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THE VINYLATION OF 4′-IODOBENZOCROWN ETHER CATALYZED BY POLYMERIC PALLADIUM CATALYSTS

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ABSTRACT: *The vinylation of 4′-iodobenzocrown ethers was achieved in good yields by using polymeric palladium catalysts P-Ph-Phen-Pd(reduced) and P-Ph-bpy-Pd(0).*

Functionalized benzocrown ethers have received much attention due to their specific property and wide applications. Kikukawa[1] and coworkers have introduced alkenyl groups to crown ether by the Heck arylation technique. The palladium catalyzed Heck arylation of olefins is a very useful reaction and has found wide application in organic synthesis.[2] Earlier investigators had noted that one of the main problems associated with this arylation catalyzed by a homogeneous catalyst is the separation of the finely divided palladium metal formed during the reaction. We encountered similar difficulties in the preparation of 4′-iodobenzo-15-crown-5 via Heck arylation of olefins (such as acrylic acid, acrylamide, methyl acrylate, and styrene) in the presence of palladium acetate and triethylamine or tributylamine. In the reaction the catalyst gradually aggregated to inactive palladium black, resulting in a poor yield. The fine palladium was hard to remove completely. Though final

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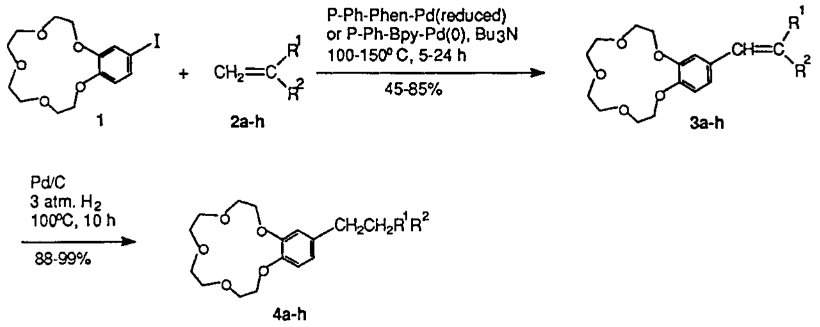
product can be purified by column chromatography, this is cumbersome and time consuming.

This problem might be overcome by using a polymer-supported palladium catalyst. We have previously described polymer-supported palladium catalysts P-Ph-Phen-Pd(reduced) **I**,[3-6] and P-Ph-bpy-Pd(0) **II**[7] and their applications in the Heck arylation. These polymeric palladium catalysts showed high activity for the reaction of various olefins with iodobenzenes, and could tolerate the presence of a variety of functional groups. As a result of the isolation of reactive species by the polymer matrix, these polymeric catalysts were very stable to air and moisture and could be stored for a long period. These results encouraged us to employ polymeric catalysts to the synthesis of functionalized benzocrown ethers. As a part of our continuing investigation, in this paper we present the vinylation of 4'-iodobenzocrown ether catalyzed by polymeric palladium catalysts.

4'-Iodobenzo-15-crown-5 **1** was treated with a variety of olefins **2a-h** in the presence of *n*-tributylamine and polymeric catalysts (Scheme 1). Both **I** and **II** could be used as catalyst, the reaction conditions and the physical data of the products **3** are summarized in Table 1. Acetonitrile was found to be the best solvent for the reaction which required solvent. When the reaction temperature was higher than 100°C, the reaction was carried out in an autoclave. In the IR spectra of product **3**, a strong band appeared in the region of 971-991 cm^{-1}, and in ^1H NMR spectra of compounds **3a-c**, the coupling constant of adjacent olefinic hydrogens was $J=16$ Hz. All these data are consistent with the (*E*)-structure.

Though heterogeneous reaction required elevated reaction temperature, the polymeric catalysts displayed some advantages over homogeneous reagents. These polymeric catalysts showed high activity, only a trace of catalyst (0.32 mol% based on crown ether **1**) was used, while the yields were higher than those obtained by



2-4	R^1	R^2	2-4	R^1	R^2
a	COOH	H	e	succinimido	H
b	COOMe	H	f	phthalimido	H
c	$CONH_2$	H	g	$(CH_2)_8COOH$	H
d	Ph	H	h	Ph	CH_3

Scheme 1

using palladium acetate. The major advantage of using polymeric catalyst is that the product is free of the contamination of palladium metal and is easy to purify. The separation of catalyst can be accomplished by simple filtration, and column chromatography is no longer necessary. It is also worth mentioning that after the reaction, the polymeric catalyst could be recovered and reused in the next run.

Alkenyl substituted crown ethers **3** could be readily reduced to alkyl derivatives in the presence of 5% Pd on charcoal at 100°C in excellent yields. The results are presented in Table 2.

Vinyl acetate **2i** did not undergo the reaction in normal manner. When it was treated with 4'-iodobenzo-15-crown-5, the reaction proceeded at 130°C to give bis-crown ether **3i** in 50% yield (Scheme 2). It could be further reduced to saturated derivative **4i**.

