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Synthesis of High-Purity *o*- and *p*-Vinyltoluenes by the Heck Palladium-Catalyzed Arylation Reaction

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A homogeneous palladium-catalyzed coupling reaction has been used to make high-purity *o*- and *p*-vinyltoluenes in high yields from bromotoluenes. The arylation reaction, first reported by Heck, was studied in 2-L reactors, and then further scaled to a 10-gallon reactor using 0.02, 2.2, and 28 mol of bromotoluene, respectively. Catalyst turnover, rate, and lifetime were significantly improved over similar arylation reactions previously reported by changing the catalyst concentration, ligand to palladium ratio, ethylene pressure, temperature, and solvent system. An inorganic base such as potassium acetate can be substituted for triethylamine in this reaction and kept soluble by using a mixture of dimethylformamide and water as solvent. Side products were due to a second addition of bromotoluene to the vinyltoluene product, which formed both *trans* and *gem* bis adducts. The formation of bisarylation products can be controlled by adjusting and/or venting ethylene pressure during the reaction. Polymerization of the monomers during the coupling reaction and distillation was minimal. This arylation reaction combined with known technology to brominate toluene and methods to equilibrate and isolate bromotoluene isomers could be a viable synthesis of vinyltoluenes.

Introduction

The palladium-catalyzed coupling reaction of aryl halides and olefins (Heck reaction) is a very efficient and practical method for synthesizing carbon–carbon bonds having a wide variety of functionalities.[1] This chemistry can be used to prepare fine organics, pharmaceuticals, and specialty monomers. For example, the reaction allows a one-step synthesis of substituted styrenes from aryl bromides[2] and is an excellent method for preparation of a wide variety of styrene derivatives.[3]

One particularly difficult monomer to make by other routes is *o*-vinyltoluene, a material with relatively low toxicity (based on vinyltoluene)[4] which is attractive as a comonomer in styrene polymers. *o*-Vinyltoluene improves heat-distortion properties of styrenes with polymerization rates similar to styrene and with little color formation or cross-linking (see Table 1).[5]

Historically, *o*-vinyltoluene has been prepared by separating the *o*-ethyltoluene obtained during the alkylation of toluene with ethylene, followed by steam cracking using similar conditions to those used to prepare styrene from ethylbenzene. Unfortunately, this process to vinyltoluenes is not very selective and generates large quantities of indan and indene during the cracking of *o*-ethyltoluene (see Scheme 1).[6] Attempts to produce *o*-vinyltoluene by this process on a pilot scale were made at The Dow Chemical Co. in the 1960s and gave less than a 60% isolated yield of *o*-vinyltoluene (from isolated *o*-ethyltoluene) because of poor pyrolysis selectivity, difficult isomer separation, and indan/indene formation. These impurities are extremely difficult to separate on an industrial scale even with extensive distillation, and they cause low molecular weight and color problems in polymerization. The final purified monomer made by this route still contained 3–7% indan and indene.

Table 1. Properties of Substituted Styrene Polymers[a]

monomer	process adaptability[b]	glass-transition temp (°C)	polymerization rate[c]
styrene	acceptable	105	
o-vinyltoluene	acceptable	140	equal
m-vinyltoluene	cross-links	75	equal
p-vinyltoluene	cross-links	115	equal
α-methylstyrene	low T_c[d]	185	slower

[a] Brandrup, J.; Immergut, E. H. *Polymer Handbook*; Wiley-Interscience: New York, 1966; Section III-71. [b] Adaptability to the bulk styrene polymerization process. [c] Relative to styrene. [d] Critical temperature of depolymerization.

The preparation of vinyltoluene directly from vinylation of bromotoluene was first reported by Heck in 1978 using a palladium-catalyzed arylation reaction.[7] The experiments were carried out by reacting *o*-bromotoluene in acetonitrile solution, with ethylene, using triethylamine as base, and 1 mol % palladium acetate, plus 2 mol % tris(*o*-tolyl)phosphine (based on the halide) as catalyst.

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1994.

(1) (a) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: London, 1985. (b) Heck, R. F. *Org. React.* **1982,** *27,* 345. (c) Heck, R. F. *Acc. Chem. Res.* **1979,** *12,* 146. (d) Heck, R. F. U.S. Patent 3,922,299, 11/25/75. (e) Liebeskind, L. S. *Advances in Metal-Organic Chemistry*; Jai Press: London, 1989; Vol. 1, pp 137–155. (f) Larock, R. C. *Pure Appl. Chem.* **1990,** *62,* 653. (g) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 720–727.

(2) (a) Spencer, A. *J. Organomet. Chem.* **1983,** *258,* 101. (b) Spencer, A. U.S. Patent 4,564,479, 1/14/86.

(3) Heitz, W.; Brugging, W.; Freund, L.; Gailberger, M.; Greiner, A.; Jung, H.; Kampschulte, U.; Niessner, N.; Osan, F.; Schmidt, H.; Wicker, M. *Makromol. Chem.* **1988,** *189,* 119.

(4) Hazardous Substance Database: (vinyltoluene) CAS Reg. No. (RN) 25013-15-4, MSDB Number (MSN) 1035, Rev. Date 9/15/93; (4-vinyltoluene) CAS Reg. No. (RN) 622-97-9, MSDB Number (MSN) 6503, Rev. Date 1/20/93.

(5) Brandrup, J.; Immergut, E. H. *Polymer Handbook*; Wiley-Interscience: New York; 1966; Section III-71.

(6) Amos, I. L.; Coulter, K. E.; Wilcox, A. C.; Soderquis, F. I. Vinyltoluene. In *Styrene: Its Polymers, Copolymers, and Derivatives*; Boundy, R. H., Boyer, R. F., Eds.; Reinhold Publishing Corp.: New York, 1952.

