Synthesis of Acetylene-Terminated α,ω-Bisphenoxyalkanes

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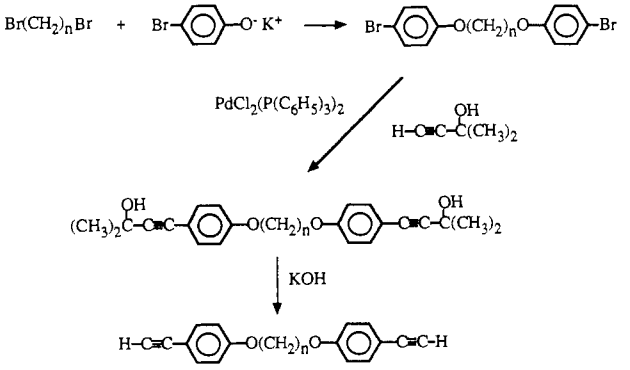
Nine α,ω-bis(4-ethynylphenoxy)alkanes were synthesized from the corresponding α,ω-dibromoalkanes by (1) reaction with *p*-bromophenol/KOH, (2) palladium-catalyzed coupling with 2-methyl-3-butyn-2-ol, and (3) caustic hydrolysis of the hydroxy intermediates. The structures of the ethynyl compounds were confirmed by IR, ^{1}H NMR, and DSC.

Aromatic acetylene-terminated (AT) systems have been an area of research interest for over a decade (*1*, *2*). Ethynyl groups have been used to thermally chain extend, rigidize, and cross-link polymers that show promise for aerospace applications. AT compounds, upon thermal polymerization, do not eliminate volatiles, giving them desirable characteristics for use as adhesives and matrix resins. We have previously reported the synthesis of diamines containing oxyethylene units (*3*). Polyimides derived from these diamines showed good isothermal stability in atmospheres of air and nitrogen in spite of the presence of nonaromatic, oxyalkylene structures. Acetylene-terminated bisphenoxyalkanes (ATPA) were first reported in 1964 (*4*). A classical series of reactions was employed which included the Friedel–Crafts generation of a diacetyl compound, chlorination of the diketone with phosphorus pentachloride followed by double dehydrochlorination with sodium amide in liquid ammonia. As part of our interest in oxyalkylene linked monomeric systems, we have synthesized a series of ATPA monomers by a three-step procedure employing catalytic reactions (*5*) and readily available starting materials, the α,ω-dibromoalkanes.

The ^{1}H NMR spectral data for each compound is shown in Table II. Thermal characterization by DSC indicated a melting endotherm followed by an exothermic transition at approximately 250 °C (Table I) in each case. The exotherm occurs in a region associated with the curing of other ethynyl-terminated systems (*1*).

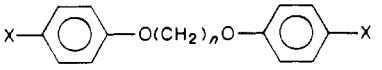


Experimental Section

Nuclear magnetic resonance (NMR, ^{1}H) spectra were obtained by employing a Varian EM-360A spectrometer using solutions of approximately 10% w/v concentration (tetramethylsilane internal standard). Infrared (IR) spectra were recorded on a Perkin-Elmer Model 1330 or Model 457 spectrophotometer. Differential scanning calorimetric (DSC) data were obtained by using a DuPont Model 900 thermal analyzer equipped with a differential scanning calorimetric cell. Elemental analyses were performed by Midwest Microlab Ltd., Indianapolis, IN. The dibromoalkanes, 2-methyl-3-butyn-2-ol, and dichlorobis(triphenylphosphine)palladium(II) were obtained from Aldrich Chemical Co. and were used as received.

Procedure for the Synthesis of Bis(4-bromophenoxy) Derivatives. In a 250-mL round-bottomed flask equipped with a magnetic stir bar and reflux condenser was placed a mixture of 0.2 mol of potassium hydroxide and 30 mL of absolute ethanol. The resulting solution was treated with 0.07 mol of the appropriate dibromoalkane and heated at reflux for 2 h. The solid that formed on cooling was collected by vacuum filtration and washed with a 10% sodium hydroxide solution and with two 100-mL portions of distilled water. The product was recrystallized from either glacial acetic acid or absolute ethanol (*6*).

