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Benzylic oxidation and photooxidation by air in the presence of graphite and cyclohexene

Grigoriy Sereda* and Vikul Rajpara

The University of South Dakota, Department of Chemistry, 414 E. Clark Street, Vermillion, SD 57069, United States

Abstract—Graphite is introduced as a convenient catalyst for cyclohexene-promoted photooxidation of *p*-xylene, ethylbenzene, and cumene by air. Availability of the reagent (air), lack of chemical waste, low toxicity, and reusability of the catalyst make the process a good green alternative of oxidation of these industrially important hydrocarbons.
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Unmodified graphite is receiving increased attention as a mild catalyst for acylation,[1] alkylation,[2] and cleavage of ethers.[3] Development of efficient catalytic systems for oxidation of aromatic hydrocarbons to peroxy- hydr-oxy-, and carbonyl compounds is an area of current interest because of its significant practical potential. Research in this field is driven by the involvement of expensive catalysts and unsatisfactory control of the synthetic outcome for current reaction conditions. Thus, use of a cobalt(II)-chelated copolymer was suggested to improve the well-known cumene peroxidation.[4] For conversion of alkylbenzenes to alcohols, aldehydes, and acids there are recently patented procedures, involving tungsten, palladium-based catalysts,[5,6] and photoox-idation.[7,8] Here we report oxidation and photooxidation of the benzylic carbon in *p*-xylene, ethylbenzene, and cumene by air, as well as the influence of unmodified graphite and cyclohexene on the reaction outcome. Passing air at the rate of 1 mL/min through refluxing *p*-xylene **1** with graphite in the presence of cyclohexene under the ambient light leads to a mixture of 4-methyl-benzyl hydroperoxide **2**,[9a] 4-methylbenzyl alcohol **3**,[10] 4-methylbenzaldehyde **4**,[11] and 4-methylbenzoic acid **5**[12] at the molar ratio of 4.5:1.5:1:1.5 (Scheme 1). After the reaction was complete, the catalyst that was filtered out and kept on air completely regained its activity.

Graphite does not seem to require a substantial activa-tion time before the reaction starts. A sample taken
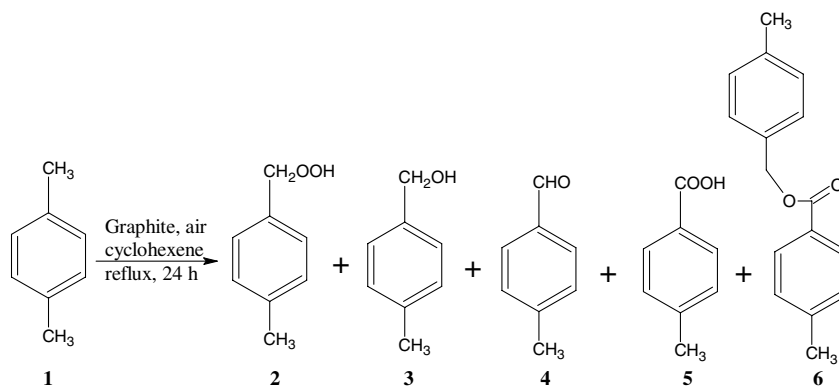
Scheme 1. Oxidation of *p*-xylene.

* Corresponding author. Tel.: +1 605 677 6190; fax: +1 605 677 6397; e-mail: gsereda@usd.edu

from the reaction mixture after 1 h has shown the presence of compounds **2–5** (by NMR). Products **4** and **5** were isolated by column chromatography in order to obtain an additional evidence of their identity.