(7) Plevyak, J. E.; Heck, R. F. *J. Org. Chem.* **1978,** *43,* 2454.

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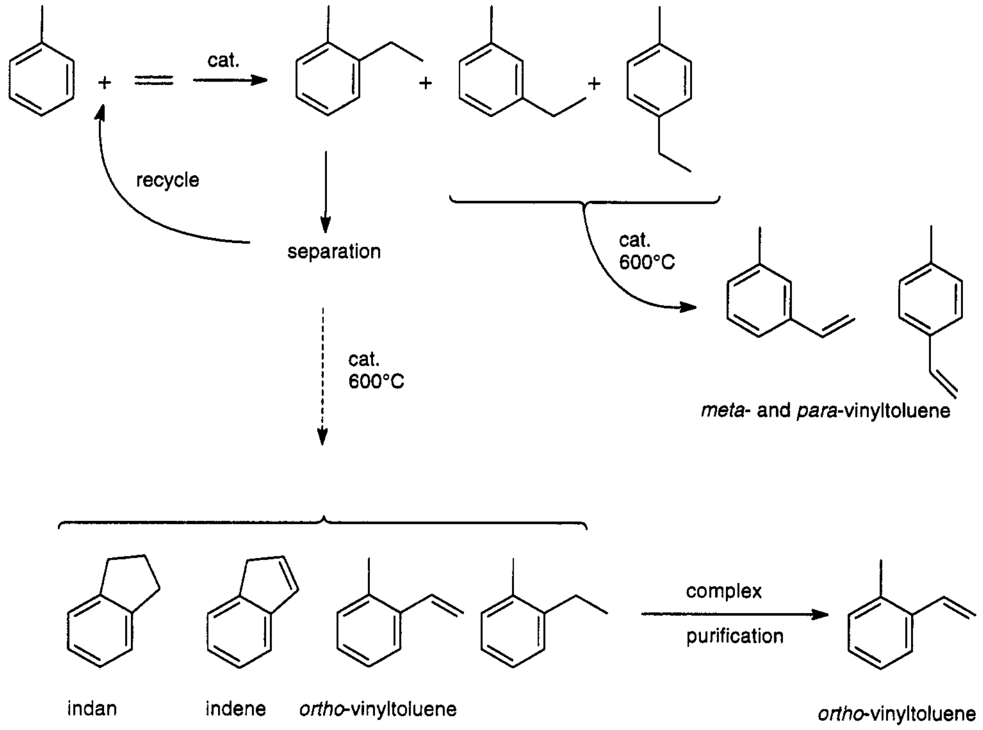
Table 2. Summary of 2-L Range-Finding Studies[a]

run no.	product	reacn temp (°C)	ethylene pressure (psig)	base[b]	solvent syst	ligand to Pd[c] ratio	time (h)	BrTol conv[d] (%)	catalyst turnovers[e]	overall turnover rate[f] (turnovers/h)	vinyltoluene selectivity[g]
1[a]	*o*-VT	125	20	TEA	CH_3CN	2 to 1	20	95.0	95/100	5	61
2[a]	*o*-VT	125	100	TEA	CH_3CN	2 to 1	7	93.0	94/100	14	89
3[a]	*o*-VT	125	120	TEA	CH_3CN	2 to 1	18	90.0	90/100	5	95
4[a]	*o*-VT	125	750	TEA	CH_3CN	2 to 1	20	60.0	60/100	3	>95
5	*o*-VT	75	75	TEA	DMF/water	4 to 1	28	91.0	757/832	18	80
6	*o*-VT	75	200	TEA	DMF/water	4 to 1	20	100.0	500/500	25	93
7	*o*-VT	120	200	TEA	DMF/water	4 to 1	5	99.0	495/500	99	76
8	*o*-VT	120	200	TEA	DMF/water	4 to 1	25	59.2	2966/5000	135	89
	o-VT	120	200	TEA	DMF/water	4 to 1	45	94.0	732/832	16	81
9	*o*-VT	125	120	TEA	CH_3CN	2 to 1	24	36.0	144/400	6	98
10	*o*-VT	125	120	TEA	CH_3CN	4 to 1	24	71.8	287/400	12	96
11	*o*-VT	80	70	TEA	DMF/water	4 to 1	25	99.7	499/500	20	65
12	*o*-VT	75	75	TEA	DMF/water	4 to 1	28	95.5	477/500	17	75.8
13	*o*-VT	85	70	TEA	DMF	4 to 1	28	91.8	459/500	10	92.6
14	*o*-VT	90	80	TEA	DMF	4 to 1	19	97.2	389/400	20	91.2
15	*o*-VT	75	100	TEA	DMF	4 to 1	24	95.0	378/400	16	94.7
16	*o*-VT	75	100	TEA	DMF	2 to 1	24	46.0	184/400	8	98
17	*p*-VT	120	200	TEA	DMF/water	4 to 1	3	99.0	495/500	165	78
18	*p*-VT	120	200	KOAc	DMF/water	4 to 1	3	96.0	478/500	159	93

[a] Plevyak, J. E.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 2454. [b] Triethylamine or potassium acetate. [c] Ratio of tris(*o*-tolyl)phosphine to palladium acetate. [d] Conversion of bromotoluene to products. [e] Moles of bromotoluene converted/moles of palladium acetate. [f] Average turnover rate over the reaction time. [g] Moles of vinyltoluene/moles of bromotoluene converted.

Scheme 1. Early Commercial Route to Vinyltoluene



The conversion of the aryl bromide was greater than 90%, with the yield of *o*-vinyltoluene in 20 h at 125 °C increasing from 54% to 86% as the ethylene pressure was increased from 20 to 120 psig, respectively. The reason for lower yields at the lower pressures was that 1,2-*trans*-bis(*o*-tolyl)ethylene was being formed as a side product by the second arylation of *o*-vinyltoluene (see Scheme 2 and Table 3).

