with dichloromethane. The combined organic fraction was dried over anhydrous sodium sulfate and concentrated in vacuo to give a white crystalline powder, which was chromatographed (ThLC), eluting with ethyl acetate–cyclohexane (1:1) to afford the two major products.

Fraction A gave the syn 2:2 macrocycle **4**, as white crystals: mp 141–142 °C ($CHCl_3$–diethyl ether); 120 mg (5.5%); R_f 0.16; NMR δ 3.86 (m, β,β'-CH_2, 8 H), 4.52 (m, α,α'-CH_2, 8 H), 6.48 (d, 5-pyr-H, J = 8.8 Hz, 2 H), 7.92 (dd, 4-pyr-H, J = 2.3, 8.8 Hz, 2 H), 8.65 (d, 2-pyr-H, J = 2.3 Hz, 2 H); IR (KBr) 1725 (vs, C=O), 1705 (s, C=O), 1605 (s, C=C), 1575 (w, C=N), 1280 (br, vs, C—O, 1135 (s, C—O), cm^{-1}; mass spectrum (70 eV), m/e (assignment, relative intensity) 419 ($M^+ + 1$, 0.6), 418 (M^+, 2.5), 417 ($M^+ - 1$, 0.4), 375 ($M^+ - C_2H_3O$, 33), 236 ($C_{12}H_{14}NO_4$, 3.2), 210 ($C_{10}H_{12}NO_4$, 8.6), 166 ($C_8H_8NO_3$, 100), 148 ($C_8H_6NO_2$, 25.1), 122 ($C_6H_4NO_2$, 71.5), 121 ($C_6H_3NO_2$, 22.0).

Anal. Calcd for $C_{20}H_{22}N_2O_8$: C, 57.41; H, 5.30; N, 6.70. Found: C, 57.28; H, 5.31; N, 6.81.

Fraction B yielded the anti 2:2 macrocycle **5** as white needles: mp 167–168 °C ($CHCl_3$); 140 mg (6.4%); R_f 0.12; NMR δ 3.92 (m, β,β'-CH_2, 8 H), 4.50 (m, α,α'-CH_2, 8 H), 6.55 (d, 5-pyr-H, J = 8.7 Hz, 2 H), 7.89 (dd, 4-pyr-H, J = 2.3, 8.7 Hz, 2 H), 8.57 (d, 2-pyr-H, J = 2.3 Hz, 2 H); IR (KBr) 1715 (vs, C=O), 1608 (s, C=C), 1575 (w, C=N), 1290 (br, vs, C—O), 1130 (s, C—O) cm^{-1}; mass spectrum (70 eV), m/e (assignment, relative intensity) 419 ($M^+ + 1$, 0.5), 418 (M^+, 1.9), 417 ($M^+ - 1$, 0.2), 375 (17.0), 236 (7.7), 210 (23.6), 166 (100), 148 (9.8), 122 (71.5), 121 (12.2).

Anal. Calcd for $C_{20}H_{22}N_2O_8$: C, 57.41; H, 5.30; N, 6.70. Found: C, 57.34; H, 5.09; N, 6.62.

Reaction of 3 with Disodium Pentaethylene Glycolate. The above cyclization procedure was conducted with **3** (2 g, 4.05 mmol) and disodium pentaethylene glycolate, generated from sodium hydride (230 mg, 9.58 mmol) and pentaethylene glycol (970 mg, 4.07 mmol), in xylene (350 mL) for 24 h. After chromatography (ThLC), three major fractions were isolated and characterized.

Fraction A gave 1:1 pentaethylene macrocycle **6** as colorless oil: 170 mg (12.3%); R_f 0.1; NMR δ 3.28 (m, ϵ-CH_2, 4 H), 3.47–3.65 (m, including a sharp spike at δ 3.62, γ,δ-CH_2, 8 H), 3.78 (m, β,β'-CH_2, 4 H), 4.54 (m, α-CH_2, 2 H), 4.83 (m, α'-CH_2, 2 H), 6.81 (d, 5-pyr-H, J = 8.7 Hz, 1 H), 8.20 (dd, 4-pyr-H, J = 2.3, 8.7 Hz, 1 H), 8.90 (d, 2-pyr-H, J = 2.3 Hz, 1 H); IR (neat) 1720 (s, C=O), 1605 (s, C=C), 1575 (w, C=N), 1275 (br, vs, C—O), 1120 (br, vs, C—O) cm^{-1}; mass spectrum (70 eV), m/e (assignment, relative intensity) 342 ($M^+ + 1$, 0.3), 341 (M^+, 0.2), 340 ($M^+ - 1$, 0.4), 298 ($M^+ - C_2H_3O$, 4.5), 210 (9.6), 166 (100), 122 (63.1), 121 (39.8).

