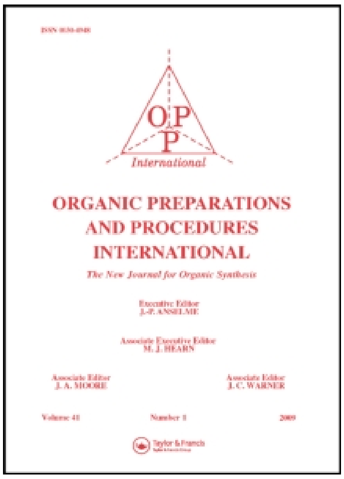

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SYNTHESIS OF PHENOXYPHENYLATED 4,4''-DICARBOXY-p-TERPHENYLS

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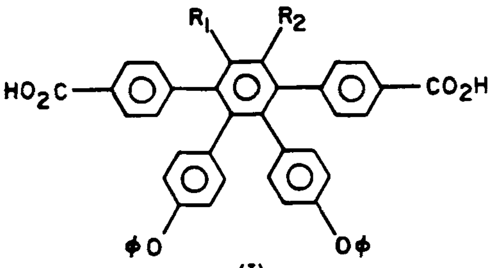
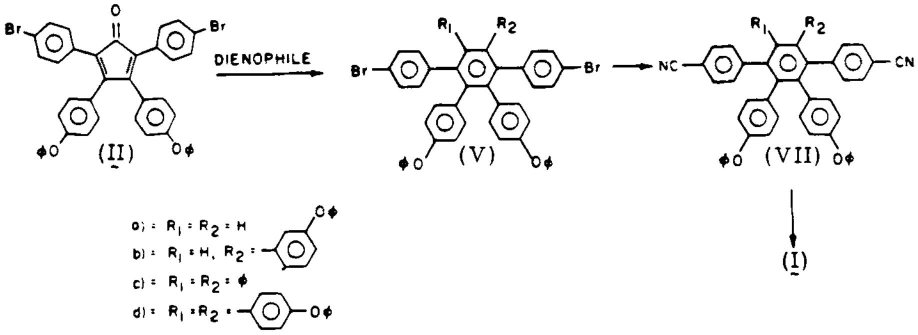
In relation to our studies on the synthesis and solution properties of high-temperature resistant heteroaromatic polymers, several phenylated poly-p-benzobisoxazoles[1] have been synthesized and shown to possess markedly improved solubility over that of p-phenylene polybenzobisoxazole[2] which was soluble only in strongly corrosive acids. Phenoxyphenylation of polybenzobisoxazole polymers could conceivably further enhance polymer solubility by the added entropy factor of the oxyphenylene linkages,[3] so that a wider range of common organic solvents could be used.

Phenoxyphenylated poly-p-benzobisoxazoles are not known. This report describes the synthesis of the diacid monomers (I) necessary for the polymerization reactions to generate the para-ordered phenoxyphenylated poly-p-benzobisoxazoles.



(I)

A key step in the synthesis of the diacids (I) is the formation of the tetracyclone (II). A double Friedel-Crafts acylation[4,5] of diphenyl ether with oxalyl chloride in carbon disulfide afforded a 2:1 mixture of 4,4'-diphenoxybenzil (III)[5] and 4,4'-diphenoxybenzophenone (IV)[5b,6] which were difficult to separate. The exact percentage of III in the mixture could be ascertained by nmr. Benzophenone IV did not interfere in the subsequent reaction and was carried through the next step before its eventual removal. Base-catalyzed condensation of III with 4,4'-dibromodibenzyl ketone[1] yielded tetracyclone II. Washing of the reaction product with hot ethanol effectively separated IV from II which was then analytically pure. In later experiments, we found that the double Friedel-Craft acylation gave only 4,4'-diphenoxybenzil when the reaction was carried out in dichloromethane.



The Diels-Alder reactions of II with norbornadiene, 3-phenoxyphenylacetylene,[7] 4,4'-diphenoxydiphenylacetylene yielded the di-, tri-, and tetra-phenoxyphenylated dibromo-p-terphenyls (V a, b, d), respectively, after subsequent decarbonylation.[8] In the first case, elimination of cyclopentadiene also took place. The reaction of II with diphenylacetylene gave the diphenyldiphenoxyphenyl derivative Vc. One of the required dienophiles, 4,4'-diphenoxydiphenylacetylene (VI), was conveniently synthesized by mercuric oxide oxidation[9] of 4,4'-diphenoxybenzil dihydrazone.

