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## The Nickel(0)-Catalyzed Addition of Phenol to Butadiene

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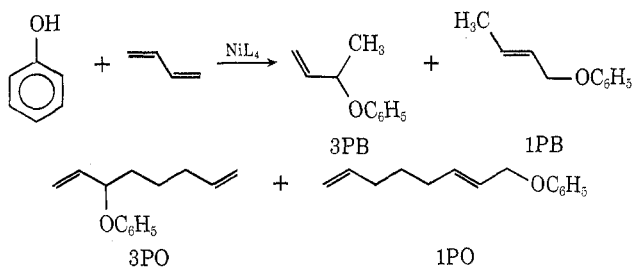
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The (organophosphorus)nickel(0)-catalyzed reaction of phenol and butadiene gives mixtures of 3-phenoxy-1-butene, 1-phenoxy-2-butene, 3-phenoxy-1,7-octadiene, and 1-phenoxy-2,7-octadiene. The formation of phenoxybutenes is favored by electron-donor ligands, excess ligand, high phenol concentration, and low conversions. A mechanism based on dual reaction pathways for an (organophosphorus)nickel intermediate is presented to explain these results.

Mechanistic understanding of transition metal catalyzed reactions is far behind other fields of chemistry. Recently elegant studies have elucidated some details by isolation and identification of intermediates in catalytic cycles.<sup>1-3</sup> Hopefully the concepts developed in such pioneering work can be broadly applied to related reactions.

Phenol reacts with butadiene in the presence of tetrakis(organophosphorus)nickel(0) to give 3-phenoxy-1-butene, *trans*-1-phenoxy-2-butene, 3-phenoxy-1,7-octadiene, and *cis*- and *trans*-1-phenoxy-2,7-octadiene.<sup>4</sup>



The goal of this work was to optimize the formation of the phenoxybutenes, as palladium seems to be a superior catalyst for the synthesis of phenoxyoctadienes.<sup>4,5</sup>

### Experimental Section

**Analytical Runs.**—A Pyrex tube was sealed with a serum stopper and evacuated. Butadiene was distilled into the tube at  $-78^\circ$  from a calibrated reservoir. Solutions of phenol in ether, nickelocene in benzene, and ligand were injected *via* syringe and the tube was sealed. The order of addition was immaterial. After warming to room temperature the tubes were heated and agitated in a thermostatted oven. After the desired reaction time the tubes were cooled to  $-78^\circ$  and opened, and the contents were examined by gas chromatography on a 6 ft  $\times$  0.25 in. column of

20% silicone 200 supported on Gas-Chrom RA (60-80) at  $180^\circ$  and 75 ml/min. The retention times (minutes) follow: phenol, 1.0; 3PB, 1.7; 1PB, 2.7; 3PO, 7.2; and 1PO, 11.7. Areas were calculated using triangular approximation of peak height times line width. Standards prepared using materials purified by preparative gas chromatography showed that area per cent calculated in this way corresponded closely to mole per cent. Precision is estimated at  $\pm 3\%$  for duplicate runs; accuracy is undoubtedly lower.

Catalyst cycles are defined as moles of products per mole of nickel charged. The yield of the phenoxybutenes and phenoxyoctadienes is essentially quantitative based on phenol consumed.

**Preparative Runs.**—A Hastelloy C bomb was charged under nitrogen with solutions of ligand, nickelocene, and phenol in ether. The bomb was sealed, evacuated, and charged with butadiene. After the reaction was complete excess butadiene was vented and the remaining contents were discharged. The ether solution was extracted with sodium hydroxide until gc showed the absence of phenol. After removal of most of the solvent, the residue was distilled through a Nestor-Faust spinning-band column at reduced pressure. Four fractions were obtained: fraction 1, 3-phenoxy-1-butene, bp  $37-40^\circ$  (1 mm),  $n_D^{25}$  1.5072 [lit.<sup>6</sup> bp  $43^\circ$  (0.8 mm)]; fraction 2, 1-phenoxy-3-butene, bp  $58-59^\circ$  (1 mm),  $n_D^{25}$  1.5173 [lit.<sup>6</sup> bp  $87^\circ$  (8 mm)]; fraction 3, 3-phenoxy-1,7-octadiene, bp  $87^\circ$  (1 mm),  $n_D^{25}$  1.5077; fraction 4, 1-phenoxy-2,7-octadiene, bp  $104^\circ$  (1 mm),  $n_D^{25}$  1.5153. The proton nmr spectrum of fraction 4 suggested the presence of 15% *cis* and 85% *trans* isomers.<sup>4</sup> No attempt was made to separate these two compounds.

