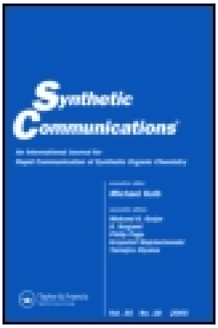

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Alcoholyses and Acetolyses of Allylic and Tertiary Benzylic Alcohols Catalyzed by 2, 3-Dichloro-5, 6-Dicyanobenzoquinone

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SYNTHETIC COMMUNICATIONS, 25(15), 2253-2260 (1995)

ALCOHOLYSES AND ACETOLYSES OF ALLYLIC AND TERTIARY BENZYLIC ALCOHOLS CATALYZED BY 2,3-DICHLORO-5,6-DICYANOBENZOQUINONE

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Abstract: Allylic and tertiary benzylic alcohols can be converted into their corresponding ethers and acetates selectively and efficiently in the presence of catalytic amounts of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).

The ready reversibility of quinone-hydroquione couple has led to the common use of quinones, especially those with electron-withdrawing substituents, as oxidizing agents in organic synthesis. Among quinones, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) has been the subject of much study. There are many examples in the literature concerning DDQ as an oxidizing and dehydrogenating agent.[1-5] Recently some new applications have been reported for DDQ such as:

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*To whom all correspondence should be addressed.

ring opening of epoxides[6] and thiiranes,[7] tetrahydropyranylation of alcohols,[8] deprotection of some protected alcohols by p-methoxybenzyl and 3,4-dimethoxybenzyl groups,[9] deprotection of acetals[10] and silyl ethers.[11]

In this paper we wish to report that catalytic amounts of DDQ can bring about an efficient transformation of allylic and tertiary benzylic alcohols to their corresponding ethers and acetates in different alcohols and acetic acid.

$$\mathbf{ROH} \xrightarrow[\text{rt or heat}]{\text{DDQ, R'OH}} \mathbf{ROR'}$$

R = allylic, 3^{0}-benzylic
R'= Me, Et, n.Pr, i.Pr, t.Bu, Cyclohexyl, Acetyl.

Alcoholyses of different classes of allylic and tertiary benzylic alcohols were performed in primary, secondary and tertiary alcohols in excellent yields. Some representative results are shown in Table 1.

Table 1: Alcoholyses of various allylic and tertiary benzylic alcohols catalyzed with 0.2 molar equivalent of DDQ.

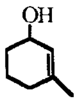
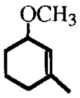
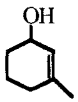
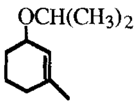
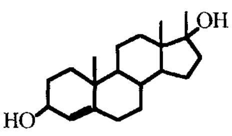
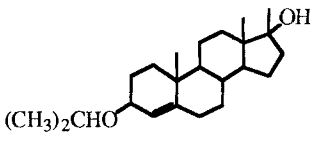
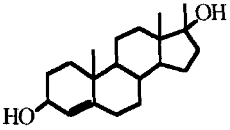
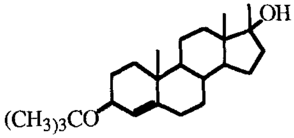
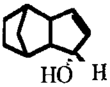
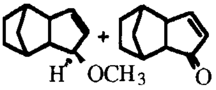
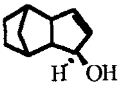
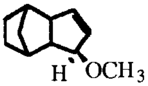
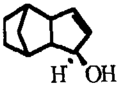
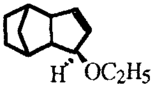
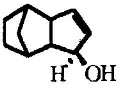
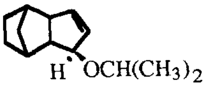
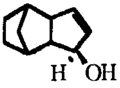
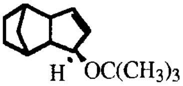
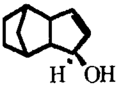
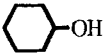
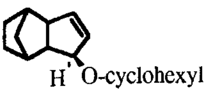
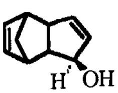
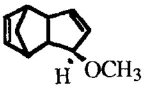
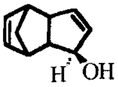
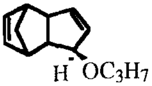
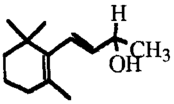
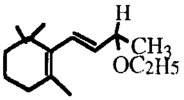
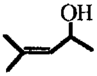
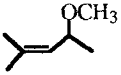
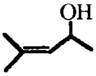
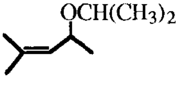
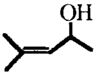
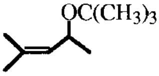
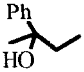
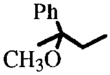
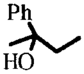
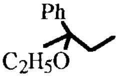
Entry	Alcohol	Solvent	Time(h)	Product[a]	Yield%[b]
1		CH_3OH	1/4		92
2		$i.C_3H_7OH$	1/4		95
3		$n.C_3H_7OH$	1		96

Table 1 continued.

