

(a) *Methyl  $\alpha$ -chloro- $\alpha$ -nitropropionate*, b.p. 25° (0.2 mm.), had  $n_D^{25}$  1.4313, yield 50%.

*Anal.* Calcd. for  $C_4H_5ClNO_4$ : C, 28.67; H, 3.61; N, 8.36. Found: C, 28.90; H, 3.59; N, 7.93.

(b) *Methyl  $\alpha$ -nitroisobutyrate*, b.p. 30° (0.1 mm.),  $n_D^{25}$  1.4195, yield 59%.

*Anal.* Calcd. for  $C_5H_9NO_4$ : C, 40.82; H, 6.16; N, 9.52. Found: C, 40.80; H, 6.41; N, 9.16.

(c) *Methyl chlorodinitroacetate*, b.p. 40° (4 mm.),  $n_D^{25}$  1.4439, yield 66%.

TABLE II

INFRARED ABSORPTION BANDS OF  $\alpha$ -NITRO ACID METHYL ESTERS<sup>a</sup>

	$\lambda_{C=O}$ , $\mu$	$\lambda_{NO_2}$ , $\mu$		Other, $\mu$
		Asym	Sym	
$CCl(NO_2)_2COOMe$	5.61	6.23	7.72	7.96
$CHCl(NO_2)COOMe$	5.66	6.32	7.45	7.67
$CMeCl(NO_2)COOMe$	5.67	6.36	7.46	7.89, 8.80, 9.08
$CMe_2(NO_2)COOMe$	5.69	6.42	7.40	7.79, 8.36, 8.56, 8.74

<sup>a</sup> Determined in capillary films.

*Anal.* Calcd. for  $C_3H_3ClN_2O_6$ : C, 18.15; H, 1.53; Cl, 17.86; N, 14.12. Found: C, 18.23; H, 1.51; Cl, 17.83; N, 13.78.

*$\alpha$ -Nitro acid amides.* The  $\alpha$ -nitro acid chlorides (0.003–0.005 mole) were converted to amides by treating their solutions in methylene chloride or chloroform with anhydrous ammonia at 0°. The residues from the evaporation of the resulting solutions were crystallized from ether.

(a)  *$\alpha$ -Chloro- $\alpha$ -nitropropionamide* was obtained in 54% yield as colorless needles, m.p. 81.5–82.5° (lit. m.p. 82°<sup>15</sup>),  $\lambda_{C=O}$  5.92 $\mu$ ,  $\lambda_{NO_2}$  6.37, 7.47 $\mu$ ,  $\lambda_{NH}$  2.99, 6.23 $\mu$ .

*Anal.* Calcd. for  $C_3H_5ClN_2O_3$ : C, 23.62; H, 3.30; N, 18.37. Found: C, 23.84; H, 3.63; N, 17.90.

(b)  *$\alpha$ -Nitroisobutyramide*, m.p. 120–121° (lit. m.p. 117–118°<sup>16</sup>), crystallized in 91% yield and had  $\lambda_{C=O}$  5.91 $\mu$ ,  $\lambda_{NO_2}$  6.47, 7.40 $\mu$ , and  $\lambda_{NH}$  2.95, 6.18 $\mu$ . Its melting point was unchanged by vacuum sublimation.

*Anal.* Calcd. for  $C_4H_9N_2O_3$ : C, 36.37; H, 6.10; N, 21.22. Found: C, 36.52; H, 6.05; N, 21.23.

*$\alpha$ -Nitro acid azides.* Chlorodinitroacetyl chloride (0.01 mole) was partially converted to the azide when it was refluxed with sodium azide (1.36 g., 0.02 mole) in alcohol-free chloroform (50 ml.) for 1 hr. The conversion was completed by displacing the solvent with carbon tetrachloride and refluxing for 4 hr. The infrared spectrum of the solution was unchanged on further heating and consisted of the following major bands (in  $\mu$ ):  $\lambda_{N_3}$  4.62 (m),  $\lambda_{C=O}$  5.75 (m),  $\lambda_{NO_2}$  6.21 (s), 7.75 (m), and 8.25 (s). Displacement of the solvent by toluene and heating to reflux temperature at 580 mm. caused complete decomposition of the azide without any evidence of isocyanate formation.

$\alpha$ -Nitroisobutyryl chloride (0.42 g., 0.00277 mole), after refluxing for 1 hr. with sodium azide (1.95 g., 0.03 mole) in alcohol-free chloroform (40 ml.), was completely converted to the known  $\alpha$ -nitroisobutyrazide<sup>6</sup> ( $\lambda_{N_3}$  4.64 $\mu$ ,  $\lambda_{C=O}$  5.81 $\mu$ ,  $\lambda_{NO_2}$  6.44, 7.45 $\mu$ ). The azide was further identified by ammonolysis with dry ammonia, which furnished the known amide<sup>16</sup> in 70% yield.

*Infrared absorption spectra* were determined with a Model 21 Perkin-Elmer spectrophotometer.

LOS ALAMOS, N. M.

(15) W. Steinkopf and A. Supan, *Ber.*, **43**, 3242 (1910).

(16) O. Piloty and B. G. Schwerin, *Ber.*, **34**, 1865 (1901)

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC.]