Phosphorus ligands and nickel(0) complexes were obtained from the same sources cited by Tolman.<sup>7</sup>

The results of the studies of several reaction variables are presented individually followed by discussion in terms of a single mechanistic proposal.

**Temperature-Time.**—Time studies at  $100^\circ$  with tetrakis(triphenylphosphite)nickel catalyst showed that the reaction was essentially complete after 2 hr, and the product composition was unchanged on extended heating. Higher temperatures gave lower conversions to the four addition products and new peaks began to appear in the gas chromatograms. Although these products have not been isolated and identified, they may result from phenol alkylation rather than addition.<sup>4</sup> Heating for 15 hr at  $90^\circ$  gave essentially identical yields and conversions as runs at  $100^\circ$ , but lower temperatures showed a sharp discontinuity. The product distribution at various temperatures for 15 hr is summarized in Table I while the product distribution as a function of time at  $70^\circ$  is given in Table II.

There is an induction period before the rapid formation of phenoxyoctadienes begins. The absolute amount of phenoxybutenes does not decline during this rapid formation of phenoxyoctadienes, but steadily increases. At low conversion the yield of 3PB is greater than that of 1PB, but later the relative amount of 1PB increases.

(6) H. L. Goering and R. R. Jacobson, *J. Amer. Chem. Soc.*, **80**, 3277 (1958).

(7) C. A. Tolman, *ibid.*, **92**, 2956 (1970).

(1) (a) Hydroformylation: R. F. Heck, *Advan. Organometal. Chem.*, **4**, 243 (1966). (b) Palladium-catalyzed oxidations: A. Aguiló, *ibid.*, **5**, 321 (1967).

(2) (a) Rhodium-catalyzed ethylene dimerization: R. Cramer, *J. Amer. Chem. Soc.*, **87**, 4717 (1965). (b) Nickel-catalyzed addition of ethylene to butadiene: C. A. Tolman, *ibid.*, **92**, 6777 (1970).

(3) For a review of the chemistry of butadiene with nickel(0) see P. Heimbach, P. W. Jolly, and G. Wilke, "Advances in Organometallic Chemistry," Vol. 8, Academic Press, New York, N. Y., 1970, pp 29-86.

(4) E. J. Smutny, H. Chung, K. C. Dewhirst, W. Keim, T. M. Shryne, and H. E. Thyret, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14** (2), B100-B111 (1969); H. Chung and W. Keim, U. S. Patent 3,636,162 (1969).

(5) Since the completion of this work, T. C. Shields and W. E. Walker, *Chem. Commun.*, 193 (1971), have described experiments in this area.

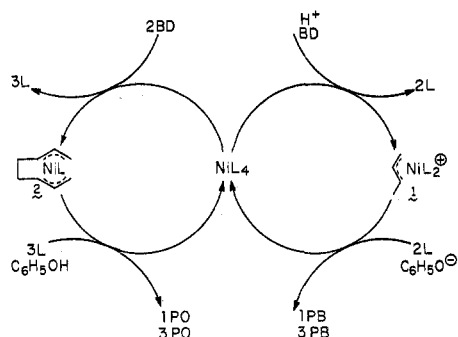


Figure 1.—Postulated mechanism for the nickel(0)-catalyzed synthesis of phenoxybutenes and phenoxyoctadienes.