Thus, the development of the Heck arylation reaction coupled to the known toluene bromination to form *o*- and *p*-bromotoluenes affords a viable route to make *o*-vinyltoluene. Bromotoluene isomers can be separated by distillation or crystal refining and then converted to the respective vinyltoluene derivatives. For example, several drums of bromotoluene isomers were made, separated, and purified at The Dow Chemical Co. in this way in 1947. Because the isomers of bromotoluene are also known to undergo isomerization in the presence of Friedel–Craft catalysts, isomerization could be used to adjust the ratio of these products to balance the demand for *o*-vinyltoluene and *p*-vinyltoluene[8] (see Scheme 3). This paper describes 2-L and 10-gallon reactor studies to product *o*- and *p*-vinyltoluene, control bisarylation products, and evaluate catalyst turnover, rate, and lifetime.

Results and Discussion

We have found in our laboratory that a two-phase solvent system using dimethylformamide (DMF) and water, with

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[8] (a) Crump, J. W. U.S. Patent 3,077,503, 2/12/63. (b) Crump, J. W.; Gornowicz, G. A. *J. Org. Chem.* **1963**, *28*, 949.

Scheme 2. Palladium-Catalyzed Arylation Reaction

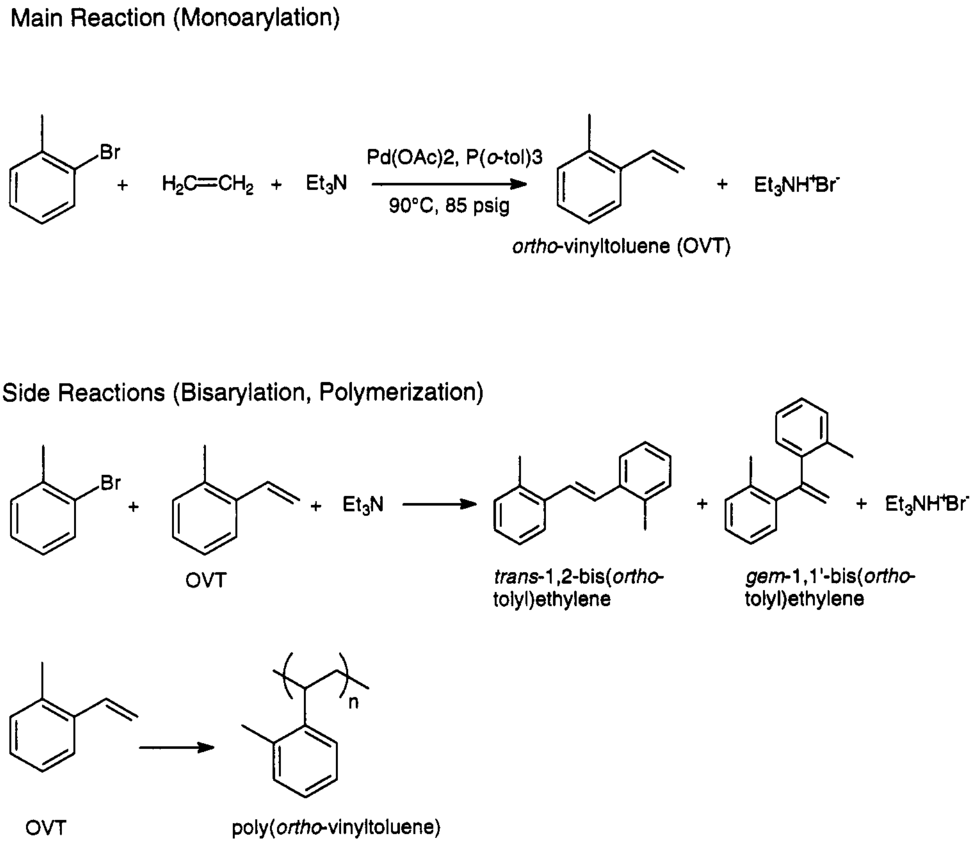

Table 3. Selectivity of 2-L Reactions

run no.	reacn temp (°C)	time (h)	ethylene pressure (psig)	solvent syst	OVT[a] (%)	BrTol[b] (%)	*gem*[c] (%)	*trans*[d] (%)	BrTol conv[e] (%)	OVT selectivity[f] (%)	turnover no.[g]
9	125	24	120	CH_3CN	33.2	64.0	0.1	0.5	36.0	98.0	144/400
10	125	24	120	CH_3CN	65.3	27.3	0.5	2.5	71.8	96.0	287/400
11	80	24.5	70	DMF/H_2O	64.0	0.3	8.9	24.4	99.7	65.0	499/500
12	75	28	75	DMF/H_2O	71.3	4.4	6.9	15.2	95.5	75.8	477/500
13	85	28	70	DMF	83.7	8.1	1.4	4.9	91.8	92.6	459/500
14	90	18.7	80	DMF	86.8	2.7	1.6	6.6	97.2	91.2	389/400
15	75	23	100	DMF	88.2	5.0	1.2	3.7	95.0	94.7	378/400
16	75	23	100	DMF	45.0	53.3	0.2	0.6	46.0	98.0	184/400

[a] *o*-Vinyltoluene. [b] *o*-Bromotoluene. [c] *gem*-1,1-Bis(*o*-tolyl)ethylene. [d] *trans*-1,2-Bis(*o*-tolyl)ethylene. [e] Conversion of bromotoluene to products. [f] Moles of product/moles of bromotoluene converted. [g] Moles of product/moles of palladium acetate and theoretical turnovers possible.

a 4 to 1 ratio of tris(*o*-tolyl)phosphine to palladium acetate, gives a faster, higher conversion, higher efficiency catalyst system than that of Heck.[9] Further modifications of this two-phase reaction have shown that alternative less-expensive inorganic bases such as sodium or potassium acetate can also be used.[10] Although the tolerance of this reaction to trace impurities and different solvents has been known for some time, the potential of running the reaction in the presence of a second water phase has not been described in the literature. Elimination of solid precipitates during the reaction is critical to high conversion, yields, and reactor efficiency. The low solubility of the base (organic or inorganic) or the salt formed can often be limiting. This improved system keeps the base and salt formed soluble throughout the reaction and has a much higher potential for commercial scale-up.

