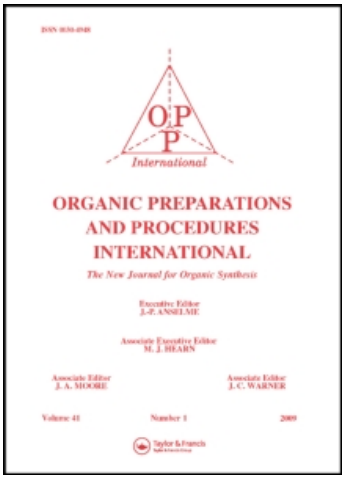


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

IODINATION OF NAPHTHOQUINONES AND COUMARIN CATALYZED BY CERIC AMMONIUM AND MERCURIC NITRATES

J. Sharma[a]; P. K. Singh[a]; K. P. Singh[a]; R. N. Khanna[a]
[a] Department of Chemistry, University of Delhi, Delhi, INDIA

To cite this Article Sharma, J. , Singh, P. K. , Singh, K. P. and Khanna, R. N.(1995) 'IODINATION OF NAPHTHOQUINONES AND COUMARIN CATALYZED BY CERIC AMMONIUM AND MERCURIC NITRATES', Organic Preparations and Procedures International, 27: 1, 84 — 86
To link to this Article: DOI: 10.1080/00304949509458181
URL: http://dx.doi.org/10.1080/00304949509458181

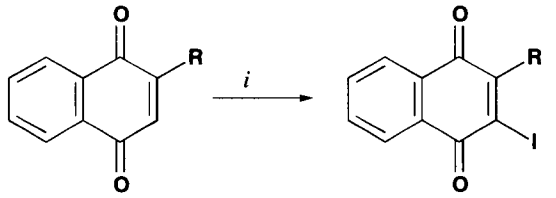
IODINATION OF NAPHTHOQUINONES AND COUMARIN CATALYZED BY CERIC AMMONIUM AND MERCURIC NITRATES

Submitted by J. Sharma, P. K. Singh, K. P. Singh and R. N. Khanna*
(01/11/94)

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

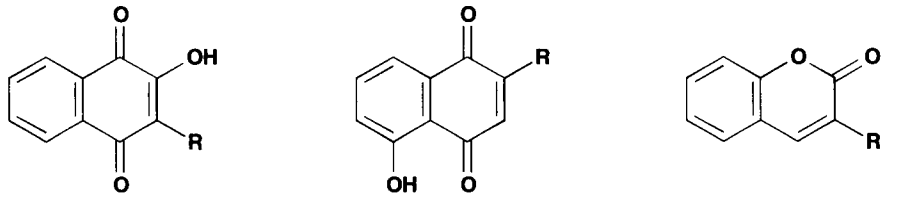
A number of halogenated quinones occur in nature.[1] Halogenated quinones have found applications as inhibitors for polymerization[2] and fire proofing dyes for woolen materials.[3] The utility of haloquinones as insecticides,[4] fungicides[5,6] and bactericides[7] has made their synthesis more urgent. Metal salts and iodine have often been used for the alkoxylation,[8] iodoalkoxylation[9] and iodination[10-12] of various organic compounds. This communication reports the synthesis of some new iodinated quinones and coumarin which have specific activity as fungicides against *Colletotrichum falcalum*[12] and *Drechslera tetramera.*

Iodine with ceric ammonium nitrate (CAN) and with mercuric nitrate [$Hg(NO_3)_2$] in aqueous acetic acid was used for the iodination at the active quinonoid position of 1,4-naphthoquinones (**1**) to give **2**.



a) R = H b) R = Me c) R = OMe
i) I_2 and CAN [or $Hg(NO_3)_2$]

1 **2**



3 **4** **5**

a) R = H b) R = I

Iodination of quinones **3a** and **4a** afforded 2-hydroxy-3-iodo-1,4-naphthoquinone (**3b**) and 5-hydroxy-2-iodo-1,4-naphthoquinone (**4b**), respectively; similarly, coumarin (**5a**) yielded 3-iodocoumarin (**5b**). The compounds were identified on the basis of their spectral data and elemental analyses. It was observed that the presence of all the reagents was essential and monoiodo products besides starting compounds were obtained The reaction was rapid at higher temperatures. Iodination of quinones **2a-c, 3a** and coumarin **5a** proceed with CAN/I_2 while for quinone **4a** proceeds

with $Hg(NO_3)_2/I_2$. Iodination of 5-methyl-1,4-naphthoquinone, halogenated 1,4-naphthoquinones and naphthazarin failed to give iodinated products with CAN/I_2. These reagents have the advantage that the reaction conditions are simple. Antifungal activity of all the products was checked on two fungi, *i. e. Colletolrichum falcatum and Drechslera tetramera* [14] All compounds except **3b** showed antifungal activity.

TABLE 1. Iodination of 1,4-Naphthoquinones **1a-c, 3a, 4a** and Coumarin **5a**

Compound	mp. (°C)	Yield (%)		Time (hrs)		Elemental Analysis (found)	
		CAN	$Hg(NO_3)_2$	CAN	$Hg(NO_3)_2$	C	H
2a	119-120	60	55	3	3	42.40(42.20)	1.76(1.70)
2b	158-160	50	50	3	4	44.44(44.30)	2.35(2.32)
2c	164-165	55	50	3	3	42.17(42.00)	2.23(2.00)
3b	177-179	50	–	3	–	40.13(40.03)	1.67(1.64)
4b	150-151	–	30	–	3	40.13(40.00)	1.67(1.65)
5b	88-89	45	40	4	4	39.85(39.70)	1.84(1.64)

