One-Pot Conversion of Phenols to Arenes

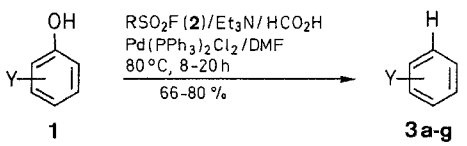
Qing-Yun Chen,* Ya-Bo He

Shanghai Institute of Organic Chemistry, Academic Sinica, 345 Lingling Lu, Shanghai, People's Republic of China

In the presence of a fluoroalkanesulfonyl fluoride and a catalytic amount of bis(triphenylphosphine)palladium dichloride, phenols reacted with triethylammonium formate in triethylamine to give arenes. Similarly, phenols reacted with alkynes or alkenes in triethylamine providing alkynyl- or alkenylarenes, respectively.

Recently, we[1] and others[2] reported that palladium could insert into the carbon–oxygen bond of phenyl fluoroalkanesulfonate (RSO_2OPh), thus the Heck reaction was accomplished by treating RSO_2OPh with alkynes or alkenes in the presence of palladium.[1a] Similarly, the removal of the hydroxy group from phenols via palladium-catalyzed reduction of RSO_2OAr by trialkylammonium formate could be carried out successfully,[1b,2] which was easier than that by using molecular hydrogen reported.[3] As an extension of our work, we wish to present a simple conversion of phenols to arenes by a one-pot reaction.

Phenols **1** reacted with fluoroalkanesulfonyl fluoride **2**[4] and triethylammonium formate catalyzed by bis(triphenylphosphine)palladium dichloride in triethylamine giving arenes in excellent yield (Table 1).



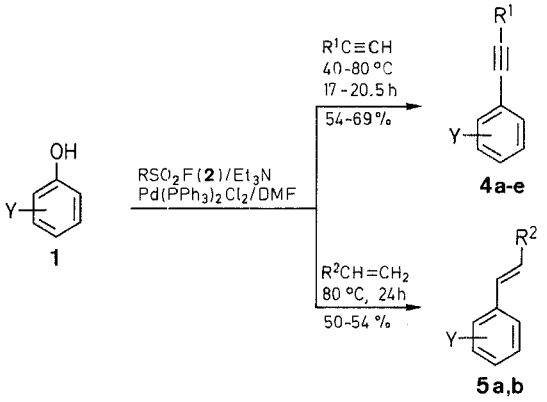
2	R	2	R
a	$HCF_2CF_2OCF_2CF_2$	c	$H(CF_2)_6OCF_2CF_2$
b	n-C_8F_{17}	d	$CF_3CF_2O(CF_2)_4OCF_2CF_2$

1, 3	Y	1, 3	Y	1, 3	Y
a	H	d	4-MeO	f	2-MeO, 4-CHO
b	4-Cl	e	3-MeO	g	2,3-(CH=CH)$_2$
c	2-Cl				

Table 1. Compounds **3** Prepared[a]

Substrate	RSO_2F	Time (h)	Product	Yield[b] (%)	bp (°C)[c] found	bp (°C)[c] reported[5]
1a	**2a**	8	**3a**	70	78–80	80
1b	**2a**	8	**3b**	78	131–133	132
1c	**2a**	8	**3c**	76	132–133	132
1d	**2a**	8	**3d**	71	153–154	154
1e	**2a**	8	**3e**	80	152–154	154
	2b	8	**3e**	75	153–154	154
1f	**2b**	20	**3f**	70	228–229	230
1g	**2a**	15	**3g**	66	mp 79–80 °C	mp 80 °C

[a] All reactions were carried out at 80 °C under nitrogen.
[b] Isolated yield based on **1**.
[c] Uncorrected.



4	Y	R^1	5	Y	R^2
a	2-Cl	CH_2OMe	a	H	CO_2Et
b	3-MeO	Ph	b	3-MeO	CO_2Et
c	4-Cl	Ph			
d	3-MeO	n-Bu			

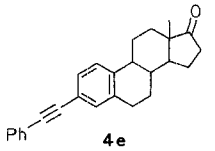


Table 2. Dehydroxy-alkynylation and -alkenylation of Phenols

RSO_2F	Reaction Conditions Temp. (°C)	Reaction Conditions Time (h)	Product	Yield[a] (%)
2a	80	19	**4a**	63
2b	80	18	**4a**	61
2c	80	18	**4a**	69
2d	80	18	**4a**	60
2a	80	17	**4b**	68
2a	80	18	**4c**	62
2a	80	18	**4d**	68
2a	55	20.5	**4d**	67
2a	40	20.5	**4d**	54
2a	80	20	**4e**	63
2a	80	24	**5a**	50
2a	80	24	**5b**	54

[a] Isolated yield.

