Mendeleev Communications

Mendeleev Commun., 2026, **36**, 47–49

2-Fluoroanthraquinone-catalyzed photooxidation of benzylic alcohols and aliphatic diols in supercritical carbon dioxide

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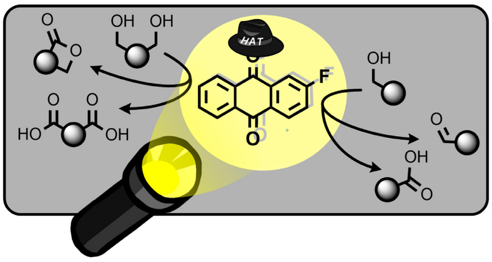
DOI: 10.71267/mencom.7855

Benzylic alcohols are oxidized with molecular oxygen to the corresponding carbonyl compounds and carboxylic acids in supercritical carbon dioxide medium in the presence of 2-fluoroanthraquinone as an organic photocatalyst. The transformation is promoted by blue light irradiation at 405 nm. The similar processing of aliphatic terminal 1,3- and 1,4-diols affords the corresponding diacids, while small changes in the procedure allows one to convert butane-1,4-diol into γ-butyrolactone in one experimental step.

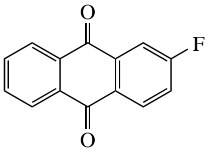


Keywords: oxidation, photocatalysis, supercritical carbon dioxide, benzylic alcohols, diols, ketones, aldehydes, lactones.

Oxidation of organic compounds is widely used to synthesize biologically active substances, polymers, and other valuable chemical products.[1] Typical perchlorates, chromates, permanganates, peroxy acids, hypervalent iodine compounds serving as oxidizers are considered hazardous due to their toxicity and the formation of a significant amount of waste, including unspent reagents, by-products, and solvents that require disposal.

A prospective integrative approach in the design of safe and effective oxidation processes is to perform them in a supercritical carbon dioxide (scCO$_2$) medium with molecular oxygen used as an oxidizer in the presence of photocatalysts.[2–5] Visible light, a renewable and non-polluting energy source, can be effectively utilized as an environmentally benign initiator for a wide range of chemical reactions.[6] At the same time, the targeted search for an organic photocatalyst should provide a higher process efficiency and, importantly, to avoid the use of toxic and expensive metal-containing reagents and catalysts. Meanwhile, the transition from traditional organic solvents to the non-flammable and naturally abundant CO$_2$ in the supercritical state as the reaction medium, which unlimitedly dissolves O$_2$ and is characterized by high heat and mass transfer coefficients,[7] minimizes the risk of fires and explosions and improves the environmental metrics of the oxidation processes.[8]

Recently, we have developed a method for the selective oxidation of aliphatic alcohols to ketones in scCO$_2$ medium using molecular oxygen as the oxidant and 2-fluoroanthraquinone (2-FAQ) as the organic photocatalyst.[9] The application of anthraquinone derivatives in photocatalytic aerobic oxidation reactions is based on their ability to be excited by near-UV and visible light and to abstract a hydrogen atom from the substrate (HAT mechanism), which triggers subsequent oxidative transformations involving molecular oxygen.[10] The mechanism features in the scCO$_2$ medium have been thoroughly studied in our previous work.[9] In the present work, we applied this method toward oxidation of benzylic alcohols and aliphatic diols. Benzylic alcohols are challenging substrates, since their oxidation is usually difficult to stop at the step of formation of carbonyl compounds which are high-demand products.[11,12] Oxidation of diols opens the way to valuable dicarboxylic acids[13] and γ-lactones[14] used to obtain polymers and drugs.



2-fluoroanthraquinone
(2-FAQ)

Based on the previous results[9] and absorption spectra of 2-FAQ (see Online Supplementary Materials, Figures S1.1 and S1.2) we chose visible light (24 W blue LEDs with 405 nm wavelength) to photoactivate 2-FAQ, since it is less hazardous and more available than UV light.[15–17] Molecule 2-FAQ is resistant to visible light and retains photocatalytic activity after a long-term storage (at least for 2 years) in a colorless transparent container.

