Asian Journal of Chemistry Vol. 22, No. 6 (2010), 4464-4468

Ring Opening by Hydrogen Peroxide in Alkaline Solution

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3,4-Diphenyl-4-hydroxy-2-cyclopentene-1-one (**1**) and 3,4-diphenyl-2-cyclopentene-1-one (**2**) give epoxides, but ketols (**3**-**22**) produce benzoic acid and its derivatives with hydrogen peroxide in alkaline solution.

Key Words: Epoxides, Benzoic acid, Hydrogen peroxide.

INTRODUCTION

Epoxides are highly useful intermediates for manufacturing of a range of important commercial products[1]. Their selective synthesis is a subject of considerable academic and industrial interest. Olefin epoxidation is one of the main routes, which leads to the production of epoxides on both a laboratory and industrial scale[2].

The use of hydrogen peroxide and peracids for direct oxidation of alkenes is the main method for industrial applications. Ethylene is commercially epoxidized by vapour-phase oxidation with oxygen or air using a supported silver catalyst[3]. However, this catalytic method is not efficient for alkenes with allylic C-H bonds due to oxidation at this position. Propylene oxide is produced by the metal catalyzed liquid phase oxidation of propylene using organic hydroperoxides produced by hydrocarbon autoxidation[4]. Homogeneous[5] Mo and heterogeneous[6] Ti are used efficiently as catalysts and *tert*-butyl hydroperoxide or ethyl benzene hydroperoxide as the oxidants, even though, the method has been widely used for the production of epoxides, it suffers from the formation of the alcohol co-product (*tert*-butanol or 1-phenylethanol).

Epoxidation of substituted alkenes widely used in the fine chemicals industry can be successfully achieved by using stoichiometric amounts of peracids such as peracetic acid and *m*-chloroperbenzoic acid[7]. However, the employment of peracids is not a clean method as equivalent amounts of acid waste are produced. There is a strong need for the development of new epoxidation methods which produce little waste. The employment of hydrogen peroxide is an attractive option both on environmental and economic grounds. It is cheap, readily available and gives water as the only by-product.

In this paper we are reporting the preparation of epoxides (**1**), (**2**) and benzoic acid and its derivatives (Table-1) by treating corresponding ketols with hydrogen peroxide.

TABLE-1
PREPARATION OF EPOXIDE, BENZOIC ACID AND ITS DERIVATIVES

Entry	G	R_1	R_2	R_3	R_4	Condition	Time (h)	Yield (%)	Product
1	H	OH	H	H	H	RT	2:20	48	Epoxide
2	H	H	H	H	H	RT	2:20	60	Epoxide
3	H	OH	CH_3	H	H	RT	4:30	60	Benzoic acid
4	H	OH	CH_3	CH_3	H	RT	5:00	55	Benzoic acid
5	Br	OH	CH_3	CH_3	H	RT	6:00	60	*p*-bromo benzoic acid
6	Cl	OH	CH_3	CH_3	H	RT	6:10	65	*p*-chloro benzoic acid
7	CH_3	OH	CH_3	CH_3	H	RT	7:00	75	*p*-methyl benzoic acid
8	OCH_3	OH	CH_3	CH_3	H	RT	7:30	65	*p*-methoxy benzoic acid
9	H	OH	H	H	CH_3	Reflux	6:00	60	Benzoic acid
10	H	OH	H	CH_3	CH_3	Reflux	8:00	65	Benzoic acid
11	H	OH	H	H	Ph	Reflux	6:00	56	Benzoic acid
12	Br	OH	H	H	CH_3	Reflux	8:00	65	*p*-bromo benzoic acid
13	Br	OH	H	CH_3	CH_3	Reflux	8:00	60	*p*-bromo benzoic acid
14	Cl	OH	H	H	CH_3	Reflux	8:00	64	*p*-chloro benzoic acid
15	CH_3	OH	H	H	CH_3	Reflux	6:30	73	*p*-methyl benzoic acid
16	OCH_3	OH	H	H	CH_3	Reflux	5:00	60	*p*-methoxy benzoic acid
17	H	H	H	H	CH_3	Reflux	6:20	–	Mixture of product
18	H	H	H	CH_3	CH_3	Reflux	6:30	–	Mixture of product
19	Br	OH	H	H	H	Reflux	7:20	68	*p*- bromo benzoic acid
20	Cl	OH	H	H	H	Reflux	6:00	55	*p*-chloro benzoic acid
21	CH_3	OH	H	H	H	Reflux	6:00	70	*p*-methyl benzoic acid
22	OCH_3	OH	H	H	H	Reflux	8:40	68	*p*-methoxy benzoic acid
23	H	OH	H	H	H	Reflux	1:00	49	Benzoic acid

