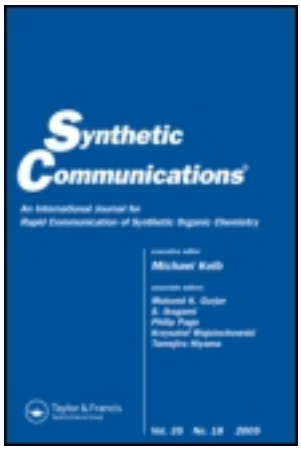


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

An Improved Iodine(III) Mediated Method for Thiocyanation of 2-Arylindan-1,3-diones, Phenols, and Anilines

Om Prakash [a] , Harpreet Kaur [a] , Rashmi Pundeer [a] , R. S. Dhillon [b] & Shiv P. Singh [a]

[a] Department of Chemistry, Kurukshetra University, Kurukshetra, India

[b] Department of Chemistry, Punjab Agricultural University, Ludhiana, India

Published online: 16 Aug 2006.

To cite this article: Om Prakash , Harpreet Kaur , Rashmi Pundeer , R. S. Dhillon & Shiv P. Singh (2003): An Improved Iodine(III) Mediated Method for Thiocyanation of 2-Arylindan-1,3-diones, Phenols, and Anilines, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 33:23, 4037-4042

To link to this article: http://dx.doi.org/10.1081/SCC-120026343

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SYNTHETIC COMMUNICATIONS®
Vol. 33, No. 23, pp. 4037–4042, 2003

An Improved Iodine(III) Mediated Method for Thiocyanation of 2-Arylindan-1,3-diones, Phenols, and Anilines

Om Prakash,[1,*] Harpreet Kaur,[1] Rashmi Pundeer,[1] R. S. Dhillon,[2] and Shiv P. Singh[1]

[1]Department of Chemistry, Kurukshetra University, Kurukshetra, India
[2]Department of Chemistry, Punjab Agricultural University, Ludhiana, India

ABSTRACT

An improved method for thiocyanation of 2-arylindan-1,3-diones, phenols, and anilines using a reagent combination of (dichloroiodo)-benzene and potassium thiocyanate in dry dichloromethane is described.

Key Words: Thiocyanation; Organohypervalent iodine; (Dichloroiodo) benzene; Potassium thiocyanate.

*Correspondence: Om Prakash, Department of Chemistry, Kurukshetra University, Kurukshetra-136119, India; E-mail: oprakash50@sify.com.

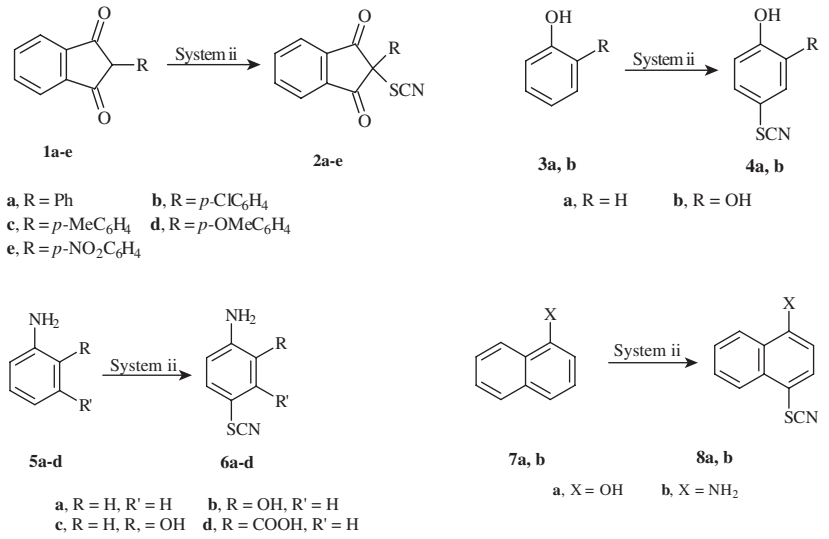
DOI: 10.1081/SCC-120026343 0039-7911 (Print); 1532-2432 (Online)

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

There is considerable recent interest in the use of organohypervalent iodine(III) compounds as oxidizing agents in organic synthesis.[1–3] We have recently reported that a combination reagent (dichloroiodo)benzene and lead thiocyanate in dichloromethane (system **i**) constitutes a very efficient reagent system for α-thiocyanation of carbonyl and β-dicarbonyl compounds.[2] The same reagent system has also been employed for the thiocyanation of phenols and anilines.[4]

In an effort to improve the experimental procedure and to avoid the use of toxic and expensive lead thiocyanate, we have now used an alternative reagent system, i.e., (dichloroiodo)benzene-potassium thiocyanate in dichloromethane (system **ii**) to effect these thiocyanations.