Treatment of the dibromo-p-terphenyls (V) with cuprous cyanide in dry N-methylpyrrolidone afforded the corresponding dicyano compounds (VII) which underwent hydrolysis with potassium hydroxide in refluxing ethylene glycol to yield the desired diacid monomers (I).

EXPERIMENTAL

4,4'-Diphenoxybenzil (III). In Carbon Disulfide.- A slurry of 64.4 g (0.482 mole) of aluminum chloride in 300 ml of carbon disulfide was stirred vigorously while 78.3 g (0.461 mole) of diphenyl ether was added. After 15 min. a pink color developed. To the slurry which was cooled to 0-5°, was added dropwise a solution of 28.2 g (0.222 mole) of oxalyl chloride in 200 ml of carbon disulfide. The resulting crimson red mixture was heated at reflux for 5 hrs., cooled and then poured into 1 ℓ. of crushed ice. The solid was collected and recrystallized from 1 ℓ. of 4:1 hexane-toluene to yield 76.4 g of crude product. Nmr analysis showed that 31% of 4,4'-diphenoxybenzophenone was present. The final product contained 70.6 wt. % of 4,4'-diphenoxybenzil which corresponded to a net yield of 61.6%.

Preparation of an analytical sample of 4,4'-diphenoxybenzil was carried out by column chromatography through silica gel using 1:1

hexane-dichloromethane as eluent. 4,4'-Diphenoxybenzil elutes before 4,4'-diphenoxybenzophenone.

In Dichloromethane.- A slurry of 21.1 g (158 mmoles) of aluminum chloride and 26.2 g (154 mmoles) of diphenyl ether in 100 ml anhydrous dichloromethane was stirred for 0.5 hr at 20°, cooled to 0-5° and treated with 9.40 g (74.0 mmoles) of oxalyl chloride in 50 ml of dichlormethane. The resulting mixture was heated at reflux for 4 hrs, cooled and poured into 0.5 ℓ. of crushed ice. The organic phase was washed with 500 ml of 10% hydrochloric acid, 500 ml of water, 500 ml of saturated sodium bicarbonate and then again with 500 ml of water. After solvent removal, the yellow solid was dissolved in 200 ml of 1:1 dichlormethane-hexane. Slow evaporation of the solvent yielded a pale yellow crystalline product melting at 113°. After removal of the first crop by filtration, the mother liquor yielded a second crop upon further concentration. The total yield was 25.5 g (87.4%). Thin-layer chromatography (silica gel, 1:1 dichloromethane-hexane) nmr and elemental analysis showed that the product was analytically pure.

2,5-Di-p-bromophenyl-3,4-di-p-phenoxyphenylcyclopentadienone (II).- A 700-ml absolute ethanol solution of 4,4'-diphenoxybenzil (containing 31 mole % of 4,4'-diphenoxybenzophenone as impurity; assay weight 32.0 g, 81.2 mmoles) and di-p-bromodibenzyl ketone (29.9 g, 81.2 mmoles) was heated at reflux before being treated with a solution of 4 g of potassium hydroxide in absolute ethanol. The dark purple solution was then stirred at reflux for 1 hr., cooled to room temperature and filtered. The crude solid was heated in 1 ℓ. boiling ethanol, filtered hot and the dark purple crystals were washed with warm ethanol (ca 60°). The mother liquor was concentrated to 500 ml to afford a second crop by filtration. Upon cooling to room temperature the mother liquor yielded white crystals of 4,4'-diphenoxybenzophenone. The dark purple crystals (38.2 g, 64.8%) of the tetracyclone (II) were analytically pure.

4,4'-Diphenoxydiphenylacetylene (VI). - The procedure for preparing diphenylacetylene from benzil was adapted.[9] Treatment of 26.0 g of 4,4'-diphenoxybenzil (18.3 g assay) with 10.0 g of 85% aqueous hydrazine hydrate in 200 ml of sec-butanol at reflux (98-100°) for 52 hrs afforded the dihydrazone derivative after recrystallization from the same solvent. yield 19.4 g, 99.6%; mp. 143°; IR (KBr) 3380, 3340, 3200 (sharp, NH_2), 1250 cm^{-1} (broad, strong). Oxidation of the dihydrazone with 25.0 g of yellow mercuric oxide in 100 ml of benzene at reflux for 5 hrs. yielded crystalline 4,4'-diphenoxydiphenylacetylene which was purified by column chromatography through silica gel using a solvent mixture of 20% dichloromethane in hexane; yield 54.1%.

