anhydrous ether was stirred mechanically while 126 g. (0.32 mol.) of 9-pentyl-9-hexyl-7-hexadecanone in 160 ml. of anhydrous ether was added at a rate sufficient to cause gentle refluxing. After the addition had been completed, the mixture was stirred at room temperature for 1 hr. and heated under reflux for an additional 5 hr. Then a 50% by volume solution of ethyl acetate in ether was added slowly until refluxing ceased. This was followed by the addition of 500 ml. of 10% sulfuric acid. The ether layer was removed, washed with water, 10% sodium bicarbonate, again with water, and was dried over anhydrous sodium sulfate. After removing the ether, the residue was distilled to give 124 g. (98%) of the carbinol; b.p. 199–203°/1 mm., n_{D}^{25} 1.4580.

Attempted reduction of 9-pentyl-9-hexyl-7-hexadecanone with sodium borohydride. The method of Chaikin and Brown[19] was followed. To a solution of 50 g. (0.13 mol.) of 9-pentyl-9-hexyl-7-hexadecanone in 50 ml. of methanol was added 2.4 g. (0.07 mol.) of sodium borohydride in 20 ml. of methanol. No reaction appeared to occur even when the mixture was heated to boiling for some time. It was heated then with 100 ml. of 10% sodium hydroxide solution for 1 hr. The organic layer was removed, taken up in 100 ml. of ether, washed with water and dried over anhydrous sodium sulfate. The ether was removed by distillation and the residue was distilled to give 48 g. of unchanged ketone.

10-Propyl-10-butyl-7(8)-eicosene. This procedure is typical of those used to obtain the mixtures of olefins given in Table VI. A mixture of 111 g. (0.3 mol.) of 10-propyl-10-butyl-8-eicosanol and 20 g. of anhydrous potassium bisulfate was heated under reduced pressure at 150–160° for 24 hr. It was allowed to cool, the liquid was decanted, and the potassium bisulfate was extracted with several small portions of ether. The oil and extracts were combined and the ether was evaporated. The residue was distilled to give 101 g. (94%) of material which boiled between 218 and 220°/2 mm., n_{D}^{25} 1.4562.

10-Butyl-10-propyleicosane. The tetraalkylmethanes in Table VII were obtained by the hydrogenation of the mixtures of olefins reported in Table VI. The preparation of 10-butyl-10-propyleicosane is representative. A mixture of 51 g. of 10-butyl-10-propyl-7(8)-eicosene, 75 ml. of methylcyclohexane, and 10 g. of Raney nickel catalyst was heated, and rocked at 180° and 3200 p.s.i. of hydrogen for 7 hr. The reaction mixture was allowed to cool, was filtered and the solvent was removed by distillation. The residual oil was washed with three 100-ml. portions of cold, concentrated sulfuric acid, then with saturated sodium chloride solution, 10% sodium bicarbonate solution, and water. It was distilled to give 45 g. (88%) of a colorless liquid; b.p. 200–201°/1 mm., n_{D}^{25} 1.4524.

COLUMBIA, MO.

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[19] S. W. Chaikin and W. G. Brown, *J. Am. Chem. Soc.*, **71**, 122 (1949).

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

Synthesis of Hydrocarbon Derivatives by the Wittig Reaction II. Diarylbutadienes and Quinquephenyls[1]

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The reaction of triphenylcinnamylphosphonium chloride and *p*-xylylenebis(triphenylphosphonium chloride) with aromatic aldehydes and cinnamaldehydes has given diarylbutadienes and 1,4-bis(4-arylbutadienyl)benzenes in yields of 60–100%. 1,4-Diphenylbutadiene, 1-(*p*-tolyl)-4-phenylbutadiene, and 1,4-bis(*p*-tolyl)butadiene were converted by the method described by Lohaus into *p*-terphenyl, 4-methylterphenyl, and 4,4″-dimethylterphenyl, respectively. This technique was extended to 1,4-bis(4-phenylbutadienyl)benzene, 1,4-bis[4-(*p*-tolyl)butadienyl]benzene, and 1,4-bis(3-methyl-4-phenylbutadienyl)benzene. *p*-Quinquephenyl, 4,4′′′′-dimethylquinquephenyl, and 2′,3′′′-dimethylquinquephenyl were obtained, respectively, in good yields. This represents the best route to this aromatic hydrocarbon system reported and the latter two methyl derivatives are the first derivatives to appear in the literature. This route is considered to be unambiguous.

Diarylbutadienes and 1,4-bis(arylbutadienyl)benzenes, $\mathrm{ArCH{=}CH{-}CH{=}CH{-}C_6H_4{-}CH{=}CH{-}CH{=}CH{-}Ar}$, have proved relatively difficult to synthesize in good yield, particularly with functional groups on the aryl rings. The dehydrogenation of 1,4-diphenylbutene-2 with *n*-butyllithium[2] gave 1,4-diphenylbutadiene in 12% yield. The Meerwein reaction between, for example, benzenediazonium chloride and cinnamylidene acetic acid,[3] has also been employed in the synthesis of diarylbutadienes. Probably the most widely used reaction has been the Perkin or Kuhn condensation of a β-arylacrolein with an arylacetic acid in the presence of lead oxide.[4,5] This is the basis of the *Organic Syntheses* preparation of diphenylbutadiene in 25% yield.[4a] A variation of this latter method is the condensation of two molecules of an aromatic aldehyde with succinic acid in the presence of lead oxide.[5] 1,4-Bis(4-phenylbutadienyl)benzene has been prepared in low over-all yield by similar techniques.[4b]

The synthesis of 1,4-diarylbutadienes and of 1,4-bis(arylbutadienyl)benzenes may be carried out conveniently in two steps, and in high over-all yields using the Wittig synthesis in an extension of

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[1] Previous paper, T. W. Campbell, and R. N. McDonald, *J. Org. Chem.*, **24**, 1246 (1959).

[2] H. Gilman and C. W. Bardley, *J. Am. Chem. Soc.*, **60**, 2333 (1938).

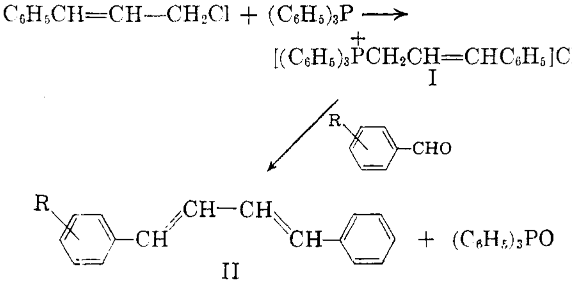
[3] C. F. Koelsch and V. Boekelheide, *J. Am. Chem. Soc.*, **66**, 412 (1944).