Anal. Calcd for $C_{16}H_{23}NO_7$: C, 56.30; H, 6.79; N, 4.10. Found: C, 56.38; H, 6.81; N, 4.00.

Fraction B gave 1:1-hexaethylene macrocycle **7**, as a viscous liquid: 20 mg (1.3%); R_f 0.06; NMR δ 3.43–3.73 (m, including sharp spikes at δ 3.43 and 3.67, γ–ζ-CH_2, 16 H), 3.86 (m, β,β'-CH_2, 4 H), 4.51 (m, α-CH_2, 2 H), 4.72 (m, α'-CH_2, 2 H), 6.82 (d, 5-pyr-H, J = 8.8 Hz, 1 H), 8.21 (dd, 4-pyr-H, J = 2.4, 8.8 Hz, 1 H), 8.88 (d, 2-pyr-H, J = 2.4 Hz, 1 H); IR (neat) 1725 (s, C=O), 1605 (s, C=C), 1575 (w, C=N), 1280 (br, vs, C—O), 1125 (br, vs, C—O) cm^{-1}; mass spectrum (70 eV), m/e (assignment, relative intensity) 386 ($M^+ + 1$, 0.3), 385 (M^+, 0.3), 384 ($M^+ - 1$, 0.5), 342 ($M^+ - C_2H_3O$, 5.1), 210 (13.4), 166 (100), 122 (68.8), 121 (44.4).

Anal. Calcd. for $C_{18}H_{27}NO_8$: C, 56.10; H, 7.06; N, 3.63. Found: C, 55.98; H, 6.94; H, 3.65.

Fraction C gave 2:2 macrocycle **8** as white crystals: mp 89–92 °C ($CHCl_3$–diethyl ether); 80 mg (6.2%); R_f 0.04; NMR δ 3.64 and 3.69 (2 br s, γ–ϵ-CH_2, 20 H), 3.82 (m, β,β'-CH_2, 8 H), 4.43 (m, α,α'-CH_2, 8 H), 6.79 (d, 5-pyr-H, J = 8.8 Hz, 2 H), 8.16 (dd, 4-pyr-H, J = 2.4, 8.8 Hz, 2 H), 8.82 (d, 2-pyr-H, J = 2.4 Hz, 2 H); IR (KBr) 1720 (s, C=O), 1605 (s, C=C), 1575 (w, C=N), 1275 (br, s, C—O), 1125 (br, vs, C—O) cm^{-1}; mass spectrum (70 eV), m/e (assignment, relative intensity) 640 ($M^+ + 2$, 0.3), 639 ($M^+ + 1$, 1.2), 595 ($M^+ - C_2H_3O$, 0.4), 342 ($C_{16}H_{24}NO_7$, 6.4), 298 ($C_{14}H_{20}NO_6$, 4.5), 210 (9.6), 166 (100), 122 (63.1), 121 (39.8).

Anal. Calcd. for $C_{32}H_{46}N_2O_{14}$: C, 56.42; H, 6.63; N, 4.39. Found: C, 56.41; H, 6.68; N, 4.18.

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Registry No. 1, 58757-38-3; **2**, 75506-48-8; **3**, 75506-49-9; **4**, 75506-50-2; **5**, 75506-51-3; **6**, 75506-52-4; **7**, 75506-53-5; **8** (isomer 1), 75506-54-6; 8 (isomer 2), 75506-55-7; diethylene glycol, 111-46-6; pentaethylene glycol, 4792-15-8; disodium diethylene glycolate, 69102-38-1; disodium pentaethylene glycolate, 70290-40-3.

Supplementary Material Available: Table 1, coordinates (× 10^4) and isotropic temperature factors for 4; Table 2, assigned coordinates (× 10^4) and thermal parameters for the hydrogen atoms for 4 (2 pages). Ordering information is given on any current masthead page.

Nickel-Catalyzed Arbuzov Reaction: Mechanistic Observations

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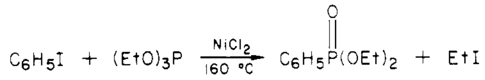
The reaction of aryl iodides or bromides with trialkyl phosphites in the presence of $NiCl_2$, as described by Tavs,[1] is the premier method[2] for preparing dialkyl arylphosphonates. The procedure is manipulatively simpler and requires less phosphite than the photolysis methods of Bunnett[3] or Griffin.[4] Since no mechanistic data is available, we have initiated an investigation of this transformation. We report here preliminary data on the profile of this reaction.

