

## Disubstituted *p*-Phenylene Monomers. $\alpha$ -Methyl- and $\alpha$ -Phenyl-vinyl Derivatives of Benzene, Biphenyl, *p*-Terphenyl, and *p,p'*-Diphenoxybiphenyl.

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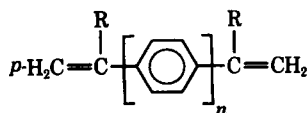
### Synopsis

The high-yield syntheses of bis[*p*-( $\alpha$ -methylvinyl)] monomers of benzene, biphenyl, *p*-terphenyl, and 4,4'-diphenoxybiphenyl are reported. Also described are the syntheses of new bis[*p*-( $\alpha$ -phenylvinyl)] monomers of biphenyl, *p*-terphenyl, and 4,4'-diphenoxybiphenyl. Infrared spectral data for the diolefinic monomers and their precursors are presented, together with brief details for the polymerization of the diolefins by means of free radical and Lewis acid catalysts.

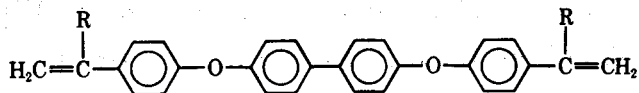
In recent years many attempts have been made to prepare easily handled and soluble polyphenylene polymers. The polyphenylenes are theoretically of interest for aerospace applications, as they are thermally and oxidatively stable, and are resistant to most corrosive environments. Unfortunately, the completely *para*-oriented polyphenylenes are characterized by extreme infusibility and intractability; and even mixed *m*- and *p*-polyphenylenes are soluble only with considerable difficulty.<sup>1,2</sup>

The observation of Mitin and Glukhov<sup>3</sup> that *p*-diisopropenylbenzene can be polymerized by Lewis acid catalysts to give polymers of unusual thermal and oxidative stability that are soluble in aromatic solvents, carbon disulfide, and carbon tetrachloride, led us to investigate the polymers that can be produced by *para*-disubstituting phenylene moieties of the type  $\text{H}-\text{C}_6\text{H}_4-\text{H}$ . Neville<sup>4,5</sup> has recently demonstrated that blocking the reactive "benzylic" position of the oxirane ring significantly enhances the thermal stability and oxidative resistance of the resulting polymers, and this reasoning was employed in the present program in which the alpha-position of the vinyl group was substituted by methyl or phenyl groups.

This article discusses the syntheses of the first three members of the homologous series:

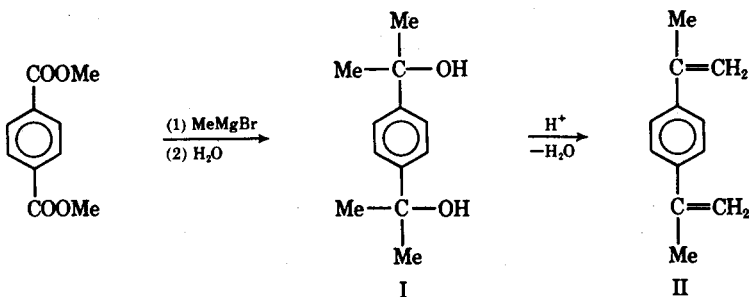


where  $R = \text{CH}_3$  ( $n = 1,2,3$ ) or  $\text{C}_6\text{H}_5$  ( $n = 2,3$ ). Owing to the insolubility of, and consequent experimental difficulty with,  $p,p'$ -quaterphenyl, the syntheses of the more readily prepared new phenoxy compounds of the following structure, are reported:



where  $R = \text{CH}_3$  or  $\text{C}_6\text{H}_5$ . It was realized, of course, that due to the aliphatic moieties, polymers produced from these monomers could not exhibit the outstanding thermal and oxidative stability of the polyphenylenes. However, such stability was not required in our present polymer program, tractability and solubility being more important prerequisites.