[4] (a) B. B. Corson, *Org. Syntheses*, **Coll. Vol. II**, 229 (1943). (b) G. Drefahl and G. Plotner, *Chem. Ber.*, **91**, 1285 (1958).

[5] S. Israelashvili, Y. Gottlieb, M. Imber, and A. Habas, *J. Org. Chem.*, **16**, 1519 (1951).

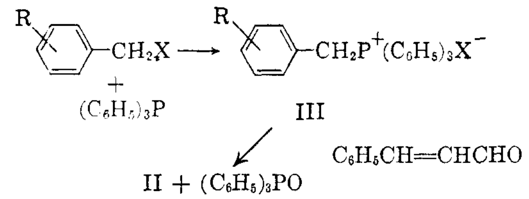
the methods used for the preparation of distyryl benzenes.[1]

One procedure (Method A) involves the preparation of triphenylcinnamylphosphonium chloride (I) from the reaction of cinnamyl chloride and triphenylphosphine. When a solution of I and benzaldehyde, or a substituted benzaldehyde, in ethanol is treated with a solution of lithium ethoxide in ethanol, a transient yellow-orange color forms. This is undoubtedly due to formation of the corresponding "ylide" of I, which then reacts with the aldehyde. As the color fades the product, diarylbutadiene (II), precipitates. Substitution of terephthalaldehyde for benzaldehyde gave the bisbutadiene.



Method A

In the other procedure (Method B) phosphonium salts from benzyl halides, exemplified by III, are allowed to react with cinnamaldehydes in the ethanol-ethoxide mixture. This gives the butadienes and triphenylphosphine oxide. Starting with substituted cinnamaldehydes, a butadiene with substituents in each ring could be made. 1,4-Bis(p-tolyl)butadiene was prepared in this manner from the reaction of (p-methylbenzyl)triphenylphosphonium bromide and p-methylcinnamaldehyde. When R in III is another $—CH_2P^+(C_6H_5)_3Cl^-$ group, the bisbutadienes are obtained.



Method B

Diarylbutadienes. The diarylbutadienes prepared during this investigation are listed in Table I. The yields in all cases surpass those reported in the literature. A point of interest is the fact that these compounds were isolated, except in the case of the p-carbomethoxy and m-nitro derivatives, as the thermodynamically more stable *trans-trans* isomers. Generally, when two isomers were possible from the Wittig reaction, they were formed in ratios varying from a 50:50 up to an 80:20 mixture, the *trans* form predominating.

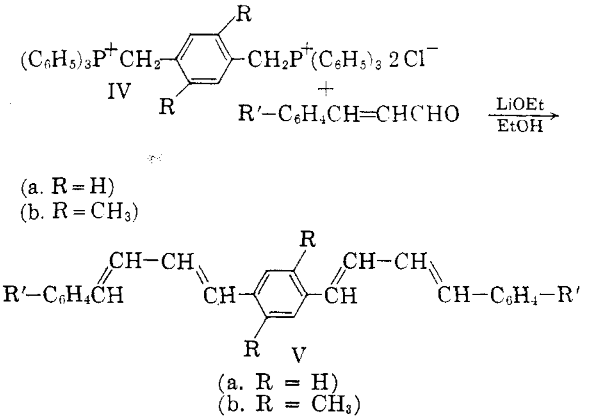
It is interesting that when the Wittig reaction is carried out in an ether solvent a temperature of about 65° is required to decompose the intermediate to products.[6] However, using the ethanol-ethoxide system the reactions proceed rapidly in about 30–60 seconds at room temperature. This rapidity of reaction in ethanol is in line with the polar nature of the reaction intermediates.

TABLE I

1,4-DIARYLBUTADIENES

R	Yield	M.P.	Method of Preparation
H	63	154–156	A
p-CH_3	76	160–161	A
p-OCH_3	63	161–162.5	A
p-$NHCOCH_3$	61	264–265	A
p-$N(CH_3)_2$	66	177–180	B
p-CO_2CH_3	38	180–180.5	B
m-NO_2	65	181.5–182	B

1,4-Bis(4-arylbutadienyl)benzenes. The next obvious extension of these reactions was the synthesis of 1,4-bis(4-arylbutadienyl)benzenes (IV). In the previous paper[1] are described the preparations of p-xylenebis(triphenylphosphonium chloride) (IVa) and 2,5-dimethyl-p-xylylenebis(triphenylphosphonium chloride) (IVb). These phosphonium salts were found to react easily with benzaldehydes to produce 1,4-distyrylbenzenes in good yields. When a solution of the phosphonium salt (IVa) and cinnamaldehyde in ethanol was treated with a lithium ethoxide solution in ethanol, the product, 1,4-bis(4-phenylbutadienyl)benzene (Va. R′ = H) precipitated in 88% yield.[7]



This reaction was found to be general for cinnamaldehydes. The compounds Vb (R′ = H) and Va, where R′ is m-nitro, p-methyl, p-methoxy, and

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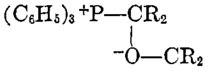
(6) In the mechanism proposed by Wittig [*Angew. Chem.*, **68**, 505 (1956); *Experientia*, **12**, 41 (1956)] for the reaction, the betaine



$$\begin{array}{l}(C_6H_5)_3\,{}^+P{-}CR_2\\ \qquad\quad\;\, |\\ \qquad\;\; {}^-O{-}CR_2\end{array}$$

is considered to be an intermediate, since in many cases a compound described as the betaine could be isolated and heating of it normally leads to olefin formation.

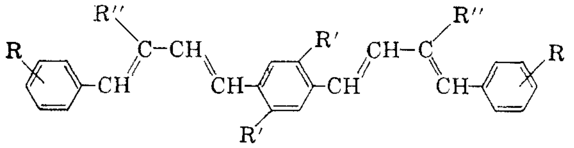
(7) This hydrocarbon was recently prepared by Drefahl and Plotner[4a] by the Perkin or Kuhn condensation in 25% yield.

p-dimethylamino have been prepared. The poor yield of the *p*-methoxy derivative is from only one experiment, and could undoubtedly be raised to the good yields as shown by the others. Another derivative of Va was obtained by replacing cinnamaldehyde in the scheme above with α-methylcinnamaldehyde to give 1,4-bis(3-methyl-4-phenylbutadienyl)benzene in 83% yield.