Table 3. Physical and Spectral Data for Compounds **4** and **5** Prepared

Product	mp (°C) or bp (°C/Torr)[a]	Molecular Formula[b] or Lit. Data	IR (film) or (KBr)[c] ν (cm^{-1})	^{1}H-NMR (solvent/TMS)[d] δ, J(Hz)	MS[e] m/z (M^+)
4a	oil	$C_{10}H_9ClO$ (180.6)	3071, 2230, 1592, 1150	CCl_4: 3.38 (s, 3H); 4.26 (s, 2H); 6.96–7.86 (m, 4H)	180
4b	74–6	$C_{15}H_{12}O$ (208.2)	3010, 2210, 1230, 860	CCl_4: 3.60 (s, 3H); 6.60–7.40 (m, 9H)	208
4c	79–81.5	81.5–82[6]	3049, 2213, 1590	CCl_4: 6.85–7.55 (m)	212
4d	oil	$C_{13}H_{16}O$ (188.1)	3072, 2230, 1576, 1287	CCl_4: 0.53–1.70 (m, 7 H); 2.03–2.53 (m, 2H); 3.64 (s, 3H); 6.47–7.24 (m, 4H)	188
4e	224–5	$C_{26}H_{26}O$ (354.3)	3054, 2205, 1731, 1595	$CDCl_3$: 0.90 (s, 3H); 1.03–3.37 (m, 15H); 7.09–7.97 (m, 8H)	354
5a	121/3	123/3[7]	3030, 1712, 1640, 1580	CCl_4: 1.22 (t, 3H); 4.13 (q, 2H); 6.30 (d, J = 16, 1H); 7.12–7.51 (m, 5H); 7.52 (d, J = 16, 1H)	176
5b	185–7/15	185–186/15[8]	3060, 1711, 1638, 1261	CCl_4: 1.18 (t, 3H); 3.63 (s, 3H); 4.07 (q, 2H); 6.21 (d, J = 16, 1H); 7.26–7.47 (m, 4H); 7.47 (d, J = 16, 1H)	206

[a] Uncorrected.
[b] Satisfactory microanalyses obtained: C ±0.34, H ±0.28.
[c] Recorded on a Perkin-Elmer 983 spectrophotometer.
[d] Recorded on EM-360 NMR spectrometer (60 MHz).
[e] Mass spectra were taken on GC-MS-4021.

Similarly, in the presence of fluoroalkanesulfonyl fluoride, phenols **1** also reacted with alkynes or alkenes catalyzed by bis(triphenylphosphine)palladium dichloride in triethylamine to provide alkynylarenes **4** or alkenylarenes **5**, respectively (Table 2).

In the above reactions, the reactants, catalyst, and solvent were added in one portion. Triethylamine could be used as both base and solvent. The products were obtained without isolating arenyl fluoroalkanesulfonate. The variation in R of fluoroalkanesulfonyl fluoride and the reaction temperature seemed to have little influence on the yields as shown in Table 2.

The novel method reported is expected to be useful for the hitherto difficult transformation of phenols to the corresponding arenes, alkynylarenes, and alkenylarene especially useful in syntheses of natural products. As an example, we chose estrone as the substrate, which reacted with phenylacetylene to give 3-phenylethynylestra-1,3,5(10)trien-17-one (**4e**) in good yield.

Arenes 3; General Procedure:
A mixture of **1** (1.5 mmol), triethylamine (2 mL), bis(triphenylphosphine)palladium dichloride (0.075 mol), fluoroalkanesulfonyl fluoride **2** (1.7 mmol) and DMF (2 mL) is placed in a Pyrex tube fitted with a screw cap under N_2. Formic acid (3 mmol) is injected in one portion. The mixture is stirred at 80 °C for the time given in Table 1, and quenched by adding 0.5 N HCl (15 mL), extracted with ether (3 × 25 mL), washed with water until neutral, dried (Na_2SO_4), and evaporated. Distillation under atmospheric pressure or column chromatography on silica gel (petroleum ether used as eluent) gives the products **3**.