## Synthesis of Hydrocarbon Derivatives by the Wittig Synthesis.

### I. Distyrylbenzenes

TOD W. CAMPBELL AND RICHARD N. McDONALD

Received March 5, 1959

*p*-Xylylene dichloride reacted quantitatively with triphenylphosphine to give *p*-xylylene bis(triphenylphosphonium chloride). This was converted to a bis-phosphonium "ylide" by lithium ethylate in ethanol, which was in turn converted to a series of disubstituted distyrylbenzenes by reaction with appropriately substituted benzaldehydes. Certain of the 1,4-distyrylbenzenes were reduced to 1,4-bis(phenethyl)benzenes.

Distyrylbenzene (III; R = X = H) has been synthesized by a variety of methods, none of which gives particularly good yields. Bisdesoxybenzoin has been reduced to the corresponding carbinol<sup>1</sup> which was in turn dehydrated to give a fair yield of distyrylbenzene. A second method has been the addition of benzylmagnesium chloride, to terephthalaldehyde<sup>2</sup> or 4-stilbenecarboxaldehyde<sup>3</sup>

followed by dehydration of the resulting carbinols. This method is limited in scope because of the reactivity of the Grignard reagent toward functional groups. A third method which has been employed is the Perkin or Kuhn condensation of phenylacetic acid and 4-stilbenecarboxaldehyde<sup>3</sup> with lead oxide accompanied or followed by decarboxylation to the olefin. Finally, the Meerwein condensation of stilbene-4-diazonium chloride with cinnamic acid has given distyrylbenzene in 35% yield.<sup>4</sup>

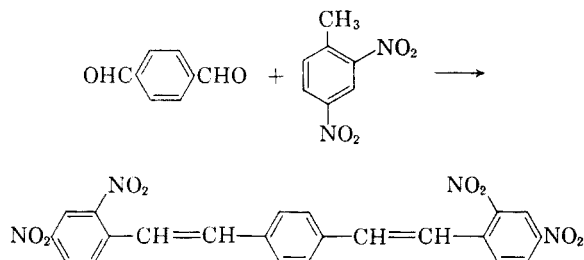
(1) J. Schmitt, P. Comoy, J. Boitard, and M. Suquet, *Compt. rend.*, **242**, 649 (1956).

(2) H. Kauffmann, *Ber.*, **50**, 515 (1917).

(3) G. Drefahl and G. Plotner, *Chem. Ber.*, **91**, 1274 (1958).

(4) P. L'Ecuyer and F. Turcotte, *Can. J. Research*, **25B**, 575 (1947).

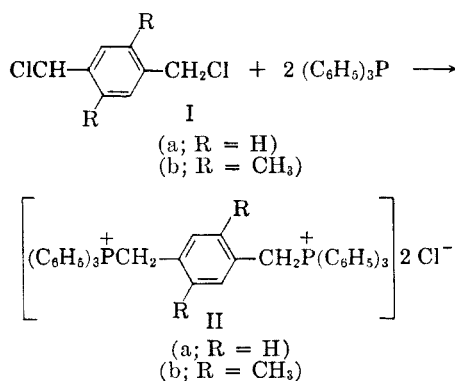
These methods are limited by their inadequacy for preparation of many functionally substituted derivatives, the nature of the reactions themselves, low yields in many cases, and the several steps required to obtain the desired intermediates. Thus, only a few substitution products of distyrylbenzene are known. Schmitt<sup>5</sup> has prepared the 4-methoxy derivative from the corresponding desoxybenzoin, while Ruggli<sup>6,7</sup> has condensed, for example terephthalaldehyde with dinitrotoluene in good yield.



We wish to report the preparation of 1,4-distyrylbenzenes (III) substituted with a variety of groups in good yields by application of the Wittig reaction to difunctional reactants.<sup>8</sup> Since the discovery of the olefin forming reaction of phosphoromethylene derivatives with carbonyl containing compounds,<sup>9</sup> there has been a rapid growth of interest in this reaction, which affords a facile and unequivocal olefin synthesis, where more conventional routes may be expected to yield ambiguous, isomeric products.

#### RESULTS AND DISCUSSION

The general procedure employed is shown in Method 1. *p*-Xylylenebis(triphenylphosphonium chloride) (IIa) was prepared by reaction of *p*-



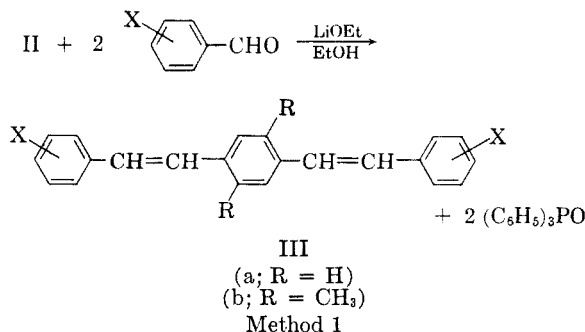
(5) J. Schmitt *et al.*, *Bull. soc. chim. France*, 636 (1956).

(6) P. Ruggli, A. Zimmerman and R. Thouray, *Helv. Chim. Acta*, **14**, 1250 (1931).

(7) P. Ruggli, and E. Wolff, *Helv. Chim. Acta*, **19**, 5 (1936).

(8) For earlier references on this reaction, see the recent review article by J. Levisalks, *Bull. soc. chim., France*, 1021 (1958). Other leading references are G. Wittig, *Angew. Chem.*, **68**, 505 (1956) and G. Wittig, *Experientia*, **12**, 41 (1956).