Two-Liter Studies To Make o-Vinyltoluene. The first reported synthesis of *o*-vinyltoluene from *o*-bromotoluene (Table 2, runs 1–4) was done by Heck at 125 °C in acetonitrile using 1 mol % palladium acetate and 2 mol % tris(*o*-tolyl)phosphine.[7] The results of this work was reported in the literature are listed in Table 2 as runs 1 through 4. This reaction was scaled approximately 100-fold to a 2-L reactor for our studies, which are shown in Table 2, runs 5 through 18. Run 5 shows that similar conversions and slightly lower selectivity can be achieved in a mixture of DMF/water as solvent under milder conditions of 75 °C and 75 psig of ethylene using only $^1/_{10}$th the catalyst loading. The reaction gave 757 catalyst turnovers vs the 90–95 reported by Heck. Because the selectivity appears to be both temperature and ethylene-pressure dependent, an additional experiment was done to increase the ethylene pressure to 200 psig (Table 2, run 6). As expected, a higher selectivity was observed, but at a slightly faster rate of turnover. The reaction profile is shown in Figure 1. Increasing the temperature to 120 °C (run 7) gave similar catalyst turnover, but lowered the selectivity to 76%. In run 8 the catalyst loading was reduced 10-fold and nearly 3000 catalyst turnovers were

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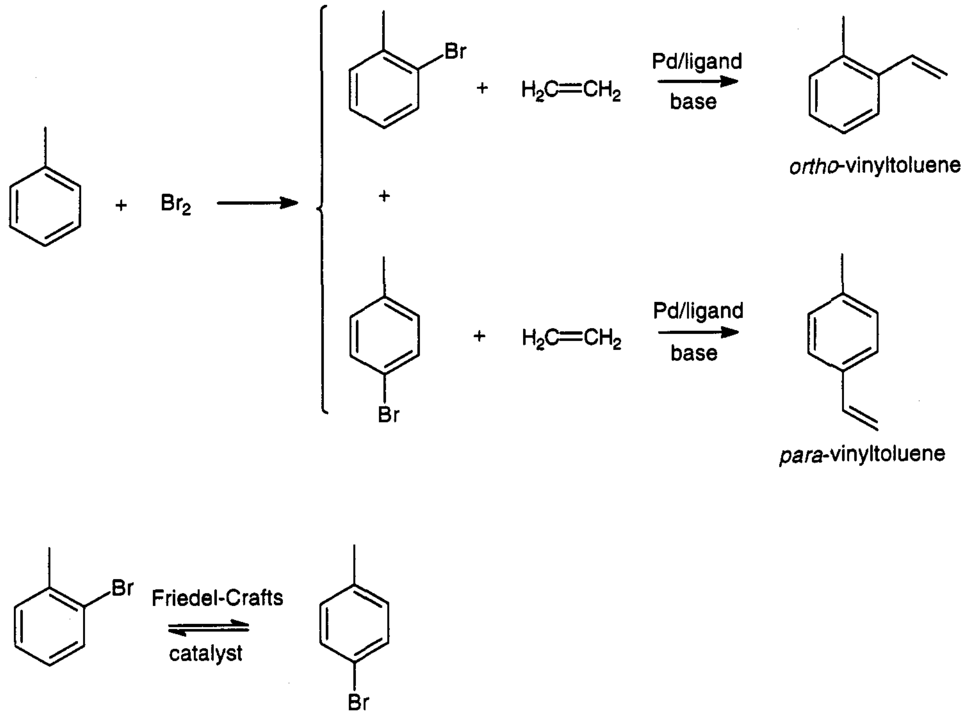
(9) DeVries, R. A.; Frick, H. R. U.S. Patent 5,243,068, 9/7/93.

(10) DeVries, R. A.; Frick, H.R. U.S. Patent 5,136,069, 8/4/92.

Scheme 3. New Toluene Route to Vinyltoluene



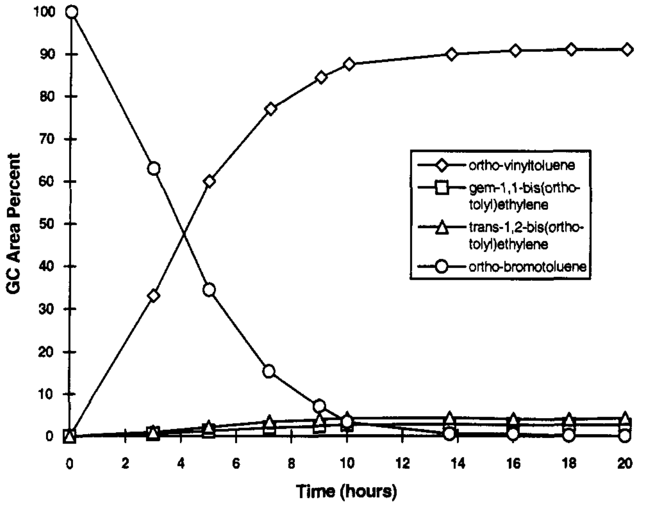


Figure 1. Reaction profile of vinylation of *o*-bromotoluene with ethylene.

obtained before deactivation. This reaction was cooled and another charge of catalyst was added to convert the remaining bromotoluene.

