compound: 193 mg, 90% yield; mp 190–191 °C dec. Anal. Calcd for $C_4H_3N_5O$: C, 35.03; H, 2.18; N, 51.09. Found: C, 35.02; H, 2.31; N, 50.33.

**1,2,4-Triazolo[3,4-*c*]pyrazine 7-Oxide (8).** To 100 mg (0.8 mmol) of 3-hydrazinopyrazine 1-oxide was added 0.5 mL (3.0 mmol) of diethoxymethyl acetate. This solution was allowed to stand at room temperature for 24 h. The light brown precipitate which formed was collected and washed with ethanol. Recrystallization from absolute ethanol yielded an off-white compound: 46 mg, 43% yield; mp 204–205 °C dec. Anal. Calcd for $C_5H_4N_4O$: C, 44.14; H, 2.94; N, 41.46. Found: C, 44.26; H, 2.61; N, 41.16.

**Registry No.** 1, 65481-57-4; 2, 14036-06-7; 3, 75431-21-9; 7, 74803-26-2; 8, 74803-29-5; 3-methoxy-1,2,4-triazine 1-oxide, 27531-67-5; hydrazine, 302-01-2; 3-chloropyrazine 1-oxide, 6863-76-9.

## Nicotinic Acid Crown Ethers.[1] Synthesis and Structural Characterization of Polyethereal Macrocyclic Lactones from 6-Chloronicotinic Acid

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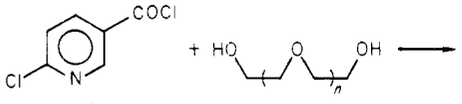
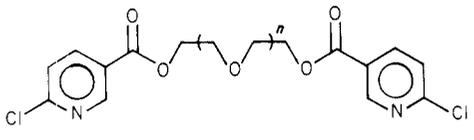
Recently, we described the synthesis of crown ethers possessing a 2-oxanicotinate moiety and demonstrated a distinct template effect on cyclization.[3] In view of the few examples of pyridine macrocyclic lactones[4] and the absence of 1,4-bridged nicotinate macrocycles, we herein describe the inclusion of a 6-oxanicotinate moiety into a novel series of cross-ring macrocycles.

6-Chloronicotinic acid was transformed (100%) in excess refluxing thionyl chloride[5] into 6-chloronicotinoyl chloride (1). Subsequent treatment of 1 with 1 equiv of disodium diethylene glycol in benzene at 78 °C afforded the 2:1 bisester 2 in nearly quantitative yields. Under these mild



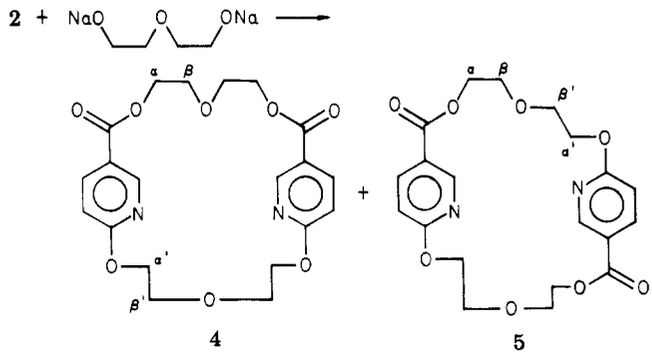
1



2, $n$ = 1
3, $n$ = 4

reaction conditions, direct heteroaryl substitution reactions are negligible. Bisester 3 was prepared (90%) in a similar manner from 1 upon treatment with pentaethylene glycol.

Cyclization was accomplished upon treatment of 2 with disodiodiethylene glycolate in refluxing xylene (138 °C) to generate isomeric 2:2 macrocycles 4 and 5 in 5.5 and 6.4% yield, respectively. Due to the similarity in physical and selected spectral (NMR and mass spectra) data,



