Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

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Prakash Chander Thapliyal [a]

[a] Department of Chemistry , University of Delhi , Delhi, 110007, India

To cite this article: Prakash Chander Thapliyal (1998) Iodine Catalyzed Chlorination of Naphthoquinones Using Metal (II) Chlorides, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 28:7, 1123-1126, DOI: 10.1080/00397919808005952

To link to this article: http://dx.doi.org/10.1080/00397919808005952

SYNTHETIC COMMUNICATIONS, 28(7), 1123-1126 (1998)

IODINE CATALYZED CHLORINATION OF NAPHTHOQUINONES USING METAL (II) CHLORIDES

Prakash Chander Thapliyal

Department of Chemistry, University of Delhi,Delhi-110007, India

Abstract : The active quinonoid position of various naphthoquinones is chlorinated by metal(II) chloride (Cu/Hg) and iodine in acetic acid in single step reaction with excellent yields.

The complex metal salts are of great synthetic utility and they have been employed in various reactions in olefins[1-5] i.e. halogenation (particularly for the synthesis of vicinal dibromo, chloro iodo, chloro bromo), nitration, cyclization, iodo-alkoxylation, oxymercuration etc. In continuation of our studies[6-8] on metal salts-quinone reactions, I report in the present communication a simple versatile reaction for the chlorination at quinonoid position in 1,4-naphthoquinone and its derivatives giving fair to good yield of the products. When a solution of 1,4-naphthoquinone (1) (0.1 mole) in acetic acid (30 ml) was stirred at 60°C in the presence of mercury(II) chloride/copper(II) chloride (0.1 mole) and iodine (0.01 mole), 2-chloro-1,4-naphthoquinone (7) was obtained in 98% yield. Similarly other naphthoquinones (2 to 6) on reaction gave corresponding chloroquinones (8 to 12).

Chlorination does not occur in the absence of any one of the reagents i.e. copper(II) chloride/mercury(II) chloride and iodine. The reaction is fast at elevated temperature rather than at room temperature. The chlorination reactions are not quenched on the addition of radical quencher implying the involvement of ionic mechanism. It has been reported[6] that the molecular iodine is activated by the complexation with the metal salts facilitating an electrophilic attack. So the initial step in this mechanism is the electrophilic attack of iodine on the quinonoid double bond, thus leading to iodonium intermediate, there is transfer of chloride ion from the metal complex to iodonium intermediate resulting in the product formation.

EXPERIMENTAL

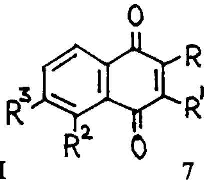
Melting points recorded are uncorrected. ^{1}HNMR spectrum was recorded on δ scale on Perkin-Elmer R-32 spectrophotometer (90 MHz) with TMS as internal standard using $CDCl_3$ as solvent. The notations used are s for singlet, m for multiplet and Ar for aromatic. IR spectrum was recorded on Perkin-Elmer spectrophotometer model 599-B in nujol and ν_{max} is in $cm^{-1.}$

General procedure : A solution of naphthoquinone (0.1 mole) in acetic acid (30 ml) is stirred vigourously at 60°C. To this metal salt (0.1 mole) and iodine (0.01 mole) are added with continuous stirring. The reaction is monitored on TLC (silica gel, pet ether) for the completion of the reaction. When the composition of the product remain unaltered on TLC, the reaction mixture is

Table : Reaction of naphthoquinones with $HgCl_2/CuCl_2$ and iodine in CH_3COOH

Reactant	Time (hrs.)	Product	Yield (%)	m.p. (°C)	Spectral Data*
1	3.0	7	98[8]		-
2	3.0	8	80[8]		-
3	3.0	9	85[8]		-
4	3.0	10	95[8]		-
5	2.5	11	98	205	^{1}HNMR : δ 3.9 (s,1H, NH_2), 7.6-8.2 (m,4H,Ar-H's). IR : 1320, 1680, 3300 cm^{-1}
6	2.5	12	50	190	^{1}HNMR : δ 3.7 (s,1H, OCH_3),7.5-8.1 (m,4H,Ar-H's). IR :1625,1680cm^{-1}

* Satisfactory CHN data found.



1 $R=R^1=R^2=R^3=H$
2 $R=CH_3, R^1=R^2=R^3=H$
3 $R=R^1=R^2=H, R^3=CH_3$
4 $R=R^1=R^3=H, R^2=OH$
5 $R=NH_2, R^1=R^2=R^3=H$
6 $R=OCH_3, R^1=R^2=R^3=H$

7 $R=Cl, R^1=R^2=R^3=H$
8 $R=Cl, R^1=CH_3, R^2=R^3=H$
9 $R=R^2=H, R^1=Cl, R^3=CH_3$
10 $R=R^3=H, R^1=Cl, R^2=OH$
11 $R=NH_2, R^1=Cl, R^2=R^3=H$
12 $R=OCH_3, R^1=Cl, R^2=R^3=H$

filtered and solvent is evaporated on rotary vaccum evaporator. The residual mixture is extracted with ether (3 X 100 ml) and the ethereal layer is washed thoroughly with water and dried over ignited sodium sulphate and the ether is evaporated and the reaction mixture is subjected to preparative TLC (silica gel;

pet. ether : benzene :: 9:1) to isolate the various chlorination products. The identification of products has been done by physical as well as chemical methods and also by comparing with the authentic samples.

Acknowledgement : The author is grateful to the CSIR, New Delhi for the award of SRF and the financial assistance rendered thereof.

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(Received in the UK 16th April, 1997)