The preparation of *o*-vinyltoluene described by Heck at 125 °C and 120 psig of ethylene pressure gave about 90% conversion of the bromotoluene at 1 mol % palladium (90 turnovers, run 3).[7] Lowering the catalyst to 0.25 mol % gave only 36% conversion (144 turnovers, run 9) before deactivation. Increasing the tris(*o*-tolyl)phosphine ligand to palladium ratio to 4 to 1 from 2 to 1 helped increase conversion to 72%, but the catalyst still underwent deactivation in acetonitrile before reaching complete reaction (runs 9 and 10). Under mild conditions of 75–80 °C and 70–75 psig of ethylene pressure in a mixture of DMF and water (runs 11 and 12), the conversion was complete after 20 h, but selectivity to *o*-vinyltoluene was only 65–76%. Increasing the pressure to 200 psig in this solvent (run 6) increased selectivity to 93%. However, high selectivity can also be achieved under low pressure if the reaction is run under anhydrous DMF as solvent (runs 13–16).

Two-Liter Studies To Make p-Vinyltoluene. Several experiments were done with *p*-bromotoluene (see Table 2, runs 17 and 18). The arylation of ethylene occurred faster than with *o*-vinyltoluene, possibly because of less steric hindrance during the oxidative addition step of the aryl bromide onto the palladium(0) complex. The turnover rate appeared to be about 65% faster than that of *o*-bromotoluene (run 7) under similar conditions. In run 18 potassium acetate was used as the base rather than triethylamine. This demonstrates that a less-expensive, nonflammable base could be substituted in these reactions when water is present without affecting the rate or conversion. The selectivity appeared to increase (78% to 93%) at 200 psig of ethylene pressure.

Regioselectivity of Bisarylation. Although the Heck vinylation reaction has been studied for many years, the isomeric makeup of the stilbene products have only recently been identified as both the 1,1-*gem*-bis(*o*-tolyl)ethylene and 1,2-*trans*-bis(*o*-tolyl)ethylene substituted derivatives.[11] As seen in Table 3, the major bisarylation product found in our studies was 1,2-*trans*-bis(*o*-tolyl)ethylene, but with significant amounts of 1,1-*gem*-bis(*o*-tolyl)ethylene. These are formed when the arylpalladium intermediate undergoes a migratory insertion by adding the second aryl group onto the more substituted olefin carbon. A mechanism based on that proposed by Heck[12] is given in Figure 2, showing the formation of the regioisomers.

Control of Bisarylation. When aryl bromides are reacted with ethylene under pressure, styrenes and/or stilbenes are formed depending on the reaction conditions. Generally, the palladium compound is employed in a quantity of at least 1 mol % based on the aryl bromide.

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(11) (a) Cabri, W.; Candiani, I.; Bedeschi, A. *J. Org. Chem.* **1992**, *57*, 3558. (b) Cabri, W.; Candiani, I.; Bedeschi, A.; Penco, S. *J. Org. Chem.* **1992**, *57*, 1481.

(12) Dieck, H. A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1133.