4 5

structural differentiation between these isomers was not possible. Thus, colorless crystals of the 141–142 °C melting isomer were grown by slow evaporation of a chloroform solution. X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromatized Mo K$\alpha$ radiation ($\lambda$ = 0.71069 Å) and a crystal of dimensions 0.40 × 0.30 × 0.22 mm. The crystal data are as follows: $C_{20}H_{22}N_2O_8$, mol wt 418.4; triclinic space group $P\bar{1}$; $a$ = 7.651 (2), $b$ = 10.237 (2), $c$ = 12.754 (2) Å; $\alpha$ = 101.51 (1), $\beta$ = 95.26 (2), $\gamma$ = 94.23 (2)°; $Z$ = 2; $d_c$ = 1.429 g cm$^{-3}$; $\mu$ (Mo K$\alpha$) = 1.04 cm$^{-1}$. Intensity data were collected by the $\theta$–$2\theta$ scan technique, employing variable scan rates, which varied from 0.80 to 10.0 deg min$^{-1}$ in order to measure all data with approximately equal precision. No significant decrease in the intensity of periodically remeasured reflections was noted. All data in one hemisphere having $2° \leq \theta \leq 20°$ were measured and corrected for background and Lorentz and polarization effects; no absorption corrections were necessary.

The structure was solved by a combination of direct (MULTAN 78)[6] and Fourier methods (SHELX).[7] Least-squares refinement was based upon $F$, and was carried out by using data having $F_{obsd} > 3\sigma(F_{obsd})$. Nonhydrogens were refined with isotropic temperature factors; hydrogen atoms were placed in calculated positions 1.08 Å from atoms to which they are bonded, and their isotropic temperature factors were refined. Convergence was achieved with $R$ = 0.061 for 967 data and 143 variables. Nonhydrogen atom positions and hydrogen atom parameters are given in the supplementary material.

The conformation of 4 is illustrated in Figure 1. The pyridine rings are nearly parallel, deviating by 7.4°, and are separated by 4.33 Å between ring centers. The ethereal linkage to the heteroaromatic ring is cis in both cases, as is generally true with similar imidate moieties in related macrocyclic systems.[8] Torsion angles are 30.4° for N1–C1–O8–C20 and 5.4° for N2–C16–O6–C17; the larger angle is indicative of the release of steric strain caused by the juxtaposition of the pyridine subunits. The two ester linkages are quite different, being anti to N1 and syn to N2, again a favorable mode to circumvent the repulsive heteroaromatic interactions. Those torsion angles are −5.0° and 180.0° for C3–C4–C6–O2 and C14–C12–C11–O5, re-

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(9) Johnson, C. K. "ORTEP", Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN., 1965.

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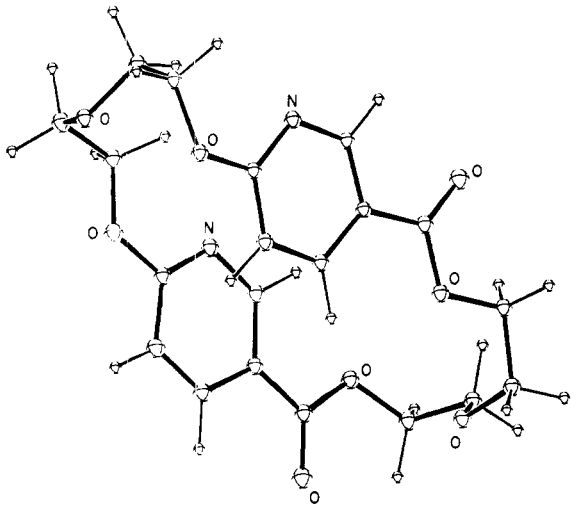
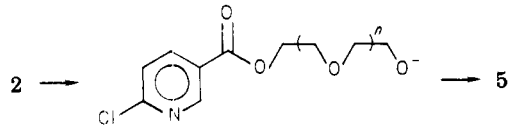


**Figure 1.** Perspective drawing[9] of the macrocycle **4**.

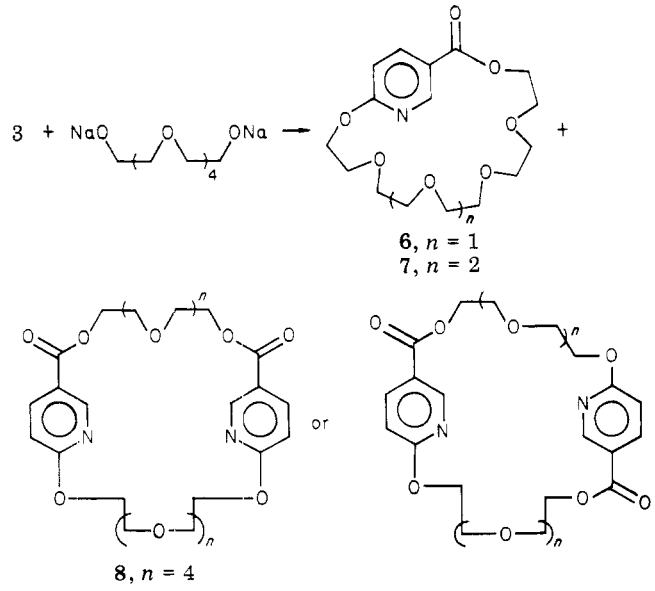
spectively. Average bond distances are 1.337 (6) Å for the pyridine C–N bond, 1.387 (6) Å for the heteroaromatic C–C, 1.502 (7) Å for the polyethereal C–C, and 1.437 (7) Å for the ethereal C–O bonds. No unusually short intermolecular contacts are present.