EXPERIMENTAL

Diethyl ether, benzil, propanone, phenyl propanone, 2-butanone, 3-pentanone, 3-methyl-2-butanone were purchased from Fluka (Switzerland) and are used without further purification, other organic compounds used in this work were prepared in the laboratory[8,9]. Melting points were measured on an electrothermal 9100 apparatus.

Elemental analyses for the C and H were performed using a heraeus CHN-O-rapid analyzer. ^{1}H NMR spectra were taken on a bruker AM-300 and chemical shifts are in ppm. IR spectra were recorded on a Perkin-Elmer 843 (ν in cm^{-1}).

Procedure A: To a stirred solution of compound (5 m mol) in methanol (75 mL) was added hydrogen peroxide (12 mL, 30 %) and aqueous sodium hydroxide (5 mL, 10 %), the reaction was followed by TLC over silica gel (4:1 cyclohexane/ethyl acetate as an eluent) and after its completion methanol was evaporated under reduced pressure. Water was added and extracted with ether. The organic phase was dried over Na_2SO_4 and evaporated under reduced pressure to give the product.

Compound (1): m.p. 115-117 °C (lit.[10] 115-116 °C). IR (KBr, ν_{max}, cm^{-1}): 3550, 1730; ^{1}H NMR ($CDCl_3$): δ 3(2H, s), 3.9 (1H, s), 3.15 (1H, s), 6.9 (10H, m).

Compound (2): m.p. 82-84 °C. IR (KBr, ν_{max}, cm^{-1}): 1750; ^1H NMR (CCl_4): δ 2.2 (1H, d), 3.1 (1H, dd), 4 (1H, d), 3.8 (1H, s), 6.8-7.6 (10H, m). (Found: C, 81.52; H, 5.63. Calcd. For $C_{17}H_{14}O_2$: C, 81.32; H, 5.66 %).

Procedure B: The reactions are performed as described in procedure A, after addition of water, the solution was washed with ether. The aqueous phase was acidified with sulfuric acid (10 %). Benzoic acid was precipitated out as pure compound and was identified by its physical data (IR, ^1H NMR and melting point).

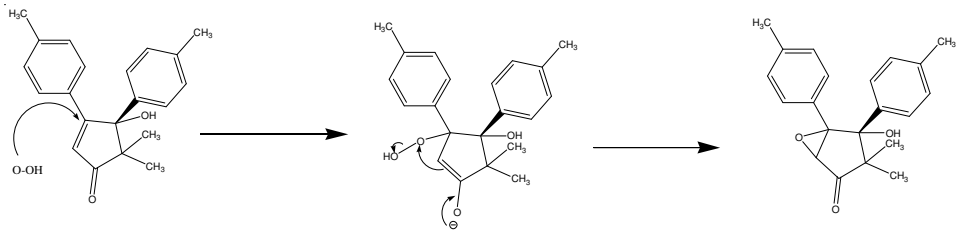
Procedure C: The reactions are performed as described in procedure B but the reaction mixture refluxed.