Table I. Properties of Selected α,ω-Bisphenoxyalkanes



	X = Br		X = -C≡C-C(OH)(CH3)2		X = -C≡C-H		DSC exotherm, °C	
n	yield,[a] (lit.) %	mp, °C (lit.)	yield,[b] %	mp, °C	yield,[c] %	mp, °C (lit.[d])	onset[e]	max
2	40 (30)[f]	132-4 (134-5)[f]	71	164-5	73	165-6 (170.5)	165	240
3	81 (81)[g]	142-3 (142-3)[g]	55	117-19	78	120-1 (124)	155	245
4	87	118-20 (118-20)[h]	48	146-7	74	116-18 (119)	155	248
5	85	59-60	57	92-3	79	92-4 (98)	150	245
6	83	105-6	64	130-2	80	108-9	160	250
8	81	99-100	52	120-1	99	108-9	170	250
9	74	69-70	46	99-100	84	71-2	150	250
10	83	89-91	55	115-16	62	110-11 (111)	165	250
12	85	91-2	61	114-15	82	90-1	150	250

[a] All yields are for isolated and purified products. [b] Not generally isolated and purified. [c] Reference *4* gives overall yields which are not directly comparable here. [d] Reference *4*. [e] Initial deflection of exotherm from base line. [f] Reference *6*. [g] Reference *7*. [h] Reference *8*.

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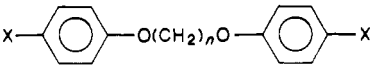
Table II. ^{1}H NMR Data[a] for Selected α,ω-Bisphenoxyalkanes



	X = $-O(CH_2)_nO-$		X = Br	X = $-C{\equiv}C-C(OH)(CH_3)_2$			X = $-C{\equiv}C-H$	
n	$-CH_2-$[b]	$-OCH_2-$[b]	$-Ar-$[c]	$-Ar-$[c]	$-CH_3$	$-OH$	$-Ar-$[c]	CH
2		4.3	7.1	7.0	1.5	2.5	7.1	2.9
3	2.3	4.2	[d]	7.0	1.5	2.2	7.0	3.0
4	1.9	4.0	7.0	6.9	1.4	2.4	7.0	3.0
5	1.7	3.9	7.0	7.0	1.6	2.4	7.0	3.0
6	1.6	3.9	7.0	7.0	1.5	2.1	7.0	3.0
8	1.5	3.9	7.0	7.0	1.5	2.2	7.0	3.0
9	1.5	3.9	7.0	7.0	1.5	2.2	7.0	3.0
10	1.4	3.9	7.0	7.0	1.5	2.0	7.0	3.0
12	1.4	3.9	7.0	7.0	1.4	2.1	7.0	3.0

[a] Downfield (ppm) from TMS. [b] These absorptions occur at the positions noted ±0.1 ppm for all three types of compounds. [c] AB quartet center. [d] The bromo compound was insoluble.

Procedure for the Synthesis of 4-(3-Methyl-3-hydroxy-1-butynyl)phenoxy Derivatives. In a dry, three-neck, 250-mL, round-bottomed flask equipped with a magnetic stir bar and fitted with a reflux condenser, nitrogen inlet, and glass stopper was placed a mixture of 0.008 mol of the appropriate bis(bromophenoxy)alkane, 0.023 mol of 2-methyl-3-butyn-2-ol, and 100 mL of triethylamine. The resulting solution was degassed with nitrogen for 20 min at room temperature and then heated to 80 °C, and then 0.2413 g of triphenylphosphine, 0.06 g of copper(I) iodide, and 0.06 g of dichlorobis(triphenylphosphine)palladium(II) was added to the homogeneous solution. The temperature of the reaction mixture was raised to 105 °C and maintained for 20 h. The resulting solution was cooled to room temperature, and triethylamine hydrobromide was removed by filtration and washed with ether until the ether washes were colorless. The triethylamine and ether were removed under reduced pressure to leave a residual solid which was taken up in 50 mL of methylene chloride and washed with three 100-mL portions of 10% sulfuric acid and finally with two 100-mL portions of distilled water. The organic layer was dried with $MgSO_4$, filtered, and concentrated to leave a crude product which was recrystallized from a mixture of methylene chloride and low-boiling petroleum ether.

Procedure for the Synthesis of Acetylene-Terminated Derivatives. In a 100-mL round-bottomed flask, equipped with a magnetic stir bar and fitted with a distilling head, was placed 0.002 mol of the appropriate butynylphenoxy derivative in 50 mL of toluene. The reaction mixture was made homogeneous by heating the solution to 70 °C at which time 20 mL of a 10% NaOH/MeOH solution was added. Toluene was distilled to half its original volume. A small sample was withdrawn from the reaction vessel and analyzed by thin-layer chromatography (TLC) using methylene chloride as eluent. The reaction flask was replenished with toluene and the distillation/TLC/addition process repeated three times. When the reaction was complete by TLC, toluene was removed at reduced pressure and the residue solid was purified by column chromatography using methylene chloride as the eluent.