We herein found (Scheme 1, Table 1) that benzylic alcohols **1a–g** can be readily oxidized in a scCO$_2$ medium under the action of molecular oxygen (4 equiv.) at 45 °C in the presence of photocatalyst 2-FAQ (1 mol%). The required pressure in the reactor was 8.6 MPa which corresponds to the previously[9] determined optimal density of the scCO$_2$ medium of ~0.3 g cm^{-3}. To achieve good conversion, the reaction time was chosen within the 0.5–2.0 h interval depending on the substituents in the aromatic ring. Under the proposed conditions, the reaction resulted in the formation of mixtures of benzaldehyde derivatives **2a–g** and the corresponding benzoic acids **3a–g** (see Scheme 1), and the selectivity of the reaction for the aldehydes changed from good to moderate with the conversion growth. It is noteworthy that among the oxidation products of 4-methylbenzyl alcohol **1f** a minor amount of terephthalic acid was detected as

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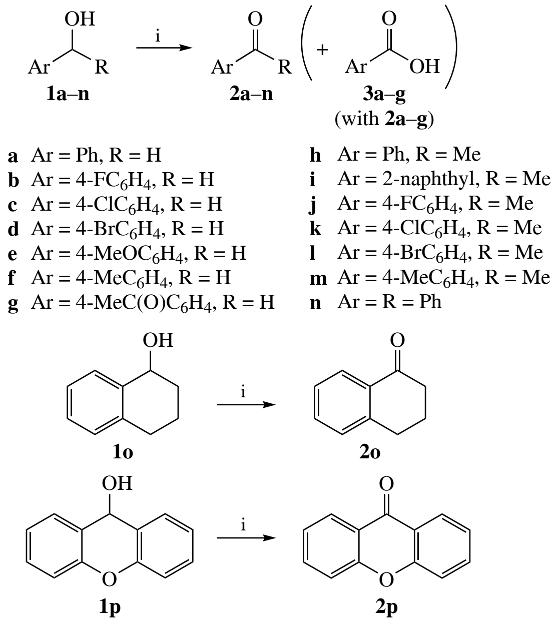


a Ar = Ph, R = H
b Ar = 4-FC_6H_4, R = H
c Ar = 4-ClC_6H_4, R = H
d Ar = 4-BrC_6H_4, R = H
e Ar = 4-$MeOC_6H_4$, R = H
f Ar = 4-MeC_6H_4, R = H
g Ar = 4-$MeC(O)C_6H_4$, R = H
h Ar = Ph, R = Me
i Ar = 2-naphthyl, R = Me
j Ar = 4-FC_6H_4, R = Me
k Ar = 4-ClC_6H_4, R = Me
l Ar = 4-BrC_6H_4, R = Me
m Ar = 4-MeC_6H_4, R = Me
n Ar = R = Ph

Scheme 1 *Reagents and conditions*: i, 2-FAQ (1%); O_2 (4 equiv.), steel autoclave with $scCO_2$ (8.6 MPa), 45 °C, LEDs 405 nm (24 W).

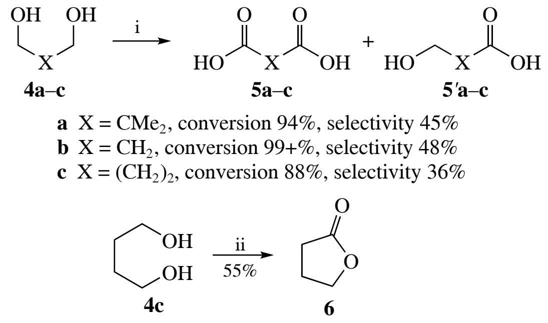
Table 1 Photooxidation of benzylic alcohols **1a**–**p** into the corresponding carbonyl compounds **2a**–**p**.

Entry	Alcohol	*t*/h	Conversion of **1** (%)	Selectivity to **2** (%)
1	**1a**	0.5	40	78
2	**1b**	1.0	58	75
3	**1c**	0.5	55	51
4	**1d**	1.5	60	42
5	**1e**	1.0	24	79
6	**1f**	0.5	67	43
7	**1g**	2.0	72	30
8	**1h**	3.0	99+	95
9	**1i**	6.0	94	72
10	**1j**	2.0	63	99+
11	**1k**	1.0	56	99+
12	**1l**	3.0	96	99+
13	**1m**	2.0	67	40
14	**1n**	2.0	98	95
15	**1o**	1.5	68	60
16	**1p**	1.0	99+	99+

a result of the competitive oxidation of the methyl group. The obtained data do not reveal any clear correlation between the nature of substituents in the aromatic ring and the efficiency of the photooxidation process. It is likely that other factors such as the solubility of the substrate and/or reaction products in the $scCO_2$ medium play a more significant role in the reaction outcome.

