Selective *o*-Vinylation of Phenols; Synthesis of 2-(1-Phenylethenyl)-phenols

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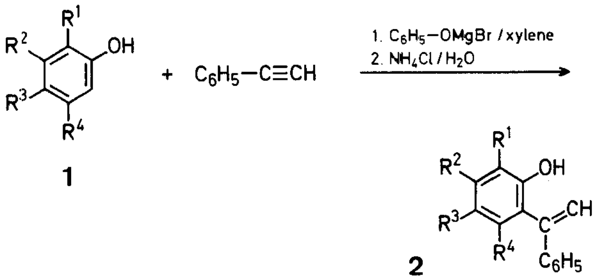
Phenol and related aromatic compounds react with alkynes to give, according to the catalyst employed, aryl vinyl ethers, 1,1-dihydroxydiarylalkanes, or highly condensed resinous products[1]. In general, no nuclear vinyl compounds are produced.

We now report a convenient and highly selective method for the direct *o*-vinylation of phenols[2] (**1**) with phenylacetylene[3] leading to 2-(1-phenylethenyl)-phenols (**2**) the synthesis of which has hitherto only been accomplished by indirect procedures[4,5]. The method consists of treatment of an equimolar mixture of phenol and phenoxymagnesium bromide with phenylacetylene in xylene under reflux; compounds **2** are obtained in 20–70% yields (56–93% based on unrecovered substrate).



As can be seen from Table 1, the reaction may be carried out with a variety of substituted phenols (**1**). However, in the case of phenols having strongly electron-withdrawing groups the yields are low or the reaction fails at all. The ratio phenol:phenoxide seriously affects the course of the reaction; both, conversion of **1** and yield of **2** are maximum at the ratio 1:1, whereas the use of smaller or larger amounts of phenoxide results in a marked decrease in yield.

Unfortunately, our attempts to extend the procedure to acetylene and to other alkynes were unsuccessful.

Table 1. 2-(1-Phenylethenyl)-phenols (**2**) prepared

2	R^1	R^2	R^3	R^4	Yield [%][a]	n_D^{20}	Molecular formula[b]
a	H	H	H	H	23 (60)[c]	1.5955[d]	$C_{14}H_{12}O$ (196.2)
b	CH_3	H	H	H	30 (75)	1.6020[e]	$C_{15}H_{14}O$ (210.2)
c	t-C_4H_9	H	H	H	60 (80)	1.5815	$C_{18}H_{20}O$ (252.3)
d	H	H	CH_3	H	35 (83)	1.6000	$C_{15}H_{14}O$ (210.2)
e	CH_3	H	H	CH_3	20 (56)	1.5995	$C_{16}H_{16}O$ (224.3)
f	t-C_4H_9	H	CH_3	H	68 (85)	1.5780	$C_{19}H_{22}O$ (266.3)
g	H	H	Cl	H	55 (81)	1.6090	$C_{14}H_{11}ClO$ (230.7)
h	H	H	OCH_3	H	20 (85)	1.6135	$C_{15}H_{14}O_2$ (226.3)
i	H	H	—CH=CH—CH=CH—		70 (93)	(m.p. 117–119°)[f]	$C_{18}H_{14}O$ (246.3)

[a] Yields of pure products. The yields in brackets are based on reacted starting phenol.

[b] The microanalyses had the following maximum deviations from the calculated values: C, ±0.33; H, ±0.33; Cl, −0.06.

[c] In boiling mesitylene (b.p. 163–166°).

[d] Ref.[4], n_D^{18}: 1.6193.

[e] Ref.[4], n_D^{20}: 1.6075.

[f] Colorless crystals from hexane.