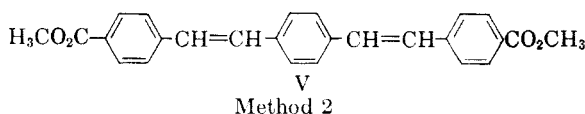
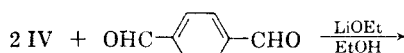
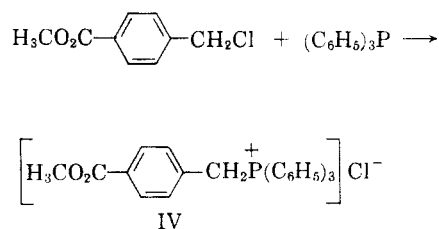
(9) G. Wittig and G. Geissler, *Ann.*, **580**, 44 (1953).



xylylene dichloride (Ia) and triphenylphosphine, preferably in boiling dimethyl formamide. Compound IIa was obtained from this medium in analytical purity, and essentially quantitatively. In like manner the bisphosphonium salt IIb was prepared from 2,5-bis(chloromethyl)-*p*-xylene (Ib).

When a solution of the bisphosphonium salt II and benzaldehyde, or a substituted benzaldehyde, in ethanol was treated with a solution of lithium ethylate in ethanol, a transient color appeared due to the formation of a phosphorus "ylide." As this color disappeared the product, 1,4-distyrylbenzene (III), precipitated from the solution.<sup>10</sup> The solution was diluted with water to about 60% ethanol which insured the precipitation of all of the product. The by-product, triphenylphosphine oxide, remained in solution at this dilution and, therefore, afforded no difficulty in separation. Filtering the solid and washing with aqueous ethanol to remove any remaining triphenylphosphine oxide gave a product essentially free of contaminants.

A second method was used in the preparation of 1,4-bis(4-carbomethoxystyryl)benzene (V). This is shown in Method 2. In this case the phospho-



nium salt IV was prepared by reaction of methyl *p*-chloromethylbenzoate with triphenylphosphine. Reaction of IV with terephthalaldehyde produced the

(10) In only one instance did the product fail to precipitate. This was in the reaction of *p*-xylylenebis(triphenylphosphonium salt) with *m*-acetamidobenzaldehyde.

desired diester in 80% yield. The isolation technique was the same as described above.

The products obtained are mixtures of *cis* and *trans* isomers, as indicated by their low melting points and amorphous appearance. This is in agreement with the observations of others as to the non-stereospecificity of the reaction. The materials were routinely isomerized to the all *trans*-configurations by digestion in benzene or xylene containing a trace of iodine. The isomerized compounds were then characterized.

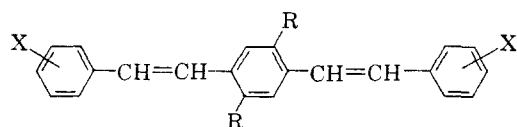
By the use of the above methods it is now possible to synthesize easily 1,4-distyrylbenzenes containing a variety of functional groups. It is not necessary to use ether as reaction medium, and an organometallic compound as base, since we are dealing with easily removed benzylic protons, stable phosphonium-ylides and reactive aromatic aldehydes.

Other advantages of this system are obvious. The separation of the triphenylphosphine oxide in the filtrate, and the ease of making up and storing the lithium ethoxide solution as opposed to that of phenyl- or butyllithium are two. Erlenmeyer flasks are the only equipment necessary in the exchange reactions, and the reactions can be run rapidly and easily at room temperature. Also, in some cases, the products obtained are in the thermodynamically stable *trans* configuration.<sup>11</sup>

The 1,4-distyrylbenzenes synthesized during this investigation are listed in Table I. The variety of functional groups illustrate the versatility of the two methods, both in products and yields. The yields given do not necessarily represent the maximum yield obtainable. In several instances, these were only single runs and little effort placed on getting out and isomerizing oils or semisolid product.

The preparation of 1,4-bis(4-aminostyryl)ben-

TABLE I  
DISTYRYLBENZENES



x	R	Yield, %	M.P.
H	H	88	268-268.5 <sup>3</sup>
H	CH <sub>3</sub>	40	203-204
<i>m</i> -NO <sub>2</sub>	H	83	260-262
<i>m</i> -NH <sub>2</sub>	H	38	269-273
<i>p</i> -CH <sub>3</sub>	H	81	307-308 <sup>3</sup>
<i>p</i> -OCH <sub>3</sub>	H	61	310-310.5
<i>p</i> -NO <sub>2</sub>	H	60	288-290
<i>p</i> -NHCOCH <sub>3</sub>	H	73	~420
<i>p</i> -CO <sub>2</sub> CH <sub>3</sub>	H	80	290-292
<i>p</i> -Cl	H	14	294-295
<i>p</i> -NH <sub>2</sub>	H	90	303

(11) R. N. McDonald and T. W. Campbell, *J. Org. Chem.*, in press. Several of the 1,4-diarylbutadienes precipitated in the *trans-trans* configuration.

