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Palladium-Catalyzed Arylation of Ethylene

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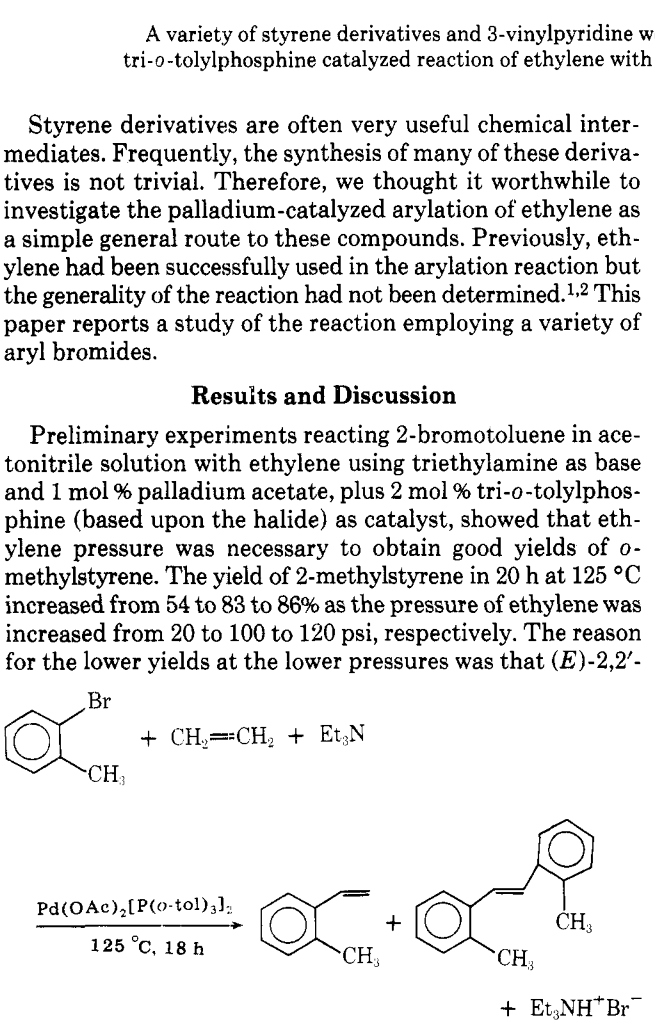
A variety of styrene derivatives and 3-vinylpyridine were prepared in moderate to good yields by the palladium–tri-*o*-tolylphosphine catalyzed reaction of ethylene with aryl bromides or 3-bromopyridine, respectively.

Styrene derivatives are often very useful chemical intermediates. Frequently, the synthesis of many of these derivatives is not trivial. Therefore, we thought it worthwhile to investigate the palladium-catalyzed arylation of ethylene as a simple general route to these compounds. Previously, ethylene had been successfully used in the arylation reaction but the generality of the reaction had not been determined.[1,2] This paper reports a study of the reaction employing a variety of aryl bromides.

Results and Discussion

Preliminary experiments reacting 2-bromotoluene in acetonitrile solution with ethylene using triethylamine as base and 1 mol % palladium acetate, plus 2 mol % tri-*o*-tolylphosphine (based upon the halide) as catalyst, showed that ethylene pressure was necessary to obtain good yields of *o*-methylstyrene. The yield of 2-methylstyrene in 20 h at 125 °C increased from 54 to 83 to 86% as the pressure of ethylene was increased from 20 to 100 to 120 psi, respectively. The reason for the lower yields at the lower pressures was that (*E*)-2,2′-dimethylstilbene was being formed as a side product by a second arylation of the 2-methylstyrene. The yields of the stilbene decreased from 34 to 10 to 4%, respectively, in the above reactions. At pressures above about 200 psi the reaction rates decreased. At 750 psi only 40% of the styrene was formed in 20 h and 60% of the starting bromide remained unreacted. The high ethylene pressure apparently deactivates the catalyst by coordination probably decreasing the rate of oxidative addition of the 2-bromotoluene.



