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1,4 - BENZOQUINONE : A NEW SELECTIVE REAGENT FOR OXIDATION OF ALCOHOLS

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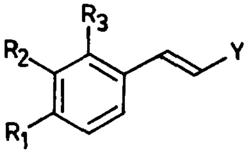
Abstract : The utility of 1,4- benzoquinone as a highly selective reagent for the oxidation of aryl conjugated primary allylic alcohols in the presence of benzylic and aryl conjugated secondary allylic alcohols is demomstrated. The reaction is clean, convenient and results in moderate to high yields.

With recent development of newer methods for oxidation of a hydroxyl group, it is possible to oxidise primary[1] or secondary[2] alcohols in presence of each other and allylic/benzylic alcohols[3] in presence of saturated ones with good selectivity. However, discrimination between primary and secondary allylic alcohols is not possible with any of these methods. In this communication a new method for oxidation of cinnamyl alcohols using 1,4 - benzoquinone, a reagent never employed before for the oxidation of alcohols[4] is described. More importantly, this method also permits selective oxidation of primary cinnamyl alcohols in presence of secondary cinnamyl alcohols under certain conditions.

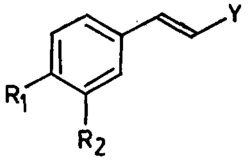
Heating the alcohols 1a-f, 2a-e and 3a-b with 1,4-benzoquinone in diglyme (Method A) produced the carbonyl compounds 4a-f, 5a-e and 6a-b respectively in 60-90% yield[5]. Benzhydrol 7d gave benzophenone 8d in 40% yield. However the benzylic alcohols 7a-c failed to yield the corresponding ketones/aldehydes under these reaction conditions. Simple allylic alcohols also remained inert to these conditions. Thus, under these conditions, the primary and secondary cinnamyl alcohols as well as the allylic alcohols conjugated to other aromatic systems, as illustrated by alcohols 3a-b, can be oxidised to the corresponding carbonyl compounds in good yields. However, benzylic alcohols (eg. 7a-c) could not be oxidised, with the exception of benzhydrol 7d, which is bibenzylic. These results were interesting since this method allows selective oxidation of aryl conjugated allylic alcohols in the presence of benzylic alcohols.

When the reaction was conducted in xylene (Method B), the primary cinnamyl alcohols 1a-f and alcohol 3d were oxidised to aldehydes 4a-f and 6a respectively in 65-90% yield but the secondary cinnamyl alcohols 2a-d did not furnish the corresponding ketones 5a-d. However, in spite of being secondary, the alcohols 2e and 3b underwent smooth oxidation to ketones 5e



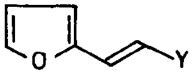
1 Y = $-CH_2OH$ 4 Y = $-CHO$

a. $R_1 = R_2 = R_3 = H$
b. $R_1 = -Me$, $R_2 = R_3 = H$
c. $R_1 = -OMe$, $R_2 = R_3 = H$
d. $R_1 = R_2 = -OMe$, $R_3 = H$
e. $R_1 = R_2 = -OCH_2O-$, $R_3 = H$
f. $R_1 = R_2 = H$, $R_3 = -NO_2$



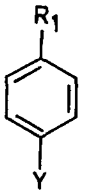
2 Y = $-CH(OH)R_3$ 5 Y = $-C(O)R_3$

a. $R_1 = R_2 = H$, $R_3 = -Me$
b. $R_1 = R_2 = -OCH_2O-$, $R_3 = -Me$
c. $R_1 = -OMe$, $R_2 = H$, $R_3 = -Et$
d. $R_1 = R_2 = -OMe$, $R_3 = -isoBu$
e. $R_1 = R_2 = H$, $R_3 = -Ph$



3 Y = $-CH(OH)R_1$ 6 Y = $-C(O)R_1$

a. $R_1 = H$
b. $R_1 = -Ph$



7 Y = $-CH(OH)R_2$ 8 Y = $-C(O)R_2$

a. $R_1 = R_2 = H$
b. $R_1 = -OMe$, $R_2 = H$
c. $R_1 = H$, $R_2 = -Me$
d. $R_1 = H$, $R_2 = -Ph$

and 6b respectively in 90% yield, most probably, due to their allylic as well as benzylic nature. The benzylic alcohols 7a-d did not react under these conditions. These results were rather fascinating because the primary allylic alcohols conjugated to aryl ring were oxidised under these conditions while similar secondary ones were not. To check this observed selectivity, an equimolar mixture of 1a and 2a was treated with 1,4 benzoquinone in xylene at 120°C. After 24 h the reaction mixture showed the formation of aldehyde 4a while 2a remained unchanged. This confirmed the observation that the primary cinnamyl alcohols can be oxidised in presence of secondary ones with complete selectivity.

In conclusion, easily available 1,4 benzoquinone is shown to oxidise mainly aryl conjugated allylic alcohols. More importantly, using method A, selective oxidation of cinnamyl alcohols could be achieved in the presence of benzylic alcohols while method B allows selective oxidation of

Table

Oxidation of aryl conjugated allylic alcohols with 1,4-Benzoquinone

Alcohol	Method	Time (Hr)	Product	Yield (%)#	Alcohol	Method	Time (Hr)	Product	Yield (%)
1a	A	12	4a	80	2d	A	26	5d	73
	B	16	-"-	75		B	--	NR	--
1b	A	18	4b	75	2e	A	06	5e	90
	B	20	-"-	67		B	08	-"-	90
1c	A	24	4c	80	3a	A	19	6a	65
	B	27	-"-	73		B	24	-"-	62
1d	A	24	4d	65	3b	A	09	6b	90
	B	27	-"-	60		B	12	-"-	70
1e	A	24	4e	60	7a	A	--	NR	--
	B	27	-"-	60		B	--	NR	--
1f	A	26	4f	96	7b	A	--	NR	--
	B	29	-"-	90		B	--	NR	--
2a	A	20	5a	82	7c	A	--	NR	--
	B	--	NR@	--		B	--	NR	--
2b	A	20	5b	84	7d	A	42	8d	40
	B	--	NR	--		B	--	NR	--
2c	A	24	5c	80					
	B	--	NR	--					

@ NR = No reaction; # Yields are of isolated pure products.

primary cinnamyl alcohols in presence of secondary cinnamyl alcohols which until now was not possible.

Representative experimental procedure :A solution of the alcohol 1a (10 mmol) and 1,4,benzoquinone (15 mmol) in diglyme (5.0 ml) (Method A) or xylene (5.0 ml) (Method B) was heated at 120°C until TLC indicated complete consumption of starting alcohol. The reaction mixture was then poured in water and extracted with ether. The ether layer was dried over anhydrous sodium sulfate, concentrated and the residue was chromatographed on silica gel using hexane:ethyl acetate mixture as solvent to afford aldehyde **4a** which was purified by distillation(b.p. $132^{o}C/10_{Torr}$).

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4) Substituted benzoquinones like DDQ and o- & p- chloranils have been used for oxidation of allylic alcohols. See 'Reagents for Organic Synthesis' vol. 1 - 14 by Fieser & Fieser, John Wiley & sons Inc.

5) All compounds gave satisfactrory spectral and microanalytical data.

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