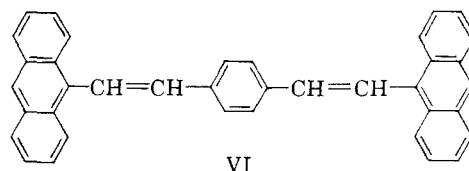
zene (IIIa;  $x = p\text{-NH}_2$ ) was accomplished by acid hydrolysis of the corresponding acetamide compound in 90% yield. This diamine, though undoubtedly forming a dihydrochloride, was insoluble in both water and concentrated hydrochloric acid. However, it was soluble in dilute sulfuric acid when the hydrolysis was carried out in this solvent.

The synthesis of the *m*- isomer, 1,4-bis(3-aminostyryl)benzene (IIIa;  $x = m\text{-NH}_2$ ) proved much more difficult. Reduction of the corresponding dinitro compound with lithium aluminum hydride, stannous chloride and hydrochloric acid, hydrazine hydrate and base, or iron powder and acetic acid failed to give any identifiable product other than starting material. Reduction with hydrazine hydrate and iron powder, and catalytic hydrogenation over Raney nickel gave the saturated diamine, 1,4-bis(3-aminophenethyl)benzene.

Success was finally achieved by catalytic reduction over Raney nickel in the presence of ammonia to inhibit reduction of the double bonds. The desired unsaturated *m*-diamine was obtained in 38% yield. Reduction of unisomerized dinitro compound led to a mixture of saturated and unsaturated diamines.

Most of the *p*-substituted compounds exhibit liquid crystalline behavior in that the products melt to a liquid which is still birefringent, indicating that a degree of order still exists in the liquid state. This behavior is characteristic of many long thin polar molecules.<sup>12</sup>

In addition to substituted benzaldehydes, 9-anthraldehyde reacted readily with *p*-xylylenebis(triphenylphosphonium chloride) to give the brick-red compound VI. Exposure to light caused



VI

the brick-red color to fade to orange, suggesting a photochemical isomerization.

Several of the 1,4-distyrylbenzenes were catalytically reduced to the 1,4-bis(phenethyl)benzenes. These are listed in Table II. Both 1,4-bis(3-

TABLE II

BIS(PHENETHYL)BENZENES

x	Yield, %	M.P.
<i>m</i> -NH <sub>2</sub>	78	150-150.5
<i>p</i> -NH <sub>2</sub>	93	187-189
<i>p</i> -CO <sub>2</sub> CH <sub>3</sub>	93	148-149
<i>p</i> -CO <sub>2</sub> H	90	~368
<i>p</i> -Cl	84	133-134

(12) G. H. Brown and W. G. Shaw, *Chem. Revs.* **57** (1957).

aminophenethyl)benzene and 1,4-bis(4-aminophenethyl)benzene were prepared from the corresponding unsaturated diamines. The diacid, 1,4-bis(4-carboxyphenethyl)benzene, was synthesized by saponification of the ester.

#### EXPERIMENTAL

*Preparation of p-xylylenebis(triphenylphosphonium chloride).* A solution of 88.0 g. (0.50 mole) of *p*-xylylene dichloride and 285.0 g. (1.09 mole) of triphenylphosphine in 1 l. of dimethylformamide was heated at reflux with stirring for 3 hr. Crystalline solid began separating after 0.5 hr. The mixture was then allowed to cool to room temperature and the colorless analytically pure crystalline product was filtered, washed with dimethylformamide followed by ether, and dried in a vacuum oven at 20 mm. pressure and 80°. The dry weight is 335–343 g. (93–98%), m.p. >400°.

*Anal.* Calcd. for  $C_{44}H_{38}Cl_2P_2$ : Cl, 10.16. Found: Cl (total), 10.04, 10.00; Cl (ionic), 10.18, 10.00.

A sample was recrystallized from water to obtain a dihydrate.

*Anal.* Calcd. for  $C_{44}H_{38}Cl_2P_2 \cdot 2H_2O$ : C, 71.8; H, 5.7; Cl, 9.7. Found: C, 71.6, 71.8; H, 5.9, 5.9; Cl (total), 9.6, 9.8; Cl (ionic), 9.7, 9.8.

*Preparation of 2,5-dimethyl-p-xylylenebis(triphenylphosphonium chloride).* A stirred solution of 262 g. (1.00 mole) of triphenylphosphine and 80.0 g. (0.39 mole) of 2,5-bis-(chloromethyl)-*p*-xylylene in 1400 ml. of dimethylformamide was heated at reflux for 2.5 hr. The thick mixture was filtered hot and the solid washed with dimethylformamide and then with ether. After drying under vacuum at 60° the weight was 270 g. (94%) of crude product. It was recrystallized from 95% ethanol and found to melt above 400°. The yield of recrystallized product was 240 g.

*Anal.* Calcd. for  $C_{48}H_{42}Cl_2P_2 \cdot H_2O$ : C, 74.1; H, 6.0; Cl, 9.5. Found: C, 73.9, 73.8; H, 6.2, 6.2; Cl, 9.0, 9.2.

In common with all of the bisphosphonium salts, this one retained water of crystallization tenaciously.

*(4-Carbomethoxybenzyl)triphenylphosphonium chloride.* Twenty-seven g. (0.15 mole) of methyl *p*-chloromethylbenzoate was mixed with 115 g. (0.44 mole) triphenylphosphine in 300 cc. of xylene and the entire mixture was stirred at reflux for 24 hr., and then was filtered. The filtrate was rejected and the crystalline xylene-insoluble product was dried. The yield of crude product was 59 g. (92%). This material was dissolved in absolute alcohol, treated with decolorizing carbon, and filtered. The filtrate was treated with ether until slightly cloudy and the mixture was then placed in the refrigerator for 24 hr. Filtration gave 43 g. of pure crystalline product, melting 240–245° (Koffler).

