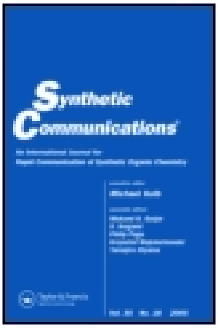

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Chlorination of Quinonoid Compounds Using Dichlorine Monoxide

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CHLORINATION OF QUINONOID COMPOUNDS USING DICHLORINE MONOXIDE

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ABSTRACT: Dichlorine monoxide is a selective reagent for the monochlorination at the active quinonoid position in benzoquinones and naphthoquinones.

A large number of halobenzoquinones and halonaphthoquinones are known to occur in nature[1,2] and some of them are of medicinal importance[3,4]. Halonaphthoquinones have also been used for the synthesis of naturally occurring anthraquinones[5].

Dichlorine monoxide is a unique selective chlorinating agent and acts at the benzylic positions of deactivated alkyl aromatics in non-polar medium. In strongly acidic media, a facile electrophilic aromatic ring chlorination occur[6].

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We have now utilized dichlorine monoxide for the chlorination of the quinonoid positions in benzoquinone, naphthoquinone and their derivatives. In all cases, monochlorination at quinonoid position took place except in the case of benzoquinone where it gave 2,5-dichloro-1,4-benzoquinone (XIII). Dichlorine monoxide was prepared in situ by passing chlorine gas through the suspended yellow mercuric oxide in carbon tetrachloride[7]. The rate of reaction was enhanced by radical initiators like benzoyl peroxide and retarded by radical quenchers like iodine. The reaction proceeded in the dark at room temperature involving the formation of ClO radical which was the hydrogen abstracting species[8]. Chlorination of quinones (I to VII) with mercuric oxide and chlorine in carbon tetrachloride gave the corresponding chlorinated quinones (VIII to XIV).

EXPERIMENTAL

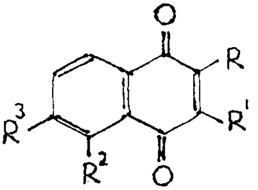
Melting points are uncorrected. ^{1}H-NMR spectra were recorded on Perkin-Elmer R-32 spectrometer (90 MHz) in $CDCl_3$ with TMS as internal standard. Chemical shift values are in δ scale. The notations used are s for singlet, d for doublet, dd for double doublet, m for multiplet and Ar for aromatic. IR spectra in KBr disc were recorded on a Perkin-Elmer spectrophotometer model 599-B and ν_{max} are in Cm^{-1}. UV spectra in ethanol were recorded on Beckmann DU-2 spectrophotometer and λ_{max} values are given in nm.

TABLE

Reaction of quinones with dichlorine monoxide in CCl_4

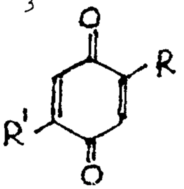
S.No.	Reactant	Time (hrs)	Product	Yield (%)	M.Pt. (°C)	Spectral data (^{1}H-NMR/IR/UV)
1.	I	0.5	VIII	100	112	^{1}H-NMR: 7.28(s,1H,C_3-H),7.78-7.98 (m,2H,$C_{6,7}$-H), 8.12-8.33(m,2H, $C_{5,8}$-H). IR: 1680,1678,1656,1582. UV: 247,258,267,313.
2.	II	0.5	IX	80	93	^{1}H-NMR: 2.4(s,3H,CH_3), 7.7-7.9(m,2H, $C_{6,7}$-H), 8-8.2(m,2H,$C_{5,8}$-H). IR: 1720,1680,1600,1578. UV: 252,270,330.
3.	III	2.0	X	60	214	^{1}H-NMR: 7.4-7.6(m,2H,$C_{5,8}$-H),7.15-7.35(m,2H,$C_{6,7}$-H), 11.6(s,1H,OH). IR: 3240,1710,1650,1631. UV: 220,230,275,463.
4.	IV	2.0	XI	70	166	^{1}H-NMR: 7.1(s,1H,C_3-H), 7.1-7.25(dd, 1H,ArH), 7.5-7.65(m,2H,Ar-H), 11.8 (s,1H,OH). IR: 1665,1640,1450,1380,1290. UV: 212,352,429.
5.	V	2.5	XII	50	92	^{1}H-NMR: 2.6(s,3H,CH_3), 7.55(s,1H, C_2-H), 7.92(d,1H,J=8Hz,C_7-H), 8.28 (s,1H,C_5-H),8.39(d,1H,J=8Hz,C_8-H). IR: 1721,1665,1584. UV: 237,269,340,390.
6.	VI	0.5	XIII	70	257	^{1}H-NMR: 7.32(s,$C_{3,6}$-H). IR: 1663,1582. UV: 265.
7.	VII	1.0	XIV	60	103	^{1}H-NMR: 2.1(s,3H,CH_3), 6.6(s,1H, C_3-H), 6.8(s,1H,C_6-H). IR: 1680,1660,1637. UV: 250,315,434.

General procedure: 5 mmol of the quinones (I to VII) was stirred continuously with 5 mmol of yellow HgO in 100 ml of CCl_4 in a 250 ml RB flask wrapped with carbon paper and chlorine gas was passed through the reaction mixture. The reaction was monitored. on TLC (thin layer chromatography; silica gel). The reaction mixture was filtered. The filtrate was evaporated under reduced pressure to give the solid which was subjected to column chromatography (silica gel, petroleum ether-benzene) to give various chloroquinones (VIII to XIV).



I $R=R^1=R^2=R^3=H$
II $R=CH_3$, $R^1=R^2=R^3=H$
III $R=OH$, $R^1=R^2=R^3=H$
IV $R=R^1=R^3=H$, $R^2=OH$
V $R=R^1=R^2=H$, $R^3=CH_3$

VIII $R=Cl$, $R^1=R^2=R^3=H$
IX $R=CH_3$, $R^1=Cl$, $R^2=R^3=H$
X $R=OH$, $R^1=Cl$, $R^2=R^3=H$
XI $R=Cl$, $R^1=R^3=H$, $R^2=OH$
XII $R=Cl$, $R^1=R^2=H$, $R^3=CH_3$



VI $R=R^1=H$
VII $R=CH_3$, $R^1=H$

XIII $R=R^1=Cl$
XIV $R=CH_3$, $R^1=Cl$

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