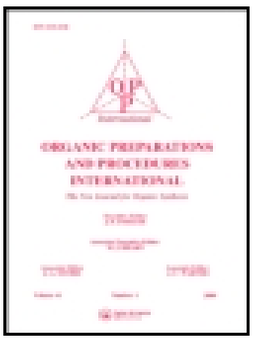

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DIRECT α-HYDROXYLATION OF ARYL KETONES USING A HYPERVALENT IODINE(III) SULFONATE

Submitted by (01/25/06)

H.-Y. Huang[†], R.-S. Hou[††] H.-M. Wang[††], and L.-C. Chen*[†]

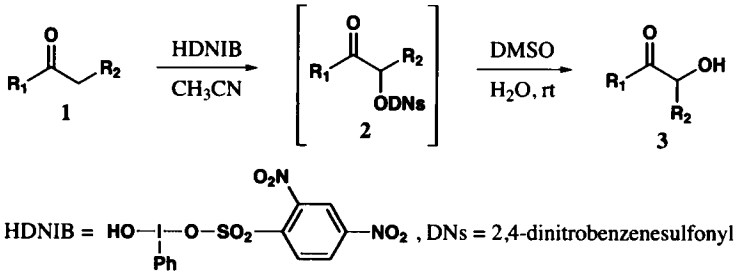
[†] *Graduate Institute of Pharmaceutical Sciences, College of Pharmacy Kaohsiung Medical University, Kaohsiung Taiwan 807, Republic of CHINA*

[††] *Chung Hwa College of Medical Technology Tainan, Taiwan 717, Republic of CHINA*

e-mail: m715003@cc.kmu.edu.tw

α-Hydroxyketones are widely used intermediates and are important constituents of many biologically important natural products.[1] The methods used for their synthesis involve the direct α-hydroxylation of ketones under basic[2] or acidic conditions.[3] Only a few reports in the literature account for the direct α-hydroxylation of ketones under neutral conditions.

Recently, hypervalent iodine(III) reagents have been used extensively in organic synthesis due to their low toxicity, ready availability and easy handling.[4] As a part of our on-going studies to utilize hypervalent iodine (III) reagents in organic synthesis, we report here a new and direct method for the synthesis of α-hydroxy aryl ketones by the reaction of aryl ketones with [hydroxy-(2,4-dinitrobenzenesulfonyloxy)iodo] benzene (HDNIB) under mild conditions. The required HDNIB was prepared in satisfactory yields from the reaction of 2,4-dinitrobenzenesulfonic acid with phenyliodine (III) diacetate (PIDA).[5] Treatment of aryl ketones (**1**) with HDNIB in CH_3CN at reflux for 1 h produced the α-(2,4-dinitrobenzenesulfonyloxy)-ketone intermediates (**2**),[5] which can then undergo hydrolysis with DMSO-H_2O system at room temperature for 2 h to give α-hydroxyaryl ketones (**3**) in good yields as shown in the *Scheme*.



a) $R_1 = C_6H_5, R_2 = H$; b) $R_1 = 4\text{-}MeC_6H_4, R_2 = H$; c) $R_1 = 4\text{-}MeOC_6H_4, R_2 = H$; d) $R_1 = 4\text{-}ClC_6H_4, R_2 = H$; e) $R_1 = 4\text{-}BrC_5H_4, R_2 = H$; f) R_1 = 3-Furyl, $R_2 = H$; g) R_1 = 3-Thienyl, $R_2 = H$; h) $R_1 = C_6H_5, R_2 = Me$; i) $R_1 = C_6H_5, R_2 = C_6H_5$

Our experiments involving a one-pot procedure for the preparation of α-hydroxy- aryl ketones (**3**) by treatment of HDNIB with aryl ketones and subsequent hydrolysis using DMSO-H_2O at room temperature was successful. The results are summarized in the Table. When the reaction was conducted by replacing HDNIB with HTIB (Koser's reagent)[6] under the same conditions, the preparation of 2-hydroxy-1-phenylethanone (**3a**) requires refluxing for 7 h. This observation clearly demonstrated that the leaving ability of –ODNs is superior to –OTs in nucleophilic substitution reactions.