TABLE I  
TEMPERATURE EFFECTS<sup>a</sup>

Temp, °C	Catalyst cycles	Yield, %			
		3PB	1PB	3PO	1PO
64	7	58	25	1	16
80	8	55	28	0	19
90	71	14	10	9	68
100	79	11	13	16	60
113	55	13	12	10	65
125	40	12	12	8	68
151	20 <sup>b</sup>	8	24	0	68

<sup>a</sup> 25 mmol of BD/10 mmol of phenol, 15 hr, 0.1 mmol of Ni-[P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>4</sub>, ether solvent. <sup>b</sup> Plus many side products.

TABLE II  
EFFECT OF REACTION TIME ON PRODUCT DISTRIBUTION<sup>a</sup>

Time, hr	Catalyst cycles	Yield, %				Absolute yield of phenoxybutene
		3PB	1PB	3PO	1PO	
4	3	55	23	6	15	2
8	5	52	16	6	26	4
16	19	32	16	8	44	9
32	72	13	10	12	64	16

<sup>a</sup> 10 mmol of C<sub>6</sub>H<sub>5</sub>OH, 25 mmol of BD, 0.1 mmol of Ni(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>, 0.4 mmol of (C<sub>6</sub>H<sub>5</sub>O)<sub>3</sub>P, 70°, ether solvent.

**Ligand to Metal Ratio.**—Initially, preformed NiL<sub>4</sub> species served as catalysts and excess ligand was added to stabilize an intermediate if excessive ligand dissociation was the mechanism of catalyst deactivation. Starting with nickel-olefin complexes, ligand-to-metal ratios lower than 4:1 could be studied. The results of varying the ratio of triphenyl phosphite to nickelocene are shown in Table III. The adducts do not form in the absence

TABLE III  
EFFECT OF LIGAND TO METAL RATIO<sup>a</sup>

Triphenyl phosphite, mmol	Catalyst cycles	Yield, %			
		3PB	1PB	3PO	1PO
0.1	6	13	5	7	75
0.2	44	11	6	11	72
0.3	38	13	7	9	71
0.4	54	10	16	23	51
0.8	59	10	16	21	53
1.2	35	28	26	9	37
2.0	15	47	40	3	10

<sup>a</sup> 0.1 mmol of nickelocene, 25 mmol of BD, 10 mmol of C<sub>6</sub>H<sub>5</sub>OH, 100°, 15 hr, ether solvent.

of a phosphorus ligand. As triphenyl phosphite is initially added, the major products are phenoxyoctadienes, and up to 8 equiv of ligand does not significantly change this product distribution, although the ratio of linear to branched products is affected. Excess ligand slows the reaction and increases the

TABLE IV  
EFFECT OF REACTANT RATIOS ON PRODUCT DISTRIBUTION<sup>a</sup>

BD/C <sub>6</sub> H <sub>5</sub> OH	Catalyst cycles	Yield, %			
		3PB	1PB	3PO	1PO
Catalyst Ni[P(OEt) <sub>3</sub> ] <sub>4</sub>					
1.25:1	46	32	54	2	10
2.5:1	84	22	36	10	32
5:1	96	21	31	8	40
Catalyst Ni[P(OC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>4</sub>					
0.67:1	14	39	33	6	23
1.25:1	49	20	21	8	52
2.5:1	79	11	13	11	60
10:1	77	13	10	12	65

<sup>a</sup> Solvent Et<sub>2</sub>O, 100°, 15 hr.

yield of phenoxybutenes. When runs with large excesses of ligand are cooled, tetrakis(triphenyl phosphite)nickel precipitates from solution.

**Reactant Ratios.**—As the ratio of butadiene to phenol is increased, the phenoxyoctadienes comprise a larger proportion of the product; however, above 3 equiv of butadiene per phenol little change in the product distribution occurs. Table IV gives the results of varying the ratio of phenol to butadiene with tetrakis(triphenyl and triethyl phosphite)nickel catalysts.

**Ligand Effects.**—Table V gives the product distribution with different phosphorus ligands. For triphenyl phosphite the yields and conversion are identical whether the catalyst was preformed or prepared *in situ* from either nickelocene or bis(cyclooctadiene)-nickel and the ligand. Preformed complexes were required for triethyl phosphite and all phosphines. For the other ligands listed *in situ* preparation was apparently adequate. Phosphines and phosphonites give high yields of phenoxybutenes. Phosphines favor 3PO while phosphonites favor 1PO. Phosphinites and phosphites give high yields of phenoxyoctadienes. By varying *only* the ligand, any of three compounds can be the major product.