*Anal.* Calcd. for  $C_{27}H_{24}O_2P$ : C, 72.5; H, 5.4; Cl, 7.95. Found: C, 72.4, 72.2; H, 5.2, 5.5; Cl, 7.96, 7.92.

Evaporation of the mother liquor gave 11.1 g. of only slightly less pure material with an ionic chlorine content of 7.71, 7.80.

*Preparation of 1,4-distyrylbenzene.* To a solution of 30.0 g. (0.043 mole) of *p*-xylylene-bis(triphenylphosphonium chloride) and 9.9 g. (0.093 mole) of benzaldehyde in 100 ml. of ethanol was added 450 ml. of 0.2M lithium ethylate in ethanol. A transient orange color developed, and then the colorless crystalline product separated from the reaction mixture. After standing for 2 hr., 400 ml. of water was added, the product filtered, washed with 200 ml. of 60% ethanol, and dried under vacuum at 60°. The filtrate containing the triphenylphosphine oxide was rejected. The yield of dry crystalline solid which melted broadly was 10.4 g. (86%). The solid which was a mixture of *cis* and *trans* isomers was recrystallized from boiling benzene in the presence of a trace of iodine to give the pure *trans-trans*-distyrylbenzene as large, faintly yellowish plates (8.6 g.), m.p. 268–268.5°.

*Anal.* Calcd. for  $C_{22}H_{18}$ : C, 93.6; H, 6.4. Found: C, 93.5, 93.3; H, 6.4, 6.4.

*Preparation of 1,4-distyryl-2,5-dimethylbenzene.* To a solution of 7.0 g. (9.6 mmole) of 2,5-dimethyl-*p*-xylylenebis-(triphenylphosphonium chloride) and 3.0 g. (28 mmole) of benzaldehyde in 25 ml. of ethanol was added a solution of 0.14 g. of lithium wire dissolved in 100 ml. of ethanol. The mixture was worked up as above and recrystallized from cyclohexane with a trace of iodine to give 1.2 g. (36%) of desired product, m.p. 203–204°.

*Anal.* Calcd. for  $C_{24}H_{22}$ : C, 92.9; H, 7.1. Found: C, 93.0, 93.0; H, 7.05, 7.07.

*Preparation of 1,4-bis(3-nitrostyryl)benzene.* Seventy g. (0.10 mole) of the *p*-xylylene bis(phosphonium salt) and 40.0 g. (0.27 mole) of *m*-nitrobenzaldehyde were dissolved in 500 cc. of absolute alcohol. An immediate yellow precipitate formed. After 24 hr., 500 cc. of water was added and the mixture was filtered. The dried solid was dissolved in xylene, treated with decolorizing carbon, filtered and digested with iodine on a hot plate. This caused gradual separation of an orange-yellow crystalline solid which was filtered after 3 hr. of digestion and cooling overnight at room temperature. The product was obtained in a yield of 31 g. (83%) with a melting point of 260–262°.

*Anal.* Calcd. for  $C_{22}H_{16}N_2O_4$ : C, 71.0; H, 4.3; N, 7.55. Found: C, 71.2, 71.2; H, 4.54, 4.31; N, 7.73, 7.68.

*Preparation of 1,4-bis(3-aminostyryl)benzene.* Five g. (0.014 mole) of 1,4-bis(3-nitrostyryl)benzene was hydrogenated with Raney nickel catalyst in the presence of ammonia in dimethylformamide solution. After filtration of the catalyst, water was added to the hot solution of the product until it became cloudy. On cooling a small amount of flocculent material (probably some saturated diamine) was filtered from the solution. This process was repeated several times until this material was eliminated. Diluting the aqueous dimethylformamide solution again at the boiling point with water finally gave pale yellow crystals. These were filtered, washed with alcohol, and dried at reduced pressure and 60° to give 1.6 g. (38%) of dry product, m.p. 263–266°. This could be recrystallized from dimethylformamide-ethanol mixture to give light tan crystals (1.2 g.), m.p. 269–273°. An analytical sample was sublimed at 250° and 0.04 mm.

*Anal.* Calcd. for  $C_{22}H_{20}N_2$ : C, 84.58; H, 6.45; N, 8.97. Found: C, 84.4, 84.6; H, 6.4, 6.5; N, 8.93, 8.97.

*Preparation of 1,4-bis(3-aminophenethyl)benzene.* Twenty g. of 1,4-bis(3-nitrostyryl)benzene was hydrogenated over palladium in dimethylformamide. The mixture was filtered free of catalyst and the filtrate was heated approximately to boiling, and then hot water was added until the mixture became cloudy. The next day the heavy pearly scales were filtered and recrystallized from about 200 ml. of absolute alcohol. The faintly pinkish product was dried and found to melt at 150.5 to 151.0°C. The yield was 14.5 g. (85%).

*Anal.* Calcd. for  $C_{22}H_{24}N_2$ : C, 83.5; H, 7.6. Found: C, 83.6, 83.3; H, 7.3, 7.6.

