

Photoacid Catalyzed Reaction of Phenol with Styrene

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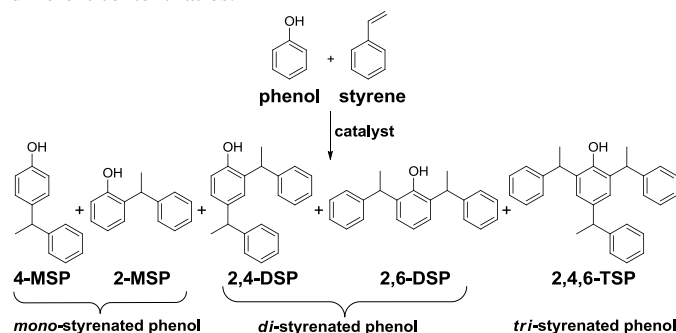
ABSTRACT: The reaction of styrene with phenol using photoacid catalyst has been investigated. Upon irradiation with 450 nm light, protonated merocyanine photoacid converts into spiropyran form with releasing proton. The reaction of styrene with phenol has been conducted under irradiation with 450 nm light using merocyanine photoacid catalyst at room temperature in comparison with the results using some selected catalysts including H₂SO₄ or FeCl₃ at the reaction temperature of 120°C.

Sterically hindered phenols are effective inhibitors of free-radical processes and light stabilizers.¹ They are widely used as antioxidants for the stabilization of polymers, rubbers, foods, fuels, and oils. The free-radical stabilizing ability mainly depends on the steric hindrance by the size of *ortho* substituents to the hydroxyl group in the hindered phenols. The presence of *ortho* bulky substituents in the hindered phenols enhances the stability of the phenoxyl radicals formed by O-H bond cleavage. These hindered phenols are often referred to as radical scavengers, since they react rapidly with peroxy radicals thereby breaking the degradation cycle.² Styrenated phenols are typical of sterically hindered phenols. Styrenated phenol derivatives or related hydroarylation products from the reaction of styrene derivatives with phenols or arenes are very important as antioxidants as well as in the chemical industry including fine chemicals, bulk chemicals, pharmaceuticals, and agrochemicals.³ Styrenated phenols are prepared by acid catalyzed reaction of phenol and styrene using Lewis acid catalysts such as FeCl₃, inorganic protic acids such as H₂SO₄, or organic protic acid catalysts such as *p*-toluenesulfonic acid.^{4,5} Most of these reactions have some drawbacks such as the need for severe reaction conditions (high temperature, strong acidic conditions), low selectivity, moisture sensitivity, high cost, and large amounts of waste materials.⁶ Therefore, great efforts have been devoted to search for the more mild reaction conditions such as low temperature, short reaction time, small amounts of catalyst, *etc.* Photoacids refer to the molecules, which undergo reversible photochemical dissociation of proton on light irradiation and thermal reassociation of proton.⁷

Proton transfer is very popular in numerous chemical reactions and biological processes.^{8,9} Photoacids releasing proton upon light irradiation make possible to control proton-required processes and could provide a way to convert photoenergy into chemical energy.⁷ Photoacids have been used to study molecular proton transfer, and have been exploited to control molecular and supramolecular events since the 1970s.¹⁰⁻¹² However, acid-catalyzed reactions using photoacids have been rarely explored because proton concentration released by photoacids has not been high enough to provoke many acid-catalyzed reactions.¹³ Another limitation is the short lifetime of the proton dissociation state. Although photoacids have relatively strong acidity in the excited state, the liberated proton does not have enough time to diffuse away from ground state conjugate base of photoacid towards the reactant mixture and thus cannot catalyze a chemical reaction. A recent work reported a photoacid with a relaxation time of the proton-dissociation state close to 1 s.¹³ In order to increase the lifetime of the proton dissociation state and stabilize the proton dissociation state, photoacids accomplishing the intramolecular photoreactions such as photochromic reactions have been explored.¹⁴⁻¹⁸ A few acid-catalyzed reaction such as esterification and cationic polymerization reaction catalyzed with protonated merocyanine photoacid has been reported as applications.^{7,19}

Herein we have reported the reaction of styrene with phenol using photoacid catalyst in comparison with the reaction employing common protic acid or Lewis acid.