4,4''-Dibromo-2',3-di-p-phenoxyphenyl-p-terphenyl (Va). - A mixture of 14.3 g (19.6 mmoles) of 2,5-di-p-bromophenyl-3,4-di-p-phenoxyphenylcyclopentadienone (II) and 24.1 g (262 mmoles) of norbornadiene in 100 ml toluene was heated at reflux for 8 hrs. The dark purple color faded to an orange-red tint. No further change was observed after 24 hrs. at reflux. Upon cooling, a white solid precipitated; it was mixed with 200 ml of methanol, collected by filtration and recrystallized from 100 ml of hexane to yield 11.4 g (79.9%) of featherlike white needles.

4,4''-Dibromo-2',3'-di-p-phenoxyphenyl-5'-m-phenoxyphenyl-p-terphenyl (Vb). - A mixture of 5.00 g (0.89 mmole) of dienone II and 4.00 g (20.6 mmoles) of m-phenoxyphenylacetylene was heated without solvent under nitrogen to a vigorous reflux for 2 minutes. The intense purple color faded to a light yellow tint. The solid obtained upon cooling was recrystallized from 50 ml of a 1:2 dichloromethane-hexane mixture to yield 5.27 g (85.5%).

4,4''-Dibromo-2',3'-di-p-phenoxyphenyl-5',6'-diphenyl-p-terphenyl (Vc). - Heating 2.00 g (2.75 mmoles) of dienone II and 2.50 g (14.0 mmoles) of diphenylacetylene in 10 g of benzophenone at reflux for 20 minutes, followed by cooling and mixing with 20.0 ml of hexane precipitated a crude product which was recrystallized from 50 ml of 2:3 benzene-hexane to yield 2.20 g (91.3%) of purified product.

4,4''-Dibromo-2',3',5',6'-tetraphenoxyphenyl-p-terphenyl (Vd). - A mixture of 3.40 g (4.68 mmoles) of II and 1.90 g (5.25 mmoles) of 4,4'-diphenoxydiphenylacetylene was heated to a gentle reflux for 15 minutes with a Bunsen flame. The white solid obtained was recrystallized from 50 ml of 1:4 dichloromethane-hexane to yield 4.16 g (83.5%).

4,4''-Dicyano-2',3'-di-p-phenoxyphenyl-p-terphenyl (VIIa). - A mixture of 10.2 g (15.5 mmoles) of 4,4''-dibromo-2',3'-di-p-phenoxyphenyl-p-terphenyl (Va) and 4.15 g (46.4 mmoles) of cuprous cyanide in 75 ml of deaerated anhydrous N-methylpyrrolidone was heated at reflux under nitrogen for 18 hrs. The dark brown mixture was cooled and poured into 200 ml of 25 g sodium cyanide in warm water. The grey precipitate was stirred for 1 hr. and allowed to cool to room temperature, filtered, washed with 100 ml of 10% sodium cyanide and then with water. The air-dried crispy grey solid was purified by column chromatography (silica gel, 1:1 dichloromethane-hexane) followed by recrystallization from 100 ml of hexane to give 8.98 g (94.2%) of long colorless needles.

4,4''-Dicyano-2',3'-di-p-phenoxyphenyl-5'-m-phenoxyphenyl-p-terphenyl (VIIb). - The dinitrile VIIb was similarly obtained from 2.98 g (3.34 mmoles) of Vb (reaction time: 48 hrs) in quantitative yield after column chromatography (silica gel, 1:1 dichloromethane-hexane) and recrystallization from 30 ml of hexane.

4,4''-Dicyano-2',3'-di-p-phenoxyphenyl-5',6'-diphenyl-p-terphenyl (VIIc). - Using the same procedure described for VIIa, dinitrile VIIc was prepared from 2.03 g (2.32 mmoles) of Vc (reaction time: 44 hrs.) in quantitative yield. The product was purified by column chromatography (silica gel, 1:1 dichloromethane-hexane) and recrystallization from 100 ml of hexane.

4,4''-Dicyano-2',3',5',6'-tetraphenoxyphenyl-p-terphenyl (VIId). - The dinitrile VIId was obtained from 2.00 g (1.89 mmole) of Vd (reaction time: 48 hrs) by the same procedure described for VIIa. The product was purified by column chromatography (silica gel, 1:1 dichloromethane-hexane) to yield 1.69 g (93.9%).