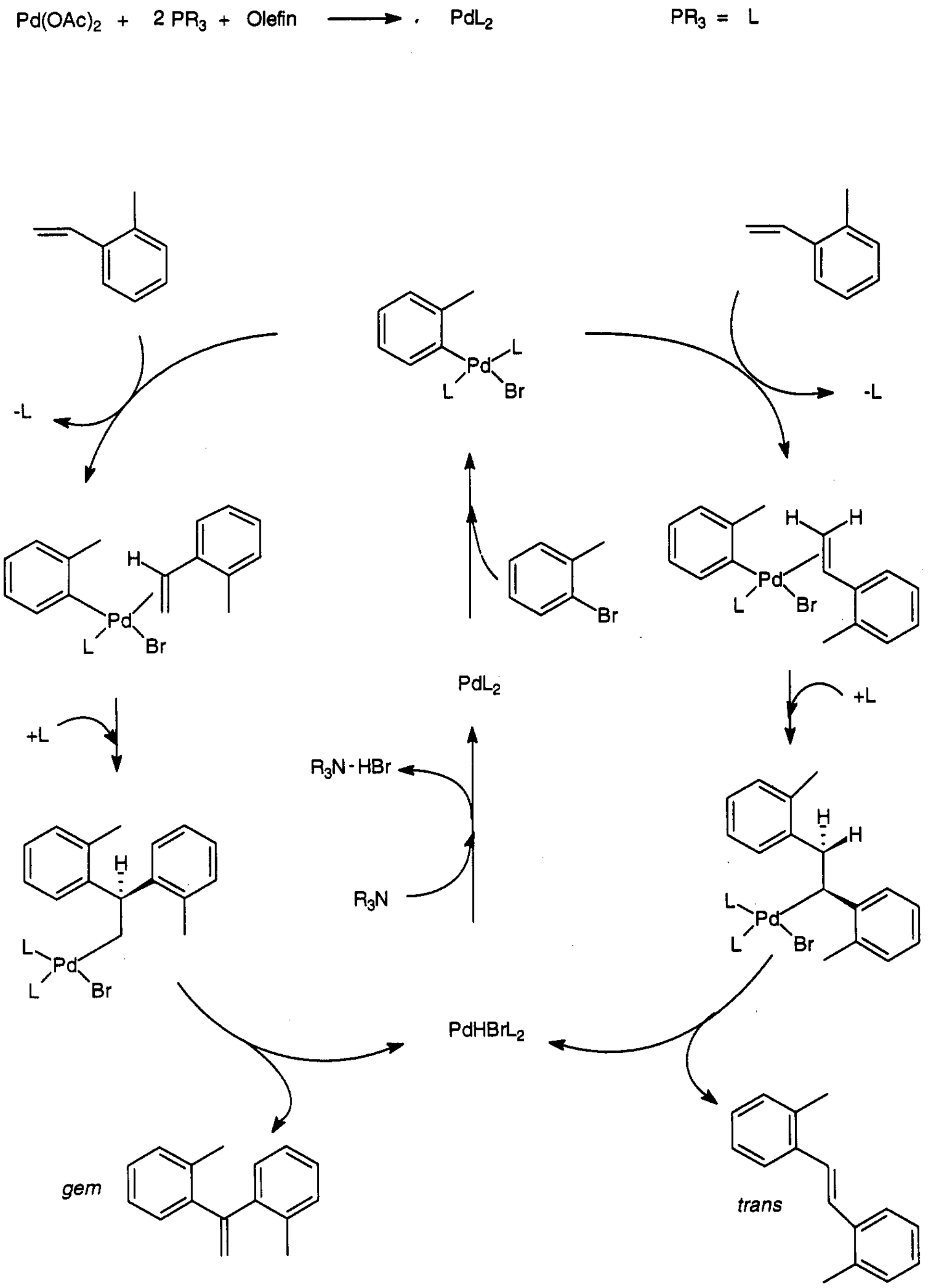

Figure 2. Mechanism of bisarylation isomer formation (based on ref 12).

Styrene derivatives are formed mainly at higher pressures. Spencer showed that stilbene derivatives are the principal products when ethylene is a reactant.[2] He also found a higher yield at lower catalyst concentrations than those reported by Heck, especially if DMF was the solvent. Spencer reported that anhydrous sodium acetate could be used as base, rather than triethylamine, but that these alkali metal salts may be only partially soluble in the reaction medium.

The selectivity between mono- and bisarylation can be driven to bisarylation (stilbene) products by monitoring the reaction conversion to about 45% and then venting the ethylene from the reactor. This leaves a 1 to 1 ratio of styrene to aryl bromide. If monoarylation is desired, the ethylene concentration relative to the aryl bromide must be increased in the reaction. At relatively low pressures, the solubility of ethylene is very dependent on the solvent. Using less aryl bromide also increases the selectivity by increasing the ratio of ethylene to aryl bromide in solution. At 100 psig of ethylene (typical pressure rating of a Pfaudler reactor), the solubility of ethylene and selectivity to monoarylation in DMF are better than in a DMF/water mixture. This is less important at higher pressures, where the use of DMF/water with water-soluble bases is advantageous. Because the 10-gallon reactor available for scale-up had a maximum working pressure rating of 100 psig, the solvent of choice for highest selectivity was DMF rather than a combination of DMF and water. The reaction was further studied in DMF at 75 °C and 100 psig ethylene with a 4 to 1 and 2 to 1 ratio of ligand to palladium (runs 15 and 16). The 4 to 1 excess of ligand was needed to maintain high conversion and selectivity for 378 turnovers in 24 h.

Ten-Gallon Studies. A series of arylations was run in a 10-gallon reactor to provide a quantity of high-purity monomer for polymerization studies. These reactions were

Table 4. Summary of 10-Gallon Reactions in DMF with TEA

run no.	reacn temp (°C)	time (h)	ethylene pressure (psig)	BrTol conv[a] (%)	OVT selectivity[b] (%)	isolated OVT yield (g)	recovered OVT (g)	actual catalyst turnovers
19	90	40	85	99.9	87.5	64.3	2152.7	399
20	90	40	85	100.0	91.4	67.2	2249.1	400
21	90	40	85	99.6	79.8	59.4	1988.9	399
22	90	40	85	99.6	92.5	65.3	2185.7	399
23[c]	90	73	85	84.0	76.0			336
		19		99.8	85.6	27.8	932.0	
24[d]	90	70	85	43.8	97.5			876/2000
		29		99.7	91.1	41.6	1392.1	400

[a] Conversion of bromotoluene to products. [b] Selectivity of converted bromotoluene to *o*-vinyltoluene. [c] Triethylamine base was reduced from a 2-fold excess to bromotoluene to a 1.5-fold excess. This reaction was slow and stopped after 73 h, so a second charge of catalyst (50% of original charge) makeup with TEA was added. [d] The catalyst was reduced to 20%, and the reaction stopped after 876 turnovers, so an additional catalyst charge (80% of the other batches) was added to complete the reaction.

done using 0.25 mol % catalyst in DMF where ethylene has a relatively high solubility at 90 °C and 85 psig to ensure complete conversion (see Table 4, runs 19 through 24). Although a higher ethylene pressure would increase selectivity, this jacketed reactor system was limited to about 100 psig. The batch size was approximately 1400 times larger than that described by Heck and would be expected to show possible scale-up limitations due to heat transfer, agitation, and diffusion problems. The product was easily purified by distillation on a short-path molecular distillation unit to greater than 99.5% purity (GLC area %) free of any indan/indene or bis(*o*-tolyl)ethylene impurities. This monomer was used to make low-color, high molecular weight homopolymer and copolymers with styrene.

In general, the arylation reactions went smoothly, duplicating results found in the 2-L Parr reactor studies. However, a buildup of salt on the agitator was sometimes observed upon inspection of the reactor. During the latter part of the reaction, salt may also have precipitated in the bottom of the reactor, causing lower thermocouple readings. These problems could be avoided by using a mixed DMF and water solvent system to dissolve any salts that form. The selectivity in run 21 was low because ethylene was not added during heat-up of the reactor. The overall isolated yields include recovery losses that occurred during sampling, phase cuts, filtration, and distillation. In run 23 the excess of base was lowered from 2-fold to 1.5-fold, which decreased the rate and gave incomplete reaction. The reactor was cooled, extra base (to make 2-fold excess) and catalyst (50% of the original charge) were added, and the reactor was heated longer for complete reaction. In run 24 an attempt was made to lower the catalyst loading to 20% of the other batches. This also slowed the reaction such that additional catalyst (80% of the other batches) was needed to complete the reaction. Isolated yields in runs 23 and 24 were much lower due to equipment problems.

