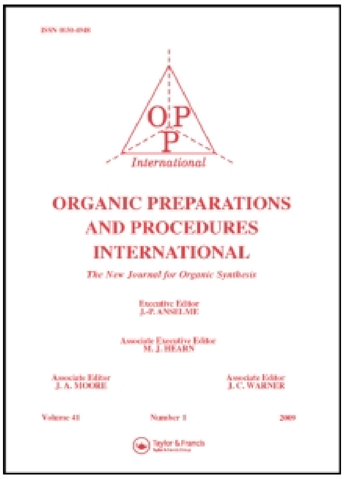
This article was downloaded by:
On: *27 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



OP
P
International
ORGANIC PREPARATIONS
AND PROCEDURES
INTERNATIONAL
The New Journal for Organic Synthesis
Executive Editor
J.-P. ANSELME
Associate Executive Editor
M. J. HEARN
Associate Editor
J. A. MOORE
Associate Editor
J. C. WARNER
Volume 41 Number 1 2009
Taylor & Francis

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

SANDMEYER TYPE REACTION IN DIMETHYL SULFOXIDE

Michio Kobayashi[a]; Eiichi Yamada[a]; Mikio Matsui[a]; Nobumasa Kobori[a]
[a] Department of Chemistry, Faculty of Science Tokyo Metropolitan University Setagaya-ku, Tokyo, Japan

To cite this Article Kobayashi, Michio , Yamada, Eiichi , Matsui, Mikio and Kobori, Nobumasa(1969) 'SANDMEYER TYPE REACTION IN DIMETHYL SULFOXIDE', Organic Preparations and Procedures International, 1: 4, 221 — 224

To link to this Article: DOI: 10.1080/00304946909458386

URL: http://dx.doi.org/10.1080/00304946909458386

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

ORGANIC PREPARATIONS AND PROCEDURES 1(4), 221-224 (1969)

SANDMEYER TYPE REACTION IN DIMETHYL SULFOXIDE

Michio Kobayashi, Eiichi Yamada,
Mikio Matsui, and Nobumasa Kobori

Department of Chemistry, Faculty of Science
Tokyo Metropolitan University
Setagaya-ku, Tokyo, Japan

Aromatic diazonium fluoborates are soluble in many aprotic polar solvents such as dimethyl sulfoxide. When these solutions are added to the solution of halides of copper or iron in the same solvent, reaction started immediately to form the aryl halides. Nitrogen evolution was almost quantitative. The reaction of the cuprous cyanide-sodium cyanide complex with diazonium salts gave aryl cyanides in good yields. In the usual Sandmeyer reaction,[1] it is recommended that freshly prepared cuprous cyanide be used and that the reaction mixture be stirred for a long time in order to secure good yields. In the present method, however, commercially available cuprous cyanide gave satisfactory yields, and the reaction was completed within a few minutes. Another interesting difference between this method and the ordinary Sandmeyer reaction is that cupric and ferric salts may be used for the preparation of aryl halides. Yields of aryl bromides with cupric bromide were sometimes almost quantitative. Moreover, the reaction with cuprous chlorides was accompanied by the formation of biaryls in a rather high yield. Halides of nickel or cobalt gave very poor yields of aryl halides. Several examples are shown in the following table.

Table

Diazonium fluoborate	Metal Salts	Main Products	bp./mmHg (mp.)	Yield[a)]
Benzene-	$FeCl_3$	Chlorobenzene		50[b)]
Benzene-	Cu_2Cl_2	Chlorobenzene Biphenyl		28;33[b)] 45;50[b)]
Biphenyl-2-	$FeCl_3$	o-Chlorobiphenyl	135-6/5	61
Biphenyl-3-	$FeCl_3$	m-Chlorobiphenyl	107-8/1	61
Biphenyl-4-	$FeCl_3$	p-Chlorobiphenyl	110/2 (76.5)	16
Biphenyl-2-	$CuBr_2$	o-Bromobiphenyl	114/2	70
Biphenyl-3-	$CuBr_2$	m-Bromobiphenyl	111/1	80
Biphenyl-4-	$CuBr_2$	p-Bromobiphenyl	(91.5-92.0)	97
Biphenyl-2-	$Cu_2(CN)_2$ NaCN	o-Cyanobiphenyl	167/5	60;74
Biphenyl-3-	$Cu_2(CN)_2$ NaCN	m-Cyanobiphenyl	146/3	55;60
Biphenyl-4-	$Cu_2(CN)_2$ NaCN	p-Cyanobiphenyl	118-120/1	62

a) Mole % based on the diazonium salts.

b) Determined by gas chromatography.

EXPERIMENTAL

Typical procedures for aryl bromides and aryl cyanides are described.

Preparation of p-Bromobiphenyl. A solution of biphenyl-p-diazonium fluoborate[2] (4.5 g) in DMSO (20 g) was added slowly to a stirred solution of cupric bromide (8.0 g) in DMSO (80 g). Rapid stirring is essential in order to obtain high yields. As soon as the addition was completed, the reaction mixture was diluted with water and extracted with benzene. Evaporation of the solvent gave 3.8 g (97%) of p-bromobiphenyl, m.p. 92° (from EtOH).

Preparation of m-Cyanobiphenyl. Commercial cuprous cyanide[3] (37 g) and finely powdered sodium cyanide (26 g) were mixed with DMSO (200 g). The viscous resin which initially precipitated gradually dissolved, and a clear homogeneous solution was obtained. To this solution was added a solution of biphenyl-m-diazonium fluoborate[4] (26 g) in DMSO (90 g) at room temperature under vigorous stirring. The reaction was very rapid in this case too, as shown by the rise in temperature; efficient cooling with ice bath was necessary. After the addition of the diazonium solution, the mixture was diluted with water and worked by as above to yield 8.5 g (50%) of m-cyanobiphenyl, b.p. 146°/3 mm.

REFERENCES

1. For example see "Organic Syntheses", Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N.Y., p. 170, 514, (1961).

2. M. F. W. Dunker, E. B. Starkey, and G. L. Jenkins, J. Am. Chem. Soc., 58, 2308 (1936).

3. Present authors used first grade product from Wako Pure Chemical Industries Ltd. (Tokyo), which may be comparable to that obtainable from Mallinckrodt Chemical Works.

4. Prepared from m-aminobiphenyl in a way similar to that of p-isomer.

(Received November 7, 1968)