Registry No. $Br(CH_2)_2Br$, 106-93-4; $Br(CH_2)_3Br$, 109-64-8; $Br(CH_2)_4Br$, 110-52-1; $Br(CH_2)_5Br$, 111-24-0; $Br(CH_2)_6Br$, 629-03-8; $Br(CH_2)_8Br$, 4549-32-0; $Br(CH_2)_9Br$, 4549-33-1; $Br(CH_2)_{10}Br$, 4101-68-2; $Br(CH_2)_{12}Br$, 3344-70-5; 4,4′-$BrC_6H_4O(CH_2)_2OC_6H_4Br$, 36506-46-4; 4,4′-$BrC_6H_4O(CH_2)_3OC_6H_4Br$, 3722-66-5; 4,4′-$BrC_6H_4O(CH_2)_4OC_6H_4Br$, 34932-24-6; 4,4′-$BrC_6H_4O(CH_2)_5OC_6H_4Br$, 117499-24-8; 4,4′-$BrC_6H_4O(CH_2)_6OC_6H_4Br$, 6943-11-9; 4,4′-$BrC_6H_4O(CH_2)_8OC_6H_4Br$, 117499-25-9; 4,4′-$BrC_6H_4O(CH_2)_9OC_6H_4Br$, 117499-26-0; 4,4′-$BrC_6H_4O(CH_2)_{10}OC_6H_4Br$, 117499-27-1; 4,4′-$BrC_6H_4O(CH_2)_{12}OC_6H_4Br$, 117499-28-2; 4-$BrC_6H_4OH$, 106-41-2; $HC{\equiv}CC(OH)(CH_3)_2$, 115-19-5; 4,4′-$(CH_3)_2C(OH)C{\equiv}CC_6H_4O(CH_2)_2OC_6H_4C{\equiv}CC(OH)(CH_3)_2$, 117499-29-3; 4,4′-$(CH_3)_2C(OH)C{\equiv}CC_6H_4O(CH_2)_3OC_6H_4C{\equiv}CC(OH)(CH_3)_2$, 117499-30-6; 4,4′-$(CH_3)_2C(OH)C{\equiv}CC_6H_4O(CH_2)_4OC_6H_4C{\equiv}CC(OH)(CH_3)_2$, 117499-31-7; 4,4′-$(CH_3)_2C(OH)C{\equiv}CC_6H_4O(CH_2)_5OC_6H_4C{\equiv}CC(OH)(CH_3)_2$, 117499-32-8; 4,4′-$(CH_3)_2C(OH)C{\equiv}CC_6H_4O(CH_2)_6OC_6H_4C{\equiv}CC(OH)(CH_3)_2$, 117499-33-9; 4,4′-$(CH_3)_2C(OH)C{\equiv}CC_6H_4O(CH_2)_8OC_6H_4C{\equiv}CC(OH)(CH_3)_2$, 117499-34-0; 4,4′-$(CH_3)_2C(OH)C{\equiv}CC_6H_4O(CH_2)_9OC_6H_4C{\equiv}CC(OH)(CH_3)_2$, 117499-35-1; 4,4′-$(CH_3)_2C(OH)C{\equiv}CC_6H_4O(CH_2)_{10}OC_6H_4C{\equiv}CC(OH)(CH_3)_2$, 117499-36-2; 4,4′-$(CH_3)_2C(OH)C{\equiv}CC_6H_4O(CH_2)_{12}OC_6H_4C{\equiv}CC(OH)(CH_3)_2$, 117499-37-3; 4,4′-$HC{\equiv}CC_6H_4O(CH_2)_2OC_6H_4C{\equiv}CH$, 93655-06-2; 4,4′-$HC{\equiv}CC_6H_4O(CH_2)_3OC_6H_4C{\equiv}CH$, 95219-64-0; 4,4′-$HC{\equiv}CC_6H_4O(CH_2)_4OC_6H_4C{\equiv}CH$, 95814-15-6; 4,4′-$HC{\equiv}CC_6H_4O(CH_2)_5OC_6H_4C{\equiv}CH$, 97432-27-4; 4,4′-$HC{\equiv}CC_6H_4O(CH_2)_6OC_6H_4C{\equiv}CH$, 96172-86-0; 4,4′-$HC{\equiv}CC_6H_4O(CH_2)_8OC_6H_4C{\equiv}CH$, 117499-38-4; 4,4′-$HC{\equiv}CC_6H_4O(CH_2)_9OC_6H_4C{\equiv}CH$, 117499-39-5; 4,4′-$HC{\equiv}CC_6H_4O(CH_2)_{10}OC_6H_4C{\equiv}CH$, 96075-28-4; 4,4′-$HC{\equiv}CC_6H_4O(CH_2)_{12}OC_6H_4C{\equiv}CH$, 117499-40-8.

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