$p$ -Diisopropenylbenzene (compound II, where  $n = 1$ ) has been prepared by catalytic dehydrogenation of  $p$ -diisopropylbenzene,<sup>6,7</sup> by catalytic demethanation of  $p$ -di-*tert*-butylbenzene,<sup>8</sup> by dehydration of  $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl- $p$ -xylene- $\alpha,\alpha'$ -diol,<sup>9-12</sup> and by the reaction of the di-Grignard reagent of  $p$ -dibromobenzene with acetone and subsequent dehydration.<sup>13</sup> By treating dimethyl terephthalate with methylmagnesium bromide, Mitin<sup>14</sup> obtained a 66% yield of  $p$ - $\text{C}_6\text{H}_4(\text{CMe}_2\text{OH})_2$  (I), which was converted to the corresponding dichloride, then dehydrochlorinated with pyridine to give a 50% yield of II. We have improved the yields of most of the foregoing syntheses by treating dimethyl terephthalate with methylmagnesium bromide, followed by hydrolysis to the di-*tert*-alcohol (I), which was then dehydrated by refluxing in toluene or xylene containing a catalytic amount of orthophosphoric acid:



Partial dehydration occurs merely by refluxing an uncatalyzed toluene or xylene solution of the dialcohol, but complete and rapid removal of the elements of water occurs only in the presence of trace amounts of acid. Although dehydration can be effected by using hydriodic, oxalic, trifluoroacetic, sulfuric, or  $p$ -toluenesulfonic acids, optimum results were obtained only when orthophosphoric acid was employed.

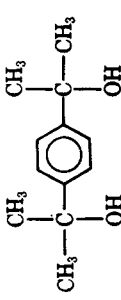
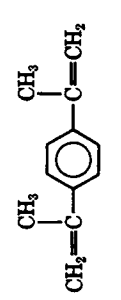
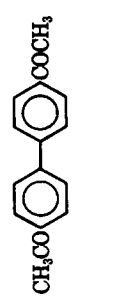
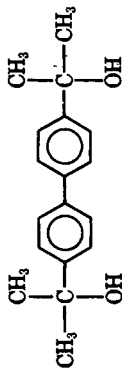
$p,p'$ -Diisopropenylbiphenyl (compound V, where  $n = 2$ ) has been synthesized in 44% yield by treating dipropylbiphenyl-4,4'-dicarboxylate with methylmagnesium bromide, followed by hydrolysis to the correspond-

ing dialcohol, conversion to the dichloride, and dehydrochlorination.<sup>14</sup> In the present program 4,4'-diacetylbiphenyl (III) was prepared in essentially theoretical yield by acetylating biphenyl in methylene chloride under Friedel-Crafts conditions. Patai et al.<sup>15</sup> and Kotlyarevskii et al.<sup>16</sup> have reported up to 63% yields of III employing carbon disulfide as the Friedel-Crafts medium, but as this gives a two-phase inhomogeneous system methylene chloride is the preferred solvent.<sup>4,17</sup> After recrystallization, pure III was obtained as colorless platelets, mp 195°C (lit. mp, 186–187°C,<sup>15</sup> 190–191°C,<sup>16</sup> 192°C<sup>18</sup>). The corresponding dialcohol (IV) was prepared in essentially theoretical yield by treating III with methylmagnesium bromide in tetrahydrofuran (THF) below 0°C. After decomposition of the Grignard complex the THF was removed without heating to yield a white solid which, on recrystallizing from benzene, yielded the dialcohol (IV) as colorless scintillating platelets, mp 161.5°C (lit. mp.<sup>14</sup> 161°C). On refluxing IV in xylene, in the presence of a catalytic amount of orthophosphoric acid, *p,p'*-diisopropenylbiphenyl (V) was formed in 80–90% yield. Recrystallization of V from toluene yielded colorless platelets, mp 182°C (lit. mp. 176–177°C,<sup>15</sup> 177–179°C,<sup>19</sup> 183°C<sup>14</sup>). The infrared spectrum of IV showed strong absorption at 3360–3370 cm<sup>-1</sup> (—OH), and V exhibited strong absorption at 1623 cm<sup>-1</sup> (>C=C<).