4		t.C_4H_9OH	11/2		90
5		CH_3OH	1/4		35+60
6		CH_3OH	1/4		92
7		C_2H_5OH	1/4		90
8		i.C_3H_7OH	11/2		91
9		t.C_4H_9OH	3		90
10			11/4		90
11		CH_3OH	1/4		95
12		n.C_3H_7OH	2		94
13		C_2H_5OH	1		72
14		CH_3OH	1/2		95

(continued)

Table 1 continued.

15		i.C_3H_7OH	2		92
16		t.C_4H_9OH	4		65
17		CH_3OH	11/4		60
18		C_2H_5OH	11/4		65
19	Ph_3COH	CH_3OH	3/4	Ph_3COCH_3	92
20	Ph_3COH	n.C_3H_7OH	1	$Ph_3COC_3H_7$	97

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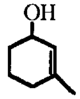
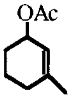
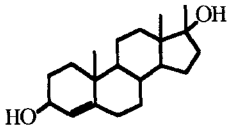
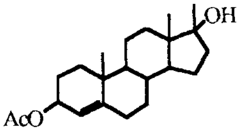
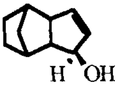
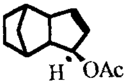
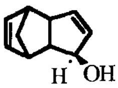
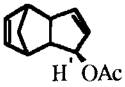
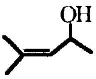
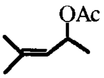
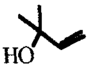
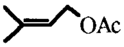
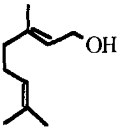
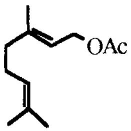
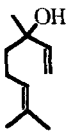
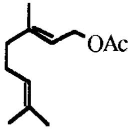
[a] The products were identified by comparison with authentic samples.

[b] Yields refer to isolated products.

The method is also very efficient and selective for acetolyses of allylic alcohols. Various allylic acetates were obtained in excellent yields from their corresponding alcohols in the presence of catalytic amounts of DDQ in acetic acid (Table 2). Formation of the isomerized, e.g. exo-methyl ether from endo-alcohol (Table 1, entry 5) and isomerized acetates of allylic alcohols (Table 2, entries 7,10) accounts for the formation of carbonium ion intermediates in these reactions. This was confirmed by the reaction of optically pure (+) endo-alcohol (Table 1, entry 5), $[\alpha]_{D}^{25}$ ($CHCl_3$) = $+169° \pm 2$ with 0.2 molar ratio of DDQ/alcohol in methanol. The obtained exo-methyl ether did not show any optical rotation. The formation of racemic ether is evidence for the formation of a symmetrical carbonium ion in

Table 2: Acetolyses of various allylic alcohols catalyzed with 0.2 molar equivalent of DDQ in acetic acid.

Entry	Alcohol	Time(h)	Product[a]	Yield(%)[b]
1		1/2		90
2		1		95
3		1/2		93
4		1/2		97
5		1/2		90
6		1		90
7		1/2		90
8		1/2		93
9		1		85
10		1		87

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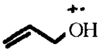
[a] The products were identified by comparison with known samples.

[b] Yield refers to isolated products.

this case. Although the exact role of DDQ is not clear, but on the basis of the above observation and the results obtained in the presence of acrylamide as a radical trapping agent,[13] we suggest that DDQ may act as a one-electron transfer agent to form the stable $\overset{-\bullet}{\text{DDQ}}$[14,15] and a radical cation () .

Carbon-oxygen bond cleavage to form stable allylic carbonium ion followed by regeneration of DDQ from the reaction of $\overset{-\bullet}{\text{DDQ}}$ and $^{\bullet}$OH may account for the above features of the reaction.

High yield of the reactions and ease of work up, availability and catalytic nature of the reagent , efficiency and selectivity of the method could make DDQ a useful reagent for selective alcoholyses of allylic and tertiary benzylic alcohols and acetolyses of only allylic alcohols .

Experimental

Products were isolated and their physical, i.r, n.m.r and mass spectral data were compared with those of known samples which were prepared according to the literature procedures.[16-20]

General Procedure for the Alcoholyses of Allylic and Tertiary Benzylic Alcohols: To a solution of alcohol (1 mmole) in the appropriate alcohol (5 ml) was added DDQ (0.2 mmole) and the mixture was stirred under reflux condition (0.25-4 h). The progress of the reaction was monitored by g.l.c and t.l.c. The Solvent was evaporated and water was added (30 ml) . Extraction with n-hexane or ether (3 x 20 ml) followed by chromatography on a short column of silica-gel gave the product in 35-96% yield.

General Procedure for the Acetolyses of Allylic Alcohols: A solution of the substrate (1 mmole) in acetic acid (5 ml) was treated with DDQ (0.2 mmole) and refluxed for 0.5-1h. The reaction was monitored with g.l.c and t.l.c . After completion of the reaction, solvent was evaporated and n-hexane or ether (30-50 ml) was added. The mixture was washed with 5% aqueous sodium bicarbonate solution and then water and dried. Evaporation of solvent followed by chromatography on a short column of silica-gel gave the corresponding acetate in 85-97% yield.

Acknowledgment:

The authors gratefully thank partial support of this work by Research Council of Shiraz University and Prof. H. Firouzabadi for his valuable comments.

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