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An Improved Route to 1,3-bis-[4-(4-Aminophenoxy)benzoyl]benzene and Related Compounds

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Abstract. The title compound is prepared in 75% overall yield in two steps. In the first step, the entire carbon framework is assembled from readily available materials with excellent regioselectivity. The second step is a simple nitro group hydrogenation.

The polyimide derived from 1,3-bis-4-[(4-aminophenoxy)benzoyl]benzene (1) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride has attracted considerable interest because it exhibits the exceptional thermal, thermoxidative, and chemical stability of polyimides but is modified by incorporation of ether and ketone functionality present in polyetherketones (PEK's).^{1,2} A particularly striking consequence of the inclusion of the PEK segments is that the polymer undergoes increases



in T_g and solvent resistance upon temperature cycling near the glass transition temperature. The property enhancements are thought to arise as a result of formation of crystalline domains brought about by reorganization of the PEK portion of the polymer chain.³ Although the



Figure 1. Improved Route to 1.

improvement in properties under conditions in which most materials undergo significant degradation makes this material particularly attractive as a matrix for aerospace composites, a significant deterrent to the more widespread study of this interesting polymer system has been the lack of availability of the starting diamine, **1**.

Hergenrother, *et. al.*, have reported the synthesis of **1** by Friedel-Crafts reaction of isophthaloyl chloride with fluorobenzene (81%) followed by treatment of the product with potassium 4-aminophenoxide in refluxing DMAc (58%). Retrosynthetic analysis of **1** indicated that disconnection at the bonds connecting the central isophthaloyl unit to the remote rings ("a") rather than at carbon-oxygen bond "b" would not only avoid harsh conditions typical of aromatic nucleophilic substitutions,⁴ but would also allow construction of the entire carbon framework in a direct and elegant fashion. Thus, reaction of isophthaloyl chloride with 4phenoxynitrobenzene followed by catalytic nitro group hydrogenation would provide a highly convergent route and would greatly simplify the second step of the reaction sequence (Figure 1).

Although considerable literature precedence suggests that acylations of 4-phenoxynitrobenzene should proceed with high para selectivity,⁵ the potential consequences of poor regioselectivity on polymer properties prompted us to examine the product distribution of acylations of this material in some detail. These reactions were performed using benzoyl chloride rather than isophthaloyl chloride to acylations of this material in a typical experiment, equimolar quantities of benzoyl chloride and 4-phenoxynitrobenzene were allowed to react in the presence of AlCl₃ and solvent under N₂ for 3 h. Extractive workup and analysis by GC indicated para selectivities of over 98% were obtained in CH₂Cl₂ (3 h, 40 °C), PhNO₂ (30 min, 100 °C) and excess PhOC₆H₄NO₂-*p* (30 min, 100 °C). Nitrobenzene was preferred based on the homogeneity of the reaction mixtures produced.

This chemistry was readily extended to diacid chlorides. Reaction of 4-phenoxynitrobenzene with isophthaloyl chloride in the presence of AlCl₃ at 50 °C for 2.25 h, followed by hydrolysis of the AlCl₃ complex of the product and removal of the nitrobenzene by steam distillation provided 1,3-bis-[4-(4-nitrophenoxy)benzoyl]benzene (2) in 81% recrystallized yield. No evidence of acylation ortho to the bridging oxygen or on the ring bearing the nitro substituent was observed by ¹H NMR spectroscopy. Analogous chemistry with terephthaloyl chloride produced the corresponding product in 72% recrystallized yield.

Hydrogenation of **2** in the presence of a platinum catalyst (96 °C, 516 psi, 13 min) produced the title compound, a bright yellow solid, in 93% yield. Polymer grade material was obtained with a single recrystallization of the crude reaction product from ethanol/toluene. This step represents a significant improvement relative to the previously reported procedure in that the use of high temperatures, basic solutions, and DMAc is avoided. Further, the yield is improved and the purity of the product is increased; reversible gel formation during polymerization, attributed to the presence of an unidentified impurity present in material prepared by the Hergenrother procedure, is not observed in polymerizations carried out with material prepared by the procedure described herein.²

Experimental Section

General Procedures. Melting points were determined with a Thomas Hoover oil immersion capillary melting point apparatus and are uncorrected. NMR spectra were recorded at ambient temperature employing a Bruker WP-200 or an IBM SY-200 FT-NMR spectrometer equipped with a 5 mm ¹H/¹⁹F dual probe or a 10 mm pretuned ¹³C probe. Chemical shifts are referenced to the chemical shift of residual solvent protons for ¹H spectra ($\delta_{DMSO} = 2.49$, $\delta_{CH_2Cl_2} = 5.32$,) or to the central resonance of the solvent multiplet for ¹³C spectra ($\delta_{DMSO} = 59.5$, $\delta_{CH_2Cl_2} = 53.8$).

SAFETY NOTE: Mixtures of nitrobenzene and aluminum chloride are thermally unstable and may lead to explosive decomposition at temperatures above 90 °C.⁶ Although the experiments to examine acylation selectivity described here were performed without incident, it is not recommended that they be repeated at 100 °C.