We have utilized Tavs' method for the synthesis of diethyl phenylphosphonate **1** and found excellent agreement with his experimental description. Slow addition of triethyl phosphite (1.15 equiv) to a mixture of iodobenzene and $NiCl_2$ (5 mol %, ≤1% H_2O) at 160 °C results in an exothermic reaction leading to a nearly quantitative yield of **1**. A slight excess of phosphite is used as some is lost via a rearrangement to diethyl ethylphosphonate at this elevated temperature. At 160 °C, $NiCl_2$ and iodobenzene appear as a light yellow heterogeneous mixture. Upon addition of a small amount of triethyl phosphite the mixture immediately darkens. After an induction period of ca. 60 s an exothermic reaction ensues, ethyl iodide distills out, and the reaction mixture fades to light yellow. A nearly theoretical amount of ethyl iodide can be collected in a cold trap upon addition of the remaining phosphite in like manner.



$$C_6H_5I + (EtO)_3P \xrightarrow[160\ °C]{NiCl_2} C_6H_5\overset{\overset{O}{\|}}{P}(OEt)_2 + EtI$$

1

Our initial question concerned the nature of the metal catalyst, specifically whether Ni(+II) might be reduced to Ni(0) under the reaction conditions. Boiling a mixture of $NiCl_2$ in excess iodobenzene for 17 h results in no detectable change in either reactant. In contrast, a mixture of $NiCl_2$ in triethyl phosphite produces a homogeneous solution upon heating. Removal of excess phosphite yields a white solid identical with an authentic sample of tetra-

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(1) P. Tavs, *Chem. Ber.*, **103**, 2428 (1970).

(2) For examples of this type reaction see: T. M. Balthazor, J. A. Miles, and B. R. Stults, *J. Org. Chem.*, **43**, 4538 (1978); T. M. Balthazor, *Ibid.*, **45**, 2519 (1980).

(3) J. F. Bunnett and X. Creary, *J. Org. Chem.*, **39**, 3613 (1974).

(4) R. Obrycki and C. E. Griffin, *J. Org. Chem.*, **33**, 632 (1968), and references therein.

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kis(triethyl phosphite)Ni(0), **2a**. To our knowledge this

$(R_3P)_4Ni$ | $ArNi(PR_3)_2I$
2a, $R = OC_2H_5$ | **3a**, $R = OC_2H_5$
b, $R = C_6H_5$ | **b**, $R = C_6H_5$
c, $R = C_2H_5$ | **c**, $R = C_2H_5$

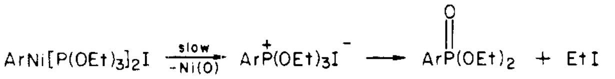
is the first example of a direct reduction of Ni(+II) to Ni(0) by phosphite in the absence of other reducing agents or amines. More to the point, **2a** is an effective catalyst for the conversion of iodobenzene to **1**. No induction period is observed with **2a** as a catalyst.

A minimum temperature of ca. 130–140 °C is required for this reaction. Below 140 °C the reaction is sporadic and below 130 °C no reaction is observed. Significantly, this is found for either $NiCl_2$ or **2a**. No reaction is found after 17 h on heating a solution of iodobenzene, triethyl phosphite, and **2a** at 98 °C.

A competitive kinetic study of three para-substituted iodobenzenes has been carried out. The relative rates for 4-iodotoluene, iodobenzene, and methyl 4-iodobenzoate are 1.5, 1.0, and 0.6, respectively. These data indicate increased positive charge character in the slow step of this transformation.

Aryl halides are known to oxidatively add to Ni(0) complexes. For example,[5,6] aryl iodides add to **2b** and **2c** to give **3b** and **3c**. Recent kinetic studies by Kochi[5] have shown the oxidative-addition of aryl iodides to **2c** follows a reaction course defined by a $\rho = 2.0$. Cassar[7] found that in the presence of excess triphenylphosphine, **3b** reacts further to give aryltriphenylphosphonium iodides. Electron-withdrawing groups on the aryl ring were found to retard the rate of formation of the phosphonium iodides.

Based on our data and the above literature precedents, a plausible working hypothesis for the formation of aryl phosphonates is a rapid oxidative addition of the aryl iodide to **2a** to give **3a** followed by slow formation of **4** with regeneration of Ni(0). Decomposition of **4** gives the arylphosphonate and ethyl iodide.[8]



3a 4

While this hypothesis is consistent with the data, several tenuous assumptions have been made. Most significant is, does the oxidative addition of aryl halides to Ni(0) phosphine complexes always proceed via a path defined by a positive ρ? Cassar[6] has found that for oxidative addition of substituted chlorobenzenes to **2b**, a plot of log k_{rel} vs. σ shows a dramatic break at $\sigma = 0.2$ (for $\sigma > 0.2$, $\rho = 8.8$; $\sigma < 0.2$, $\rho \simeq 0$), indicative of a change in mechanism. Changing from phosphine to phosphite ligands on nickel might also have a radical effect on the mechanism.[9] No reports of oxidative additions with **2a** are currently available.