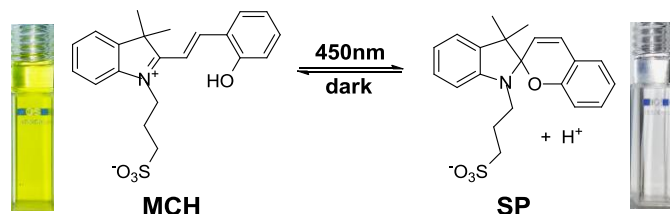
Reaction of phenol with styrene in the presence of catalyst yields the mixture of *mono*-, *di*-, and *tri*-styrenated phenol as shown in Scheme 1. Styrenated phenols are commercially provided as mixtures with different content ratios.



Scheme 1. Styrenated phenols from the reaction of phenol with styrene

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A protonated merocyanine MCH with a propyl sulfonate substituents on the indoline nitrogen was employed as photoacid. MCH was prepared following the literature method.⁷ MCH undergoes reversible photochromic reaction between yellow MCH form and colorless SP (spiropyran) form (Scheme 2).



Scheme 2. Photochromic reaction of MCH

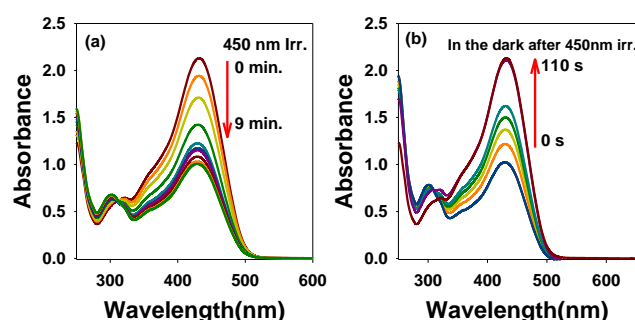


Figure 1. Absorption spectral changes of photoacid MCH in acetonitrile/water (7/3) (a) after irradiation with 450 nm light and (b) in the dark after irradiation with 450 nm light for 9 min.

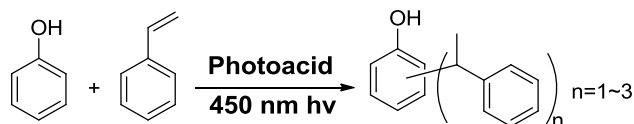
Photochromic reaction was monitored by UV-Vis absorption spectroscopy. As MCH converts to SP under 450 nm irradiation, absorption of MCH at 430 nm decreases. As keeping in the dark, absorption at 430 nm increases and the original spectrum of MCH is recovered (Figure 1).

For the comparison of photoacid with common protonic acid or Lewis acid for the acid-catalyzed reaction of phenol with styrene, photoacid MCH, protonic acid catalyst H_2SO_4 , or Lewis acid FeCl_3 was employed as an acid catalyst.

When H_2SO_4 or FeCl_3 was used, reactions of styrene with phenol was conducted in the following reaction condition; reaction temperature is 120°C , reaction time is 6 hrs, no solvent is added to the reaction mixture, reactant mole ratio is styrene/phenol=2/1, and catalyst amount is 0.1 mol per 1 mol phenol.

The reaction using photoacid MCH was run on the irradiation with 450 nm light using the same reaction conditions as above, except the use of solvent (acetonitrile/water=7/3) and the reactions at room temperature. The results are summarized in Table 1. Conversion of phenol was obtained from GC analysis.

Table 1. Conversion of phenol in the reaction of styrene with phenol using photoacid MCH, compared with using H_2SO_4 or FeCl_3 .



Acid	Reaction Time, hr	Temperature, $^\circ\text{C}$	Conversion, %
MCH	1	r.t. (450 nm hv)	15
H_2SO_4	6	120	97
H_2SO_4	1	r.t.	no reaction
FeCl_3	6	120	96
FeCl_3	1	r.t.	no reaction

As shown in Table 1, whereas the reaction of styrene with phenol is almost completed using H_2SO_4 or FeCl_3 catalyst, the conversion of starting compound phenol is very low using photoacid catalyst MCH. For comparison with photoacid catalyst, the reactions of styrene with phenol were conducted using H_2SO_4 or FeCl_3 catalyst for 1 hr at room temperature and no reactions were observed. Although styrenated phenols are produced in small amount with photoacid catalyst, the results might be meaningful in aspect that photoacid could be applicable in acid-catalyzed reaction. The proton concentration could be simply controlled by switching on-off of light. In summary, for the reaction of styrene and phenol, three catalysts of photoacid MCH, H_2SO_4 , and FeCl_3 were employed. Photoacid-catalyzed reaction of phenol with styrene is very inefficient in this study. In this stage, only the possibility of the photoacid-catalyzed reaction was examined. The exploration for searching better reaction condition is under investigation. Light-controllable acid-catalyzed reaction might be possible by using both the photoacid and light.