In view of the X-ray analysis, the other isomer (mp 167–168 °C) must possess the anti configuration, e.g., **5**,



which results from either a transesterification or -etherification reaction under the cyclization conditions. Although transetherification reactions can be easily circumvented by reduction in the temperature, facile transesterification even under mild reaction conditions (25 °C) would still be operative and detrimental to the preparation of a single (cis) isomer.[3]

Treatment of **3** with disodiopentaethylene glycolate gave as the major (12%) product the 1:1 macrocycle **6** along with traces of the hexabridged **7**. An isomeric mixture of dimers (**8**) was also isolated (6%); however, no attempts were



made to separate the pure components. The relatively low yield of the 1:1 macrocycle **6** compared with that of the 2-oxo isomer[3] may be due to the lesser reactivity of the 6-position than that of the 2-position of nicotinic ester and the minor template effect on the 1,4-cyclization process. In **6**, the 1,4-bridge crosses over the face of the pyridine nucleus as supported by the dramatic upfield shift ($\Delta\delta$ = 0.3~0.4) of the $\epsilon$-methylene singlet, when compared to the position for either **3** or dimer **8**, in which the central bridge protons are not confined to the environment of the heteroaryl $\pi$ system. Similar but lesser shifts are demonstrated for both the $\gamma$ and $\delta$ methylene groups.

From low-temperature VT NMR studies on **6**, the upfield shift for the $\epsilon$-$CH_2$ suggests that upon cooling, the terminal oxygen (O1–O6) distance contracts from 8.42 to 6.94 Å; thus the $\epsilon$-methylene hydrogens are forced into a closer proximity to the pyridine $\pi$ electrons, giving rise to the apparent chemical shift ($\Delta\delta$ = 0.2–0.3). This effect is less pronounced than expected, since a portion of the contraction process can be absorbed by rotation of the carbonyl group into a more orthogonal orientation.

## Experimental Section

**General Comments.** All melting points were taken in capillary tubes with a Thomas-Hoover Uni-Melt apparatus and are uncorrected. $^1H$ NMR spectra were obtained in $CDCl_3$ solution with $Me_4Si$ as the internal standard ($\delta$ 0) and were recorded on either a Varian Associates A-60A or a Bruker WP 200 spectrometer. Infrared (IR) spectra were recorded on a Beckman IR-7 spectrometer. Mass spectra and molecular-weight data were obtained on a Hewlett-Packard Model 5992 GC/MS by Mr. D. Patterson. Reported $R_f$ values more ascertained by a standardized thin-layer chromatography (TLC) procedure: 0.25-mm Brinkman silica gel HF-254-366 plates eluting with ethyl acetate–cyclohexane (1:1). For the preparative thick-layer chromatography (ThLC), 2-mm Brinkman silica gel PF-254+366 plates were used, eluting with the stipulated solvent system. Elemental analyses were performed by Mr. R. Seab in these laboratories.

Sodium hydride (57% oil dispersion) was washed with dry petroleum ether (bp 30–60 °C) and then dried under nitrogen prior to the reaction. All the reaction solvents were distilled from sodium wire under a nitrogen atmosphere.