EXPERIMENTAL

(*E*)-4'-Carboxyvinylene-benzo-15-crown-5 3a; Typical Procedure:

A mixture of 4'-iodo-benzo-15-crown-5 (**1**, 1.40 g, 3.5 mmol), acrylic acid (**2a**, 0.05 g, 7.0 mmol), *n*-tributylamine (5 mL, 21.0 mmol), and catalyst (**I**, 0.05 g, 0.024 mmol%)

Table 1. 4'-Alkenyl-benzo-15-crown-5 **3** Prepared

Product	Reaction Conditions		Yield[a] (%)	mp (°C) (Lit. mp)/ Molecular Formula[b]	IR ν (cm^{-1})	^{1}H NMR (CDCl$_3$/TMS) δ, J (Hz)	MS(70 eV) m/z (M$^+$)
	Cat.	Temp.(°C)/ Time(h)					
3a	I II	150/5 135/8	67 45	190-192 (190-191[1])	3200-2700 1694, 1625, 1597, 1582, 1142, 975, 850, 804	3.70-4.20(m, 16H, 4xOCH$_2$CH$_2$O), 6.20(d, 1H, J=16, CH=), 6.70-7.20(m, 3H, ArH), 7.70(d, 1H, J=16, CH=),	-
3b	I[c] II[c]	120/10 120/10	82 79	83-85 (80-83[8])	1700, 1629, 1595, 1585, 1141, 979, 854, 808	3.80(s, 3H, CH$_3$O), 3.90-4.30(m, 16H, 4xOCH$_2$CH$_2$O), 6.30(d, 1H, J=16, CH=), 6.80-7.30(m, 3H, ArH), 7.70(d, 1H, J=16, CH=),	352
3c	I[c] II[c]	100/48 100/48	85 82	170-172 $C_{17}H_{23}NO_6$	3319, 3156, 1667, 1592, 1123, 991, 864, 805	3.70-4.20(m, 16H, 4xOCH$_2$CH$_2$O), 6.10-6.80(m, 2H, CONH$_2$), 6.60(d, 1H, J=16, CH=), 7.10-7.70(m, 3H, ArH), 7.80(d, 1H, J=16, CH=),	337
3d	I II	120/24 120/24	80 82	106-107 (108-109[1])	3025, 1593, 1585, 1138, 979, 846, 802, 749, 690	3.70-4.20(m, 16H, 4xCH$_2$OCH$_2$O), 6.70-7.50(m, 10H, ArH, CH=),	-
3e	I II	140/20 140/24	65 67	134-136 $C_{20}H_{25}NO_7$	1702, 1648, 1602, 1583, 1140, 975, 851, 796	2.80(s, 4H, CH$_2$CH$_2$), 3.70-4.20(m, 16H, 4xOCH$_2$CH$_2$O), 6.80-7.80(m, 5H, ArH, CH=),	391
3f	I II	140/24 140/24	85 82	136-138 $C_{24}H_{25}NO_7$	1712, 1649, 1600. 1582, 1143, 983, 834, 806, 714	3.70-4.20(m, 16H, 4xOCH$_2$CH$_2$O), 6.60-7.80(m, 9H, ArH, CH=),	439
3g	I II	125/24 130/24	63 65	$C_{25}H_{38}O_7$[d]	1707, 1653, 1602, 1583, 1139, 979, 845, 803, 725	1.20-1.50(m, 8H, 4xCH$_2$), 1.80-2.30(m, 8H, 4xCH$_2$), 3.70-4.10(m, 16H, 4xOCH$_2$CH$_2$O), 6.40-8.10(m, 5H, ArH, CH=),	450
3h	I[c] II[c]	135/24 135/16	65 62	94-96 $C_{23}H_{28}O_5$	1598, 1575, 1510, 1139, 982, 848, 805, 769, 700	2.30(s, 3H, CH$_3$), 3.70-4.10(m, 16H, 4xOCH$_2$CH$_2$O), 6.80-7.60(m, 9H, ArH, CH=),	384
3i	I[c] II[c]	130/16 130/16	50 50	195-197 (190-192[9])	1602, 1513, 1127, 971, 870, 806	3.70-4.20(m, 32H, 8xOCH$_2$CH$_2$O), 6.80-8.00(m, 8H, ArH, CH=)	560

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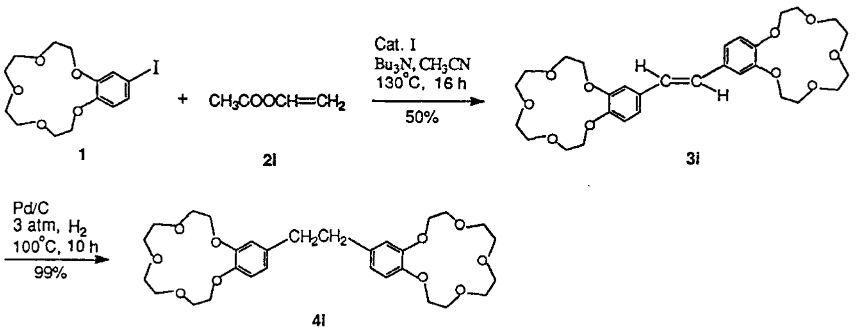
[a] Yield of isolated product 3 based on 1. [b] Satisfactory microanalyses obtained: C±0.32, H±0.17, N±0.04.
[c] Acetonitrile was added as solvent. When the reaction temperature was heigher than 100°C, the reaction was carried out in an autoclave. [d] Viscous oil.