4,4''-Diacetylterphenyl (IV) has been prepared by treating *p*-terphenyl with acetic anhydride<sup>15</sup> or acetyl chloride<sup>20</sup> under Friedel-Crafts conditions. During the present investigation VI was synthesized in almost theoretical yield by treating *p*-terphenyl with acetyl chloride in methylene chloride, with aluminum chloride as catalyst. Sublimation of the crude product gave pure VI as colorless prisms, mp 288°C (lit. mp, 268–269°C,<sup>15</sup> 278–280°C<sup>20</sup>). 1,4-Bis(4-isopropenylphenyl)benzene (compound VIII, *n* = 3) was produced in 93.7% yield by treating VI with methylmagnesium bromide, followed by the usual work-up to give the dialcohol (VII) as cream-colored platelets (mp 224°C), then dehydration in xylene solution in the presence of a trace of orthophosphoric acid. Thus prepared and recrystallized from dimethylformamide (DMF), VIII was obtained as iridescent platelets, mp 285°C (lit. mp, 268–269°C<sup>15</sup>).

The marked insolubility of *p*-quaterphenyl precluded our extending the series of *p*-diisopropenylphenylenes to the fourth homolog (*n* = 4). In place of *p*-quaterphenyl the diisopropenyl derivative of 4,4'-diphenoxybiphenyl (IX) was prepared. A 90% yield of IX was obtained by the reaction of potassium phenoxide with 4,4'-dibromobiphenyl by using a suitably modified version of the Ullman synthesis.<sup>4</sup> After recrystallization from tetrachloroethylene, IX was obtained as a white microcrystalline solid, mp 152°C (lit. mp, 152°C,<sup>16</sup> 155°C<sup>21</sup>). Kotlyarevskii et al.<sup>16</sup> have reported the preparation of 4,4'-bis(4-acetylphenoxy)biphenyl (X) in 36% yield by the Friedel-Crafts reaction of acetyl chloride with IX in 1,2-dichloroethane. Using methylene chloride as the Friedel-Crafts medium, we obtained twice that yield (approx. 70% crude) of X which, after recrystallization from DMF and charcoal, gave a 59% yield of iridescent platelets, mp 225°C

TABLE I  
 $\alpha$ -Methylvinyl *p*-Phenylene Monomers and Precursors

Compound no.	Compound	Description	Reactants	Yield, Mp, %	Infrared absorption, $\text{cm}^{-1}$	Analysis			
						Calculated	Found		
						C, %	H, %		
I		Colorless needles	$p\text{-C}_6\text{H}_4(\text{COOMe})_2$ ; 100 g (0.4 mole) MeMgBr(2M), 1600 ml (3.2 mole)	100 141	3310 ( $-\text{OH}$ )	74.24	9.27	74.21	9.75
II		Colorless iridescent platelets	I, 61 g (0.314 mole); $\text{H}_3\text{PO}_4$ , 12 drops xylene, 500 ml.	60 65	1621 [ $>\text{C}=\text{C}<$ ]	91.15	8.85	91.11	8.94
III		Colorless platelets	$\text{C}_6\text{H}_5$ , $\text{C}_6\text{H}_5$ , 425 g (2.75 mole) $\text{CH}_3\text{COCl}$ , 454 g (5.77 mole) $\text{AlCl}_3$ , 908 g (6.8 mole) $\text{CH}_2\text{Cl}_2$ , 1000 ml	93 195	1680 ( $>\text{C}=\text{O}$ )	80.68	5.88	80.67	5.63
IV		Colorless scintillating platelets	III, 144 g (0.6 mole) MeMgBr(2M), 1500 ml (3 mole)	95 161.5	3360-70 ( $-\text{OH}$ ) 1500 (arom.)	80.01	8.14	79.97	8.21


