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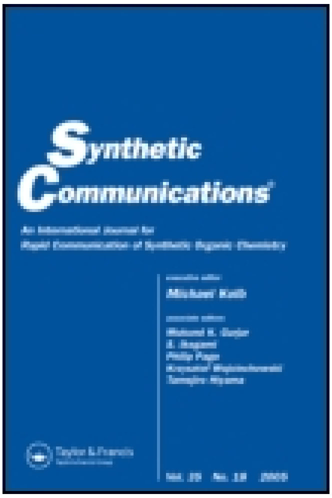

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Epoxidation of 1,4-Diaroyl Ethene Derivatives in the Presence of UHP or H_2O_2

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EPOXIDATION OF 1,4-DIAROYL ETHENE DERIVATIVES IN THE PRESENCE OF UHP OR H_2O_2

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Hydrogen peroxide (H_2O_2) or urea–hydrogen peroxide (UHP) in basic media react with carbon–carbon double bonds of 1,4-diaroyl ethenes to produce the corresponding epoxides.

***Keywords*:** 1,4-Diaroyl ethenes; epoxidation; hydrogen peroxide; UHP

Epoxides are well known as valuable building blocks that can be used as intermediates and precursors for chemical production. Therefore, the epoxidation reaction is an important transformation of carbon–carbon double bonds. Many epoxidation reactions have been done on the carbon–carbon double bonds using sodium hypochlorite,[1] sodium peroxide,[2] m-chloroperbenzoic acid,[3] oxone,[4] dimethyloxirane,[5] hydrogen peroxide,[6] and urea–hydrogen peroxide (UHP).[7] Bentley et al. reported epoxidation of chalcones with UHP in an organic solvent in the presence of 1,8-diazabicycloundec-7-ene (DBU) and poly-(L)-leucine in 1997.[8] Recently, Jin et al. reported epoxidation of chalcones with UHP under ultrasound irradiation.[7] Some epoxidations have been done on α,β-unsaturated compounds including hydrogen peroxide,[9] poly-L-leucine/H_2O_2 (Julia–Colonna epoxidation)[8] for ennantiomeric epoxidation, NaOCl,[10] and H_2O_2/[c_nMIm][PF_6].[11]

RESULTS AND DISCUSSION

To contribute to these epoxide syntheses, we decided to transform some 1,4-diaroyl ethenes (**1**) to their epoxides (**2**) utillizing two available reagents and considering their reactions time and yields. So far, no published methodology in the literature for epoxidation of 1,4-diaroyls had been reported. For this epoxidation, our adopted two reagents were (1) H_2O_2/Na_2CO_3 and (2) urea–hydrogen peroxide (UHP)/NaOH (Scheme 1). Hydrogen peroxide has an active oxygen content about as high as molecular oxygen, and the waste product by employing this oxidant is plain water. UHP is a white crystalline solid formed from urea and hydrogen

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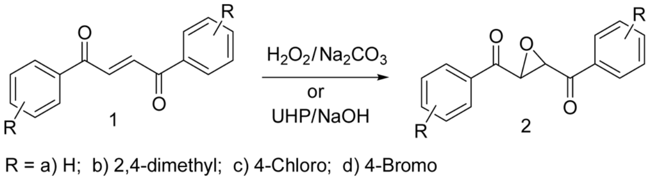


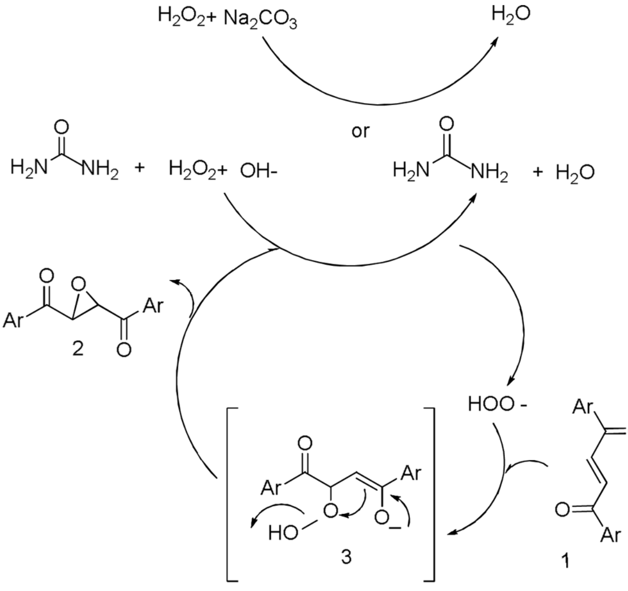
Scheme 1. Two adopted reagents for epoxidation of 1,4-diaroyl ethenes.

peroxide.[7] This solid has a high hydrogen peroxide content and releases it in a controlled manner, with green by-products. In comparison with many epoxidation reactions that used MeOH,[12] toluene,[10] and CH_2Cl_2[10] as solvents, in our procedure EtOH worked excellently.

The produced epoxides are symmetric and have two identical carbonyl groups; these functional groups have potential for subsequent reactions and produce various compounds. For example, like in some reactions that have been done on epoxy ketones, they can be hydrolised,[13] converted to corresponding esters by Baeyer–Villiger oxidation,[14] and undergo epoxy ring opening by nucleophilic addition.[15]

The 1,4-diaroyl compounds were prepared according to the literature[16] and then underwent epoxidation. The mechanism for epoxidation by either H_2O_2 or UHP is depicted in Scheme 2.

In either method, first OOH^- is formed in situ and then added to the unreactive enone unit (**1**) to generate intermediate hydroperoxide enolate (**3**). This reactive enolate, by excluding the OH^-, led to the formation of the epoxide (**2**) (Scheme 2).