Table 2. 4'-Alkylbenzo-15-crown-5 **4** Prepared

Product	Yield[a] (%)	mp (°C) (Lit. mp)/ Molecular Formular[b]	IR ν (cm^{-1})	^{1}H NMR (CDCl$_3$/TMS) δ	MS(70 eV) *m/z* (M$^+$)
4a	88	92-94 (96-98)[10]	3250-2750, 1694, 1625, 1145, 851 805	2.60-3.10(m, 4H, CH_2CH_2), 3.80-4.40(m, 16H, 4xOCH_2CH_2O), 6.80-8.00(m, 3H, ArH)	-
4b	90	47-49 $C_{18}H_{26}O_7$	1731, 1589, 1515, 1138, 855, 808	2.70-3.10(m, 4H, CH_2CH_2), 3.80(s, 3H, CH_3O), 3.90-4.40(m, 16H, 4xOCH_2CH_2O), 6.80-7.70(m, 3H, ArH)	-
4c	98	122-123 $C_{17}H_{25}NO_6$	3397, 3207, 1664, 1592, 1520, 1141, 860, 802	2.30-3.00(m, 4H, CH_2CH_2), 3.80-4.30(m, 2H, 4xOCH_2CH_2O), 5.70-6.30(m, 2H, $CONH_2$), 6.90(m, 3H, ArH)	339
4d	92	64-65 $C_{22}H_{28}O_5$	1603, 1590, 1133, 852, 793, 753, 696	2.90(s, 4H, CH_2CH_2), 3.80-4.40(m, 16H, 4xOCH_2CH_2O), 6.90-7.60(m, 8H, ArH)	372
4e	90	108-109 $C_{20}H_{27}NO_7$	1697, 1589, 1516, 1136, 853, 782	2.10-3.00(m, 8H, 4xCH_2), 3.70-4.20(m, 16H, 4xOCH_2CH_2O), 6.60-7.30(m, 3H, ArH)	393
4f	96	106-107 $C_{24}H_{27}NO_7$	1721, 1607, 1591, 1141, 867, 815, 716	2.90-3.20(m, 4H, CH_2CH_2), 3.80-4.40(m, 16H, 4xOCH_2CH_2O), 7.00-8.20(m, 7H, ArH)	441
4i	99	107-108 (107-109)[11]	1592, 1518, 1137, 853, 803	2.90(s, 4H, CH_2CH_2), 3.70-4.30(m, 32H, 8xOCH_2CH_2O), 6.90-7.60(m, 6H, ArH)	-

[a] Yield of isolated product **4** based on **3**. [b] Satisfactory microanalyses obtained: C±0.35, H±0.38, N±0.14.



Scheme 2

was stirred at 150°C for 5 h. The reaction mixture was cooled to room temperature, and sodium bicarbonate solution (2 g in 20 mL of water) was added. The catalyst was recovered by filtration, the aqueous layer of the filtration was acidified to pH 3.0 with 3 M HCl. After standing overnight, the precipitated product **3a** was isolated by suction and recrystallized from anhydrous EtOH; yield: 0.80 g (67%); mp 190-192°C.

4'-Alkyl-benzo-15-crown-5 4; General Procedure:

A mixture of 4'-alkenyl-benzo-15-crown-5 or bis-crown ether (**3a-i**, 1.0 mmol), Pd/C (5%, 0.20 g) and anhydrous EtOH (25 mL) was stirred under hydrogen pressure (3 atm.) at 100°C for 10 h. The catalyst was filtered off, the solvent was evaporated, and the crude product **4** was crystallized from EtOH. In the cases of **4a** and **4b**, **4c**, toluene and acetone were used, respectively.

(*E*)-1,2-vinyl-bis(4'-benzo-15-crown-5) 3i:

A mixture of 4'-iodo-benzo-15-crown-5 (**1**, 1.40 g, 3.5 mmol), vinyl acetate (2 mL, 8.4 mmol), *n*-tributylamine (3 mL, 12.6 mmol), catalyst (**I**, 0.05 g, 0.024 mmol%), and acetonitrile (15 mL) was stirred at 130°C in an autoclave for 16 h. The polymeric catalyst was removed by filtration, and the solvent was evaporated. After standing at 4°C overnight, the precipitated crude product **3i** was isolated by suction, washed with anhydrous EtOH, and recrystallized from anhydrous EtOH/CH_2Cl_2; yield: 0.98 g (50%); mp 195-197°C.[9]

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