**Reaction of 6-Chloronicotinoyl Chloride with Diethylene Glycol. General Esterification Procedure.** A solution of 6-chloronicotinoyl chloride (mp 49–51 °C; 5 g, 28.4 mmol) and diethylene glycol (1.51 g, 14.2 mmol) in benzene (50 mL) was refluxed for 6 h. After concentration, the residue was extracted with dichloromethane, washed with diluted aqueous sodium carbonate, dried over anhydrous sodium sulfate, and concentrated in vacuo to give the desired ester, **2**, as white crystals, which were recrystallized from diethyl ether: mp 104.5–105.5 °C; 4.83 g (88%), NMR $\delta$ 3.89 (m, $\beta$-$CH_2$, 4 H), 4.50 (m, $\alpha$-$CH_2$, 4 H), 7.39 (d, 5-pyr-H, $J$ = 8.3 Hz, 2 H), 8.22 (dd, 4-pyr-H, $J$ = 2.3, 8.3 Hz, 2 H), 9.01 (d, 2-pyr-H, $J$ = 2.3 Hz, 2 H); IR (KBr) 1725 (vs, C=O), 1587 (s, C=C), 1570 (w, C=N), 1290 (br, vs, C—O), 1130 (br, vs, C—O) $cm^{-1}$.

Anal. Calcd for $C_{16}H_{14}N_2O_5Cl_2$: C, 49.89; H, 3.66; N, 7.27. Found: C, 49.76; H, 3.68; N, 7.42.

**Reaction of 6-chloronicotinoyl chloride with pentaethylene glycol** followed the above general esterification procedure except for the substitution of pentaethylene glycol (3.39 g, 14.2 mmol), affording (90%) the desired ester, **3**, as a viscous colorless oil. Without further purification, the following spectral data were obtained: NMR $\delta$ 3.57 (s, $\epsilon$-$CH_2$, 4 H), 3.62 (br s, $\gamma,\delta$-$CH_2$, 8 H), 3.80 (m, $\beta$-$CH_2$, 4 H), 4.46 (m, $\alpha$-$CH_2$, 4 H), 7.42 (d, 5-pyr-H, $J$ = 8.3 Hz, 2 H), 8.07 (dd, 4-pyr-H, $J$ = 2.3, 8.3 Hz, 2 H), 8.95 (d, 2-pyr-H, $J$ = 2.3 Hz, 2 H); IR (neat) 1725 (s, C=O), 1585 (s , C=C), 1575 (w, C=N), 1280 (br, vs, C—O), 1110 (br, vs, C—O) $cm^{-1}$.

**Reaction of 2 with Disodium Diethylene Glycolate. General Procedure of Macrocycle Preparation.** To a suspension of sodium hydride (300 mg, 12.5 mmol) in xylene (300 mL) was slowly added diethylene glycol (555 mg, 5.23 mmol) under nitrogen. The mixture was stirred at 20 °C for 30 min and then **2** (2 g, 5.19 mmol) in xylene (50 mL) was added dropwise. The mixture was refluxed for 24 h, cooled, and quenched with water. The organic layer was separated and the aqueous layer extracted

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 $\delta$ 3.86 (m, $\beta,\beta'$-$CH_2$, 8 H), 4.52 (m, $\alpha,\alpha'$-$CH_2$, 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 $\delta$ 3.92 (m, $\beta,\beta'$-$CH_2$, 8 H), 4.50 (m, $\alpha,\alpha'$-$CH_2$, 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 $\delta$ 3.28 (m, $\epsilon$-$CH_2$, 4 H), 3.47–3.65 (m, including a sharp spike at $\delta$ 3.62, $\gamma,\delta$-$CH_2$, 8 H), 3.78 (m, $\beta,\beta'$-$CH_2$, 4 H), 4.54 (m, $\alpha$-$CH_2$, 2 H), 4.83 (m, $\alpha'$-$CH_2$, 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 $\delta$ 3.43–3.73 (m, including sharp spikes at $\delta$ 3.43 and 3.67, $\gamma$-$\zeta$-$CH_2$, 16 H), 3.86 (m, $\beta,\beta'$-$CH_2$, 4 H), 4.51 (m, $\alpha$-$CH_2$, 2 H), 4.72 (m, $\alpha'$-$CH_2$, 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 $\delta$ 3.64 and 3.69 (2 br s, $\gamma$-$\epsilon$-$CH_2$, 20 H), 3.82 (m, $\beta,\beta'$-$CH_2$, 8 H), 4.43 (m, $\alpha,\alpha'$-$CH_2$, 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.

**Acknowledgment.** We are grateful to the National Institutes of Health and the National Science Foundation for partial support of this work.

**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 ($\times 10^4$) and isotropic temperature factors for **4**; Table 2, assigned coordinates ($\times 10^4$) 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.

$$C_6H_5I + (EtO)_3P \xrightarrow[160\ °C]{NiCl_2} C_6H_5P(OEt)_2 + EtI$$

**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-

(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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