All of the products were obtained as mixtures of *cis* and *trans* isomers which were routinely isomerized, except for the dimethylamino derivative, to the all *trans* configuration by digestion in boiling xylene containing a trace of iodine. The dimethylamino compound, due to its reaction with iodine, could not be isomerized in this manner. It did, however, isomerize when recrystallized from dimethylformamide. The compounds obtained are listed in Table II. The yields are based on crude product, while the melting points are those of the isomerized materials, which were obtained with essentially no loss.

TABLE II

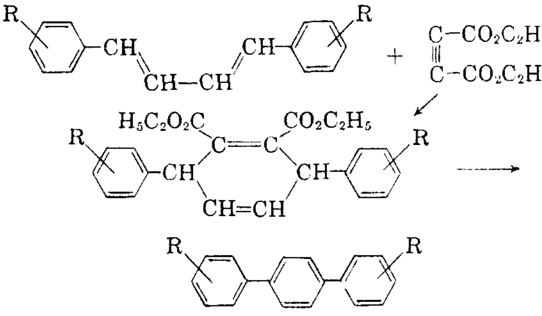
1,4-BIS(ARYLBUTADIENYL)BENZENES



R	R′	R″	Yield, %	M.P.
H	H	H	88	290–293
p-CH_3	H	H	100	315–319
H	CH_3	H	75	246–247
H	H	CH_3	83	235–237
m-NO_2	H	H	65	260–264
p-OCH_3	H	H	13	304–306
p-$N(CH_3)_2$	H	H	100	314–315

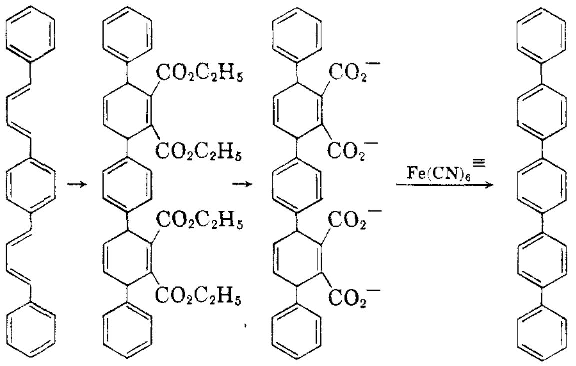
Terphenyls and Quinquephenyls. In 1935 Lohaus[8] reported a convenient method for the preparation of *p*-terphenyl from 1,4-diphenylbutadiene. This involved the Diels-Alder reaction of the diene with diethyl acetylenedicarboxylate to give a 90% yield of diethyl 3,6-diphenyldihydrophthalate. Saponification and acidification gave the corresponding diacid. When this diacid was dissolved in aqueous carbonate and treated with a solution of potassium ferricyanide, a quantitative yield of terphenyl resulted.

We have repeated this synthesis without isolation of intermediates and have obtained a 60% yield of terphenyl. Application of this procedure to 1-(*p*-tolyl)-4-phenylbutadiene and 1,4-bis(*p*-tolyl)-butadiene resulted in a 70% yield of 4-methylterphenyl and a 42% yield of 4,4″-dimethylterphenyl, respectively. This appears to be a fairly general route to terphenyls not containing groups attacked by ferricyanide.



It was of interest to see if this technique could be extended to the bisbutadienyl system to obtain *p*-quinquephenyls.[9] Previous methods of synthesis of this interesting polyphenyl have been laborious and have resulted in the production of trace amounts or, at best, very poor yields. These have included the reaction of biphenyllithium with cyclohexandione-1,4 followed by dehydration and air oxidation,[10] the Gatterman coupling reaction of benzenediazonium formate with copper[11]; the Ullmann coupling of 4-iodoterphenyl and 4-iodobiphenyl with silver[11]; the catalytic reduction of *p*-dibromobenzene[12]; and the Friedel-Crafts reaction of cyclohexene with terphenyl followed by dehydrogenation.[13]

The synthesis of quinquephenyl was carried out as follows. 1,4-Bis(4-phenylbutadienyl)benzene was condensed with two equivalents of diethyl acetylenedicarboxylate in boiling *o*-dichlorobenzene. The resulting mixture was saponified with alcoholic potassium hydroxide to give a brilliant yellow solution of the potassium tetrahydroquinquephenyl tetracarboxylate. This solution was readily decarboxylated and aromatized by reaction with potassium ferricyanide to give quinquephenyl. The product from four experiments was combined and sublimed to give a 52% yield of pure hydrocarbon. This rep-



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[8] H. Lohaus, *Ann.*, **516,** 295 (1935).

[9] This material has been previously published in a Communication, T. W. Campbell and R. N. McDonald, *J. Org. Chem.*, **24,** 730 (1959).

[10] E. Miller and T. Topel, *Chem. Ber.*, **72B,** 273 (1939).

[11] O. Gerngrass and M. Dunkel, *Chem. Ber.*, **57B,** 739 (1924).

[12] M. Busch, W. Weber, C. Darboven, W. Renner, H. J. Hahn, G. Mathauser, F. Stratz, K. Zitzmann, and H. Engelhardt, *J. prakt. Chem.*, **146,** 1 (1936).

[13] Buu-Hoï and P. Cagniant, *Compt. rend.*, **216,** 381 (1943).

resents by far the best synthesis of this polyphenyl of which we are aware.

Applying this synthesis to 1,4-bis[4-(*p*-tolyl)butadienyl]benzene and 1,4-bis(3-methyl-4-phenylbutadienyl)benzene gave 4,4''''- and 2',3'''-dimethylquinquephenyl, respectively.

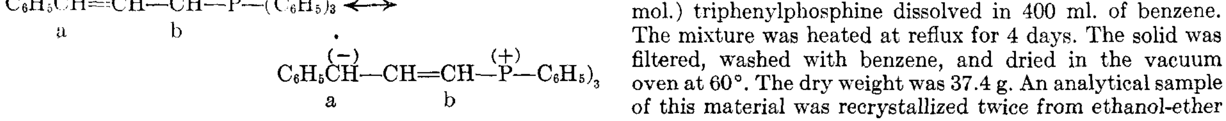
These two methylated derivatives of *p*-quinquephenyl represent the first derivatives of the hydrocarbon reported in the literature. It is also worth noting that they were synthesized under mild conditions and in what we consider an unambiguous manner.