In one experiment, the use of triphenylphosphine rather than the tri-*o*-tolylphosphine gave product at only half the rate. Therefore, subsequent experiments were carried out with 100–200 psi of ethylene with tri-*o*-tolylphosphine in the catalyst.

Ethylene was arylated with seven different aryl bromides and 3-bromopyridine as shown in Table I. The isolated yields of distilled styrene products ranged from 45 to 86%. The stilbene yields were also obtained by isolation. Unreacted aryl bromides were determined by GLC. These are relatively good yields considering the fact that the reactions were carried out on only a 10–20 mmol scale and some polymerization often occurred. 3-Bromopyridine yielded the 3-vinyl derivative in 52% yield (isolated as the picrate). Styrene derivatives with methyl, nitro, acetamide, amino, formyl, and carboxyl substituents also were prepared. *o*-Divinylbenzene was obtained from *o*-dibromobenzene in 76% (isolated) yield. Thus, the palladium-catalyzed arylation of ethylene appears to be an excellent method for the preparation of a wide variety of styrene derivatives.

Experimental Section

Reagents. All of the aryl bromides were commercial products which were used without further purification. The ethylene, triethylamine, and acetonitrile were reagent grade materials and were used as received. The tri-*o*-tolylphosphine was prepared by the Grignard procedure described previously.[3] The palladium acetate was prepared by the published method.[4]

General Procedure for the Arylation of Ethylene. A 45-mL T-303 stainless steel bomb (Parr Instrument Company) containing a Teflon-coated magnetic stirring bar was charged with 20 mmol of

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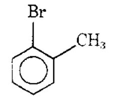
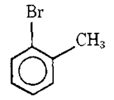
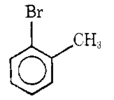
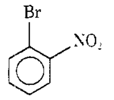
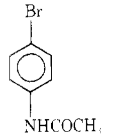
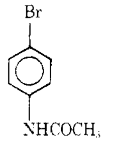
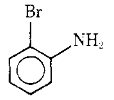
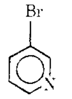
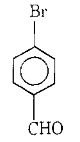
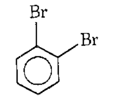
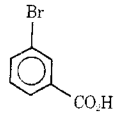
Table I. Reactions of Various Aryl Bromides with Ethylene[a,b]

Aryl bromide	Registry no.	Ethylene pressure, psi	Solvent	Time, h	% yield for product		
					Styrene	Stilbene	Unreacted RX (by GLC)
	95-46-5	20	5 mL of CH_3CN	20	54	34	5
		100	5 mL of CH_3CN	7	83	10	7
		120	5 mL of CH_3CN	18	86	4	10
	577-19-5	120	8 mL of CH_3CN	2	55	5	
		120	10 mL of DMF	23	59	20	
	103-88-8	120	5 mL of CH_3CN	2		48	
	615-36-1	200	10 mL of CH_3CN	30	45		15[c,d]
	626-55-1	200	10 mL of CH_3CN	66	52[b]		20
	1122-91-4	200	10 mL of CH_3CN	48	53[e]	11	
	583-53-9	200	10 mL of CH_3CN	15	78[f]		
 [g]	585-76-2	200	10 mL of CH_3CN	4	51	12	

[a] Reactions were carried out at 125 °C with 20 mmol of the aryl bromide (10 mmol of *o*-dibromobenzene), 1 mol %, based upon the aryl bromide, palladium acetate, and 2 mol % of tri-*o*-tolylphosphine. [b] Isolated as the picrate. [c] 14% aniline was also formed. [d] ~20% polymer was obtained. [e] Polymer formed also. [f] 12% *o*-Bromostyrene also formed. [g] 8 mL of Et_3N was used. [h] Registry No.—Ethylene, 74-85-1.

