

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



Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

SELECTIVE PREPARATION. 44. PREPARATION OF 4-HYDROXYPHENYL PHENYL THIOETHER USING *t*-BUTYL FUNCTION AS A POSITIONAL PROTECTIVE GROUP

Masashi Tashiro^a; Haruo Yoshiya^a

^a Research Institute of Industrial Science, and Department of Molecular Science and Technology, Graduate School of Engineering Sciences Kyushu University, Kasuga-shi, Fukuoka, Japan

To cite this Article Tashiro, Masashi and Yoshiya, Haruo(1983) 'SELECTIVE PREPARATION. 44. PREPARATION OF 4-HYDROXYPHENYL PHENYL THIOETHER USING *t*-BUTYL FUNCTION AS A POSITIONAL PROTECTIVE GROUP', *Organic Preparations and Procedures International*, 15: 4, 276 – 278

To link to this Article: DOI: 10.1080/00304948309356655

URL: <http://dx.doi.org/10.1080/00304948309356655>

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.

SELECTIVE PREPARATION. 44.

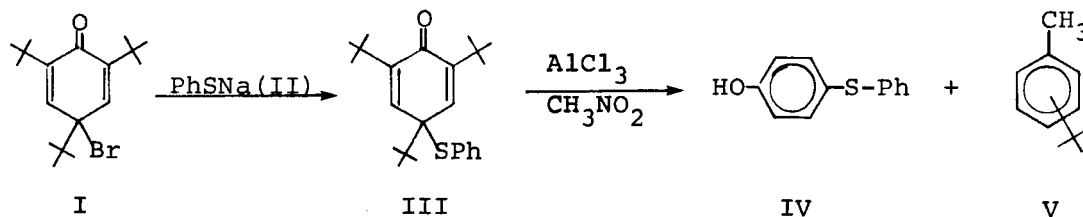
PREPARATION OF 4-HYDROXYPHENYL PHENYL THIOETHER USING
t-BUTYL FUNCTION AS A POSITIONAL PROTECTIVE GROUP[†]

Submitted by Masashi Tashiro* and Haruo Yoshiya
(1/28/83)

Research Institute of Industrial Science, and
Department of Molecular Science and Technology
Graduate School of Engineering Sciences
Kyushu University 86
Sakamoto, Kasuga, Kasuga-shi, Fukuoka 816, JAPAN

The aluminum chloride-catalyzed transalkylation of 4-aryl-oxy-2,4,6-tri-t-butyl-2,5-cyclohexadien-1-ones, which were prepared by reaction of 4-bromo-2,4,6-tri-(t-butyl)-2,5-cyclohexadien-1-one (I) with the corresponding sodium phenoxides, afforded the corresponding 4-hydroxyphenyl aryl ethers.¹

In the present work, the title compound (III) was prepared from I by application of the above reaction.



When I was reacted with sodium thiophenoxide (II) in THF at 70° for 5 min, the expected III was obtained together with IV and V. However, compound III was so labile that its purification could not be carried out by recrystallization or chromatography on silica gel.² Therefore, transalkylation of the crude III was carried out in toluene in the presence of AlCl₃-CH₃NO₂ catalyst at 60° for 3 hrs. The desired compound IV was obtained in 48% yield calculated from I together with V.

EXPERIMENTAL SECTION

Reaction of I with II.- To a solution of NaOCH_3 in methanol, prepared by addition of 0.67 g of Na in 20 ml of methanol, was added 3.2 g (20 mmol) of thiophenol under cooling with ice-water. The mixture was evaporated in vacuo to give sodium salt II. After a mixture of the obtained II and 9.9 g (20 mmol) of I in 60 ml of THF was heated at 70° for 5 min, the precipitated NaBr was filtered. The filtrate was evaporated in vacuo to give 3.8 g of crude III, which was used as a starting compound for preparation of IV without purification.

Transalkylation of III.- After a mixture of 3.8 g of the crude III and $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ catalyst (AlCl_3 4.1 g and CH_3NO_2 6 ml) in 163 ml of toluene was heated at 60° for 3 hrs with stirring, it was poured into a large amount of water and extracted with ether. The ethereal extract was extracted with aq. 10% NaOH. The alkaline solution was acidified with aq. 10% HCl and extracted with ether. The ethereal extract was washed with water, dried over Na_2SO_4 and evaporated in vacuo to leave the residue which was chromatographed on silica gel using benzene as an eluent to give 2.5 g (48% calculated from II used) of IV as a pale brown oil. IR(NaCl): ν_{OH} 3430 cm^{-1} ; $^1\text{H-NMR}(\text{CDCl}_3)$: δ 6.32 (s, 1H, OH) and 6.78 ~ 7.48 (m, 9H, aromatic protons). The IR spectrum of IV agreed with that of an authentic sample.³

REFERENCES

- Part 43, M. Tashiro, K. Nakayama and G. Fukata, To be published.
1. M. Tashiro, H. Yoshiya and T. Yamato, *Synthesis*, 399 (1978).

2. For example, chromatography on silica gel using a mixture of hexane and benzene (1:1) as eluent, gave diphenyldisulfide and 2,4,6-tri-(*t*-butyl)phenol in 63% and 69% yields respectively.
3. O. Hinsberg, Ber., 36, 107 (1903).

SYNTHESIS OF 3-ACETOXY-1-METHYL AND 1-ETHYLINDOLES

Submitted by Roy W. Daisley* and Zaha A. Elagbar
(12/14/83)

Department of Pharmacy, Brighton Polytechnic
Lewes Road
Brighton, Sussex, BN2 4GJ, ENGLAND

Indol-3(2H)-ones (indoxyls) (II) may be synthesized by the cyclization of the appropriate phenylglycines (I) or the appropriate 2-carboxyphenylglycine. Cyclizing agents for the former include sodium or potassium hydroxide¹ at 260° or soda-mide with cyanide moderators;² however, the indoxyl once formed has a great tendency to oxidize to indigo unless air is rigorously excluded from the reaction and work-up procedures and yields tend to be low. Although cyclization of 2-carboxyphenylglycines proceeds smoothly using acetic anhydride and sodium acetate at reflux temperatures,^{3,4} the corresponding *N*-substituted 2-carboxyphenylglycines are not readily available and