We, first carried out the reaction with 2-phenylindan-1,3-dione (**1a**) as a typical example of α-substituted β-dicarbonyl compounds, to afford 2-phenyl-2-thiocyanatoindan-1,3-dione (**2a**) in 85% yield. Other 2-arylindan-1,3-diones (**1b–e**) also reacted smoothly with system **ii** to give 2-aryl-2-thiocyanatoindan-1,3-diones (**2b–e**). The scope of this reagent system was further extended for thiocyanation of phenols and anilines. Only representative cases were investigated and it was found that system **ii** efficiently converts phenol (**3a**), catechol (**3b**), α-naphthol (**7a**), aniline (**5a**), substituted anilines (**5b–d**), α-naphthylamine (**7b**) to the corresponding *p*-thiocyanato derivatives **4a**, **4b**, **6a**, **6b–d**, **8a**, **8b** respectively (Sch. 1). The yields using system **ii** are comparable with



Scheme 1.

those obtained by using system **i** (Table 1). However, the same approach involving either systems **i** or **ii**, failed to convert other substrates such as *o*-phenylenediamine, *p*-phenylenediamine, and *p*-aminophenol to thiocyanato products; rather an inseparable mixture of several products was obtained.

Interestingly, in certain other cases such as β-naphthol **9** and hydroquinone **11**, these thiocyanation procedures using systems **i**/**ii** lead to the formation of oxathiole **10** and bisoxathiole **12** as outlined in Eqs. (1) and (2). Obviously intramolecular cyclization of thiocyanato or dithiocyanato product might have led to the formation of the corresponding oxathioles.

Earlier, thiocyanation of phenols and anilines has been reported (i) by using dichlorourea and NH_4SCN,[5] (ii) with Cu $(SCN)_2$,[6] (iii) by reaction with NaSCN and Br_2.[7]

EXPERIMENTAL

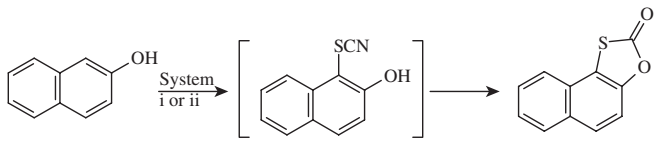
Melting points were taken in open capillaries and are uncorrected. Most of the chemicals were obtained from commercial suppliers. 2-Arylindan-1,3-diones (**1a–e**) were prepared according to the literature methods.[8,9]

Table 1. Physical data of thiocyanated products.

Compd. no.	M.p. (°C)	Lit. m.p. (°C)	Yield (%) system **i**	Yield (%) system **ii**
2a	124–125	124–126[10]	86	85
2b	124–125	127[10]	90	88
2c	108–110	108–110[2]	90	88
2d	139–140	138–140[10]	84	87
2e	125–127	126–128[10]	87	90
4a	58	59–60[4]	78	72
4b	142	142[4]	87	79
6a	102	97–98[11]	72	69
6b	100	98[4]	80	86
6c	106	107–109[4]	76	72
6d	171	168–170[5]	71	73
8a	110–112	113[7]	65	69
8b	147–148	146–147[7]	70	74
10	104	106[12]	73	77
12	303	308–309[13]	72	75

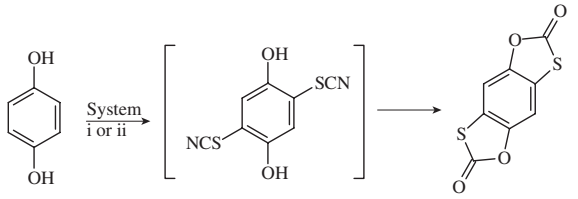
General Procedure for Thiocyanation Using $PhICl_2$-KSCN/CH_2Cl_2 (System ii)

To a suspension of potassium thiocyanate (464 mg, 4.8 mmol) in dichloromethane (10 mL), (dichloroiodo)benzene (656 mg, 2.4 mmol) was added at 0°C. The mixture was stirred at the same temperature for 15–20 min. Then the substrate (**1a–e**, **3a–b**, **5a–d**, **7a–b**, **9**, **11**) (2 mmol) (in case of **11**, 1 mmol) was added to it and stirring was continued for 30 min, completion of reaction was monitored by TLC. The reaction mixture was filtered and filtrate was adsorbed on silica gel and chromatographed using hexane:ethyl acetate (9:1) as eluent. The thiocyanato products (**2a–e**, **4a–b**, **6a–d**, **8a–b**) and oxathioles (**10** and **12**) were identified by comparison of their melting points (Table 1) and spectral data with those reported in literature. IR spectra of all the products showed a characteristic sharp SCN absorption band at ~2160 cm^{-1}.