4,4''-Dicarboxy-2',3'-di-p-phenoxyphenyl-p-terphenyl (Ia). - A slurry of 3.00 g (4.87 mmoles) of 4,4''-dicyano-2',3'-di-p-phenoxyphenyl-p-terphenyl (VIIa) and 10 g potassium hydroxide in 75 ml ethylene glycol was heated at 175° for 24 hrs. The resulting orange-colored solution

Physical Properties of Compounds

Compound	mp, °C	Yield (%)	ir(KBr) in cm^{-1}	Elemental Analysis^a			
				C	H	N	Br
II	193-194°	64.8	1700, 1590, 1485, 1240	65.97	3.62		21.27
				(66.15)^b	(3.79)		(21.47)
III	113-114°	83.8^d	1660, 1580, 1245	79.24	4.70		
				(79.17)	(4.60)		
IV	146-147^e	–	1640, 1590, 1265				
VI	167-168°	54.1	1590, 1515, 1490, 1260	86.44	5.10		
				(86.16)	(5.01)		
Va	197°	79.9	1590, 1510, 1490, 1235	69.58	3.62		21.92
				(69.63)	(3.90)		(22.06)
Vb	194°	85.8	1590, 1505, 1490, 1240	72.65	4.08		17.90
				(72.66)	(4.06)		(17.90)
Vc	281°	91.3	1590, 1510, 1490, 1235	73.73	3.82		18.44
				(73.98)	(4.14)		(18.23)
Vd	285-286°	83.5	1590, 1235	74.50	3.85		
				(74.72)	(4.18)		
VIIa	212.5°	94.2	2240, 1240	85.74	4.20	4.26	
				(85.69)	(4.58)	(4.54)	
VIIb	201-202°	100	2220, 1240	85.94	4.36	3.35	
				(85.69)	(4.62)	(3.57)	
VIIc	255-256°	100	2220, 1240	87.69	4.37	3.40	
				(87.48)	(4.72)	(3.64)	
VIId	199-200°	93.9	2230, 1230	85.47	4.35	2.78	
				(85.69)	(4.65)	(2.94)	
Ia	346-347°	84.5	3500-2550, 1690, 1280, 1240	80.79	4.69		
				(80.72)	(4.62)		
Ib	339-340°	89.4	3400-2550, 1685, 1270, 1235	81.54	4.28		
				(81.74)	(4.65)		
Ic	384-386°	88.1	3500-2550, 1685, 1280, 1240	83.90	4.44		
				(83.36)	(4.75)		
Id	368-370°	59.6	3300-2550, 1685, 1275, 1235	82.21	4.40		
				(82.41)	(4.68)		

[a] Theoretical values are in parenthesis.

[b] Calculation for compound II is based on $C_{41}H_{26}Br_2O_3H_2O$.

[c] Literature value: 116°C (reference 5a); 118-9°C (reference 5b); 116-7°C (reference 5c); 119.5-121°C (reference 5d).

[d] Yield was based on reaction carried out in dichloromethane.

[e] Literature value: 147°C (reference 6a); 146-7°C (reference 6b); 145-6°C (reference 6c); 139°C (reference 6d); 148°C (reference 5b).

was poured into 300 ml of warm 20% hydrochloric acid with stirring. Stirring was continued for 2 hrs at *ca.* 60°, then the mixture was cooled to room temperature and filtered. The air-dried solid was mixed with 175 ml toluene and 75 ml ethanol and heated to boiling with 1 g of charcoal and filtered while hot. The filtrate collected was concentrated to 100 ml. Crystals formed upon cooling in an ice bath. After filtration, washing with cold 95% ethanol and drying, the white powdery product weighed 2.69 g (84.5%).

4,4''-Dicarboxy-2',3'-di-p-phenoxyphenyl-5'-m-phenoxyphenyl-p-terphenyl (Ib). - Using the procedure described for Ia, the diacid Ib was prepared from 4.88 g (6.22 mmoles) of VIIb in 89.4% yield after recrystallization from 100 ml of 2:1 toluene-ethanol.

4,4''-Dicarboxy-2',3'-di-p-phenoxyphenyl-5',6'-diphenyl-p-terphenyl (Ic). - From 3.84 g (4.38 mmoles) of VIIc, the diacid Ic was similarly prepared in 88.1% yield after recrystallization from 200 ml of 1:1 toluene-ethanol.

4,4''-Dicarboxy-2',3',5',6'-tetra-p-phenoxyphenyl-p-terphenyl (Id). - From 4.60 g (4.83 mmoles) of VIId, the diacid Id was similarly prepared in 87.8% yield after recrystallization from 100 ml of 1:1 toluene ethanol.

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