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AN EFFICIENT SYNTHESIS OF SOME 1-NAPHTHYLALKYL KETONES AND THEIR AUTOOXIDATION IN BASIC MEDIUM

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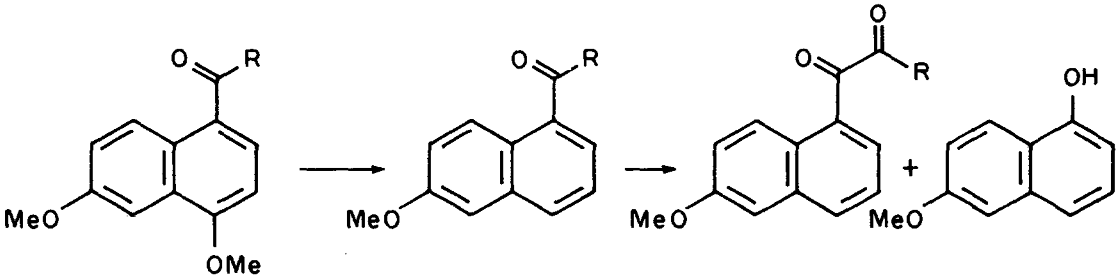
The title compounds (II) which are not easily accessible by other methods, have now been synthesised in fair to good yields through Birch reduction of 4,6-dimethoxy-1-naphthylalkyl ketones of the type (I). It has been reported [1] earlier that during metal-ammonia reduction, a p-acyl group can labilise a p-methoxy group to hydrogenolysis to some extent, but it has not been intensively investigated.

The dimethoxy ketones (I)[2] were easily available through Friedel-Crafts acylation of 1,7-dimethoxynaphthalene. Under specific conditions (see Table 1), reductive removal of 4-methoxy group from (1) by Na in liquid ammonia provided the desired ketones (II) in respectable yields. Under certain conditions, however, the main products isolated were the acid[3] (IIe), diketones (III), and interestingly the phenol[4] (IV), as a result of oxidative degradation of the desired ketones (II) in alkaline solution. It should be mentioned that this is probably the first report of phenol formation through autooxidation of aryl alkyl ketones.

A typical reduction procedure is described here for the ketone (Ib). To an efficiently stirred mixture of liquid ammonia (undistilled) (500 ml) and a solution of the ketone (Ib; 1 g) in dry THF (50 ml) and absolute EtOH (11.6 ml) was added sodium metal (1 g) in small pieces within 2-3 min. After the disappearance of the blue colour, NH_4Cl (500 mg)[5] was added all at a time. Ammonia was then evaporated, and THF was removed under reduced pressure.

The resulting residue was treated with water and the alkaline mixture (pH 10 - 12) was extracted with ether to give the neutral product/products. Usual processing of the alkaline solution afforded the phenol (IV), and the acid (IIe).



I II III IV

R

a: $(CH_2)_3CO_2H$
b: $(CH_2)_2Me$
c: $CH(Me)_2$
d: CH_2Ph
e: OH

a: $R = CH_2Me$
b: $R = Ph$

The results are summarised in Table 1, and the following comments may be made. Autooxidation of (II) is minimum when Et_2O is used as the co-solvent (entry 6). Long exposure of the homogeneous alkaline solution (when THF is used) to atmospheric oxygen leads preferentially (entries 3 and 8) to oxidative degradation of the desired products (II). The carbanion formation from (IIc) is unfavourable, and this accounts for the excellent yield of (IIc) (entry 7).

Autooxidation of ketones in basic media rapidly forms hydroperoxides which are known[6] to yield α-diketones, and acidic products. Low yield of phenol (IV) in all cases (see Table 1) presumably reflects the intermolecular pathway (Scheme - 1) for its formation.

TABLE - 1

Entry	Ketone	g.atom of Na per mole of ketone	Co-solvent	Time for evaporation of ammonia	Products^{a} (%)		
					(II)	(III)^{b}	(IV)
1.	1a	10	THF	4.0 hr.	IIe (52)	-	(3)
2.	1a	10	THF	1.5 hr.	IIa (38) IIe (31)	-	(3)
3.	1b	10	THF	4.0 hr.	IIb (12) IIe (29)	IIIa^{e} (7)	trace^{c}
4.	1b	5	THF	0.5 hr.	IIb (60)	-	(1.5)
5.	1b	10	THF	1.5 hr.	IIb (7) IIe (25)	IIIa^{e} (18)	trace^{c}
6.	1b	10	Et_2O	4.0 hr.	IIb (68) IIe (4.5)	-	(9.6)
7.	1c	10	THF	4.0 hr.	IIc (70) IIe (6.4)	-	trace^{c}
8.	1d	10	THF	4.0 hr.	IId (13) IIe (24) Benzoic acid (24)	IIIb^{d} (11)	(13.1)

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[a] Products so far isolated and characterised.

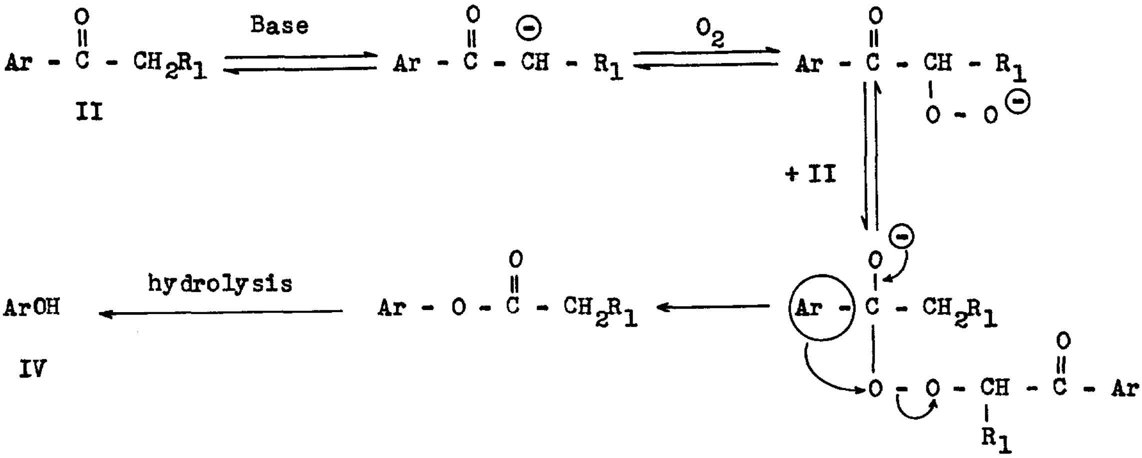
[b] The percentages of the diketones (III) were determined from the acid (IIe) obtained through alkaline H_2O_2 oxidation of the total neutral product.

[c] Trace amount was characterised through comparative tlc.

[d] Oxidation of this diketone with alkaline H_2O_2 gave IIe and benzoic acid (1:1).

[e] This diketone was isolated in pure form.

SCHEME - 1



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