When 1,4-bis[4-(3-nitrophenyl)butadienyl]benzene was used, none of the 3,3''''-dinitroquinquephenyl, resulted. It is felt that the nitro groups deactivated the diene system sufficiently so that the Diels-Alder reaction did not occur as expected.

The condensation of 1,4-bis[4-(4-*N*,*N*-dimethylaminophenyl)butadienyl]benzene with diethyl acetylenedicarboxylate and saponification seemed to proceed as expected. But, on subsequent treatment with potassium ferricyanide, a black, unidentified material was obtained. Apparently the dimethylamino groups were oxidized along with the anticipated decarboxylation and aromatization. However, little effort was expended in attempted identification of this material.

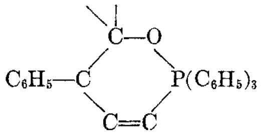
Miscellaneous. In continuing the extension of the Wittig reaction to higher polyenes, 1,6-diphenylhexatriene and 1-(3-nitrophenyl)-6-phenylhexatriene were prepared by reaction of triphenylcynnamylphosphonium chloride with cinnamaldehyde and *m*-nitrocinnamaldehyde, respectively. Since the yields of these reactions reported are from single experiments with little care taken to insure proper conditions, these do not by any means represent the maximum yields obtainable. A single attempt to prepare 1,6-diphenylhexatriene by reaction of 1,4-bis(triphenylphosphonium chloride)butene-2 and benzaldehyde gave only a brown resin as product. A similar product was obtained when the synthesis of 1,10-diphenyldecapentaene from the butene-bisphosphonium salt and cinnamaldehyde was attempted.

In connection with triphenylcinnamylphosphonium chloride, it is interesting to consider what the structure of the intermediate phosphonium ylide



$$\underset{a}{C_6H_5CH}{=}CH{-}\underset{b}{\overset{(-)}{CH}}{-}\overset{(+)}{P}{-}(C_6H_5)_3 \longleftrightarrow \underset{a}{C_6H_5\overset{(-)}{CH}}{-}CH{=}\underset{b}{CH}{-}\overset{(+)}{P}{-}C_6H_5)_3$$

might be. When prepared in alcohol solution in the absence of aldehyde, it is brilliant red-orange and stable for long periods. It is evident from the color that the ylide can resonate as indicated, in a manner similar to cinnamyl anion.[14] Such being the case, reaction can occur with the carbonyl group at both positions (a) and (b); *via* an intermediate such as;



as well as the conventional 4-ring intermediate. Evidence for such intermediates has not been observed in the products, hence it must not be capable of collapsing to products other than the original ylide and carbonyl compound.[15]

EXPERIMENTAL

Melting points were determined on the Kofler Hot Stage.

Preparation of (*p-nitrobenzyl*)*triphenylphosphonium bromide.* A mixture of 25.0 g. (0.12 mol.) of *p*-nitrobenzyl bromide and 33.0 g. (0.13 mol.) of triphenylphosphine in 300 ml. of xylene was refluxed and stirred for 26 hr. The tan crystalline solid was filtered, washed with xylene, and dried. The yield was 51.2 g. (95%) of a product melting at 275 to 275.5°.

Anal. Calcd. for $C_{25}H_{21}NO_2Br$: C, 63.0; H, 4.0; N, 2.93. Found: C, 62.6, 62.7; H, 4.4, 4.5; N, 3.14, 3.24.

The tan solid was readily soluble in alcohol. Treatment of an alcoholic solution of the phosphonium salt with lithium ethylate solution gave a very intense cherry-red color which persisted in the solution for nearly an hour.

Preparation of (*p-methylbenzyl*)*triphenylphosphonium bromide.* A mixture of 80.0 g. (0.43 mol.) of α-bromo-*p*-xylene and 140 g. (0.54 mol.) of triphenylphosphine in 500 ml. of dimethylformamide was heated under reflux for 3 hr. After cooling to room temperature the salt was filtered, washed with ether, and dried under reduced pressure at 65°. The dry weight was 147.4 g. (76%), m.p. 277–277.5°. An analytical sample was recrystallized from dimethylformamide to give clusters of colorless crystals, m.p. 276–277°.

Anal. Calcd. for $C_{26}H_{24}BrP$: C, 69.80; H, 5.41; Br, 17.87. Found: C, 69.96, 69.91; H, 5.96; Br (ionic), 17.86, 17.41; Br (total), 17.95, 18.09.

1,4-Bis(*triphenylphosphonium chloride*)*butene-2.* A mixture of 1400 ml. of xylene, 200 g. (0.75 mol.) of triphenylphosphine, and 30 g. (0.24 mol.) of 1,4-dichlorobutene-2 was refluxed for 60 hr. The slightly discolored crystalline solid was refluxed for 60 hr. The slightly discolored crystalline solid was filtered, dried, and recrystallized from a mixture of isopropanol and ether. The nicely crystalline product was obtained in a yield of 102 g. (65%). For analysis the sample was dried for 3 hr. at 110° in a high vacuum.

Anal. Calcd. for $C_{40}H_{36}P_2Cl_2$: C, 73.9; H, 5.5; Cl, 10.9. Found: C, 73.6, 73.9; H, 5.5, 5.7; Cl, 10.92, 10.88.

Preparation of ethylene-bis(*triphenylphosphonium bromide*). To a solution of 37.8 g. (0.201 mol.) of ethylene bromide in 300 ml. of benzene was added a solution of 140.0 g. (0.534 mol.) triphenylphosphine dissolved in 400 ml. of benzene. The mixture was heated at reflux for 4 days. The solid was filtered, washed with benzene, and dried in the vacuum oven at 60°. The dry weight was 37.4 g. An analytical sample of this material was recrystallized twice from ethanol-ether mixture to give colorless crystals, m.p. 280–295°.

Anal. Calcd. for $C_{38}H_{34}Br_2P_2$: C, 64.06; H, 4.81; Br, 22.44. Found: C, 64.1, 64.2; H, 4.83, 5.11; Br (ionic) 22.62.

The benzene filtrate was evaporated and on dilution with ether yielded considerably more product.

Preparation of triphenylcinnamylphosphonium chloride. To a solution of 40 g. (0.263 mol.) of (3-chloropropenyl)-benzene in 200 ml. of xylene was added a solution of 92 g.

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(14) T. W. Campbell and W. G. Young, *J. Am. Chem. Soc.*, **69**, 688 (1947); **69**, 3066 (1947); **71**, 296 (1949); **74**, 608 (1952).

