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DIMETHYL SULFOXIDE AND ANHYDROUS COPPER (II) SULFATE AS ALKYLATING REAGENT FOR 1,4-QUINONES

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ABSTRACT: 1,4-Quinones and its derivatives have been alkylated by dimethyl sulfoxide in the presence of anhydrous copper(II) sulfate at the active quinonoid position selectively, in a facile single step reaction with good yields.

Numerous alkyl quinones are known to occur in nature[1]. They possess biological activities viz. antibiotic[2], insecticidal[3], molluscicidal[4] and antihaemmorhage[5]. Copper(II) sulfate has been used for oxidation[6], generation of carbene[7], rearrangement[8], hydration[9], protection[10] and hydrolysis[11].

In the present communication, we report the use of dimethyl sulfoxide in the presence of anhydrous copper(II) sulfate for the direct and regioselective alkylation of 1,4-quinones. The advantage of this reaction is the

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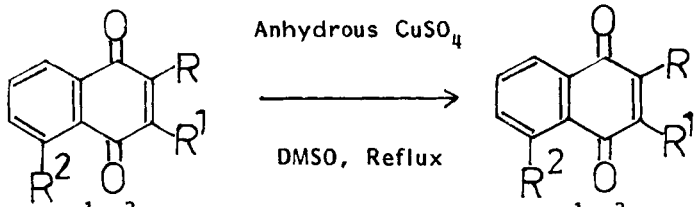
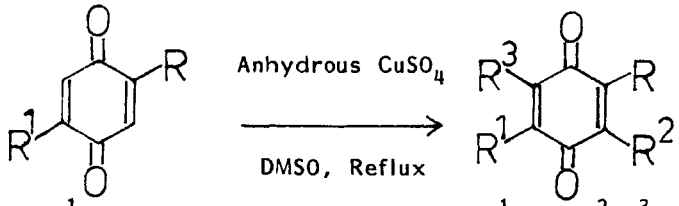


I	$R=R^1=R^2=H$	IX	$R=CH_3, R^1=R^2=H$
II	$R=CH_3, R^1=R^2=H$	X	$R=R^1=CH_3, R^2=H$
III	$R=R^1=H, R^2=OH$	XI	$R=CH_3, R^1=CH_3, R^2=OH$
IV	$R=OH, R^1=R^2=H$	XII	$R=OH, R^1=CH_3, R^2=H$
V	$R=Cl, R^1=R^2=H$	XIII	$R=Cl, R^1=CH_3, R^2=H$
VI	$R=Br, R^1=R^2=H$	XIV	$R=Br, R^1=CH_3, R^2=H$



VII	$R=R^1=H$	XV	$R=R^1=CH_3, R^2=R^3=H$
VIII	$R=R^1=OCH_3$	XVI	$R=R^1=OCH_3, R^2=R^3=CH_3$

absence of side products, mild reaction conditions and higher regioselectivity. Products are isolated in good yields by simple filtration and solvent evaporation. The reaction gets quenched by the addition of radical quenchers, like iodine and benzoyl peroxide, which proves the free radical mechanism for the reaction.

In a typical procedure, 1,4-naphthoquinone (I) (1 mmol) was refluxed at 50°C, with anhydrous copper

(II) sulfate (5 mmol) and dimethyl sulfoxide (10 ml) for 1 hr to give 2-methyl-1,4-naphthoquinone (IX) (yield 60%) and 2,3-dimethyl-1, 4-naphthoquinone (X) (yield 40%). Other 1,4-quinones (II to VIII) under similar conditions (refer table below) gave corresponding monomethyl-1, 4-quinones (X to XVI) except juglone (III) which gave 2,3-dimethyljuglone (XI). Compounds IX[12], X[13], XI[14], XII[12] and XVI[15] are naturally occurring compounds.

TABLE

S.NO.	Reactant	Time (hrs.)	Product/s	Yield (%)	M.Pt.* (^{o}C)
1.	I	1.0	IX	60	105
			X	40	128
2.	II	2.0	X	90	128
3.	III	2.0	XI[14]	80	110
4.	IV	2.5	XII	90	173
5.	V	2.0	XIII	90	93
6.	VI	2.0	XIV	90	154
7.	VII	1.0	XV	60	Gummy Solid
8.	VIII	1.5	XVI	80	132

* The melting points are uncorrected.

^{1}H-NMR spectra were recorded on δ scale on Perkin-Elmer R-32 spectrophotometer (90 MHz) with TMS as internal standard using $CDCl_3$ as solvent unless otherwise stated. The notations used are s for singlet, m for multiplet and Ar for aromatic. IR spectra were recorded in nujol on Perkin-Elmer Spectrophotometer model 599-B and ν_{max} values are given in cm^{-1}.

General Procedure : In a 50 ml dry R.B. flask, anhydrous copper (II) sulfate (5 mmol) and a solution of 1,4-quinones (1 mmol) in dimethyl sulfoxide (10 ml), were added and the mixture was refluxed at 50°C for 1-3 hrs. The reaction was monitored on TLC (silica gel, benzene-ethyl acetate). When the starting material disappeared, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The concentrate was diluted with 250 ml of water and the mixture extracted with 5 X 100 ml of ethyl acetate. The organic extract was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure to give the solid which was purified by column chromatography to give the pure methylated products.

Spectral data of the products:

Compound IX : 2-Methyl-1,4-naphthoquinone. ^{1}H-NMR : 2.3 (s,3H, C_2-CH_3), 6.3(s,1H, C_3-H), 7.4-7.6(m, 2H,

$C_{6,7}$-H's), 7.7-7.9 (m, 2H, $C_{5,8}$-H's). IR: 1662, 1618 1585.

Compound X : 2,3-Dimethyl-1,4-naphthoquinone. ^{1}H-NMR: 2.6(s, 6H, $C_{2,3}$-2xCH_3), 7.3-7.6(m, 2H, $C_{6,7}$-H's), 7.7-7.9 (m, 2H, $C_{5,8}$-H's). IR: 1658, 1618, 1594.

Compound XII : 2-Hydroxy-3-methyl-1,4-naphthoquinone ^{1}H-NMR(CD_3SOCD_3) : 2.25(s, 3H, C_3-CH_3), 7.6-8.25 (m, 4H, Ar-H's). IR: 3408, 1658, 1640, 1590.

Compound XIII : 2-Chloro-3-methyl-1,4-naphthoquinone. ^{1}H-NMR : 2.3(s,3H, C_3-CH_3), 7.6-7.8 (m,2H, $C_{6,7}$-H's), 7.9-8.1 (m,2H, $C_{5,8}$-H's). IR: 1670, 1655, 1581.

Compound XIV : 2-Bromo-3-methyl-1,4-naphthoquinone. ^{1}H-NMR: 2.3(s,3H, C_3-CH_3), 7.4-7.7(m,2H, $C_{6,7}$-H's), 7.8-8.0(m,2H, $C_{5,8}$-H's). IR : 1680, 1660, 1575.

Compound XV: 2,5-Dimethyl-1,4-benzoquinone. ^{1}H-NMR: 2.2(s,6H, $C_{2,5}$-2xCH_3), 7.2(s,2H, $C_{3,6}$-H's). IR: 1680.

Compound XVI : 2,5-Dimethoxy-3,6-dimethyl-1,4-benzoquinone. ^{1}H-NMR : 2.2(s,6H, $C_{3,6}$-2xCH_3), 4.1(s,6H, $C_{2,5}$-2xOCH_3). IR : 1680, 1660.

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