Scheme 2. The mechanism for epoxidation of 1,4-diaroyl ethenes using either H_2O_2 or UHP.

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Table 1. Epoxidation of 1,4-diaroyl ethenes

Substrate	Product	Reagent	Time (h)	Yield (%)
1a	**2a**	H_2O_2/Na_2CO_3	8	60
		UHP/NaOH	6	76
1b	**2b**	H_2O_2/Na_2CO_3	10	90
		UHP/NaOH	14	75
1c	**2c**	H_2O_2/Na_2CO_3	10	55
		UHP/NaOH	15	60
1d	**2d**	H_2O_2/Na_2CO_3	14	70
		UHP/NaOH	20	55

A few minutes after adding of reagents to the compound **1a**, the color of the solution changed from deep yellow to white. This demonstrated that the intermediate (**3**) instantaneously was formed. Monitoring a reaction with thin-layer chromatography (TLC) indicated that a trace of **1a** still was present. However, for **2a** after 6 h, TLC did not show any **1a**. Table 1 shows that compound **1a** has the shortest and **1d** has the longest reaction time.

As expected, both our adapted reagents attacked the double bond of **1a–d** from both side of **1** equally, so for the epoxids **2a–d**, a mixture of symmetrical racemic compounds was obtained.

CONCLUSION

In conclusion, for the first time some new epoxides were synthesized from premade 1,4-diaroyl ethenes (**1**) through a safe and green procedure utillizing available and cheap reagents. These epoxidation reagents are environmentally friendly and useful for the industrial proposes.

EXPERIMENTAL

Melting points were measured on a Mettler Fp5 apparatus and are uncorrected. The infrared (IR) spectra were recorded on a Shimadzu IR-470 spectrophotometer. The ^1H NMR spectra were recorded on a Bruker 500-MHz instrument using solvent as internal standard ($CDCl_3$ at 7.31 ppm).

General Procedure for the Formation of Epoxides 2a–d Utilizing H_2O_2/Na_2CO_3

To a solution of sodium carbonate (0.25 g) in water (1 ml), hydrogen peroxide (30%, 0.25 ml) was added. This mixture was added to corresponding but-2-ene-1,4-diones **1a–d** (1 mmol) in ethanol (3 ml). The mixture was vigorously stirred at room temperature; after completion of the reaction (monitored by thin-layer chromatography, TLC, petroleum ether/ethyl acetate 3:1), the precipitate solid was filtered and washed with water. Then solid was recrystallized from ethanol to yield the desired compound.

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General Procedure for the Formation of Epoxides 2a–d Utilizing UHP

An aqueous solution of NaOH (4%, 0.2 ml) and UHP (0.15 g) was added to a solution of corresponding but-2-ene-1,4-diones **1a–d** (1 mmol) in ethanol (5 ml). The mixture was vigorously stirred at room temperature. After completion of the reaction (monitored by TLC, petroleum ether/ethyl acetate 3:1), the precipitate solid was filtered and washed with water. The solid was recrystallized from ethanol to yield the desired compound.

The produced epoxides utilizing UHP have the same melting points, IR, and ^{1}H NMR spectra as the epoxides produced by H_2O_2/Na_2CO_3.

Selected Data

2,3-Epoxy-1,4-diphenyl-1,4-butanone 2a. Yield 60%, mp 130–131 °C, white solid. IR (KBr, ν/cm^{-1}): 3080, 1670, 1600, 1240, 940, 880. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.54 (s, 1H), 7.58 (t, 2H, $J = 8$ Hz), 7.71 (t, 1H, $J = 7.4$ Hz), 8.11 (d, 2H, $J = 7.2$ Hz). Anal. calcd. for $C_{16}H_{12}O_3$; C, 76.18; H, 4.79; found: C, 76.20; H, 4.80.

2,3-Epoxy-1,4-(2,4-dimethyl)diphenyl-1,4-butanone 2b. Yield 85%, mp 80–81 °C, white solid. IR (KBr, ν/cm^{-1}): 3050, 2980, 1670, 1560, 1440, 1280, 1220, 890. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.43 (s, 6H), 2.56 (s, 6H), 4.31 (s, 2H), 7.17 (d, 2H, $J = 7.4$ Hz), 7.78 (d, 2H, $J = 8.1$ Hz). Anal. calcd. for $C_{20}H_{20}O_3$; C, 77.90; H, 6.54; found: C, 77.93; H, 6.56.

2,3-Epoxy-1,4-(4-chloro)diphenyl-1,4-butanone 2c. Yield 55%, mp 175–176 °C, white solid. IR (KBr, ν/cm^{-1}): 3050, 1670, 1590, 1400, 1090, 890.^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.47 (s, 1H), 7.56 (d, 2H, $J = 8.5$ Hz), 8.06 (d, 2H, $J = 8.5$ Hz). Anal. calcd. for $C_{16}H_{10}Cl_2O_3$: C, 59.84; H, 3.14; Cl, 22.08; found: C, 59.86; H, 3.17; Cl, 22.11.

2,3-Epoxy-1,4-(4-bromo)-diphenyl-1,4-butanone 2d. Yield 65%, mp 187–188 °C, white solid. IR (KBr, ν/cm^{-1}): 3100, 3050, 1670, 1585, 1400, 890. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.46 (s, 1H), 7.73 (d, 2H, $J = 8.5$ Hz), 7.98 (d, 2H, $J = 8.5$ Hz). Anal. calcd. for $C_{16}H_{10}Br_2O_3$: C, 46.86; H, 2.46; Br, 38.97; found: C, 46.89; H, 2.47; Br, 38.99.

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