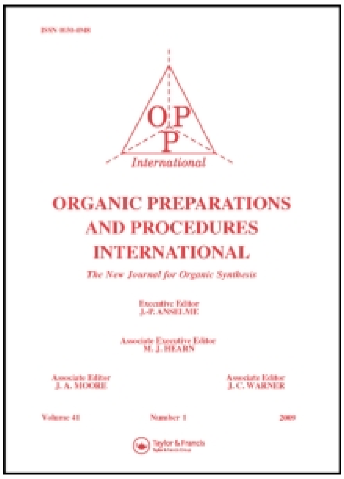
This article was downloaded by:
On: *27 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

AN IMPROVED SYNTHESIS OF 2-METHALLYLOXYPHENOL

V. B. Deodhar[a]; V. S. Dalavoy[a]; U. R. Nayak[a]
[a] National Chemical Laboratory, Pune, INDIA

To cite this Article Deodhar, V. B. , Dalavoy, V. S. and Nayak, U. R.(1993) 'AN IMPROVED SYNTHESIS OF 2-METHALLYLOXYPHENOL', Organic Preparations and Procedures International, 25: 5, 583 — 585
To link to this Article: DOI: 10.1080/00304949309458004
URL: http://dx.doi.org/10.1080/00304949309458004

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.

EXPERIMENTAL SECTION

Melting point are uncorrected and were taken on a Büchi 535 apparatus. Elemental analyses were carried out on a Carlo Erba 1106 apparatus. IR spectra were determined on a Shimadzu IR-435 spectrophotometer. ^{1}H NMR spectra were recoded on a Bruker QC-P200 spectrometer in $CDCl_3$ using TMS as internal standard.

General Procedure for the Synthesis of bis(3-Aryl-3-oxo-l-propenyl)benzenes.- A mixture of **1** (0.5 mmol), **2** (1 mmol) and BMPTO (0.03g)[3] in DMSO (5 mL) was stirred at 80°; the progress of the reaction was monitored by TLC. When the reaction was complete, water (5 mL) was added and precipitated the product was collected and dried. The pure products (**4** and **5**) were obtained by column chromatography on silica gel (1:2 petroleum ether-dichloromethane).

REFERENCES

1. a) S. V. Tsukerman, V. M. Nikitchenko, V. P. Maslennikova and V. F. Lavrnshin, *Khim. Geterotsikl. Soedin.*, **7**, 1094 (1971); *Chem. Abs.*, **76**, 34158s (1972); b) S. F. Chang and K. K. Hsu, *Taiwan Ko Hsueh*, **32**, 87 (1978); *Chem. Abs.*, **91**, 91448v (1979).

2. Q. Zhong and R. J. Lu, *Chin. J. Appl. Chem.* 7, 89 (1990); *Chem. Abs*, **114**, 61639j (1991); Q. Zhong, J. G. Shao and C. Q. Liu, *ibid.*, **8**, 17 (1991); *Chem. Abs.*, **116**, 83329b (1992); Q. Zhong, Y. J. Lu, C. Q. Liu, W. G. Tao and Y. J. Zhou, *Chin., Chemical Lett.*, **2**, 683 (1991); *Chem. Abs.*, **116**, 173723e (1992).

3. N. Petragnani and J. V. Comasseto, *Synthesis*, 29 (**1986**).

4. A. I. Makhotilo and V. G. Tishchenko, *Zh. Org. Khim.*, **9**, 1730 (1973).

Downloaded At: 09:17 27 January 2011

****

AN IMPROVED SYNTHESIS OF 2-METHALLYLOXYPHENOL[†]

Submitted by (01/19/93)

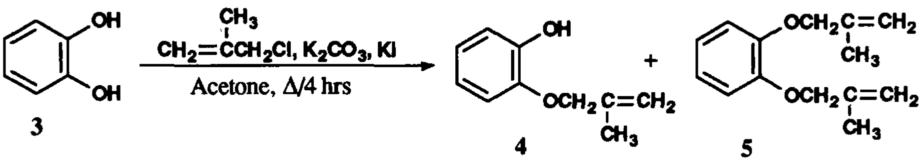
V. B. Deodhar*, V. S. Dalavoy, U. R. Nayak

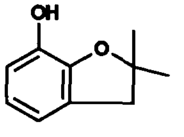
National Chemical Laboratory
Pune-411 008, INDIA

2,2-dimethyl-2,3-dihydro-7-hydroxybenzofuran (1),[1] a synthon for the insecticide carbofuran (2)[2] is obtained by Claisen rearrangement-cyclization of 2-methallyloxyphenol (4).[1] Various methods have been reported for the preparation of 4 by monoalkylation[3] of catechol by β-methallyl chloride. All reported methods are patented and involve long reaction time[3a,c] or preparation *in situ*,[3e] or water-

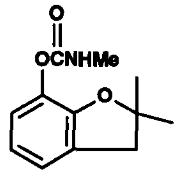
Downloaded At: 09:17 27 January 2011

aided preparation of 4[3f] in 48% conversion. We now report the preparation of 4 from catechol in 70% conversion by refluxing an acetone solution of catechol with β-methallyl chloride in the presence of K_2CO_3 for 4 hrs. A simple work-up allows the clean separation of the products in 54% yield. The reported procedure in contrast gives 44% yield after refluxing the reaction mixture for 30 hrs and lengthy work-up involving standing for 18 hrs followed by filtration, concentration and extraction of the filtrate with $CHCl_3$.