Protection from light does not affect the overall extent of conversion, but significantly impacts the reaction product distribution (Table 1, entries 2 and 3). Ester **6** was the major product of oxidation in the dark, while hydroperoxide **2** was not detected among the products (entry 2). The presence of ester **6**[13] in the reaction mixture was additionally confirmed by mass-spectrometry. In a control experiment, no autooxidation of *p*-xylene was observed in the absence of carbonaceous catalysts under the ambient light (Table 1, entry 1). Cyclohexene plays a significant role in the oxidation of *p*-xylene. No reaction takes place without cyclohexene, or a complex mixture of unidentified products is formed (Table 2). The content of phenolic products in the reaction mixture was estimated by the integral intensity of a ^{1}H multiplet at 6.8–6.9 ppm.

The known tendency of cyclohexene to form relatively stable allylic radicals upon irradiation or in the presence of peroxides[14] and the ability of graphite to produce hydroperoxy-surface groups upon oxidation by air[15] offer an explanation of their synchronous catalytic activity toward free-radical oxidation of *p*-xylene with air. The exact mechanism of this reaction is yet unclear, however, lack of light may allow for accumulation of the surface peroxy-groups, which, in turn, induce decomposition of hydroperoxide **2** (Table 1, entry 2).

As opposed to *p*-xylene **1**, oxidation of ethylbenzene **7** under ambient light proceeds without carbonaceous catalysts and produces a mixture of 1-phenylethyl hydroperoxide **8**,[16] 1-phenylethanol **9**,[17] and acetophenone **10**[18] (Scheme 2) at the molar ratio of 2:0.2:1. (Table 3, entry 2). The distilled out unreacted ethylbenzene did not contain any impurities (by NMR).

We believe that hydroperoxide **8** is formed by the common radical mechanism followed by decomposition as outlined in Scheme 3. The reaction was almost completely suppressed when run with light protection (source of free radicals, Table 3, entry 1), or in the presence of cyclohexene (interceptor of free radicals, Table 4, entry 2). Interestingly, cyclohexene has the opposite effect on oxidation of *p*-xylene (Tables 1,2), where it seems to play an essential role in the formation of free radicals. Black particles of graphite absorb the ambient light and, therefore, stop oxidation of ethylbenzene (Table 3, entries 5 and 6).

Interestingly, simultaneous action of light, cyclohexene, and graphite leads to significant oxidation of ethylbenzene to practically important acetophenone **10** as the major reaction product (Table 4, entry 6). This reaction results from the unique combination of controversial effects of cyclohexene (generator and interceptor of free radicals) and graphite (generator, interceptor of free radicals, absorbent of light and, possibly, reaction intermediates). The exact reason of such synchronous behavior remains unknown.

Because of the formation of a stable tertiary benzylic free radical, cumene **11** was more active toward oxidation than ethylbenzene **7** (Tables 3 and 4). After refluxing for 24 h with or without light protection, the reaction led to mixtures of products **14**,[19] **12**,[20] and **10** (Scheme 4).

Table 1. Oxidation of *p*-xylene in the presence of cyclohexene

Catalyst	Light protection	Peroxide	Alcohol	Aldehyde	Acid	Ester	Total yield (g)	Entry
None	No	0	0	0	0	0	0	**1**
Graphite	Yes	0	1	1	1.7	1.7	0.23	**2**
	No	4.5	1.5	1	1.5	0	0.23	**3**

Table 2. Oxidation of *p*-xylene (24 h, no light protection)

Catalyst	Peroxide	Alcohol	Aldehyde	Acid	Ester	Phenolic products	Total yield (g)
None	0	0	0	0	0	0	0
Graphite	0.5	0.5	1	0.5	0	2	0.06[a]