Table. Preparation of α-Hydroxyketones **3a-i**

Cmpd[a]	Yield (%)	mp. (°C)	*lit.* mp. (°C)
3a	88	87-88	80-82[7]
3b	85	79-80	81-83[7]
3c	83	104-105	99-101[7]
3d	86	120-121	118-120[7]
3e	84	133-134	134-136[7]
3f	78	80-81	79-81[7]
3g	76	71-72	73-74[8]
3h	82	Oil	Oil[7]
3i	72	129-131	126-128[7]

a) All products are known compounds and their physical constants, IR and ^1H NMR spectra correspond to those reported in literature.

In summary, the method described herein provides a good approach for the synthesis of α-hydroxyarylketones by the reaction of aryl ketones with hypervalent iodine(III) sulfonate (HDNIB) and subsequent hydrolysis using DMSO-H_2O at room temperature in a one-pot procedure.

EXPERIMENTAL SECTION

All melting points are uncorrected. The IR spectra were recorded on a Shimadzu IR-27 G spectrophotometer. ^{1}H NMR spectra were recorded on a Varian Unity Plus 400 MHz. Chemical shifts (δ) were measured in ppm with respect to TMS. MS were obtained on a JEOL JMS D-300 instrument.

Typical Procedure.- A mixture of acetophenone (120 mg, 1.0 mmol) and HDNIB (468 mg, 1.0 mmol) in acetonitrile (20 mL) was heated at reflux for 1 h. After the reaction mixture had been cooled to room temperature, 12 mL of DMSO-H_2O (1 : 2) was added and the mixture was stirred at room temperature for 2 h. After removal of acetonitrile under reduced pressure, the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure. The resulting residue was then dissolved in Et_2O, washed with H_2O, and dried over $MgSO_4$. The solvent was evaporated off and the residue was purified by chromatography on silica gel eluting with AcOEt-*n*-hexane (1:3) to give 120 mg (88%) of **3a**. IR (KBr): 3425, 1684 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.25-3.75 (br s, 1H), 4.88 (s, 2H), 7.49-7.94 (m, 5H); MS (EI) m/z : 136 (M^+), 105, 83, 57, 45.

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IMPROVED METHOD FOR THE CYCLIZATION OF *ortho*-ALKYNYLBENZENEDIAZONIUM SALTS

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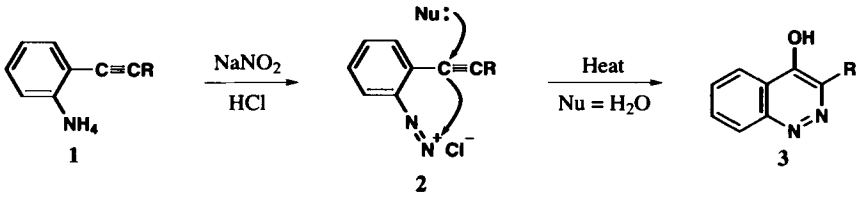
Nataliya A. Zolnikova, Lidiya G. Fedenok* and Nikolay E. Polyakov

Institute of Chemical Kinetics and Combustion,
Siberian Branch of Russian Academy of Sciences
Institutskaya 3, 630090 Novosibirsk, RUSSIA
e-mail: fedenok@kinetics.nsc.ru

In the last decade, the Richter reaction has elicited considerable interest among chemists for two reasons: 1) the requirement to produce condensed heteroaromatic compounds with high biological activity, and 2) creation of convenient methods for introduction of alkyne groups into the aromatic ring, thereby making *vic*-alkynylaminoarenes accessible.[1] The cyclization of *ortho*-alkynylbenzenediazonium salts, discovered by Richter,[2] has been applied to the preparation of 4-hydroxycinnoline derivatives (*Eq. 1*).[3,4]



1 2 3 (1)

In the standard procedure, the conversion of anilines **1** into cinnolines **3** can be realized in a one-pot preparation. At the same time, the Richter reaction for the preparation of some cinnoline derivatives is limited because of its rigorous conditions. Acidity and high temperature lead to poor results in the conversion of *vic*-alkynylaminoarenes because of the concurrent hydrolysis of some functional groups. Transformation of the amino group (compound **1**) to the diazonium salt (compound **2**) enhances the reactivity of substituents; for example, all attempts to perform the cyclization of the 3-diethylamino-6-(heptyn-1-yl)-1,4-naphthoquinone-5-diazonium