In contrast to primary benzylic alcohols **1a–g**, secondary ones **1h–p** underwent oxidation much more selectively yielding the corresponding ketones **2h–p** as the main products. Some decrease in selectivity in the case of alcohol **1i** can be attributed to the tendency of the naphthalene fragment to undergo oxidative destruction of the aromatic system.[18] The lower selectivity in the oxidation of substrates **1m** and **1o** is caused by side oxidative conversion into 4-acetylbenzoic acid and 1,4-naphthalenediol, respectively, similarly to the results of **1f** oxidation.

Noteworthy, 4-nitrobenzyl alcohol and fluoren-9-ol did not undergo the oxidation under the proposed conditions, presumably due to their poor solubility in $scCO_2$. Importantly, none of the used substrates **1a–p** underwent significant oxidation in the absence of the catalyst. When performed in conventional solvents, *i.e.*, *n*-hexane or acetonitrile, the photocatalytic processing of **1a** for 0.5 h gave only 7 and 9% substrate conversion, respectively, thereby demonstrating the superior performance of $scCO_2$ as the reaction medium.



a X = CMe_2, conversion 94%, selectivity 45%
b X = CH_2, conversion 99+%, selectivity 48%
c X = $(CH_2)_2$, conversion 88%, selectivity 36%

Scheme 2 *Reagents and conditions*: i, 2-FAQ (1%); O_2 (4 equiv.), steel autoclave with $scCO_2$ (8.6 MPa), 45 °C, LEDs 405 nm (24 W), 4 h for **4a**,**b** or 8 h for **4c**; ii, similarly but O_2 (16 equiv.) and CO_2 total pressure to 9.8 MPa, 4 h.

The method was found applicable for the oxidation of aliphatic 1,3- and 1,4-diols **4** (Scheme 2). These reactions proceed more slowly than the oxidation of benzylic alcohols **1** and cannot be halted at the aldehyde formation step. Over 4–8 h, the reactions furnished the corresponding dicarboxylic acids **5a–c** in moderate yields. Hydroxy acids **5′** were detected among the side products. While optimizing the reaction conditions, we discovered that larger excess of oxygen (see Scheme 2, conditions ii) allowed for the one-pot conversion of 1,4-butanediol **4c** into γ-butyrolactone **6** with a 55% yield. The obtained result has a high application potential, since compound **6** and its derivatives are widely used in food, cosmetic, agrochemical, and perfume industries, as well as in pharmaceuticals as antihypertensive, antibiotic, antifungal, antiparasitic, and anticancer drugs.[14]

To summarize, the oxidation of benzylic alcohols and aliphatic diols with molecular oxygen in $scCO_2$ medium has been carried out in the presence of 2-fluoroanthraquinone as the organic photocatalyst upon activation with visible light. The data obtained can be useful for the design of oxidation processes that meet strict environmental and industrial safety criteria.

This work was supported by The Russian Science Foundation (project no. 23-73-00071).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7855.

References

1 *The Organic Chemistry of Medicinal Agents*, ed. A. Renslo, McGraw-Hill, New York, 2016; https://accesspharmacy.mhmedical.com/content.aspx?bookid=1731.

2 E. A. Ivanova, M. N. Zharkov, V. G. Merkulov, V. I. Gladilina, I. V. Kuchurov, P. S. Artemova, E. O. Pentsak and S. G. Zlotin, *Russ. J. Phys. Chem. B*, 2024, **18**, 1830; https://doi.org/10.1134/S1990793124701719.

3 H. Q. Martínez, E. Pájaro, E. A. Páez-Mozo, H. A. Lambis-Miranda and F. O. Martínez, *Catal. Today*, 2025, **455**, 115305; https://doi.org/10.1016/j.cattod.2025.115305.

4 L. Wu, B. L. Abreu, A. J. Blake, L. J. Taylor, W. Lewis, S. P. Argent, M. Poliakoff, H. Boufroura and M. W. George, *Org. Process Res. Dev.*, 2021, **25**, 1873; https://doi.org/10.1021/acs.oprd.1c00111.

5 I. V. Kuchurov, M. N. Zharkov and S. G. Zlotin, *Russ. Chem. Bull.*, 2025, **74**, 1914; https://doi.org/10.1007/s11172-025-4678-3.

