; H, 4.99%).

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