TABLE 2. Spectral Data of Compounds **2a-c, 3b, 4b** and **5b**

Cmpd	NMR(δ)[a]	UV (nm)	IR (cm^{-1})
2a	7.27 (s, 1H, C_3-H), 7.8-7.9 (m, 2H, $C_{6,7}$-H), 8.15-8.29 (m, 2H, $C_{5,8}$-H)	247,258,267, 313,314	1587,1656, 1680,1682
2b	2.38 (s, 3H, CH_3), 7.69-7.78 (m, 2H, $C_{6,7}$-H), 8.1-8.3 (m, 2H, $C_{5,8}$-H)	247,262,272,337	1720
2c	3.1(s,3H. OCH_3) 7.7-7.8 (m ,2H, $CH_{6,7}$-H), 8.1-8.3(m, 2H, $C_{5,8}$-H)	247,260, 273,336	1680,1720
3b	7.35-7.6(m,2H, $C_{5,8}$-H), 7.8-8.6 (m, 2H, $C_{6,7}$-H)	270,275,300,320	1650, 1710
4b	7.1 (s, 2H, Q_n-H), 7.15-7.30 (m, 1H, C_7-H), 7.6 (m, 2H, $C_{6,8}$-H), 11.83 (s, 1H,-OH)	245,270,406,428	1585, 1656, 1675,3360
5b	7.0-7.6 (m, 4H, $C_{5,6,7,8}$-H's), 8.1 (s, 1H, C_4-H)	—	1730

a) Q = quinonoid

EXPERIMENTAL SECTION

Melting points are uncorrected. IR spectra were recorded on a PE Model 137/Shimadju IR 435 spectrometer (Nujol, cm^{-1}). UV spectra were recorded in methanol on a Beckman DU-2 spectrophotometer and PMR spectra were obtained on a PE R-32 (90MHz) in $CDCl_3$ (except for **5b** where $(CD_3)_2CO$ was used), using TMS as internal standard. Chemical shifts were recorded in δ scale. Notations used are s, singlet; d, doublet; m, multiplet.

General Procedure.- To a solution of 1 mmol of the substrate in 30% aq. acetic acid (20 mL) were added ceric ammonium nitrate (1 mmol) or mercuric nitrate (1 mmol) and iodine (0.1 mmol). The

solution was stirred vigorously at 80° using a magnetic stirrer for the specified time (see Table 1). The reaction mixture was filtered and the filtrate was extracted with ether and the ethereal layer was washed with water and dried over anhydrous sodium sulfate. Evaporation of solvent under reduced pressure gave a residue which was chromatographed on silica gel column and the products eluted with petroleum ether (100 mL) and subsequently with 2:1 petroleum ether-benzene (150 mL).

REFERENCES

1. E. Yosioko, H. Yamauchi, K. Morimoto and I. Kitagawa, *Tetrahedron Lett.*, 1149 (**1968**); H. J. Banks, D. W. Cameron, J. S. Edmonds and W. D. Ravetry, *Australian J. Chem.*, **29**, 2225 (1976); H. Nakano, T. Komiya and S. Shibata, *Phytochemistry*, **11**, 3505 (1972); G. Bobman, *Acta Chem Scand.*, **23**, 2241 (1969); C. H. Fox, W. S. G. Maass and T. P. Forrest, *Tetrahedron Lett.*, 919 (**1969**); T. Bruun, D. P. Hollis and R. Rhyage, *Acta Chem. Scand.*, **19**, 839 (1965); A. Calderbank and D.W. Cameron, *J. Chem. Soc.*, 80 (**1964**).

2. B. A. Renato and A. Scaramucci, *Ger. Often.*, 2,210,423 (1972); *CA*, **78**, 4,753f (1973).

3. V. K. Kruglov, R. P. Rilo, N. O. Pastushak and V. S. Gorbatyuk, *Otkrytiya Izobret. Prom. Obraztsy Tovarnye Znaki*, **24**, 133 (1982); *CA*, **98**, 5444f (1983).

4. H. Julius, US Patent, 2,507 (1950); *CA*, **44**, 9617f (1950).

5. C. L Elbert and P H. Marlin, US Patent, **2**, 430,722 (1947); *CA*, **42**, 1014e (1948)

6. J. Sharma, R. N Khanna, S. Sakhuja and K. G. Mukerji, *Incompatibility Newsletter* (State University College, Cortland, New York), **25**, 35 (1993).

7. J. I. G. Cadogan, R. A. Raphel, C. W. Rees, *Dictionary of Organic Compounds* (Chapman and Hall), Fifth Edition, Vol. 1, C-01802 (1982).

8. R. N. Khanna, K. P. Singh, S. K. Yadav and S. Srinivas, *Synth. Commun.*, **19**, 3151 (1989).

9. a) C. Georgoulis, E. Paillaseur and J. M. Valery, *Synthesis*, 67 (**1979**); b) C. Georgoulis and J. M. Valery, *ibid.*, 402 (**1978**).

10. T. H. Kim, T. Asakawa and Y. Asaka, Chemical Express, **5 (4)**, 221 (1990); *CA.*, **113**, 78046r (1990).

11. M. S. Shvartsberg, A. V. Piskunov and A. A. Moroz, *Izv. Akad. Nauk SSSR, Set. Khim*, **5**, 1101 (1990); *CA*, **113**, 131699j (1990).

12. Z. Fangjie and L. Y Chin, *Chemistry Lett.*, **2**, 763 (1991); *CA*, **116**, 193976t (1992).

13. J. Sharma, R. N. Khanna S. Sakhuja and K. G. Mukerji, *Incompatibility Newsletter*, (State University College, Cortland, New York), **24**, 51 (1992).

14. J. Sharma, Ph. D. Thesis (Delhi University), 1991.