Mixtures of ligands give intermediate product distributions. Addition of triphenyl phosphite to tetrakis(triphenylphosphine)-nickel or triphenylphosphine to tetrakis(triphenyl phosphite)-nickel gave essentially the same product distribution.

**Solvent.**—Diethyl ether was generally used, but the reaction proceeded well in hydrocarbons or with no added solvent. Protic solvents promote the formation of octatrienes. Halogenated solvents such as carbon tetrachloride or chloroform were unsatisfactory, possibly because of oxidation of the nickel(0) species. Traces of water inhibit this reaction and all reagents and reaction vessels must be dried.

**Equilibration.**—Heating solutions of either phenoxybutene in ether with catalytic amounts of tetrakis(triphenyl phosphite)-nickel establishes an equilibrium of 65% 1PB and 35% 3PB. Some leakage to the phenoxyoctadienes and butadiene dimers and phenol occurs, but the equilibrium could be established from both 1PB and 3PB. Equilibration was much slower than the addition reaction, requiring several days at 100° with 1 mol % catalyst. The phenoxybutenes are not equilibrated if butadiene is present, nor are phenoxyoctadienes formed. Attempts to equilibrate the phenoxyoctadienes gave only octatrienes and phenol.

## Discussion

Figure 1 summarizes the mechanism postulated for the tetrakis(organophosphorus)nickel-catalyzed reaction of phenol with butadiene. The initial steps leading to complex 1 are probably identical with those postulated by Tolman in the nickel(0)-catalyzed addition of ethylene to butadiene.<sup>2</sup> The subsequent steps must differ because in Tolman's mechanism the nickel becomes bonded to the ethylene carbons in the newly coupled product. The  $\pi$ -allyl complex 1 may react with phenoxide anion and lose phenoxybutene to reform the nickel(0) species. This intermediate can react in either of two ways to produce two interwoven catalytic cycles. Protonation continues the phenoxybutene reaction.

TABLE V  
 LIGAND EFFECTS ON PRODUCT DISTRIBUTION<sup>a</sup>

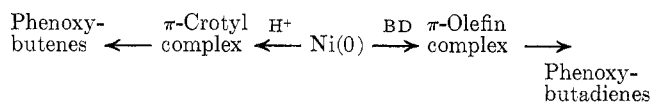
Phosphorus ligand PR <sub>1</sub> R <sub>2</sub> R <sub>3</sub>			Catalyst cycles	Yield, %			
R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>		3PB	1PB	3PO	1PO
OC <sub>6</sub> H <sub>5</sub>	OC <sub>6</sub> H <sub>5</sub>	OC <sub>6</sub> H <sub>5</sub>	74	10	12	18	60
C <sub>6</sub> H <sub>5</sub>	OC <sub>6</sub> H <sub>5</sub>	OC <sub>6</sub> H <sub>5</sub>	80	9	13	22	55
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	OC <sub>6</sub> H <sub>5</sub>	62	29	22	16	33
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	36	71	9	7	12
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	45	27	46	8	19
C <sub>6</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	48	25	45	9	21
OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	80	21	35	9	31
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	OCH <sub>3</sub>	67	21	34	12	32
C <sub>6</sub> H <sub>5</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>	51	47	28	8	18
C <sub>6</sub> H <sub>5</sub>	O- <i>n</i> -C <sub>4</sub> H <sub>9</sub>	O- <i>n</i> -C <sub>4</sub> H <sub>9</sub>	59	22	41	9	27
C <sub>6</sub> H <sub>5</sub>	O- <i>i</i> -C <sub>3</sub> H <sub>7</sub>	O- <i>i</i> -C <sub>3</sub> H <sub>7</sub>	54	23	41	10	26
(O(4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )) <sub>3</sub>			66	9	17	21	52
CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	36	74	13	8	4
CH <sub>3</sub>	OC <sub>6</sub> H <sub>5</sub>	OC <sub>6</sub> H <sub>5</sub>	34	44	39	4	13
C <sub>2</sub> H <sub>5</sub>	OC <sub>6</sub> H <sub>5</sub>	OC <sub>6</sub> H <sub>5</sub>	51	13	23	21	43

<sup>a</sup> 25 mmol of BD, 10 mmol of C<sub>6</sub>H<sub>5</sub>OH, 0.1 mmol of Ni, 0.4 mmol of ligand, ether solvent, 100°, 15 hr.