Determination of Acylation Selectivity. A 25 mL twonecked round-bottomed flask equipped with addition funnel, reflux condenser, and magnetic stirrer was charged with 4phenoxynitrobenzene (2.15 g, 10.0 mmol), AICl₃ (1.47 g, 11.0 mmol), and solvent (10 mL). The solution was heated to the desired temperature and benzoyl chloride (1.16 mL, 1.41 g, 10 mmol) was added dropwise via the addition funnel. After the desired time had expired, the reaction was cooled to room temperature, quenched carefully with 100 mL of 10% HCl, and diluted with an additional 100 mL of CH₂Cl₂. The mixture was transferred to a separatory funnel and the organic layer was separated. dried over MgSO₄, filtered, and analyzed by GLC. The identity of the products was verified by GCMS. The results are presented in the text.

1,3-bis-[4-(4-Nitrophenoxy)benzoyl]benzene (2). A solution of isophthaloyl dichloride (20.3 g, 0.10 mol) in 50 mL of nitrobenzene was added over 5 min to a solution of $AlCl_3$ (29.4 g, 0.22 mol) and 4-phenoxynitrobenzene (43.0 g, 0.20 mol) in nitrobenzene (100 mL) heated to 50 °C. The dark solution was heated at 50 °C for 2.25 h, cooled to room temperature, and treated carefully with 400 mL of 10% HCl. A tan, two-phase mixture resulted.

The reaction vessel was fitted with a Dean-Stark trap and condenser and its contents were heated to reflux; the lower, nitrobenzene layer in the trap was drained occasionally. After all of the nitrobenzene had been removed, the still-warm reaction mixture was extracted with hot toluene. The hot toluene solution was washed with hot H₂O, hot 10% NaOH solution, and hot H₂O, and then was diluted with 400 mL of absolute EtOH and cooled to room temperature. The resulting off-white powder was collected and washed with three portions of EtOH and dried under vacuum to afford 45.43 g (81%) of off-white powder: mp 140-142 °C; ¹H NMR (CD₂Cl₂) δ 8.26 (4H, m) 8.18 (1H, t) 8.02 (2H, dd) 7.91 (4H, m) 7.69 (1H, t) 7.21 (4H, m) 7.17 (4H, m); ¹³C NMR δ 194.43, 162.03, 159.41, 143.91, 138.12, 133.86, 133.63, 132.92, 131.15, 128.99, 126.34, 118.87; Anal. Calcd for $C_{32}H_{20}N_2O_8$: C 68.57; H 3.60; N 5.00; O 22.83. Found: C 68.78; H 3.63; N 4.55.

1,4-bis-[4-(4-Nitrophenoxy)benzoyl]benzene. A warm solution of terephthaloyl dichloride (10.15 g, 0.050 mol) in 50 mL of nitrobenzene was added over 15 min to a 75 °C solution of 4-phenoxynitrobenzene (21.5 g, 0.10 mol) and AlCl₃ (14.7 g, 0.11 mol) in nitrobenzene (50 mL). The solution was heated at 75 °C for 30 min, cooled to room temperature and quenched with 200 mL of 10% HCI.

The nitrobenzene was removed from the resulting mixture by steam distillation. The solid was collected by filtration, washed thoroughly with H₂O and three portions of MeOH, and recrystallized from 250 mL of N,N-dimethylacetamide. The solid was filtered and washed with three 50 mL portions of acetone and dried in a vacuum oven to provide 20.06 g (72%) of pink solid: mp 269-275 °C; ¹H NMR (DMSO-*d*₆, 115 °C) 8.28 (4H, m) 7.92 (8H, m), 7.32 (8H, m); ¹³C NMR (DMSO-*d*₆, 115 °C) 193.32, 160.66, 158.37, 143.16, 139.86, 132.68, 131,68, 128.55, 125.41, 118.76, 118.52; Anal. Calcd for $C_{32}H_{20}N_2O_8$: C 68.57; H 3.60; N 5.00; O 22.83. Found: C 67.97; H 3.65; N 5.00.

1,3-bis-[4-(4-Aminophenoxy)benzoyl]benzene.(1). A 100 mL stainless steel Parr autoclave was charged with 1,3-bis-[4-(4-nitrophenoxy)benzoyl]benzene (7.50 g, 13.4 mmol), Pt/CP-56 (Engelhard Catalyst Co., 99 mg) and tetrahydrofuran (37.5 mL). The reactor was sealed and the contents were heated to 96 °C. H₂ gas (516 psi) was admitted to the reactor and stirring was increased to 700 rpm. After 13 min, H₂ uptake had ceased. The contents were removed from the reactor and the catalyst was removed by filtration. The solvent was removed *in vacuo* and the residual oil was recrystallized from 40 mL of 50/50 (V/V)

EtOH/toluene and isolated by filtration to afford 4.78 g of yellow powder with properties identical to a sample of the diamine prepared using the previously published procedure¹. Concentration of the mother liquor provided 1.44 g of additional material (total yield 93%).

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