Conclusions

The Heck palladium-catalyzed arylation reaction has been used to make high-purity, indene-free, *o*- and *p*-vinyltoluenes in high yields from *o*- and *p*-bromotoluenes. Catalyst turnover, rate, and lifetime were significantly improved over similar previously reported arylation reactions by changing the catalyst concentration, ligand to palladium ratio, ethylene pressure, temperature, and solvent system. An inorganic base such as potassium acetate can be substituted for triethylamine in this reaction and kept soluble by using a mixture of DMF and water as solvent. Side products formed are from a second addition of bromotoluene to the vinyltoluene product, making both *trans* and *gem* bis adducts. The formation of bisarylation products can be controlled by adjusting and/or venting ethylene pressure during the reaction. Polymerization of the monomers during the coupling and distillation was minimal. The Heck arylation reaction has been scaled 1400-fold to a 10-gallon reactor to make pound quantities of *o*-vinyltoluene for polymerization studies.

Experimental Section

Analytical Equipment. Routine gas–liquid chromatographic (GLC) analysis was performed on a Hewlett-Packard 5890 gas chromatograph with a flame ionization detector, a 7676A automatic sampler, and a Hewlett-Packard 3390 integrator using known standards of pure bromotoluene and vinyltoluene isomers. The column was a 15-m by 0.32-mm fused silica capillary column bonded with DB-5 (0.1-μm film). The heat program was held for 2 min at 70 °C and then ramped at 8 °C/min up to 230 °C. The order of elution was *o*-vinyltoluene (0.9 min), *o*-bromotoluene (1.1 min), 1,1-*gem*-bis(*o*-tolyl)ethylene (10.3 min), 1,2-*trans*-bis(*o*-tolyl)ethylene (13.3 min), tris(*o*-tolyl)phosphine (18 min), and tris(*o*-tolyl)phosphine oxide (20 min).

Materials. 2-Bromotoluene and 4-bromotoluene (98%) were obtained from Aldrich or Austin Chemical. Triethylamine (reagent grade), silica gel (chromatographic 644 grade), and *N*,*N*-dimethylformamide (reagent grade) were purchased from Fisher Scientific. Potassium acetate (reagent grade) was purchased from J. T. Baker. The catalyst was prepared in the reactor from palladium acetate obtained from Engelhard and tris(*o*-tolyl)phosphine (99.0%) from Strem Chemical. Ethylene (CP grade, 99.5%) was purchased from Scott Gas. All materials were used as received.

General Procedures for the Arylation of Ethylene. Two-Liter Reactor. The reactions were run in a stainless-steel 2-L Parr reactor located in a high-pressure cubicle area. The reactor was equipped with an air-motor-driven stirring shaft, gas inlet tube equipped to purge both nitrogen and ethylene, pressure gauge, sampling system, internal thermowell, blow-out frangible, and a vent to the roof. An electrically heated mantle was used which was connected to a high-temperature-limit shutoff and a West temperature controller attached to a Molytek Model 2702 recorder.

Two-Liter Preparation of *o*-Vinyltoluene. To the reactor was charged 374 g (2.187 mol) of 2-bromotoluene, 442 g (4.376 mol) of triethylamine, 0.59 g (0.0026 mol) of palladium acetate, 3.18 g (0.0104 mol) of tris(*o*-tolyl)phosphine, 600 mL of *N*,*N*-dimethylformamide, and 300 mL of deionized water. The reactor was sealed and attached to the reactor system. After stirring was initiated, the contents of the vessel was purged with nitrogen (75 psig) five times. The nitrogen was vented and the reactor charged with ethylene to 75 psig and held at this pressure. A sample of about 5 mL was removed from a double-valved sample dip tube and used as the initial feed sample. Additional samples were taken during the reaction. The temperature controller was set at 75 °C, and heating was initiated. The contents of the reactor reached the selected temperature after 30 min and was maintained at that temperature for the duration of the run. The contents of the reactor was cooled to room temperature with stirring and the excess ethylene vented off. The reaction vessel was detached and opened in a hood.

The contents of the reactor was poured into a 5-L, three-necked, glass, round-bottom flask containing 1 L of methylene chloride and 1 L of water. The flask had a bottom dump valve and was mechanically stirred with an air motor, and the top aqueous phase was discarded. The organic phase was washed two more times with 1.5-L washes of water, followed by a wash with 250 mL of 5 N HCl in 1250 mL of water, and then another two washes with 1.5-L washes of water. A filtration was done on a short column prepared using a 300-mL Fisherbrand microfiltration system with a 5-μm membrane filter containing 150 mL of silica topped with 60 mL of magnesium sulfate. This system filtered any residual solids or catalyst and dried the solution. The methylene chloride was removed by a rotary evaporator at 40 °C and 15 mmHg, yielding 227 g of crude product. This was distilled from a 500-mL round-bottom flask attached to an 8-in. Bantamware column packed with glass helices attached to a one-piece Bantamware distillation unit equipped with a vacuum-jacketed Vigreaux section and fraction cutter. The product was distilled overhead at 55 °C and 0.35 mmHg to give 166.3 g of pure (99.8% by GPC) *o*-vinyltoluene. The proton and carbon NMR were compared against known standards. The pot residue at the end of the distillation contained 53.2 g of material, which crystallized upon cooling. Analysis by capillary GLC and GC/MS against known standards showed this to contain *o*-vinyltoluene (3.5 area %), 1,2-*trans*-bis(*o*-tolyl)ethylene (60%), 1,1-*gem*-bis(*o*-tolyl)ethylene (30%), and tris-(*o*-tolyl)phosphine (4%). The isolated yield of *o*-vinyltoluene was 166.3 g or 64% of the 258 g theoretical. The results are shown in Table 2, run 5.