the aryl bromide (10 mmol in the *o*-dibromobenzene reaction), 0.045 g (0.20 mmol) of palladium acetate, 0.122 g (0.40 mmol) of tri-*o*-tolylphosphine, 5–10 mL of acetonitrile (DMF was used instead in one example because it was a better solvent for the aryl bromide), and 5 mL of triethylamine (8 mL of amine were used with *m*-bromobenzoic acid). The air in the bomb was flushed out with a stream of argon while the cap was put on. Ethylene was then added to the desired pressure with stirring to saturate the solution. The bomb was stirred magnetically in an oil bath at 125 °C until no more gas was absorbed. Additional ethylene was added periodically to keep the pressure at the initial level. The bomb was then cooled to room temperature, vented, and opened. The contents were rinsed into a round-bottomed flask with ether. Water was added to the mixture and the product was extracted with ether. The extracts were dried ($MgSO_4$) and then either distilled under reduced pressure or if solid they were recrystallized. The pot residues or the less soluble fractions from the recrystallizations contained the stilbene derivatives. These were purified by recrystallization.

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Registry No.—Palladium acetate, 3375-31-3; *o*-vinyltoluene, 611-15-4; 1,2-di-*o*-tolylethene, 20657-42-5; *o*-vinylnitrobenzene, 579-71-5; 1,2-bis(*o*-nitrophenyl)ethene, 6275-02-1; *N*-(*p*-vinylphenyl)acetamide, 53498-47-8; 1,2-bis(*p*-acetamidophenyl)ethene, 33267-39-9; *o*-vinylaniline, 3867-18-3; 3-vinylpyridine picrate, 66018-22-2; *p*-vinylbenzaldehyde, 1791-26-0; *o*-divinylbenzene, 91-14-5; *m*-vinylbenzoic acid, 28447-20-3.

Supplementary Material Available: Properties of the products prepared bp or mp NMR data, and molecular weights (Table II) (3 pages). Ordering information is on any current masthead page.

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Synthesis of Macrocyclic Polyether–Diester Compounds with an Aromatic Subcyclic Unit[1]

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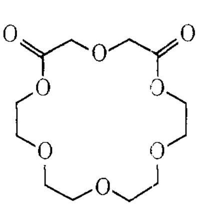
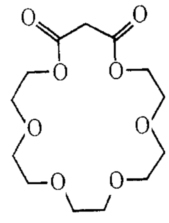
New series of macrocyclic polyether–diester ligands have been prepared by reacting isophthaloyl chloride and 5-nitroisophthaloyl chloride with tri-, tetra-, penta-, and hexaethylene glycols and one sulfur-substituted analogue (compounds **4–13**), terephthaloyl chloride with tetra-, penta-, and hexaethylene glycols (**14–16**), phthaloyl chloride with penta- and hexaethylene glycol (**17–18**), and 1,8-naphthaloyl chloride with pentaethylene glycol (**19**). All macrocyclic diesters were found to be 1:1 adducts except for the terephthalate prepared from tetraethylene glycol, which was found to be a 2:2 adduct.

The synthesis and unique cation complexing properties of the macrocyclic polyethers, first reported by Pedersen,[2] have been the object of intensive research.[3-7] The majority of work has concerned macrocyclic polyethers, the so-called crown compounds, although many aza[8] and thia crown compounds have been studied.[6,9-13]

We have recently reported the synthesis and cation complexing properties of macrocyclic polyether–diester compounds.[14,15] These compounds have proved to be of interest because stabilities for the ligand–metal complexes are somewhat different than those of the typical crown ethers. Thus, the diketo–crown compounds **1** and **2** gave stability orders of $K^+ \approx Ba^{2+}$ and $K^+ > Ba^{2+}$, respectively, while 18-crown-6 has $Ba^{2+} > K^+$.[14] The inclusion of a pyridine moiety in the macrocyclic compound (**3**) greatly increases the cation complexing ability in methanol.[15]