[a] Substantial amounts of unidentified products were formed.
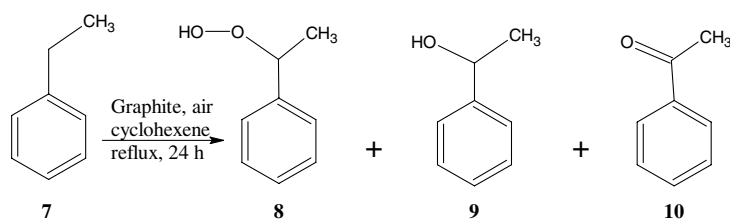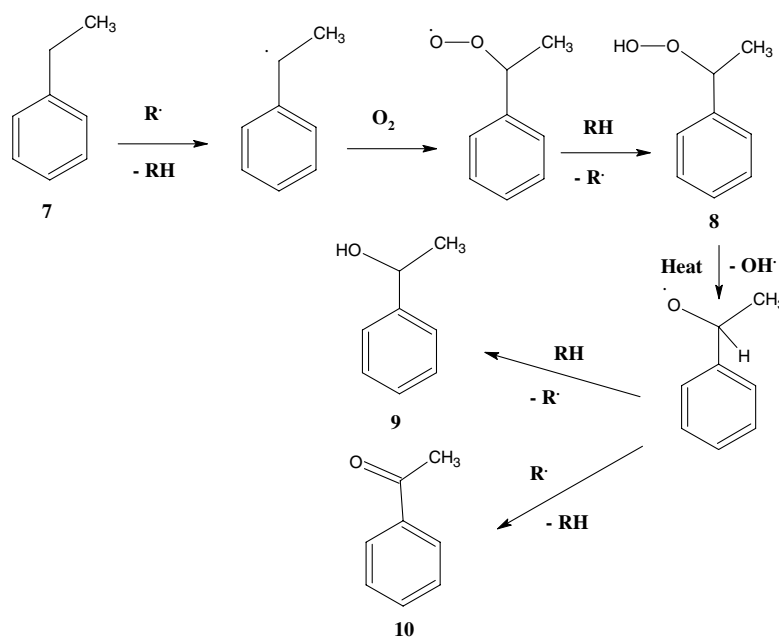

Scheme 2. Oxidation of ethylbenzene.

Table 3. Oxidation of ethylbenzene and cumene

Catalyst	Substrate	Light protection	t (h)	Peroxide	Alcohol	PhAc	Total yield (g)	Entry
None	Ethylbenzene	Yes	18	10	5	1	0.03	**1**
		No	24	2	0.2	1	1.2	**2**
	Cumene	Yes	24	0.7	0.7	1	0.08[a]	**3**
		No	24	0	1.5	1	2.0	**4**
Graphite	Ethylbenzene	Yes	23	0	0	0	0	**5**
		No	24	0	0	0	0	**6**
	Cumene	Yes	24	1	1	1	0.07[b]	**7**
		No	20	0.25	1	1	0.66	**8**

[a] 0.7 equiv of 2,2-dimethyl-2,3-diphenylbutane **13** is also formed.
[b] 1 equiv of 2,2-dimethyl-2,3-diphenylbutane is **13** also formed.

Scheme 3. Mechanism of oxidation of ethylbenzene by air.

Table 4. Oxidation of ethylbenzene and cumene in the presence of cyclohexene

Catalyst	Substrate	Light protection	Peroxide	Alcohol	PhAc	Phenolic products	Total yield (g)	Entry
None	Ethylbenzene	Yes	1	1	1	0	0.13	**1**
		No	20	1	1	0	0.1	**2**
	Cumene	Yes	0.3	1.8	1	0	0.97	**3**
		No	0	0.7	1	0.1	1.84	**4**
Graphite	Ethylbenzene	Yes	0	0	0	0	0	**5**
		No	0.06	0.3	1	0.1	0.79	**6**
	Cumene	Yes	—	—	—	—	0.09[a]	**7**
		No	0	0.3	1	0	2.20	**8**

[a] Only unidentified products were formed.