*1,4-Bis(4-nitrostyryl)benzene.* To a solution of 35.0 g. (0.23 mole) of *p*-nitrobenzaldehyde and 70.0 g. (0.10 mole) of *p*-xylylenebis(phosphonium salt) in 500 ml. of absolute alcohol was added 1100 ml. of 0.2M lithium ethoxide. An immediate yellow precipitate formed which after 24 hr. was filtered and dried. The solid (36.5 g.) was dissolved in xylene and the decolorized solution was digested for about 4 hr. in the presence of a trace of iodine. The product slowly crystallized as orange leaflets melting at 285 to 288°. This compound exhibited liquid crystalline behavior in that the melt remained birefringent for 15° to 20° above the melting point. The yield of product was 22.4 g. (60%). An analytical sample (0.62 g.) was recrystallized from 200 ml. of xylene containing a trace of iodine. The melting point was 288 to 290°.

*Anal.* Calcd. for  $C_{22}H_{16}N_2O_4$ : C, 71.0; H, 4.3. Found: C, 71.24, 71.25; H, 4.57, 4.49.

*1,4-Bis(4-aminophenethyl)benzene.* A 36.0 g. (0.097 mole) sample of 1,4-bis(4-nitrostyryl)benzene was hydrogenated in dimethylformamide over palladium. The solution was filtered using "Celite" and diluted with water at the boiling point. The diluted solution was allowed to crystallize overnight. The solid (28.0 g.) was filtered and recrystallized from 1 liter of absolute alcohol. The product was obtained in a yield of 24.1 g. (80%), m.p. 189–190°.

*Anal.* Calcd. for  $C_{22}H_{24}N_2$ : C, 83.5; H, 7.6. Found: C, 83.78, 83.30; H, 8.07, 7.73.

The diacetyl derivative was obtained by boiling a mixture of 100 mg. of the diamine with 10 ml. of pyridine and 2 ml. of acetic anhydride for 30 min. The solution was poured into water and the solid was recrystallized from aqueous dimethyl formamide. The product melted at 295° to 297°.

*Anal.* Calcd. for  $C_{26}H_{28}N_2O_2$ : N, 6.99. Found: N, 7.14, 7.08.

*Preparation of 1,4-bis(4-acetamidostyryl)benzene.* To a solution of 14.0 g. (0.020 mole) of *p*-xylylenebis(phosphonium salt) and 7.5 g. (0.046 mole) of *p*-acetamidobenzaldehyde in 100 ml. of ethanol was added 230 ml. of 0.2M lithium ethoxide. After standing overnight 150 ml. of water was added and the pale yellow solid filtered, washed with 50 ml. of 60% ethanol and dried at reduced pressure and 60°. The dry weight was 5.7 g. (72%). No effort was made to isomerize this material, but the infrared spectrum indicated mainly the *trans* configuration present and the melting point was diffuse. A sample was recrystallized from dimethyl sulfoxide to give product, m.p. ~420°.

*Anal.* Calcd. for  $C_{26}H_{24}N_2O_2$ : N, 7.07. Found: N, 6.90, 6.87.

*Preparation of 1,4-bis(4-aminostyryl)benzene.* Five g. (0.013 mole) of 1,4-bis(4-acetamidostyryl)benzene and 150 ml. of concentrated hydrochloric acid were heated at reflux for 40 hr. A small amount of Dow Corning "Antifoam A" was added to eliminate the frothing. The mixture was poured into 500 ml. of water. The solid was then filtered, washed until basic with dilute aqueous sodium carbonate, then with water until neutral, and dried at reduced pressure and 60°. The dry weight was 3.6 g. (90%). It was recrystallized from dimethylformamide-ethanol mixture to give 3.4 g. of golden crystals, m.p. 299–300° (dec.). An analytical sample was sublimed at 265° and 0.05 mm. to give yellow needles, m.p. 303° (dec.).

*Anal.* Calcd. for  $C_{22}H_{20}N_2$ : C, 84.58; H, 6.45; N, 8.97. Found: C, 84.5, 84.3; H, 6.58, 6.55; N, 8.97, 9.06.

It was later found that 95% of the crude could be sublimed at 300° and 0.03 mm. as the best means of purification.

*1,4-Bis(4-chlorostyryl)benzene.* To a solution of 28.2 g. (0.20 mole) of *p*-chlorobenzaldehyde and 70.0 g. (0.10 mole) of *p*-xylylenebis(phosphonium salt) in 500 ml. of ethanol was added 1 l. of 0.2M lithium ethoxide. After 24 hr. the solution was concentrated to about 500 ml. total volume, then diluted with an equal volume of water. A considerable amount of an unidentified oil which may have been low melting geometric isomers was rejected. The solid was pale yellow and slightly pasty although it was strongly crystalline under a polarizing microscope. The solid was decolorized and recrystallized from xylene in the presence of a trace of iodine. The product was obtained in a yield of 4.9 g. (13%), m.p. 294–295°. The molten product was highly birefringent indicating that the product formed liquid crystals. This liquid birefringence remained to about 310°. An analytical sample was recrystallized from xylene containing a trace of iodine, m.p. 294–295°.

*Anal.* Calcd. for  $C_{22}H_{16}Cl_2$ : C, 75.2; H, 4.6. Found: C, 75.2, 75.4; H, 4.8, 4.8.