1



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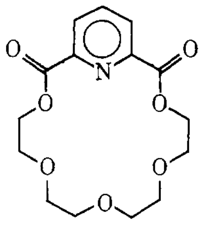
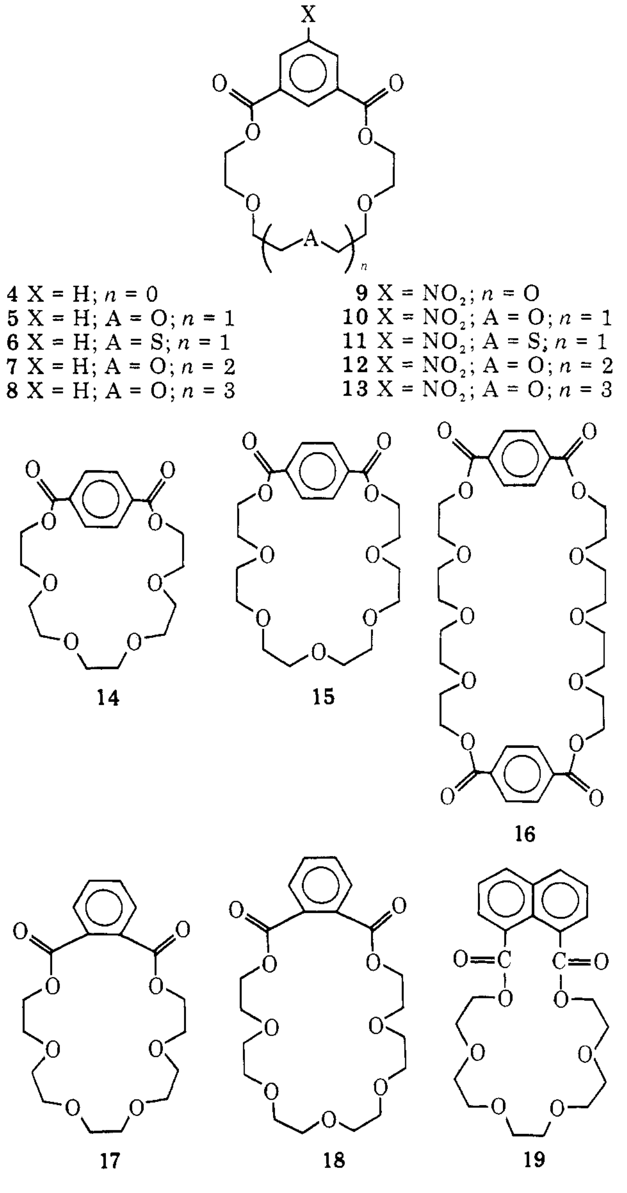


3

We have previously reported the synthesis of a wide variety of macrocyclic polyether–diester compounds including ether-esters,[14,16-21] thioether-esters,[15,17,19,21] ether–thiol esters,[17,21] amine–esters,[18] ether–ester–amides,[18] ester–amides,[18] and an ether–ester compound with a pyridine subcyclic unit.[15] In this paper we are reporting the synthesis of macrocyclic polyether–diester compounds containing benzene and, in one case, naphthalene subcyclic units (compounds **4–19**, Chart I).

Some macrocyclic diester compounds prepared from aromatic dicarboxylic acid moieties have been reported. Drewes and co-workers have prepared a number of different phthalate and bisphthalate compounds by treating the dipotassium phthalates with various alkyl dihalides.[22-26] None of their phthalate compounds contains the repeating ethylene oxide moiety, although they have reported the preparation of two

Chart I



4 X = H; $n = 0$
5 X = H; A = O; $n = 1$
6 X = H; A = S; $n = 1$
7 X = H; A = O; $n = 2$
8 X = H; A = O; $n = 3$
9 X = NO_2; $n = 0$
10 X = NO_2; A = O; $n = 1$
11 X = NO_2; A = S; $n = 1$
12 X = NO_2; A = O; $n = 2$
13 X = NO_2; A = O; $n = 3$

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