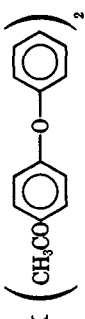
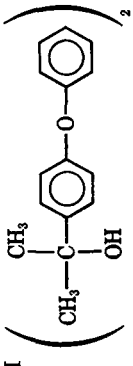
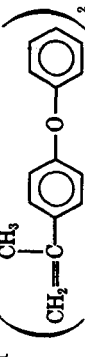
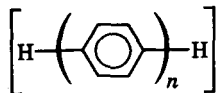
V		Colorless platelets	IV, 36 g (0.13 mole) H <sub>3</sub> PO <sub>4</sub> , 12 drops xylene, 500 ml	93	182	1623 (>C=C<) 1620 sh (arom.)	91.53	7.67	91.54	7.57
VI		Colorless prisms	<i>p</i> -C <sub>6</sub> H <sub>5</sub> ·C <sub>6</sub> H <sub>4</sub> ·- C <sub>6</sub> H <sub>5</sub> , 200 g (0.86 mole) CH <sub>3</sub> COCl, 137 g (1.75 mole) AlCl <sub>3</sub> , 367 g (2.75 mole)	89	288	1670(>C=O) 1595 (arom.)	84.09	5.73	83.85	5.80
VII		Cream- colored platelets	VI, 141.5 g (0.45 mole) MeMgBr(2 <i>M</i> ), 1125 ml (2.35 mole)	100	224	3360-80 (-OH) 1490 (arom.)	83.25	7.51	83.39	7.64
VIII		Colorless iridescent platelets	VII, 81.0 g (0.233 mole) H <sub>3</sub> PO <sub>4</sub> , 35 drops xylene, 1300 ml	94	285	1623 (>C=C<)	92.91	7.09	92.73	7.18
IX		White micro- crystalline	C <sub>6</sub> H <sub>5</sub> OH, 550 g (5.5 mole) KOH, 340 g (5.3 mole)  , 500 g (1.14 mole)	90	152	1598 (arom.) 1591	85.22	5.32	84.89	5.40

TABLE I (continued)  
 $\alpha$ -Methylvinyl *p*-Phenylene Monomers and Precursors

Compound no.	Compound	Description	Reactants	Yield, Mp, % °C	Infrared absorption, cm <sup>-1</sup>	Analysis			
						Calculated	Found		
						C, %	H, %		
X		Colorless iridescent platelets	IX, 169 g (0.5 mole) CH <sub>3</sub> COCl, 94.2 g (1.2 mole) AlCl <sub>3</sub> , 187 g (1.4 mole) CH <sub>2</sub> Cl <sub>2</sub> , 1500 ml	95 225	1680 (>C=O) 1600 (arom.)	79.63	5.21	79.96	5.34
XI		Colorless platelets	X, 90 g (0.213 mole) MeMgBr (2M), 568 ml (1.136 mole)	100 169	3370-90 (-OH)	79.31	6.60	79.44	6.73
XII		White micro-crystalline	XI, 71 g (0.156 mole) H <sub>3</sub> PO <sub>4</sub> , 30 drops xylene, 1000 ml	90 213	1627 (>C=C<) 1600 (arom.)	86.13	6.22	85.97	6.27

(lit. mp, 223°C<sup>16</sup>). The hitherto unrecorded dialcohol (XI) and 4,4'-bis(4-isopropenylphenoxy)biphenyl (XII) were synthesized by procedures similar to those described for the preparation of the *p*-phenylene analogs.