(15) Compare F. Bohlmann, *Chem. Ber.*, **89**, 2191 (1956).

(0.350 mol.) of triphenylphosphine in 300 ml. of xylene. The mixture was heated at reflux with stirring overnight. The colorless crystalline product was filtered, washed with xylene, and dried in the vacuum oven. The dry weight was 99–101 g. (91–93%), m.p. 224–226°. A sample was recrystallized twice from ethanol ether to give colorless rosettes of needles, m.p. 224–226°.

Anal. Calcd. for $C_{27}H_{24}ClP$: C, 78.15; H, 5.83; Cl, 8.55. Found: C, 76.58, 76.58; H, 6.13, 6.26; Cl (ionic) 8.22, 8.36; O, 3.54 (direct analysis).

The poor analyses, plus presence of oxygen, suggest solvation.[1]

A solution of triphenylcinnamylphosphonium chloride in absolute ethanol gave an intense red color when treated with lithium ethoxide, which persisted for some time. In the following reactions, it was noted that reaction of the cinnamyl "ylide" with aromatic aldehydes was qualitatively much slower than the corresponding reaction of the bis "ylide" from *p*-xylylene-bis(triphenylphosphonium chloride).[1]

In addition to the products described in more detail below, triphenylcinnamylphosphonium chloride underwent the following reactions. Eight g. of this salt was condensed with 2.9 g. of *p*-nitrobenzaldehyde to give 3.1 g. of pure 1-(4-nitrophenyl)-4-phenylbutadiene melting at 181–182°. In addition, 0.82 g. of a yellow, crystalline solid melting at 165–175° was obtained from the filtrate as well as some unidentified oil.

Similarly, reaction of the cinnamyl phosphonium salt with terephthalaldehyde gave the previously known 1,4-bis-(4-phenylbutadienyl)benzene, m.p. 276–281. The yield was only 0.8 g. from 1.2 g. of terephthalaldehyde (27%).

Preparation of 1,4-diphenylbutadiene. A solution of 60 g. (0.145 mol.) of triphenylcinnamylphosphonium chloride and 16.4 g. (0.155 mol.) of benzaldehyde in 200 ml. of alcohol was treated with 760 ml. of 0.2*M* lithium ethoxide in ethanol. After allowing this mixture to stand over the week end at room temperature, 700 ml. of water was added and the solid filtered, washed with 150 ml. of 60% alcohol, and dried in a vacuum oven at 65°. The yield of product was 17.9–19.9 g. (60–66%). Recrystallization from cyclohexane gave colorless needles, m.p. 154–155° (reported[4a] m.p. 152.5–153.5°). The product is in the *trans-trans* form of the diene.

Preparation of 1-(4-methoxyphenyl)-4-phenylbutadiene. To a solution of 15.0 g. (0.0363 mol.) of triphenylcinnamylphosphonium chloride and 5.26 g. (0.0387 mol.) of anisaldehyde in 50 ml. of alcohol was added 190 ml. of 0.2*M* lithium ethoxide in ethanol. After standing at room temperature over the week end, 150 ml. of water was added and the crystalline solid filtered, washed with 100 ml. of 60% alcohol, and dried in the vacuum oven at 60°. The dry weight was 5.4 g. (63%). The solid was recrystallized from benzene-cyclohexane mixture to give colorless crystals, m.p. 162–162.5°. An analytical sample was recrystallized from the same solvent mixture to give colorless crystals, m.p. 162–162.5°.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.3, 86.5; H, 6.89, 6.91.

Preparation of 1-(4-acetamidophenyl)-4-phenylbutadiene. To a solution of 15.0 g. (0.0363 mol.) of triphenylcinnamylphosphonium chloride and 6.4 g. (0.392 mol.) of *p*-acetamidobenzaldehyde in 50 ml. of alcohol was added 190 ml. of 0.2*M* lithium ethoxide in ethanol. After standing overnight at room temperature, 150 ml. of water was added and the solid filtered, washed with 100 ml. of 60% alcohol and dried in the vacuum oven at 60°. The dry weight was 5.8 g. (61%). Recrystallization from dimethylformamide-ethanol mixture gave light yellow needles (4.9 g.), m.p. 264–265°. An analytical sample was recrystallized from the same solvent mixture, m.p. 267–268°.

Anal. Calcd. for $C_{18}H_{17}ON$: C, 82.09; H, 6.51; N, 5.32. Found: C, 82.31, 82.33; H, 6.55, 6.58; N, 5.32, 5.38.

Preparation of 1-(p-tolyl)-4-phenylbutadiene. To a solution of 60 g. (0.145 mol.) of triphenylcinnamylphosphonium chloride and 19.2 g. (0.16 mol.) of *p*-tolualdehyde in 200 ml. of alcohol was added 760 ml. of 0.2*M* lithium ethoxide in ethanol. After 24 hr., an equal volume of water was added, and the crystalline product was filtered, washed with 60% aqueous ethanol, and dried in a vacuum at 60°. The yield was 24.3 g. (76%). After recrystallization from cyclohexane, colorless needles resulted, m.p. 160–161° (reported[4b], m.p. 159–160°).

Anal. Calcd. for $C_{17}H_{16}$: C, 92.70; H, 7.30. Found: C, 92.44, 92.41; H, 7.36, 7.37.

Preparation of 1-(4-dimethylaminophenyl)-4-phenylbutadiene. To a solution of 20.0 g. (0.051 mol.) of triphenylcinnamylphosphonium chloride and 9.5 g. (0.053 mol.) of *p*-dimethylaminobenzaldehyde in 200 ml. of ethanol was added 260 ml. of 0.2*M* lithium ethoxide. In about 4 min. a yellow-tan crystalline precipitate appeared. After standing overnight 250 ml. of water was added, the solid filtered, washed with 100 ml. of 60% ethanol and dried at reduced pressure and 60°. The dry weight was 8.5 g. (66%). This was recrystallized from a benzene-cyclohexane mixture to give golden needles, m.p. 177–180°. An analytical sample was recrystallized from dimethylformamide, m.p. 180–182°.

Anal. Calcd. for: $C_{18}H_{19}N$: C, 86.7; H, 7.8; N, 5.6. Found: C, 86.6, 86.9; H, 7.8, 7.6; N, 5.7, 5.7.