RESULTS AND DISCUSSION

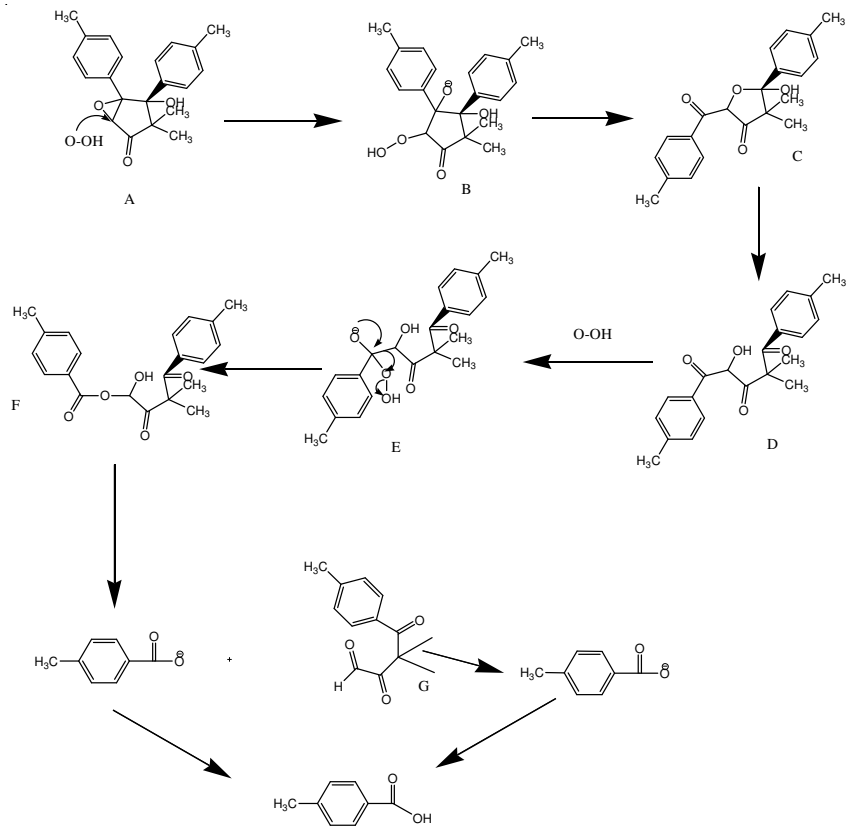
In conclusion, Padwa and co-workers have prepared epoxide of ketol (**1**) by treating 3,4-diphenyl-4-hydroxy-2-cyclopentene-1-one with hydrogen peroxide in alkaline solution. This epoxide was prepared by a modified method in shorter period of time (Table-1, procedure A). By treating ketone (**2**) with hydrogen peroxide at room temperature, epoxide of ketone **2** was obtained, but when ketols such as (**3**-**8**) were used in the same condition, benzoic acid and its derivatives resulted instead (procedure B). It is believed that the methyl groups, due to their steric hindrance effect, make epoxides unstable and decompose them to benzoic acid. To obtain the epoxides of these ketols, the reaction carried out at low temperature in an ice-bath, hydrogen peroxide did not have any effect on ketols. At an elevated temperature of 70 °C, ketols (**9**-**16**) converted to benzoic acid and its derivatives (procedure C). It should be mentioned that these ketols remained unchanged, at room temperature, due to the steric hindrance caused by the methyl and phenyl groups on the ethylenic carbon, which is in accordance with fioroni report in epoxidation of α,β- unsaturated ketones in water[10]. Hydrogen peroxide did not have any effect on ketones (**17**) and (**18**) at room temperature. But they produced a mixture by reacting with hydrogen peroxide at 70 °C which is not studied. Ketol (**1**) and its epoxide and ketols (**19**-**22**) produced benzoic acid and its derivatives at the same temperature (Table-1).

The reaction of ketols (**19**-**22**) with hydrogen peroxide at room temperature is under studies. In all of the present utilized cyclopentenone systems, the C-C double bond is conjugated with an aryl substituent, beyond the carbonyl moiety. These high conjugated alkene systems are presumably less reactive than simple cyclopentenones. On the other hand, steric repulsion around the cyclopentenone ring is one other possible reason for the observed results. Since these materials were α-β unsaturated ketones, due to delocalizing π bond in conjugated system and decreasing of electeron density of π bond, rate of epoxidation decrease.

It is expected that this reaction carried out under mechanism in **Scheme-I** and epoxide produced. But, we obtained only benzoic acid. This observation may be rationalized by taking in account the oxidative cleavage of cyclopentenone in the presence of hydrogenperoxide. So we propose that, at first epoxide produced and which with below mechanism changed to benzoic acid (**Scheme-II**).



Scheme-I: Epoxidation mechanism of cyclopentenones



Scheme-II: Mechanism for converting epoxide to benzoic acid and its derivatives

Conclusion

In conclusion we have developed facile, environmentally safe and practical method for opening the five membered rings and prepared a new compound (**2**).

ACKNOWLEDGEMENT

The authors are grateful to Tarbiat Moallem University Research Council for partial support of this work.

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(*Received*: 27 August 2009; *Accepted*: 12 February 2010) AJC-8432