Received December 30, 2015; Revised February 17, 2016;
Accepted March 18, 2016

KEYWORDS: Photoacid, Catalyst, Styrenated phenols

ACKNOWLEDGEMENT

This work was supported by the Human Resource Training Program for Regional Innovation and Creativity through the Ministry of Education and National Research Foundation of Korea (NRF-2014H1C1A1066844).

REFERENCES AND NOTES

- Pritchard, G. *Plastic Additives, An A-Z reference*, Springer, England, 1998.
- Manedova, P. Sh.; Farzaliev, V. M.; Velieva, F. M.; Babaev, E. R. *Petroleum Chemistry*, **2007**, *47*, 55-60.
- Weissermel, K.; Arpe, H. J. *Industrielle Organische Chemie*, 5th ed., Wiley-VCH, Weinheim, Germany, 1988, p. 167.
- Bandini, M.; Emer, E.; Tommasi, S.; Umani-Ronchi, A. *Eur. J. Org. Chem.*, **2006**, 3527–3544.
- Kischel, J.; Jovel, I.; Mertins, K.; Zapf, A.; Beller, M. A. *Org. Lett.*, **2006**, *8*(1), 19-22.
- Mohan, D. C.; Patil, R. D.; Adimurthy, S. *Eur. J. Org. Chem.*, **2012**, 3520–3525.
- Shi, Z.; Peng, P.; Strohecker, D.; Liao, Y. *J. Am. Chem. Soc.* **2011**, *133*, 14699–14703.
- Ramsey, S.; Mokrab, Y.; Carvacho, I.; Sands, Z. A.; Sansom, M. S. P.; Clapham, D. E. *Nat. Struct. Mol. Biol.* **2010**, *17*, 869–875.
- Li, J.; Liu, Z.; Tan, C.; Guo, X.; Wang, L.; Sancar, A.; Zhong, D. *Nature* **2010**, *466*, 887–890.
- Tolbert, L.; Solntsev, K. M. *Acc. Chem. Res.* **2002**, *35*, 19–27.
- Dempsey, J. L.; Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **2010**, *132*, 16774–16776.

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12. Morimoto, M.; Irie, M. *Chem. Commun.* **2011**, 47, 4186–4188.
 13. Nunes, R. M. D.; Pineiro, M.; Arnaut, L. G. *J. Am. Chem. Soc.* **2009**, 131, 9456–9462.
 14. Duerr, H.; Bouas-Laurent, H. *Photochromism : Molecules and Systems*, Revised Edition, Elsevier, Amsterdam, The Netherlands, 2003.
 15. Gil, M.; Ziolk, M.; Organero, J. A.; Douhal, A. *J. Phys. Chem. C* **2010**, 114, 9554–9562.
 16. Silvi, S.; Arduini, A.; Pochini, A.; Secchi, A.; Tomasulo, M.; Raymo, F. M.; Baroncini, M.; Credi, A. *J. Am. Chem. Soc.* **2007**, 129, 13378–13379.
 17. Raymo, F. M.; Alvarado, R. J.; Giordani, S.; Cejas, M. A. *J. Am. Chem. Soc.* **2003**, 125, 2361–2364.
 18. Emond, M.; Sun, J.; Gregoire, J.; Maurin, S.; Tribet, C.; Jullien, L. *Phys. Chem. Chem. Phys.* **2011**, 13, 6493–6499.
 19. Nakashima, T.; Tsuchie, K.; Kanazawa, R.; Li, R.; Iijima, S.; Galangau, O.; Nakagawa, H.; Mutoh, K.; Kobayashi, Y.; Abe, J.; Kawai, T. *J. Am. Chem. Soc.* **2015**, 137, 7023–7026.