As opposed to the common acid-catalyzed rearrangement of hydroperoxides involving migration of the phenyl group, homolytic cleavage of **14**, followed by the loss of the methyl radical, led to acetophenone **10**. Transfer of the methyl radical at the last step of the C–C bond cleavage takes place in the known reactions of oxidation of cumene **11** to acetophenone.[21] This reaction proceeds through cumene hydroperoxide **14**, generated by Mn(III)-catalyzed oxidation of **11** by iodosobenzene. We determined the molar ratio of the hydroperoxide **14** and alcohol **12** by integration of the inverse-gated broad band decoupled ^{13}C NMR spectrum with the relaxation delay of 2 s. The inverse-gated decoupling was employed to prevent influence of the NOE-effect on the integral intensities of the signals. To insure practically complete relaxation, the sp^3 quaternary carbons in **14** and **12** were integrated in the array of experiments with different relaxation delays until the results became consistent, according to the known technique.[22]
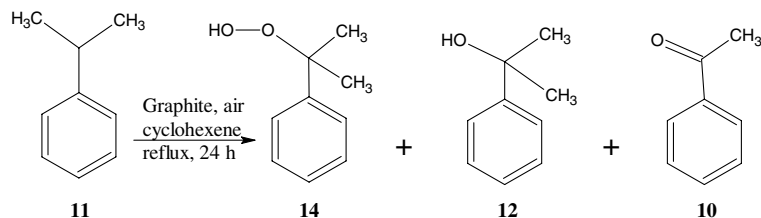
Scheme 4. Oxidation of cumene.

Oxidation of cumene was significantly suppressed when run with light protection (similarly to ethylbenzene) and produced a significant amount (0.7 equiv with respect to acetophenone, Table 3, entries 3 and 4) of 2,3-dimethyl-2,3-diphenylbutane **13**,[23] the product of dimerization of the α,α-dimethylbenzyl radical. This observation indicates that in the presence of light, the concentration of α,α-dimethylbenzyl radicals significantly drops, probably, due to the hydrogen abstraction from the oxidation products **10**, **12**, and **14**. Similarly to ethylbenzene, graphite retards oxidation of cumene in the presence of light, but does not suppress it completely (Table 3, entry 8).

In the presence of cyclohexene, cumene **11** is efficiently oxidized by air regardless of the exposure to light (Table 4, entries 3 and 4). Oxidation of cumene in the presence of cyclohexene in the dark was suppressed by graphite (Table 4, entries 3 and 7), which emphasizes the role of graphite as an interceptor of radicals as opposed to a plain light absorbent.

Similarly to ethylbenzene, the retarding effect of graphite on photooxidation of cumene (Table 3, entries 4 and 8) was lifted in the presence of cyclohexene (Table 4, entries 4 and 8), and the composition of the reaction mixture was significantly shifted toward acetophenone. Therefore, the synchronous action of light, cyclohexene and graphite on the oxidation of cumene again led to a practical procedure for the preparation of acetophenone (Table 4, entry 8).

Neither p-xylene, ethylbenzene, nor cumene undergo oxidation in the inert atmosphere of argon, which rules out the role of oxygen, pre-adsorbed on the surface of graphite. Toluene was unreactive under the reaction conditions, probably, due to its lower boiling point (110–111 °C).

In conclusion, we explored the catalytic activity of unmodified graphite toward oxidation and photooxidation of the benzylic carbon in p-xylene, ethylbenzene and cumene with and without the presence of cyclohexene. In the presence of cyclohexene, graphite catalyzes oxidation (ester **6** is among the major products) and photooxidation (major product is hydroperoxide **2**) of p-xylene. Graphite-catalyzed photooxidation of ethylbenzene and cumene leads to acetophenone **10** as the major product. The presence of both graphite and cyclohexene is necessary for the oxidation and photooxidation of p-xylene and for the significant oxidation of ethylbenzene. Cyclohexene itself catalyzes the oxidation of cumene. The distribution of photooxidation products of ethylbenzene and cumene is significantly affected by cyclohexene and the graphite catalyst.

Supplementary data

Experimental procedures for oxidation, for synthesis of carbon nanofibers, ^{1}H and NMR spectra for all reaction products. ^{1}H and ^{13}C NMR spectra of hydroperoxide **8**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.03.072.

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