Table 2. Significant Spectrometric Data of Compounds **2**

Compound	Mass Spectra[a] m/e (M^+)	I.R. (film)[b] ν_{max} [cm^{-1}]	U.V. (C_2H_5OH)[c] λ_{max} [nm] (log ε)	^{1}H-N.M.R. ($CDCl_3$)[d] δ [ppm]
2a	196	1639, 1428, 905	226 (3.98), 245 (3.89)[i], 280 (3.45)[i]	4.67 (s, 1H, OH); 5.38, 5.82 (dd, 2H, CH_2, $J = 1.8$ Hz); 6.6–7.1 (m, 4H_{arom}); 7.21 (bs, 5H, phenyl)
2b	210	1639, 1449, 925	230 (4.07), 247 (3.98)[i], 278 (3.44)[i], 288 (3.24)[i]	2.23 (s, 3H, CH_3); 5.21 (s, 1H, OH); 5.36, 5.82 (dd, 2H, CH_2, $J = 1.8$ Hz); 6.5–7.2 (m, 3H_{arom}); 7.22 (bs, 5H, phenyl)
2c	252	1639, 1449, 925	221 (4.16), 234 (4.08)[i], 248 (3.99)[i], 278 (3.51)[i]	1.35 (s, 9H, t-C_4H_9); 5.46 (s, 1H, OH); 5.39, 5.90 (dd, 2H, CH_2, $J = 1.8$ Hz); 6.6–7.0 (m, 3H_{arom}); 7.21 (bs, 5H, phenyl)
2d	210	1613, 1460, 917	234 (3.99), 249 (3.89)[i], 289 (3.44)	2.21 (s, 3H, CH_3); 4.95 (s, 1H, OH); 5.35, 5.79 (dd, 2H, CH_2, $J = 1.8$ Hz); 6.6–7.1 (m, 3H_{arom}); 7.26 (bs, 5H, phenyl)
2e	224	1626, 1418, 921	227 (4.01), 248 (4.02), 278 (3.47)[i], 289 (3.22)[i]	1.90 (s, 3H, CH_3); 2.21 (s, 3H, CH_3); 5.19 (s, 1H, OH); 5.23, 6.00 (dd, 2H, CH_2, $J = 1.8$ Hz); 6.50, 6.87 (two d, 2H_{arom}, $J = 8.0$ Hz); 7.25 (bs, 5H, phenyl)
2f	266	1640, 1452, 923	230 (4.12), 248 (4.01)[i], 278 (3.55)[i], 299 (3.28)[i]	1.40 (s, 9H, t-C_4H_9); 2.23 (s, 3H, CH_3); 5.26 (s, 1H, OH); 5.37, 5.87 (dd, 2H, CH_2, $J = 1.8$ Hz); 6.75, 7.03 (two d, 2H_{arom}, $J = 2.0$ Hz); 7.29 (bs, 5H, phenyl)
2g	230	1612, 1449, 925	231 (4.08), 250 (3.84)[i], 293 (3.37)	5.02 (s, 1H, OH); 5.43, 5.76 (dd, 2H, CH_2, $J = 1.8$ Hz); 6.6–7.2 (m, 3H_{arom}); 7.28 (bs, 5H, phenyl)
2h	226	1613, 1428, 925	240 (4.00), 302 (3.53)	3.67 (s, 3H, OCH_3); 4.79 (s, 1H, OH); 5.35, 5.80 (dd, 2H, CH_2, $J = 1.8$ Hz); 6.5–6.9 (m, 3H_{arom}); 7.30 (bs, 5H, phenyl)
2i	246	1613, 1430, 917	235 (4.65), 278 (3.85), 289 (3.77), 334 (3.53)	5.52 (s, 1H, OH); 5.46, 6.26 (dd, 2H, CH_2, $J = 1.8$ Hz); 7.0–7.9 (m, 11H, all other protons)

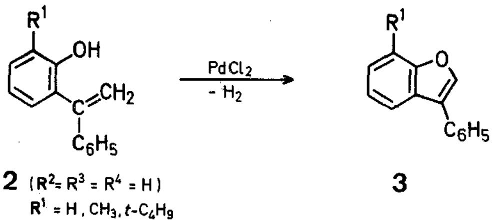
[a] Recorded on a Varian CH5 instrument.

[b] Recorded on a Perkin-Elmer 137 instrument.

[c] Recorded on a Perkin-Elmer 475 instrument; [i]indicates an inflection.

[d] Recorded on a Varian XL 100 instrument at 100 MHz, TMS as internal standard.

The structures of all products **2** were established by a detailed analysis of their 100 MHz ^{1}H-N.M.R. spectra (Table 2); analytical data, I.R., U.V., and mass spectra further confirmed the proposed structures. The purity of all compounds prepared was checked by T.L.C. and G.L.C. techniques. An additional proof of the structure was obtained by cyclodehydrogenation of three of the products **2** to give 3-phenyl-1-benzofurans (**3**) using the procedure of Cardillo et al.[6].



2 ($R^2 = R^3 = R^4 = H$)
$R^1 = H, CH_3, t\text{-}C_4H_9$

3

Preparation of 2-(1-Phenylethenyl)-phenols (2); General Procedure: The phenoxymagnesium bromide (0.02 mol) is prepared from phenol (0.02 mol) and ethylmagnesium bromide (0.02 mol) in ether (50 ml) at room temperature. Then, the ether is removed in vacuo, and anhydrous xylene (mixture of isomers, b.p. 136–140°; 100 ml), phenol (0.02 mol), and phenylacetylene (0.04 mol) are added and the mixture is heated under reflux for 24 h. After cooling, the reaction mixture is poured into an excess of saturated aqueous ammonium chloride and extracted with ether. The ether layers are washed with water, dried with magnesium sulfate, and rotary-evaporated to give an oily residue from which **2** can be easily separated by column or preparative thin-layer chromatography on silica gel using hexane/ethyl acetate (9:1). For liquid compounds, further purification can be accomplished by bulb-to-bulb distillation under reduced pressure (60–80°/0.01 torr).

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[2] For the synthesis of *o*-vinylphenols (in general) see: A. R. Bader, *J. Am. Chem. Soc.* **77**, 4155 (1955), and references therein.

[3] For the reaction of phenol with phenylacetylene under acidic conditions see:
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