(1)

9 **10**



(2)

11 **12**

System i = $PhICl_2$, $Pb(SCN)_2/CH_2Cl_2$

ACKNOWLEDGMENTS

We are thankful to DRDO, New Delhi, India for financial assistance to support this work.

REFERENCES

1. (a) Moriarity, R.M.; Vaid, R.K.; Koser, G.F. [Hydroxy(organosulfonyloxy)iodo] arenes in organic synthesis. Synlett. **1990**, 365–383; (b) Prakash, O.; Rani, N.; Sharma, P.K. Hypervalent iodine reagents in the synthesis of heterocyclic compounds. Synlett. **1994**, 221–227; (c) Varvoglis, A. *Hypervalent Iodine in Organic Synthesis*; Academic Press: London, 1997; (d) Varma, R.S.; Dhaiya, R.; Saini, R.K. Iodobenzene diacetate on alumina: rapid oxidation of alcohols to carbonyl compounds in solventless system using microwaves. Tetrahedron Lett. **1997**, *38*, 7029–7032; (e) Ochiai, M.; Akibia, K., Eds. In *Chemistry of Hypervalent Compounds*; VCH Publishers: New York, 1999; Chapter 13, 359–387; (f) Koser, G.F. [Hydroxy(tosyloxy)iodo]benzene and closely related iodanes: the Second Stage of Development. Aldrichimica Acta **2001**, *34*, 89–102; (g) Zhdankin, V.V.; Stang, P.J. Recent developments in the chemistry of polyvalent iodine compounds. Chem. Rev. **2002**, *102*, 2523–2584.
2. Prakash, O.; Kaur, H.; Batra, H.; Rani, N.; Singh, S.P. α-Thiocyanation of carbonyl and β-dicarbonyl compounds using (dichloroiodo)benzene-lead(II) thiocyanate. J. Org. Chem. **2001**, *66*, 2019–2023.
3. Kita, Y.; Takeda, Y.; Okunu, T.; Egi, M.; Iio, K.; Kawaguchi, K.; Akai, S. An efficient *p*-thiocyanation of phenols and naphthols using a reagent combination of phenyliodine dichloride and lead(II) thiocyanate. Chem. Pharm. Bull. **1997**, *45*, 1887–1890.
4. Neu, R. Aryl iododichlorides. Ber. **1939**, *72B*, 1505–1512.
5. Likhosherstov, M.V.; Petrov, A.A. The preparation of aromatic thiocyanates with the aid of dichlorourea. J. Gen. Chem. (USSR) **1933**, *3*, 183–197.
6. Kaufmann, H.P.; Kulchler, K. A further new method for the thiocyanation of organic compounds. Ber. **1934**, *67B*, 944–948.
7. Kaufmann, H.P.; Oehring, W. New method for the thiocyanation of organic compounds. Ber. **1926**, *59B*, 187–194.
8. Bailey, D.M.; Johnson, R.E. Reduction of cyclic anhydrides with sodium borohydride. Versatile lactone synthesis. J. Org. Chem. **1970**, *35*, 3574–3576.
9. Crabb, T.A.; Roxburgh, C.J.; Newton, R.F. The synthesis and stereochemistry of derivatives of 1,2,3,4,6,11,12,13,14,14a-decahydropyrido[1,2-b][2]benza zonine. Crystal structure of 1,2,3,4,4a,5,6,7,7a,12-decahydro-7-phenylisoindolo[1,2-d]quinolizin-1,3-ium tosylate. J. Chem. Soc. Perkin Trans I **1989**, 2431–2435.

10. Vanags, G.; Gudriniece, E.; Arens, A.; Arens, B. Thiocyanation of 2-aryl-1,3-indandiones. Doklady Akad. Nauk S.S.S.R. **1960**, *130* (315); Chem. Abstr. **1960**, *54*, 10974.
11. Wood, J.L. Substitution and addition reactions of thiocyanogen. *Org. React.*; Wiley: New York, 1946; Vol. 6, 240–266.
12. Stevenson, H.A.; Smiles, S. β-Naphtha-1-thioquinone and dehydro-2-naphthol 1-disulfide. **1930**, 1740–1745.
13. Fiedler, H. Jahrg. Preparation of hydroxy-2-oxo and 2-thiono-1,3-benzoxathioles. **1962**, *95*, 1771.