Preparation of 1-(4-carbomethoxyphenyl)-4-phenylbutadiene. A solution of 47.4 g. (0.11 mol.) of (4-carbomethoxybenzyl)triphenylphosphonium chloride[1] and 16.0 g. (0.12 mol.) of cinnamaldehyde in 100 ml. of ethanol was treated with 60 ml. of a 0.2*M* solution of lithium ethoxide. Immediately, a nearly colorless crystalline precipitate separated. After 0.5 hr., 100 ml. of water was added, the solution was filtered and dried to give 10.4 (37%) of product which on recrystallization from benzene-cyclohexane mixture (50/50) in the presence of a trace of iodine gave a product melting at 180–180.3°.

Anal. Calcd. for: $C_{18}H_{16}O_2$: C, 81.8; H, 6.07. Found: C, 81.8, 81.9; H, 6.10, 6.32.

Preparation of 1-(4-nitrophenyl)-4-phenylbutadiene. To a solution of 45.8 g. (0.96 mol.) of (*p*-nitrobenzyl)triphenylphosphonium bromide and 15.0 g. (0.114 mol.) of cinnamaldehyde in 250 ml. of ethanol was added a solution of 0.78 g. (0.114 mol.) of lithium wire dissolved in 400 ml. of ethanol. The mixture turned to a deep wine which faded as yellow crystals formed. After standing overnight, 250 ml. of water was added, the solid was filtered, washed with 100 ml. of 60% ethanol, and dried. The dry weight was 18.7 g. (72%). This was recrystallized from benzene-cyclohexane mixture containing a trace of iodine. The yield of product was 16.5 g., m.p. 181.5–182°.

Anal. Calcd. for: $C_{16}H_{13}NO_2$: C, 76.49; H, 5.18. Found: C, 76.26, 76.45; H, 5.17, 5.33.

Preparation of 1,4-bis(p-tolyl)butadiene. To a solution of 50.0 g. (0.11 mol.) of (*p*-methylbenzyl)triphenylphosphonium bromide and 17.3 g. (0.12 mol.) of *p*-methylcinnamaldehyde in 75 ml. of ethanol was added 550 ml. of a 0.2*M* lithium ethoxide solution. After standing overnight 400 ml. of water was added, and the crystals were filtered, washed with 100 ml. of 60% ethanol, and dried at reduced pressure and 65°. The dry weight was 17.1 g. (68.5%), m.p. 198–200°.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.50, 92.51, H, 7.71, 7.73.

Preparation of 1,4-bis(4-phenylbutadienyl)benzene. To a solution of 70.0 g. (0.10 mol.) of *p*-xylylene-bis-(triphenylphosphonium chloride)[1] and 35.0 g. (0.26 mol.) of cinnamaldehyde in 250 ml. of ethanol was added a solution of 1.74 g. (0.25 mol.) of lithium wire dissolved in 1 l. of ethanol. After standing overnight the yellow solid was filtered, washed with 300 ml. of 60% ethanol, and dried under reduced pressure at 70°. The dry weight was 29–32 g. (87–95%). The solid was dissolved in boiling xylene, treated with decolorizing carbon, filtered, and the filtrate digested for 3 hr. in the presence of a trace of iodine. Bright yellow leaflets were obtained (23–25 g.), m.p. 285–287°. An analytical sample was recrystallized from dimethylformamide, m.p. 290–293° (reported[4b] m.p. 288°).

Preparation of 1,4-bis-(4-phenylbutadienyl)-2,5-dimethylbenzene. To a solution of 72.7 g. (0.10 mol.) of 2,5-dimethyl-*p*-xylylenebis(triphenylphosphonium chloride)[1] and 30.4 g. (0.23 mol.) of cinnamaldehyde in 1050 ml. of ethanol was added 1150 ml. of 0.2*M* lithium ethoxide. After standing overnight, 600 ml. of water was added, the yellow precipitate filtered, washed with 400 ml. of 60% ethanol, and dried at reduced pressure and 65°. The dry weight was 27.1 g. (75%). This was recrystallized from xylene containing a trace of iodine to give the all *trans* product, m.p. 246–247°.

Anal. Calcd. for: $C_{28}H_{26}$: C, 92.8; H, 7.18. Found: C, 92.9, 92.8; H, 7.13, 7.15.

The preparation of 1,4-bis[4-(3-nitrophenyl)butadienyl]-benzene. To a solution of 70.0 g. (0.1 mol.) of *p*-xylylene-bis-(triphenylphosphonium chloride)[1] and 37.0 g. (0.209 mol.) of *m*-nitrocinnamaldehyde in 500 ml. of absolute alcohol was added 1 l. of 0.2*M* lithium ethoxide in ethanol. After standing overnight at room temperature, 200 ml. of water was added and the solid filtered. It was washed with 100 ml. of 60% alcohol. The yellow precipitate was dried in the vacuum oven at 60°. The dry weight was 27.7 g. (65%). The yellow solid was isomerized in boiling xylene with a trace of iodine. The resulting orange-brown crystals weighed 17.5 g., m.p. 260–264° (dec.). An analytical sample was recrystallized twice from dimethylformamide, m.p. 267–267.5°.

Anal. Calcd. for: $C_{26}H_{20}O_4N$: C, 73.5; H, 4.75; N, 6.60. Found: C, 73.77, 73.78; H, 4.90, 4.75; N, 6.59, 6.64.

Preparation of 1,4-bis[4-(p-tolyl)butadienyl]benzene. To a solution of 70.0 g. (0.10 mol.) of *p*-xylylene-bis(triphenylphosphonium chloride)[1] and 32.4 g. (0.22 mol.) of *p*-methylcinnamaldehyde in 250 ml. of alcohol was added 1100 ml. of 0.2*M* solution of lithium ethoxide in ethanol. After standing overnight, 680 ml. of water was added and the light yellow solid filtered, washed with 250 ml. of 60% alcohol, and dried in the vacuum oven. The weight of product was 36.0 g. (99%). This was recrystallized from xylene with a trace of iodine. The resulting crystals were filtered and washed with benzene to give 26.1 g. of product, m.p. 315–319°. An analytical sample was recrystallized from dimethylformamide to give yellow leaflets, m.p. 315–320°.

Anal. Calcd. for: $C_{28}H_{26}$: C, 92.8; H, 7.23. Found: C, 92.6, 92.7; H, 7.14, 7.52.