The *p*-disubstituted  $\alpha$ -phenylvinyl derivatives of phenylenes



(in which R = C<sub>6</sub>H<sub>5</sub>, and *n* = 1,2,3) have been the subject of very few investigations. Although 2,2'-bis( $\alpha$ -phenylvinyl)biphenyl has been prepared by the Wittig reaction of 2,2'-dibenzoylbiphenyl with methylenetriphenylphosphorane,<sup>22,23</sup> this compound appears to be the only example of a disubstituted  $\alpha$ -phenylvinylphenylene compound so far reported.

4,4'-Bis(1-phenyl-1-hydroxyethyl)biphenyl (XIII) was prepared in theoretical yield by treating 4,4'-diacetylbiphenyl (III) with 3*M* phenylmagnesium bromide, hydrolyzing the Grignard complex in the usual manner, and removing the solvent *in vacuo*. XIII was obtained as a pale amber gum, which was dissolved in xylene containing a trace of orthophosphoric acid, then heated at reflux to remove the elements of water. 4,4'-Bis(1-phenylvinyl)biphenyl (XIV) was thus formed as a white crystalline solid which was recrystallized from alcohol to yield colorless iridescent platelets, mp 196°C.

Similarly prepared from the corresponding diacetyl compounds were the *p*-terphenyl and 4,4'-diphenoxybiphenyl derivatives, namely, 1,4-bis[4(1-phenylvinyl)phenyl]benzene (XVI) and 4,4'-bis[4(1-phenylvinyl)phenoxy]biphenyl (XVIII), respectively.

Both the isopropenyl and the  $\alpha$ -phenylvinyl monomers can be readily polymerized by heating with benzoyl peroxide,<sup>24</sup> di-*tert*-butyl peroxide,<sup>25</sup> or Lewis acid catalysts (e.g., SnCl<sub>4</sub>-HCl).<sup>26</sup> A report on the formation of polymers, physical and chemical properties, thermogravimetric (TGA) and differential thermal analysis (DTA) data will be published in a subsequent paper.

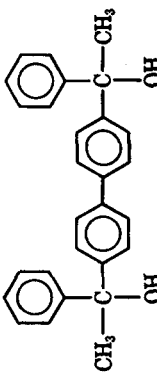
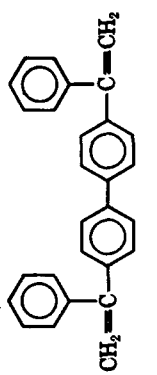
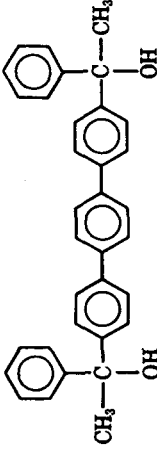
## EXPERIMENTAL

Directions for the synthesis of 1,4-bis[4(1-methylvinyl)phenyl]benzene (VIII) are given below. The corresponding  $\alpha$ -phenylvinyl compounds were similarly prepared. Other compounds listed in Tables I and II were prepared by analogous procedures, and physical data are presented therein.

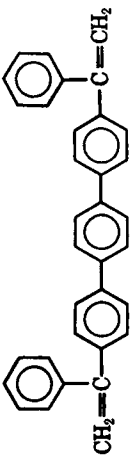
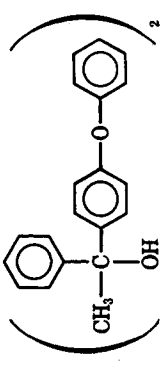
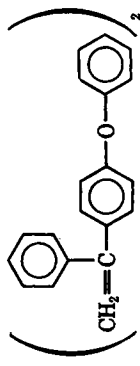
### 4,4''-Diacetylterphenyl (VI)

Finely powdered anhydrous aluminum chloride (367 g; 2.75 mole), anhydrous methylene chloride (2 liters), and redistilled acetyl chloride (137 g; 1.75 mole) were cooled to -15°C. *p*-Terphenyl (200 g; 0.86 mole) in methylene chloride was added dropwise with stirring during 20 min, the temperature being maintained at -15 to -10°C. The mixture was stirred