*1,4-Bis(4-chlorophenethyl)benzene.* A solution of 4.0 g. (0.011 mole) of 1,4-bis(4-chlorostyryl)benzene in dimethylformamide was hydrogenated over palladium. After the catalyst was removed by filtration, the colorless product was isolated by precipitation with water. The solid was recrystallized from cyclohexane after decolorization and yielded

3.4 g. (85%), m.p. 132–134°. An analytical sample was recrystallized twice from the same solvent, m.p. 133–134°.

*Anal.* Calcd. for  $C_{22}H_{20}Cl_2$ : C, 74.4; H, 5.6. Found: C, 74.0, 74.4; H, 5.7, 5.9.

*Preparation of 1,4-Bis(4-carbomethoxystyryl)benzene.* To a solution of 54.0 g. (0.121 mole) of (4-carbomethoxybenzyl)-triphenylphosphonium chloride and 6.0 g. (0.0448 mole) of terephthalaldehyde in 600 ml. of ethanol was added 600 ml. of 0.2M of lithium ethoxide. An immediate pale yellow crystalline precipitate formed. After 0.5 hr. 600 ml. of water was added, the solid filtered, washed with 200 ml. of 60% ethanol, and dried at reduced pressure and 60°. The dry weight was 13.0 g. (73%). No attempt was made to isomerize this material since the infrared spectrum indicated mostly the *trans* configuration present. An analytical sample was recrystallized from aqueous dimethylformamide, m.p. ~290°.

*Anal.* Calcd. for  $C_{26}H_{22}O_4$ : C, 78.3; H, 5.5. Found: C, 78.3, 78.5; H, 5.5, 5.7.

*Preparation of 1,4-bis(4-carbomethoxyphenethyl)benzene.* A solution of 10.0 g. (0.0251 mole) of 1,4-bis(4-carbomethoxystyryl)benzene in dimethylformamide was reduced over palladium on carbon. The catalyst was filtered, the organic filtrate heated to boiling and water added until the hot solution maintained its cloudiness. The product crystallized at room temperature and the crystals were filtered, washed with water, and dried in the vacuum oven at 60°. Weight 9.3 g. (93%), m.p. 131–137°.

It was difficult to remove some dark colored impurity by normal charcoal treatment. The colored impurity was removed, however, by dissolving the material in dichloromethane and filtering it through an alumina column. An analytical sample was recrystallized from dimethylformamide-methanol to give colorless needles, m.p. 148–149°.

*Anal.* Calcd. for  $C_{26}H_{26}O_4$ : C, 77.6; H, 6.5. Found: C, 77.5, 77.4; H, 6.7, 6.6.

*Preparation of 1,4-bis(4-carboxyphenethyl)benzene.* A mixture of 8.1 g. (0.0202 mole) of 1,4-bis(4-carbomethoxyphenethyl)benzene and 10.0 g. of potassium hydroxide in 250 ml. of methanol was refluxed with stirring overnight. It was then poured into water and filtered to remove a small amount of unreacted ester. The filtrate was acidified with concentrated hydrochloric acid and the flocculent acid filtered, washed with water, and dried in the vacuum oven at 70°. The weight of product was 6.8 g. (90%). It melted at about 386° (hot bar). An analytical sample was recrystallized from dimethylformamide.

*Anal.* Calcd. for  $C_{24}H_{22}O_4$ : C, 77.0; H, 5.9. Found: C, 76.6, 76.8; H, 5.7, 5.6.

*Preparation of 1,4-bis(4-methylstyryl)benzene.* To a solution of 30.0 g. (0.0429 mole) of *p*-xylylenebis(triphenylphosphonium chloride) and 11.0 g. (0.0915 mole) of *p*-tolualdehyde and 100 ml. of ethanol was added 450 ml. of 0.2M lithium ethoxide. After standing overnight at room temperature, 250 ml. of water was added. The solid was filtered, washed with 150 ml. of 60% alcohol, and dried in the vacuum oven at 85°. Weight 10.8 g. (81%). This was recrystallized from benzene containing a small amount of iodine to give light yellow-green plates (7.8 g.), m.p. 304–306° (Kofler). Further evaporation of the solvent yielded another 2.7 g., m.p. 306–308° (Kofler). An analytical sample was recrystallized from dimethylformamide giving yellow-green plates, m.p. 306–308° (Kofler).

*Anal.* Calcd. for  $C_{24}H_{22}$ : C, 92.86; H, 7.14. Found: C, 92.88, 92.95; H, 7.30, 7.24.

*Preparation of 1,4-bis(4-methoxystyryl)benzene.* To a solution of 30.0 g. (0.0429 mole) of *p*-xylylenebis(triphenylphosphonium chloride) and 12.5 g. (0.0925 mole) of anisaldehyde in 100 ml. of alcohol was added 450 ml. 0.02M lithium ethoxide. The mixture was allowed to stand overnight, after which the yellow solid was filtered, weight 9.0 g. (61%). This solid was recrystallized from xylene containing a small amount of iodine. It was filtered, washed with ben-

zene, and dried in a vacuum oven at 65°, weight 7.0 g. An analytical sample was recrystallized from dimethylformamide giving yellow-green plates, m.p. 305–307° (Kofler).

*Anal.* Calcd. for  $C_{24}H_{22}O_2$ : C, 84.18; H, 6.48. Found: C, 84.40, 84.30; H, 6.68, 6.67.