Preparation of 1,4-bis(3-methyl-4-phenylbutadienyl)benzene. To a solution of 35.0 g. (0.050 mol.) of *p*-xylylene-bis(triphenylphosphonium chloride)[1] and 16.4 g. (0.11 mol.) of α-methylcinnamaldehyde in 150 ml. of alcohol was added 500 ml. of a 0.2*M* lithium ethoxide solution. After standing overnight 400 ml. of water was added and the yellow solid was filtered, washed with 150 ml. of 60% ethanol, and dried in a vacuum oven at 65°. The dry weight was 15.1 g. (83%). This was recrystallized from a mixture of benzene cyclohexane containing a trace of iodine after digesting for 5 hr. The resulting yellow leaflets weighed 12.0 g., m.p. 217–218°. An analytical sample was recrystallized from dimethylformamide, m.p. 235–237°.

Anal. Calcd. for: $C_{28}H_{26}$: C, 92.8; H, 7.23. Found: C, 92.8, 92.8; H, 7.50, 7.31.

Preparation of 1,4-bis[4-(4-N,N-dimethylaminophenyl)-butadienyl]benzene. To a solution of 30.0 g. (0.043 mol.) of *p*-xylylene-bis(triphenylphosphonium chloride)[1] and 17.5 g. (0.10 mol.) of *p-N,N*-dimethylaminocinnamaldehyde in 350 ml. of alcohol was added 500 ml. of a 0.2*M* lithium ethoxide solution. After standing overnight 500 ml. of water was added and the orange precipitate was filtered, washed with 200 ml. of 60% alcohol, and dried in a vacuum oven at 70°. The dry weight was 17.7 g. (100%). This was not isomerized except for the analytical sample which apparently did so when recrystallized from dimethylformamide to give red-orange leaflets, m.p. 314–315°.

Anal. Calcd. for: $C_{30}H_{32}N_2$: C, 85.6; H, 7.67; N, 6.66. Found: C, 85.5, 85.3; H, 7.87, 7.78; N, 6.66, 6.65.

Preparation of 1,4-bis[4-(4-methoxyphenyl)butadienyl]-benzene. To a solution of 23.0 g. (0.033 mol.) of *p*-xylylenebis(triphenylphosphonium chloride)[1] and 11.0 g. (0.068 mol.) of *p*-methoxycinnamaldehyde was added a solution prepared by dissolving 0.236 g. (0.033 mol.) of lithium dissolved in 100 ml. of alcohol. After standing over the week end, the lemon yellow precipitate was filtered, washed with 50 ml. of 60% alcohol, and dried in the vacuum oven at 60°. The weight of product was 1.7 g. (13%).

This yellow solid was recrystallized from xylene with a trace of iodine after digesting for 3 hr. The resulting yellow plates were filtered, washed with benzene, and dried in the vacuum oven. Weight 1.0 g., m.p. > 300°. A sample was recrystallized from dimethylformamide, m.p. 304–306.

Anal. Calcd. for $C_{28}H_{26}O_2$: C, 85.25; H, 6.65. Found: C, 84.82, 84.99; H, 6.58, 6.73.

The infrared spectrum shows aromatic ether present and the butadiene system as *trans-trans*.

Preparation of p-terphenyl. The conversion of 1,4-diphenylbutadiene to *p*-terphenyl was repeated following the method of Lohaus.[8] The yield of *p*-terphenyl without isolation of intermediates was 1.5 g. (60% from diphenylbutadiene), m.p. 211–212° (reported by Lohaus,[8] m.p. 211° on recrystallized material).

Preparation of 4-methyl-p-terphenyl. A mixture of 2.2 g. (0.01 mol.) of 1-(*p*-tolyl)-4-phenylbutadiene and 1.7 g. (0.01 mol.) of diethyl acetylenedicarboxylate was heated in an oil bath maintained at 140–150° for 5 hr. Fifty ml. of alcohol along with 2 g. of potassium hydroxide was added and the mixture was refluxed for 11 hr. Most of the solvent was evaporated under nitrogen on the steam bath, the damp residue dissolved in water, some insoluble material was extracted with ether, and the aqueous layer was acidified with dilute hydrochloric acid. The solid acid was filtered, washed until neutral with water, and dried in the vacuum oven at 60°. Weight 3.2 g. (97% yield).

The acid was dissolved in a solution of 7 g. sodium carbonate in 200 ml. of water. To the filtered solution was added a solution of 20.0 g. of potassium ferricyanide in 50 ml. of water. The solid methylterphenyl separated almost at once. After heating on the steam bath for 0.5 hr. and allowing to stand at room temperature overnight, the product was filtered, washed with water, and dried in the vacuum oven at 80°, weight 1.7 g. (70% based on the butadiene). The solid was recrystallized from alcohol plus a small amount of dimethylformamide to give colorless crystals, m.p. 209–209.5° (reported,[16] m.p. 207–208°).

Preparation of 4,4″-dimethyl-p-terphenyl. A mixture of 4.68 g. (0.020 mol.) of 1,4-bis(*p*-tolyl)butadiene and 3.50 g. (0.020 mol) of diethyl acetylenedicarboxylate in 20 ml. of *o*-dichlorobenzene was heated under reflux for 4 hr. To this was added 100 ml. of ethanol and 5.0 g. of potassium hydroxide and the mixture was heated under reflux for 6 hr. The solvent was practically evaporated on the steam bath under nitrogen and the residual solid dissolved in 200 ml. of water. Extraction of the solution twice with ether removed a trace of solid and the *o*-dichlorobenzene. The aqueous solution was treated with dilute hydrochloric acid until just cloudy and then 5.0 g. of sodium carbonate was added. Thirty g. of potassium ferricyanide was dissolved in 200 ml. of water and this was added to the above solution. The mixture became turbid almost at once. After standing overnight it was centrifuged, the solid washed once with water by centrifugation and then dried in a vacuum oven at 80°. The dry weight was 2.2 g. (42%). This was sublimed at 220° and 0.02 mm. to give an almost colorless sublimate, m.p. 255–257°.

Anal. Calcd. for: $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.84, 92.88; H, 7.08, 7.08.