Alternatively, reaction with butadiene may begin a catalytic cycle leading to phenoxyoctadienes. The sequence of steps leading to Wilke intermediate 2 is straightforward.<sup>3</sup> At this point ring closure can give vinylcyclohexene or 1,5-cyclooctadiene. Protonation of the nickel followed by the transfer of the proton to the interior position of the allyl ligand leads to an intermediate analogous to 1. Elimination of a nickel hydride would form linear butadiene dimers.<sup>3</sup> The steps leading to the phenoxyoctadienes are now similar to those which convert 1 to phenoxybutenes.

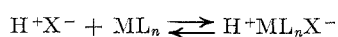
Several observations suggest that the phenoxybutenes and phenoxyoctadienes are formed in separate, yet interrelated pathways. Both phenoxybutenes have methyl groups while neither of the phenoxyoctadienes has a methyl group, either terminal or internal. It is very difficult to conceive of a mechanism leading from  $\pi$ -allyl complex 1 to a product which does not contain a methyl group. The concentration of phenoxybutenes never declines during the reaction, though if the phenoxybutenes were intermediates in the formation of phenoxyoctadienes, their concentration would be expected to reach a maximum at some point. The phenoxybutenes do not react with butadiene under the reaction conditions to give phenoxyoctadienes.

Two competing reactions for a coordinatively unsaturated nickel(0) species are postulated to determine the course of the reaction.



The effects of the relative concentrations of phenol and butadiene are easily seen; the effects of reaction time and ligand are more subtle.

The equilibrium constant for the protonation of an organometallic complex depends on the protonating



species, the metal, and its associated ligands. The equilibrium constant for the protonation of tetrakis-

(phosphorus)nickel(0) correlates with the CO stretching frequency of Ni(CO)<sub>3</sub>L and has the order P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> > P(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub> > P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>.<sup>8</sup> Nickel is more basic than palladium,<sup>9</sup> which favors phenoxybutene formation. Initially a large proportion of the nickel may be protonated, thus forming phenoxybutenes. From the behavior of the product distributions with time the rate of the cycle producing phenoxyoctadienes appears to be faster than the cycle producing phenoxybutenes, though in the absence of data on the relative amounts of the various forms of nickel(0) actually present, absolute rate factors cannot be determined.

The  $\pi$ -allyl complex 1 has two ligands per nickel, while the Wilke intermediate 2 has only one. If the steps leading to 2 are reversible until the two butadienes are coupled, excess ligand would favor phenoxybutene formation.

### Conclusion

Phenoxybutenes can be made the main product of the nickel(0)-catalyzed addition of phenol to butadiene by the use of excess phosphorus ligands, good electron-donor ligands, or a high ratio of phenol to butadiene. Phosphine ligands produce a high yield of 3-phenoxy-1-butene in a kinetically controlled process while phosphonites, phosphinites, and phosphites produce phenoxybutenes in proportions approaching thermodynamic equilibrium.

**Registry No.**—Nickel, 7440-02-0; phenol, 108-95-2; butadiene, 106-99-0; 3-phenoxy-1-butene, 22509-78-0; 1-phenoxy-3-butene, 2653-89-6; 3-phenoxy-1,7-octadiene, 15972-91-5; 1-phenoxy-2,7-octadiene, 13846-40-7.

**Acknowledgments.**—We wish to thank C. A. Tolman and G. W. Parshall for valuable discussions.

(8) C. A. Tolman, submitted for publication in *Inorg. Chem.*

(9) C. A. Tolman, W. C. Seidel, and D. H. Gerlach, *J. Amer. Chem. Soc.*, **94**, 2669 (1972).