*Reaction of p-xylylenebis(phosphonium salt) with 9-anthraldehyde.* To a solution of 7.0 g. (0.01 mole) of the bis(phosphonium salt) in 100 cc. of alcohol was added 5.0 g. (0.024 mole) of 9-anthraldehyde and 100 ml. of 0.2M lithium ethoxide solution. The mixture turned immediately an orange-red color and a brick red precipitate formed. This was allowed to stand overnight and was filtered. It was noted that the product was light sensitive changing from brick red to yellow orange on exposure to light. The yield

was 4.25 g. (88%) of a product melting at 300° on the hot bar. The product was recrystallized from dimethyl sulfoxide to give well developed yellow-orange crystals melting sharply at 320–322°.

*Anal.* Calcd. for  $C_{28}H_{26}$ : C, 94.34; H, 5.66. Found: C, 94.28, 94.32; H, 5.60, 5.70.

*Acknowledgments.* We wish to thank Dr. W. B. McCormack, Organic Chemical Department, for generously supplying the triphenylphosphine used. Also, to Dr. C. Sly of Pressure Research Laboratory who carried out all of the catalytic hydrogenations.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE ILLINOIS STATE GEOLOGICAL SURVEY]

## Oxidation of 2,6-Di-*tert*-butyl-4-methylphenol. The Structure of $C_{14}H_{22}O_3$ <sup>1</sup>

G. R. YOHE, J. E. DUNBAR,<sup>2</sup> MYRA W. LANSFORD,<sup>2</sup> R. L. PEDROTTI,<sup>2</sup> F. M. SCHEIDT,<sup>2</sup> FRED G. H. LEE,<sup>2</sup>  
AND EARLE C. SMITH<sup>2</sup>

Received March 9, 1959

The acidic compound  $C_{14}H_{22}O_3$ , previously reported without assignment of structure as an oxidation product of 2,6-di-*tert*-butyl-4-methylphenol, is now believed to be *DL-trans*-5,6-di-*tert*-butyl-2-hydroxy-1,4-diketo-2-cyclohexene (I). Chemical properties are described and infrared spectra are presented in support of this structure.

This structure is of interest in relation to the problem of the existence of *o*-di-*tert*-alkylbenzene derivatives. The relatively easy racemization of optically active I suggests that its completely enolized form, 5,6-di-*tert*-butyl-1,2,4-trihydroxybenzene, is capable of transitory existence.

A previous publication<sup>3</sup> described the formation of a compound  $C_{14}H_{22}O_3$  by the oxidation of 2,6-di-*tert*-butyl-4-methylphenol in aqueous sodium hydroxide with oxygen gas at about 100°. It was also pointed out that this same compound could be made by similar oxidation of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, 3,5-di-*tert*-butyl-4-hydroxybenzoic acid, and 2,6-di-*tert*-butyl-1,4-benzoquinone. Some of the properties of this compound were described briefly, but no attempt was made to assign a structure to it. The present paper gives the results of a detailed study of its properties, and proposes that it has the structure of *dl-trans*-5,6-di-*tert*-butyl-2-hydroxy-1,4-diketo-2-cyclohexene (I).

I is a nearly white, crystalline compound capable of being sublimed at diminished pressure; it melts at 134–135°. Its solutions in organic solvents are pale yellow. Its percentage composition confirms the molecular formula  $C_{14}H_{22}O_3$ , and the determined molecular weight (250) indicates that it is monomeric.

It reacts as a monobasic acid of sufficient strength to dissolve in aqueous sodium bicarbonate. Its neutral equivalent in aqueous solution (241) agrees with the calculated formula weight (238.32), and

the fact that it titrates as a monobasic acid (neut. equiv. 232) with sodium aminoethoxide in ethylenediamine indicates the absence of additional (*e.g.*, hindered) acidic groups. Its saponification equivalent (244) indicates the absence of saponifiable groups or acidic hydrogens other than that involved in its patent acidic properties. It gives a positive (red) enol test with ferric chloride, but a negative phosphomolybdic acid test for the phenol structure.

It shows absorption in the infrared at 3400  $cm^{-1}$  (position unchanged upon dilution), consistent with the presence of a hydroxyl situated as shown in the formula (I), and carbonyl absorption at 1670 and 1650  $cm^{-1}$ . Peaks at 1470, 1395, and 1370  $cm^{-1}$  are consistent with the presence of *tert*-butyl groups. Absorption characteristic of the carboxyl group is absent.

It forms a chloride (II) upon reaction with thionyl chloride; this chloride in turn reacts with methanol to form the methoxyl compound (III) which may also be made by the reaction of I with diazomethane or with methanol and hydrochloric acid. Saponification of III reconverts it to I.

III shows no hydroxyl absorption in the infrared. The presence of three peaks in the carbonyl region (1685, 1650, and 1610  $cm^{-1}$ ) is not readily explained; possibly one of them is to be ascribed to the carbon-carbon unsaturation.

Compound I forms a monoacetate (IV) with

(1) Publication authorized by the Chief, Illinois State Geological Survey.

(2) Formerly research assistant.

(3) G. R. Yohe, J. E. Dunbar, R. L. Pedrotti, F. M. Scheidt, Fred G. H. Lee, and Earle C. Smith, *J. Org. Chem.*, **21**, 1289 (1956).