6 T. P. Yoon, M. A. Ischay and J. Du, *Nat. Chem*, 2010, **2**, 527; https://doi.org/10.1038/nchem.687.

7 E. S. Alekseev, A. Yu. Alentiev, A. S. Belova, V. I. Bogdan, T. V. Bogdan, A. V. Bystrova, E. R. Gafarova, E. N. Golubeva, E. A. Grebenik, O. I. Gromov, V. A. Davankov, S. G. Zlotin, M. G. Kiselev, A. E. Koklin, Y. N. Kononevich, A. E. Lazhko, V. V. Lunin, S. E. Lyubimov, O. N. Martyanov, I. I. Mishanin, A. M. Muzafarov, N. S. Nesterov, A. Yu. Nikolaev, R. D. Oparin, O. O. Parenago, O. P. Parenago, Y. A. Pokusaeva, I. A. Ronova, A. B. Solovieva, M. N. Temnikov, P. S. Timashev, O. V. Turova, E. V. Filatova, A. A. Philippov, A. M. Chibiryaev and A. S. Shalygin, *Russ. Chem. Rev.*, 2020, **89**, 1337; https://doi.org/10.1070/RCR4932.

8 S. G. Zlotin, K. S. Egorova, V. P. Ananikov, A. A. Akulov, M. V. Varaksin, O. N. Chupakhin, V. N. Charushin, K. P. Bryliakov, A. D. Averin, I. P. Beletskaya, E. L. Dolengovski, Yu. H. Budnikova, O. G. Sinyashin, Z. N. Gafurov, A. O. Kantyukov, D. G. Yakhvarov, A. V. Aksenov, M. N. Elinson, V. G. Nenajdenko, A. M. Chibiryaev, N. S. Nesterov, E. A. Kozlova, O. N. Martyanov, I. A. Balova, V. N. Sorokoumov, D. A. Guk, E. K. Beloglazkina, D. A. Lemenovskii, I. Yu. Chukicheva, L. L. Frolova, E. S. Izmest'ev, I. A. Dvornikova, A. V. Popov, A. V. Kutchin, D. M. Borisova, A. A. Kalinina, A. M. Muzafarov, I. V. Kuchurov, A. L. Maximov and A. V. Zolotukhina, *Russ. Chem. Rev.*, 2023, **92**, RCR5104; https://doi.org/10.59761/RCR5104.

9 V. G. Merkulov, M. N. Zharkov, O. V. Turova, R. E. Ivanov, I. V. Kuchurov and S. G. Zlotin, *ChemPhotoChem*, 2024, **8**, e202300233; https://doi.org/10.1002/cptc.202300233.

10 J. Cervantes-González, D. A. Vosburg, S. E. Mora-Rodriguez, M. A. Vázquez, L. G. Zepeda, C. Villegas Gómez and S. Lagunas-Rivera, *ChemCatChem*, 2020, **12**, 3811; https://doi.org/10.1002/cctc.202000376.

11 J. Soares, V. M. Costa, M. D. L. Bastos, F. Carvalho and J. P. Capela, *Arch. Toxicol.*, 2021, **95**, 2895; https://doi.org/10.1007/s00204-021-03083-3.

12 L. Xiong and J. Tang, *Adv. Energy Mater.*, 2021, **11**, 2003216; https://doi.org/10.1002/aenm.202003216.

13 H. Liu and H. Tan, *J. Ind. Eng. Chem.*, 2025, **149**, 16; https://doi.org/10.1016/j.jiec.2025.01.048.

14 S. K. Sartori, M. A. N. Diaz and G. Diaz-Muñoz, *Tetrahedron*, 2021, **84**, 132001; https://doi.org/10.1016/j.tet.2021.132001.

15 G. E. M. Crisenza and P. Melchiorre, *Nat. Commun.*, 2020, **11**, 803; https://doi.org/10.1038/s41467-019-13887-8.

16 L. Candish, K. D. Collins, G. C. Cook, J. J. Douglas, A. Gómez-Suárez, A. Jolit and S. Keess, *Chem. Rev.*, 2022, **122**, 2907; https://doi.org/10.1021/acs.chemrev.1c00416.

17 R. Cannalire, S. Pelliccia, L. Sancineto, E. Novellino, G. C. Tron and M. Giustiniano, *Chem. Soc. Rev.*, 2021, **50**, 766; https://doi.org/10.1039/D0CS00493F.

18 F. Soana, M. Sturini, L. Cermenati and A. Albini, *J. Chem. Soc., Perkin Trans. 2*, 2000, 699; https://doi.org/10.1039/a908945d.

Received: 20th June 2025; Com. 25/7855