The crystals from the distillation bottoms were separated, washed, and analyzed and found to be mainly *trans*-1,2-bis(*o*-tolyl)ethylene: CAS Reg. No. 20657-42-5; MS *m/e* 200; mp 81–83 °C; ^{1}H NMR: 2.3 (triplet, methyl), 6.8–7.5 (multiplet, methine and aromatic) ppm.

Two-Liter Preparation of *p*-Vinyltoluene. The reaction was run as in run 5, except that *p*-bromotoluene was used instead of *o*-bromotoluene and 0.98 (0.0044 mol) of palladium(II) acetate and 5.32 g of tris(*o*-tolyl)phosphine were used as catalyst. The reaction was run at 120 °C and 200 psig of ethylene. Samples were taken at 0, 3, and 5 h and used for GLC analysis. At the end of 3 h, the GLC showed 77.65% *p*-vinyltoluene, less than 0.5% *p*-bromotoluene, 18.1% of the *trans*-1,2-bis(*p*-tolyl)ethylene adduct, and 3.0% of the *gem*-1,1-bis(*p*-tolyl)ethylene adduct. The reaction was stopped and worked up as in run 5, except that 1.5 L of additional methylene chloride was used to dissolve the precipitated solids. The solids were isolated, purified, and characterized as the *trans*-1,2-bis(*p*-tolyl)ethylene: CAS Reg. No. 18869-29-9; mp 179–180 °C (51 g). The total yield of isolated crude products was 225.5 g, comprising 72.9% *p*-vinyltoluene, 22.0% *trans*-1,2-bis(*p*-tolyl)ethylene, 3.2% of the *gem*-1,1-bis(*p*-tolyl)ethylene adduct, and 1.2% tris(*o*-tolyl)phosphine. The results are shown in Table 2, run 17.

Two-Liter Preparation of *p*-Vinyltoluene with Potassium Acetate. The reaction was run as in run 9, except that 429 g (4.37 mol) of potassium acetate was used, instead of triethylamine. At the end of 3 h, the reaction mixture contained 88.9% *p*-vinyltoluene, 4.5% *p*-bromotoluene, 3.76% of the *trans*-1,2-bis(*o*-tolyl)ethylene adduct, and 2.26% of the *gem*-1,1-bis(*o*-tolyl)ethylene adduct. The reaction was stopped after 7 h and worked up to give 225.3 g of crude product comprising 82.8% *p*-vinyltoluene, 8.4% *trans*-1,2-bis(*o*-tolyl)ethylene adduct, 3.86% *gem*-1,1-bis(*o*-tolyl)ethylene adduct, and 3.21% tris(*o*-tolyl)phosphine. The results are shown in Table 2, run 18.

Ten-Gallon Reactions. The reactions were run in a computer-controlled, agitated, 10-gallon, jacketed Pfaudler glass-lined reactor located in a high-pressure cubicle area. All materials were vacuum-loaded in the following order: palladium acetate (15.9 g) and tris(*o*-tolyl)phosphine (86.22 g) in 1 gallon of DMF, 2-bromotoluene (4847 g), triethylamine (5733 g), and then another 4 gallons of DMF (total of 11 786 g). This gave a ratio of palladium to tris(*o*-tolyl)phosphine to bromotoluene of 1 to 4 to 400. The reactor was purged by twice evacuating to −10 psig and then pressurizing to 10 psig with nitrogen and then put under 10 psig of ethylene. During this purging and heat-up step, ethylene was controlled manually and gradually increased to 85 psig. The reactor was heated using a mixture of hot and cold Dowtherm (trademark of The Dow Chemical Co.) J heat-transfer fluid pumped through a jacketed shell on the system. Heat-up to 90 °C took 1 h and 20 min with no apparent exotherm observed during this period. After reaching the desired temperature and pressure, the computer control was activated to maintain these conditions. Progress of the reaction was monitored by taking samples from the reactor bottom valve using an evacuated 125-mL sample cylinder. These reactions were run up to 40 h to achieve complete conversion, except runs 23 and 24, where the amount of base and catalyst was lowered, respectively.

After the desired conversion was reached, the reactor was cooled to room temperature and 2 gallons of water was added. The aqueous phase of this mixture was then separated and the organic phase washed with 1.5 gallons of 6 N HCl added slowly to neutralize any excess base. The aqueous phase was again separated and the organic phase washed twice more with water. The organic phase was then passed through 200 mL (dry volume) of silica gel topped with 60 mL of anhydrous magnesium sulfate and then through a 5-μm membrane filter, to remove any residual solids and to dry the solution.

The crude *o*-vinyltoluene was distilled on a Leybold-Heraus short-path molecular distillation system (model KDL-4) at 70 °C and 5 mmHg at a feed flow rate of 10 mL/min (1.2 lb/h). The feed flow rate was adjusted to control precipitation of bis(*o*-tolyl)ethylene adducts on the walls. The distillate and material captured in the dry-ice trap were clear, colorless, high-purity (>99.2%) *o*-vinyltoluene. The crude and final products were inhibited with 100 ppm of 4-methoxyphenol (MEHQ) to prevent polymerization and stored cold. The remainder, which was mainly *trans*-1,2- and *gem*-1,1-bis(*o*-tolyl)ethylene, was a viscous, brown liquid which precipitated some solids upon cooling.

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