Synthesis of quinquephenyl. A mixture of 3.40 g. (0.02 mol.) of diethyl acetylenedicarboxylate and 3.34 g. (0.01

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(16) H. France, I. M. Heilbron, and D. H. Hey, *J. Chem. Soc.*, 1283 (1939).

mol.) of 1,4-bis-4(phenylbutadienyl)benzene was refluxed with 20 ml. of *o*-dichlorobenzene for 3 hr. The mixture was cooled and a trace of crystalline solid was filtered and discarded. The filtrate was refluxed with 100 ml. of absolute alcohol containing 5 g. of potassium hydroxide. The solvent was practically evaporated under nitrogen and the damp residue was extracted with water. The aqueous layer was separated from water insoluble matter by the addition of a little ether. The intense yellow aqueous phase was treated with a little decolorizing carbon, filtered, and the filtrate was then neutralized with dilute hydrochloric acid and then made basic again by the addition of 5 g. of sodium carbonate. Thirty g. of potassium ferricyanide was dissolved in 200 ml. of water and the two solutions were mixed. The mixture rapidly turned milky, but the very finely divided precipitate could not be satisfactorily filtered. The suspension was centrifuged and the deposited solid was washed several times by centrifugation. The precipitated solid was dried in a vacuum oven to give 3.6 g. (theory 3.8 g.) of a green tinged solid. An analytical sample was prepared by subliming 0.3 g. at 0.2 mm. and 300°. The yellowish solid melted at 380–390° on the hot bar. Further purification was carried out by recrystallizing the product from dimethylsulfoxide from which it was obtained as large well defined leaflets. The infrared and ultraviolet spectra were consistent with the structure of quinquephenyl. No carbonyl bands could be detected in the infrared.

Anal. Calcd. for $C_{30}H_{22}$: C, 94.24; H, 5.76. Found: C, 94.19, 94.27; H, 5.95, 5.96.

The over-all yield of sublimed quinquephenyl in several preparations was 50% based on 1,4-bis(4-phenylbutadienyl)benzene.

Preparation of 4,4''''-dimethylquinquephenyl. This synthesis was carried out as described for the preparation of quinquephenyl only using 3.63 g. (0.010 mol.) of 1,4-bis[4-(*p*-tolyl)butadienyl]benzene instead of 1,4-bis(4-phenylbutadienyl)benzene. The total products (17.3 g.) from four experiments on this scale were combined and sublimed at 350° and 0.07 mm. The light yellow crystalline sublimate weighed 6.9 g. (42%), m.p. > 400°. This could be recrystallized from tetramethylenesulfone to give light yellow leaflets.

Anal. Calcd. for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.59, 93.65; H, 6.48, 6.57.

Preparation of 2',3'''-dimethylquinquephenyl. The synthesis of this compound was carried out as described for the preparation of quinquephenyl only using 3.63 g. (0.010 mol.) of 1,4-bis(3-methyl-4-phenylbutadienyl)benzene in place of 1,4-bis(4-phenylbutadienyl)benzene. The yield of crude product was 4.7 g. This was sublimed at 210° and 0.05 mm. The colorless sublimate weighed 3.5 g. (85%), m.p. 217–218°.

Anal. Calcd. for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.57, 93.61; H, 6.43, 6.48.

Attempted nitration of p-quinquephenyl. One-half g. of *p*-quinquephenyl was heated for 1 hr. with 100 ml. of concentrated nitric acid under reflux. Five ml. of concentrated sulfuric acid was added and heating continued for 26 hr. At the end of this time there was some crystalline solid present which was removed by filtration. It was washed with water and a little acetone and dried in the vacuum oven. Weight 0.1 g. (A).

The mother liquor was poured into water and the resulting fluffy precipitate filtered, washed with water and dried in the vacuum oven. Weight 0.4 g (B).

The infrared spectra of both A and B are quite similar both showing nitro groups present, but impossible to determine sites of substitution since both *m*- and *p*-substitution appear. (B) shows some carbonyl (probably acid) present.

Preparation of 1,6-diphenylhexatriene. A mixture of 8.0 g. (0.019 mol.) of triphenylcinnamylphosphonium chloride, 2.6 g. (0.020 mol.) of cinnamaldehyde, 50 ml. of ethanol, and 100 ml. of 0.2*M* lithium ethoxide reacted rapidly with separation of a pastel pink solid. This product was recrystallized from xylene in the presence of iodine to give the all-*trans*-diphenylhexatriene as pale yellow leaflets, m.p. 206–207° (hot bar). The yield of pure product was 0.90 g. and product of lesser purity (m.p. 180–185°) was 2.2 g. An analytical sample melting at 203° was obtained by recrystallization from cyclohexane-benzene mixture.

Anal. Calcd. for $C_{18}H_{16}$: C, 93.07; H, 6.93. Found: C, 93,10, 93.09; H, 7.00, 7.01.

Preparation of 1-(3-nitrophenyl)-6-phenylhexatriene. A mixture of 5.6 g. (0.013 mol.) of triphenylcinnamylphosphonium chloride and 2.4 g. (0.013 mol.) of *m*-nitrocinnamaldehyde in 50 ml. of ethanol was treated with 80 ml. of 0.2*M* lithium ethoxide. The reaction proceeded normally and after 1 hr. it was diluted with an equal volume of water and the solid was filtered. The solid was dissolved in boiling xylene and the wet solution was dried with magnesium sulfate, decolorized, and cooled. Approximately 0.9 g. of an offcolor, yellow crystalline solid separated which was filtered and the filtrate was rejected. The solid melted in the range of 175–180°. It was recrystallized from 20 ml. of xylene to give 0.3 of stubby yellow needles, m.p. 182–184°. An analytical sample was obtained by recrystallizing again from boiling xylene followed by drying at 110° for 4 hr. This product melted at 184–185.5°.

Anal. Calcd. for: $C_{18}H_{15}NO$: C, 78.0; H, 5.4. Found: C, 78.36, 78.48; H, 5.68, 5.65.

Reaction of benzaldehyde with 1,4-bis(triphenylphosphonium chloride)butene-2. In the reaction of benzaldehyde and the subject phosphonium salt, a low melting crystalline solid was obtained which was dissolved in benzene to give a lemon yellow solution. A crystal of iodine was then added which brought about the immediate precipitation of a crystalline solid of a more orange color. This was allowed to stand in the air for a short time. However, the next day only a brown gum remained in the dish.

Only a brown resin was obtained with cinnamaldehyde.

WILMINGTON 98, DEL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO AND THE ARGONNE NATIONAL LABORATORY]

Beckmann Rearrangement in Hydrogen Fluoride

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In contrast to benzophenone oxime, cyclohexanone oxime does not undergo the Beckmann rearrangement in hydrogen fluoride solution. The *O*-benzoyl derivatives of both oximes rearrange readily.

Most of the reagents that are commonly used to effect the Beckmann rearrangement of oximes, *e.g.*, concentrated sulfuric acid, polyphosphoric acid, and acid chlorides, are capable of producing