1



2

EXPERIMENTAL SECTION

Petroleum ether refers to fraction of bp. 60-80°. IR spectra were recorded on a Pye-Unicam SP-3 IR spectrophotometer. NMR spectra were obtained on a Varian T-60 spectrometer using TMS as an internal standard. The mass spectra were recorded on a CEC spectrometer model 21-110B using an ionizing voltage 70 eV and a direct inlet system. Yields are based on catechol consumed.

2-Methallyloxyphenol (4).- A mixture of catechol (5.5 g, 0.05 mol), K_2CO_3 (6.9 g, 0.05 mol), KI (8.3 g, 0.05 mol) and β-methallyl chloride (5 g, 0.055 mol) in 31.25 mL of acetone was refluxed for 4 hrs cooled and diluted with water (70 mL). The solution was acidified with conc. HCl and extracted in sequence with petroleum ether (3 x 60 mL) and ethyl acetate (3 x 60 mL). The latter extract was washed with water, brine and dried (Na_2SO_4). Removal of solvent gave 1.2 g (22%) of unchanged catechol, mp. 105°. The petroleum ether extract was washed successively with 20% KOH (3 x 25 mL), water, brine and dried (Na_2SO_4). The solvent was removed and the residue was distilled to give 1,2-dimethallyloxybenzene (5), bp. 120° (bath)/2.5 mm, as a pale yellow oil (1.4 g, 15%). IR (neat): 3100, 3040, 1675, 1610, 1510, 1140, 920, 810 and 760 cm^{-1}. ^1H NMR (CCl_4): δ 1.75 (s, 6H, 2 x $C\underline{H}_3$-C=), 4.3 (s, 4H, 2 x-$OC\underline{H}_2$), 4.8 and 5.03 (4H, 2 x =$C\underline{H}_2$), 6.7 (s, 4H, aromatic). MS: M^+ 218.
Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 7.37. Found: C, 77.28; H, 7.25

The alkaline layer was acidified with conc. HCl and extracted with petroleum ether (3 x 60 mL). The organic layer was washed with water, brine and dried (Na_2SO_4). Removal of solvent and the distillation of the residue furnished a pale yellow oil (4.41 g, 70%) of 2-methyallyloxyphenol (4), bp. 110-120°/2.5mm. lit.[1] bp. 78.5-85°/0.55mm. IR (neat): 3540, 3060, 1670, 1610, 1510, 1120, 920, 790 and 750 cm^{-1}. H NMR (CCl_4): δ 1.8 (s, 3H, CH_3-C=), 4.46 (s, 2H, -OCH_2), 4.9, 5 (2H, CH_2=C<), 5.46 (s, 1H, OH), 6.76 (m, 4H, aromatic).

REFERENCES

† NCL Communication No.5710

1. M. Sittig, "*Pesticide Manufacturing and Toxic Material Control Encyclopedia*" p. 144; Noyes Data Corporation Park Ridge, NJ, USA (1980).

2. C. R. Worthing, "*The Pesticide Manual*", 7th Ed. p. 91; British Crop Protection Council, Croydon (1983).

3. a) FMC Corp. Neth. 6,500,340 (1965); *C. A.*, **64**, 3484 (1966); b) FMC Corpn. Neth. 76,03,042 (1976); *C. A.*, **86**, 166412m (1977); c) G. Toth, J. Csazar, I Turcscan, I Jelinek, E. Somfai, G. Szabo, L. Nagy, I. Toth and T. Montory, *Hung Teljes*, 15718 (**1978**); *C. A.*, **91**, 51U6c (1979); d) G. Buettner, K. F. Christman, M. F. Lenthe and U. Allenbach, *Ger. Offen.* 2,932,458; (1981); *C. A.*, **95**, 7040h (1981); e) S. Canpolmi, V. Carletti, M. Marchi, *Eur.*, 40,400 (**1981**), *C. A.*, **96**, 85241j (1982); f) P. B. Hobson, R. E. Keay, FMC Corp. USA, US, 4,618,728 (1986); *C. A.*, **106**, 101866z (1987).

****

Downloaded At: 09:17 27 January 2011

SYNTHESIS OF 1-HYDROXY-7-PHENOXYNAPHTHALENE

Submitted by
(01/19/93)

Alan R. Katritzky*[§], Marudai Balasubramanian[§] and Michael Siskin*[#]

[§] *Center for Heterocyclic Compounds, Department of Chemistry*
University of Florida, Gainesville, FL 32611-2046

[#] *Corporate Research Science Laboratory*
Exxon Research and Engineering Company, Annandale, NJ 08801

Cleavage of diaryl ethers containing one-to-three rings and a hydroxyl group is an important pathway for depolymerization of low rank coals, and oil shales, into synthetic liquid fuels.[1] There are no reports in the literature on the synthesis of such structures to allow study of their reactivity. Preparation of 7-phenoxy-1-hydroxynaphthalene (**5**) is now reported *via* the synthesis of a tetralone derivative (**4**) in which the phenoxy group is already built in the bicyclic system.

Treatment of the diphenyl ether (**1**) with succinic anhydride in the presence of $AlCl_3$ by a literature procedure[2] gave 3-(p-phenoxybenzoyl)propionic acid (**2**) in 90% yield. Clemmensen reduction[3] of the carbonyl function of **2** gave (**3**) 4-(4-phenoxyphenyl)butyric acid[3] in only 40% yield. However,