TABLE II  
 $\alpha$ -Phenylvinyl *p*-Phenylene Monomers and Precursors

Compound No.	Compound	Description	Reactants	Yield, Mp, % °C	Infrared absorption, cm <sup>-1</sup>	Analysis	
						Calculated	Found
						C, %	H, %
XIII		Amber gum	III, 100 g (0.416 mole) PhMgBr(3 <i>M</i> ), 1250 ml (3.78 mole) C <sub>6</sub> H <sub>6</sub> , 1000 ml	—	3550(—OH)	85.29	6.59
				100		85.11	6.45
XIV		Colorless iridescent platelets	XIII, 40 g (0.1 mole) H <sub>2</sub> PO <sub>4</sub> , 15 drops Xylene, 250 ml	94	1603 (>C=C<)	93.86	6.14
				196		93.59	6.26
XV		Amber gum	VI, 47.2 g (0.15 mole) PbMgBr(3 <i>M</i> ), 300 ml (0.9 mole)	100	3555(—OH)	86.82	6.38
				—		86.56	6.28



XVI		Colorless iridescent platelets	XV, 70.5 g (0.15 mole) H <sub>3</sub> PO <sub>4</sub> , 35 drops xylene, 250 ml	87	173.5	1608 (>C=C<)	94.01	5.99	93.40	6.11
XVII		Yellow gum	X, 32 g. (0.076 mole) PhMgBr (3 <i>M</i> ), 133 ml (0.406 mole) C <sub>6</sub> H <sub>6</sub> , 1000 ml	100	—	3560(—OH) 1597(arom.)	83.06	5.88	83.25	6.10
XVIII		Colorless iridescent platelets	XVII, 42 g (0.073 mole) H <sub>3</sub> PO <sub>4</sub> , 12 drops xylene, 500 ml	90	198.5	1604 (>C=C<) 1598(arom.)	88.57	5.53	88.31	5.56

at  $-10$  to  $+5^{\circ}\text{C}$  for approximately 3 hr, then left unstirred at  $20^{\circ}\text{C}$  overnight. The dark-red solution was poured onto crushed ice, extracted with methylene chloride, washed to pH 7 with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed and 240 g (89%) of crystalline product was obtained. Purification was effected by subliming the solid, and in this manner compound VI was obtained as colorless prisms, mp  $288^{\circ}\text{C}$ . The infrared spectrum showed strong absorption at  $1670\text{ cm}^{-1}$  ( $>\text{C}=\text{O}$ ).

#### 1,4-Bis[4(1-methyl-1-hydroxyethyl)phenyl]benzene(VII)

Methylmagnesium bromide (2M in THF, 1125 ml, 2.25 mole, 150% excess) was cooled to  $-10^{\circ}\text{C}$ , then compound VI (141.5 g, 0.45 mole) in anhydrous benzene (1200 ml) was added dropwise with stirring during 45 min at  $-10^{\circ}\text{C}$ . The mixture was stirred for 1 hr, then poured onto a mixture of crushed ice (ca. 1 kg) and concentrated sulfuric acid (100 ml). The organic layer was separated, washed to pH 7 with water, dried over magnesium sulfate, and filtered. The solvent was removed by means of a rotary evaporator, *without* heating, to give a quantitative yield of the dialcohol. The pale cream-colored solid was recrystallized from acetone and yielded colorless platelets, mp  $224^{\circ}\text{C}$ .

#### 1,4-Bis[4(1-methylvinyl)phenyl]benzene (VIII)

A solution of the dialcohol (81.0 g; 0.233 mole) in xylene (1300 ml) containing orthophosphoric acid (35 drops) was heated at reflux for 3 hr, and the water formed during the reaction was collected in a Dean-Stark trap. The xylene was removed and the product (68.0 g, 93.7%) was recrystallized from dimethylformamide to yield iridescent platelets, mp  $285^{\circ}\text{C}$ .

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