Alkynylarenes 4 or alkenylarenes 5; General Procedure:
A mixture of phenols **1** (2 mmol), triethylamine (2 mL), bis(triphenylphosphine)palladium dichloride (0.12 mmol), fluoroalkanesulfonyl fluoride **2** (2.2 mmol), the appropriate alkyne or alkene (3 mmol), and DMF (2 mL) is placed in a Pyrex tube fitted with a screw cap under N_2. The mixture is stirred for the reaction temperature and time given in Table 2 and quenched by adding 0.5 N HCl (15 mL), extracted with ether (3 × 25 mL), washed with water until neutral, dried (Na_2SO_4) and evaporated. Column chromatography of the residue on silica gel using petroleum ether/EtOAc (10:1) as eluent provides the products **4** or **5**.

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(1) a) Chen, Q.Y., Yang, Z.Y. *Tetrahedron Lett.* **1986**, *27*, 1171.
b) Chen, Q.Y., He, Y.B., Yang, Z.Y. *J. Chem. Soc. Chem. Commun.* **1986**, 1452.
(2) Cacchi, S., Ciattini, P.G., Morera, E., Ortar, G. *Tetrahedron Lett.* **1986**, *27*, 3931.
(3) Subramanian, L.R., Martinez, A.G., Fernandez, A.H., Alvarez, R.M. *Synthesis* **1984**, 481.
(4) $HCF_2CF_2OCF_2CF_2SO_2F$ (**2a**) was easily obtained by the reduction of $ICF_2CF_2OCF_2CF_2SO_2F$, which, a commercial product in China, was prepared according to references:
Bargigia, G.A., Laporiccio, G., Pianca, M. *J. Fluorine Chem.* **1982**, *19*, 403.
Perfluorosulfonic Acid Group, Academia Sinica, *Scientic Sinica(B)* **1978**, *21*, 773.
(5) *Vogel's Textbook of Practical Organic Chemistry Including Qualitative Organic Analysis*, Longman, London, 1978, pp.1160, 1180, 1186, 1192.
(6) Newman, M.S., Reid, D.E. *J. Org. Chem.* **1958**, *23*, 665.
(7) Otsu, T., Yamada, T., Nozaki, T. *Kogyo Kagaku Zasshi* **1967**, *70*, 1941; *C.A.* **1968**, *68*, 114995.
(8) *Dictionary of Organic Compounds*, 5th ed., Chapman and Hall, New York, M-00700.

1988

- Chen, Q.-Y., He, Y.-B. *Synthesis* **1988**, 896. On page 897 the amount of $Pd(PPh_3)_2Cl_2$ in the general procedure for Arenes **3** should be 0.075 mmol.

1989

- Bhaha, S.K., Hajdu, J. *Synthesis* **1989**, 16. Throughout the paper thioacetyl should be replaced by acetylthio. Hence **7** is named 2-*S*-acetyl-1-*O*-hexadecyl-L-2-thioglycerol.

- Burger, A., Hetru, C., Luu, B. *Synthesis* **1989**, 93. On page 94 the formulae of the Horner–Emmons reagent used is:

$$(EtO)_2\overset{O}{\overset{\|}{P}}CCl_2Li$$

and the correct name in the experimental section p. 96 is: diethyl dichloromethylphosphonate.

- Schinzer, D. *Synthesis* **1989**, 179. On page 180 compound **14b** is (2*R*,3*RS*,4*SR*)-3-hydroxy-2,4,6-trimethyl-5-heptenoyltriethylsilane.

- Cristau, H.J., Fonte, M., Torreilles, E. *Synthesis* **1989**, 301. On page 301 compound **7** is 2-(2-benzylaminoethoxy)-1-[(2-methyl-1,3-dioxolan-2-yl)methyl]ethyltriphenylphosphonium iodide.

- Zhou, W.-S., Zhou, Y.-P., Jiang, B. *Synthesis* **1989**, 426. On page 427 compound **8** is (22*E*,24*R*)-3α,5-cyclo-5α-ergosta-7,22-dien-6-one and **9** is (22*E*,24*R*)-3α5-cyclo-5α-ergost-22-en-6-one.

- Stuart, J.G., Nicholas, K.M. *Synthesis* **1989**, 454. In the title abstract and text propargyl nitriles should read propargyl cyanides.

- Schick, H., Eichhorn, I., *Synthesis* **1989**, 477. On page 481 the final entry to Table 4 should read:
$CH_2CH{=}CH-(CH_2)_3CO_2Me$