We have shown that **2a** is involved in the conversion of aryl iodides to arylphosphonates. We suggest that until more data is available on the chemistry of **2a** and **3a**, the mechanism proposed above should be viewed with suspicion. These studies are underway in our laboratory.

Experimental Section

General. All manipulations were carried out under a nitrogen or argon atmosphere. Samples of diethyl phenyl-, diethyl 4-(methylphenyl)- and diethyl 4-[(carbomethoxy)phenyl]-phosphonate were prepared by literature methods.[10]

Tetrakis(triethyl phosphite)nickel(0). A stirred mixture of $NiCl_2$ (5 g, 38.5 mmol) in $(EtO)_3P$ (60 mL) was slowly heated to reflux. At ambient temperature the mixture was light yellow and heterogeneous. At 80 °C, a heterogeneous black mixture resulted. A clear homogeneous solution was found at 150 °C. After 1 h at reflux, the solution was cooled and excess phosphite removed to give a white solid. The solid was triturated with acetonitrile, collected, and washed with cold methanol to give 4.6 g of **2a**, mp 106–109 °C (lit.[11] mp 108 °C). This material is identical by ^1H and ^{31}P NMR with an authentic sample prepared by the method of Vinal and Reynolds.[11]

Diethyl Phenylphosphonate. To a hot (160 °C) stirred solution of **2a** (10 mg) in iodobenzene (10 g, 49.0 mmol) was slowly added $(EtO)_3P$ (9.37 g, 56.4 mmol) in small portions (ca. 5 drops). The solution became deep red upon each addition of phosphite. The color rapidly faded to yellow, ethyl iodide was distilled into a cold trap, and an exotherm was observed. After complete addition, GLC assay indicated <1% iodobenzene remained. Distillation [bp 94–101 °C (0.1 mm); lit.[10] bp 97 °C (0.1 mm)] gave 9.88 g (46.1 mmol, 94%) of diethyl phenylphosphonate identical (GLC, ^1H NMR) with an authentic sample.[10]

Competitive Kinetics. A mixture of 1 equiv each of two aryl iodides and 5 mol % $[(EtO)_3P]_4Ni$ was heated to 160 °C. Triethyl phosphite, 1 equiv, was added in small portions. After the mixture was cooled, the relative concentrations of aryl iodides and arylphosphonates were determined by GLC assay and checked versus NMR peak areas.

Acknowledgment. We thank Dr. S. Tremont (Monsanto) for helpful discussions.

Registry No. 1, 1754-49-0; **2a**, 14839-39-5; **3a**, 75507-28-7; **4**, 75556-05-7; 4-iodotoluene, 624-31-7; iodobenzene, 591-50-4; methyl 4-iodobenzoate, 619-44-3; $NiCl_2$, 7718-54-9; $(EtO)_3P$, 122-52-1.

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(5) T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, 101, 6319 (1979).

(6) M. Foa and L. Cassar, *J. Chem. Soc., Dalton Trans.*, 2572 (1975).

(7) L. Cassar and M. Foa, *J. Organomet. Chem.*, 74, 75 (1974).

(8) (a) If an oxidative addition mechanism is operative, the reactive nickel species is probably coordinatively unsaturated, i.e., $[(EtO)_3P]_3Ni$. See ref 5. (b) The phosphite that becomes **4** may be externally or internally derived.

(9) An example of the significant dissimilarity of **2a** and **2b** is the K_{eq} for $P_4Ni \rightleftarrows P_3Ni + P$ (P = triphenylphosphine or triethyl phosphite). For **2b** the compound is extensively dissociated in solution; for **2a** $K_{eq} \leq 3 \times 10^{-7}$M: C. A. Tolman, *J. Am. Chem. Soc.*, 92, 2956 (1970).

(10) G. M. Kosolapoff and L. Maier, Eds., "Organic Phosphorus Compounds", Vol. 7, Wiley-Interscience, New York, 1976, Chapter 18, and references therein.

(11) R. S. Vinal and L. T. Reynolds, *Inorg. Chem.*, 3, 1062 (1964).

Reaction of *o*-Diiodobenzene with Alkynes and Nickel Carbonyl. Synthesis of Substituted Indenones

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Nickel carbonyl reacts with iodobenzene to produce a benzoylnickel complex (**1**, Scheme I) which decomposes to benzil in aprotic solvents (THF) or undergoes alcoholysis to methyl benzoate in methanol.[1] However, in the presence of an alkyne, the benzoylnickel intermediate is trapped, undergoing insertion of the alkyne followed by an insertion of CO to yield nickel complex **2** which then decomposes to organic products.[2]

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(1) N. L. Bauld, *Tetrahedron Lett.*, 1841 (1963).

(2) P. W. Jolly and G. Wilke "The Organic Chemistry of Nickel", Vol. II, Academic Press, New York, 1975, p 358.

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