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Synthesis of Bis(propynoyloxy) Aromatics

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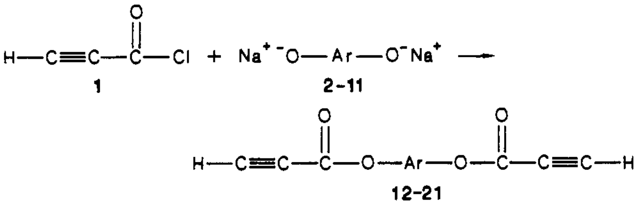
Ten bis(propynoyloxy) aromatics were prepared, in yields ranging from 28% to 68%, from propynoyl chloride and the disodium salt of the corresponding dihydroxy aromatic. The structures of these ethynyl compounds were confirmed by IR, ^{1}H NMR, and DSC.

Ethynyl groups have received much attention as a function capable of thermal chain extension and cross-linking by an addition process. Many ethynyl or acetylene-terminated (AT) aromatic systems show promise for uses in composite applications because they have been shown or proposed to form highly cross-linked matrices when heated above 200 °C (*1*–*6*). The use of propynoic acid as an acetylene-terminating agent appeared attractive because (1) propynoic acid is readily available and (2) methyl propynoate and allyl propynoate have been reported (*7*) to undergo linear polymerization in the presence of tetracarbonylnickel to give polyene oligomers that are similar to those reported as products in the thermal curing of other AT systems. In addition, a polyene structure was proposed for the product in the triethylamine-catalyzed polymerization of 9-anthramethyl propynoate (*8*). The synthesis of monofunctional propynoyloxy aromatics have been reported by Miller (*9*).

Our procedure for the preparation of aryl propynoates employed the reaction of the disodium salts of a dihydroxy aromatic **2-11** with propynoyl chloride (**1**) in toluene. The reaction was exothermic and sodium chloride was observed as a precipitate.



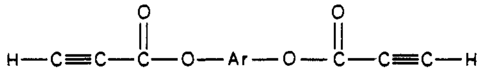
1

2-11

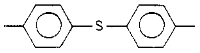
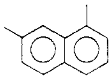
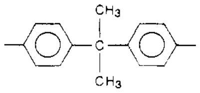
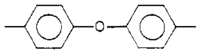
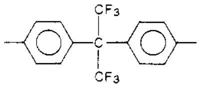
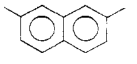
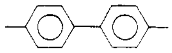
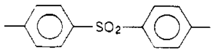
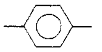
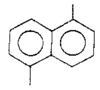
12-21

Thermal characterization by DSC indicated that bis(propynoyloxy) aromatics **12–19** each exhibit a melting endotherm in the range 97–188 °C (Table I), the position of which appears to be related to the rigidity of the aromatic function. The only exception is **20**, which distills during the DSC determination and therefore is not directly comparable.

Table I. Physical Properties of Bis(propynoyloxy) Aromatics 12-21



$$\mathrm{H{-}C{\equiv}C{-}\overset{O}{\overset{\|}{C}}{-}O{-}Ar{-}O{-}\overset{O}{\overset{\|}{C}}{-}C{\equiv}C{-}H}$$

compd	-Ar-	yield, %	mp, °C	DSC exotherm, °C		IR, cm^{-1}			^{1}H NMR, δ	
				onset[a]	max	C-H	C≡C	C=O	≡CH	Ar[b]
12		28	97	160	256	3260	2120	1725	4.07	7.36
13		47	110	160	245	3265	2128	1720	4.10	7.75
14		41	116	175	261	3260	2125	1720	3.90	7.05
15		52	125	170	257	3245	2130	1714	4.03	7.17
16		63	134	175	267	3240	2125	1720	4.12	7.47
17		39	151	165	253	3235	2125	1720	4.00	7.51
18		34	153	170	257	3263	2120	1720	3.96	7.34
19		55	158	175	238	3280	2135	1730	4.48	7.66
20		46	159	225	254[c]	3260	2110	1715	4.07	7.32
21		68	188	190	247	3270	2120	1722	4.41	7.73

[a] Initial deflection of exotherm from the base line. [b] Center of the aromatic multiplet. [c] Distills near exotherm onset.

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Experimental Section

Nuclear magnetic resonance (NMR, ^1H) 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 spectrophotometer. Differential scanning calorimetric (DSC) data was 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. All new compounds exhibited acceptable (0.5%) elemental analyses. The compounds 1,5-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 4,4′-thiobis(phenol), 2,2-bis(4-hydroxyphenyl)propane, 4,4′-bis(phenol), 4,4′-sulfonylbis(phenol), and 1,4-dihydroxybenzene were obtained from Aldrich Chemical Co. and used without further purification. The compounds 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane and 4,4′-oxybis(phenol) were obtained from B. A. Reinhardt at Wright Patterson AFB and were used without furthur purification.

***Propynoyl Chloride* (*1*).** A 500-mL three-necked, round-bottomed flask, equipped with a drying tube, a nitrogen inlet, and a dropping funnel was charged with 1 mol of phosphorus pentachloride (*10*). The flask was flushed with nitrogen for 10 min. One mole of propynoic acid was added via the dropping funnel over a 4-h period at room temperature. The flask was then attached to a small vacuum line equipped with a trap cooled with a dry ice/2-propanol followed by a trap cooled with liquid nitrogen. The contents of the flask were distilled by warming to room temperature. Both phosphorus oxychloride and propynoyl chloride were collected in the dry ice cooled trap, the former as a white solid and the latter as a clear, colorless liquid. The propynoyl chloride was pipetted from the phosphorus oxychloride and redistilled in identical fashion. After two distillations, the yield of clear, colorless, fuming liquid varied from 45% to 70%. A working solution was prepared by placing the doubly distilled propynoyl chloride in enough toluene to make 100 mL of solution, and the solution was stored at 0 °C until use (the solution was stable for several weeks at 0 °C).

***General Procedure for the Synthesis of Bis(propynolyoxy) Aromatics*.** One equivalent of the dihydroxy aromatic was dissolved in 100 mL of deoxygenated water containing 2 equiv of sodium hydroxide. The resulting solution was evaporated to dryness under vacuum. The salt obtained was pulverized and heated under vacuum at 125 °C in order to complete drying. The sodium salt (0.05 mol) was added in small portions over 2 h to a vigorously stirred toluene solution of propynoyl chloride (0.02 mol) contained in a round-bottomed flask equipped with a drying tube and a magnetic stirrer. The mixture was stirred for 12 h, treated with 100 mL of 1 N sodium hydroxide, and stirred for an additional 2 h. Crude product was isolated by separation and evaporation of the toluene. Recrystallization from cyclohexane provided pure products and analytical samples.

Registry No. **1**, 50277-65-1; **2**, 2664-63-3; **3**, 575-38-2; **4**, 80-05-7; **5**, 1965-09-9; **6**, 1478-61-1; **7**, 582-17-2; **8**, 92-88-6; **9**, 80-09-1; **10**, 123-31-9; **11**, 83-56-7; **12**, 117583-42-3; **13**, 117583-43-4; **14**, 745-13-1; **15**, 117583-44-5; **16**, 117583-45-6; **17**, 117583-46-7; **18**, 740-56-7; **19**, 117583-47-8; **20**, 721-95-9; **21**, 117583-48-9.

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