The Preparation of Stereoisomeric α,ω-Diphenylpolyenes and Related Compounds by Means of the Wittig Reaction

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As reported in a previous paper, the authors have found in the synthesis of polystilbenes that the Wittig reaction gave almost the same amount of cis and trans isomers simultaneously with regard to the ethylenic linkage formed by the particular reaction[1]. The method seemed to be promising for the preparation of geometrical isomers of a wide variety of compounds. It is well-known that the cis isomers of α, ω-diphenylpolyene can be obtained by the semihydrogenation[2] of the corresponding acetylenic compounds on Lindlar's catalyst or by the photoisomerization of the all-trans isomer[2a,3]. The fact that the latter method essentially gives a mixture of several cis isomers reduces the practical value of this process for preparative purpose. On the contrary, the Wittig reaction is advantageous in view of the introduction of cis and trans ethylenic linkages at a definite position in the molecule by the reaction of a carbonyl component with an appropriate yield moiety. The present paper deals with the syntheses of stereoisomeric α,ω-diphenylpolyenes and related compounds according to this procedure.

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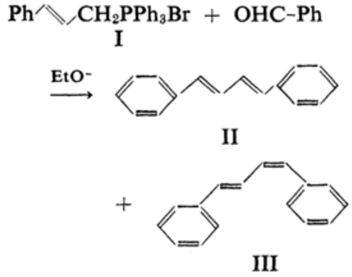
[1] S. Misumi, M. Kuwana and M. Nakagawa, This Bulletin, **34**, 1833 (1961); **35**, 135, 143 (1962).

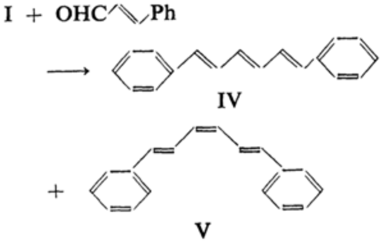
[2] a) J. H. Pinckard, B. Wille and L. Zechmeister, *J. Am. Chem. Soc.*, **70**, 1938 (1948); b) M. Akhtar, T. A. Richard and B. C. L. Weedon, *J. Chem. Soc.*, **1959**, 933.

[3] L. Zechmeister and A. L. LeRosen, *J. Am. Chem. Soc.*, **64**, 2755 (1942), **76**, 2308, 4144 (1954); *Acta Chem. Scand.*, **8**, 1421 (1954).

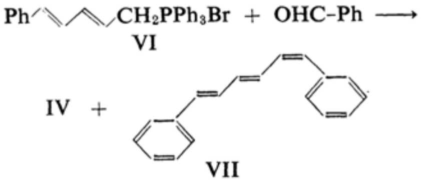
The synthesis of *trans, trans*-1,4-diphenylbutadiene (II) has been reported recently by Campbell employing triphenylcinnamylphosphonium chloride and benzaldehyde⁴⁾. The present authors have confirmed the simultaneous formation of trans, trans and trans, cis isomers (II and III) by the reaction of triphenylcinnamylphosphonium bromide (I) with the aldehyde. The combined yield was found as high as 77%.



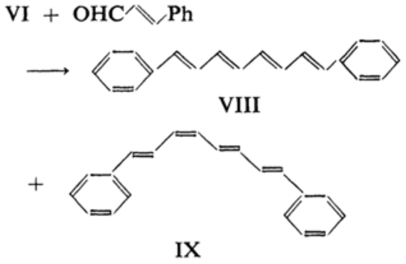
Similarly, the reaction of phosphonium bromide I with cinnamaldehyde afforded two isomers of 1,6-diphenylhexatriene, trans, trans, trans (IV) and trans, cis, trans (V), in nearly the same yield.



The third isomer, *trans, trans, cis*-diphenylhexatriene (VII) was obtained by the reaction of triphenyl-5-phenyl-2, 4-pentadienylphosphonium bromide (VI) with benzaldehyde and purified by chromatography on alumina. The cis isomer VII, colorless liquid, exhibited the identical electronic spectrum with that of the specimen prepared by Zechmeister and his coworkers³⁾, and it transformed into an all-trans isomer on exposure to light.

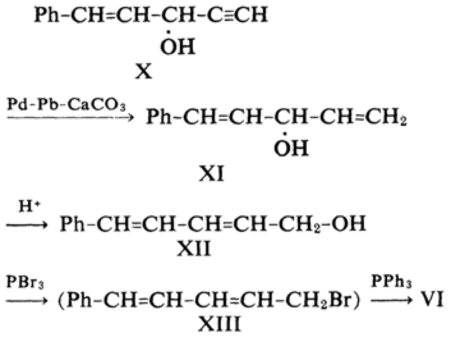


Similarly, the reaction of phosphonium bromide VI with cinnamaldehyde gave two stereoisomers, all-trans (VIII) and trans, cis, trans, trans (IX), of 1,8-diphenyloctatetraene in about the same yield.



The melting points and the electronic spectra of all above-mentioned stereoisomeric diphenylpolyenes were found to be identical with those of the reported values³⁾.

The synthesis of phosphonium salt VI was carried out according to the following scheme. 5-Phenyl-2, 4-pentadienol (XII)⁵⁾, obtained by semihydrogenation and anionotropic rearrangement of ethynylstyrylcarbinol (X)⁶⁾, was treated successively with phosphorus tribromide and triphenylphosphine yielding the phosphonium bromide VI.



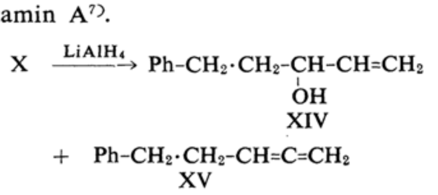
$$\underset{\text{X}}{\text{Ph-CH=CH-}\underset{\text{OH}}{\text{CH}}\text{-C}\equiv\text{CH}}$$

$$\xrightarrow{\text{Pd-Pb-CaCO}_3} \underset{\text{XI}}{\text{Ph-CH=CH-}\underset{\text{OH}}{\text{CH}}\text{-CH=CH}_2}$$

$$\xrightarrow{\text{H}^+} \underset{\text{XII}}{\text{Ph-CH=CH-CH=CH-CH}_2\text{-OH}}$$

$$\xrightarrow{\text{PBr}_3} \underset{\text{XIII}}{(\text{Ph-CH=CH-CH=CH-CH}_2\text{Br})} \xrightarrow{\text{PPh}_3} \text{VI}$$

The intermediate, XII and XIII, were used without purification for further reactions owing to their thermal instability. The reduction of ethynylcarbinol X with lithium aluminum hydride afforded unexpectedly 5-phenyl-1-penten-3-ol (XIV) in a 78% yield. The structure of this carbinol XIV was confirmed by elemental analysis, electronic and infrared spectra (Fig. 1). The same type of unusual reduction of $-\text{CH=CH-CH(OH)-C}\equiv\text{CH}$ grouping by the hydride has been found by Attenburrow in the course of the synthesis of Vitamin A⁷⁾.



$$\text{X} \xrightarrow{\text{LiAlH}_4} \underset{\text{XIV}}{\text{Ph-CH}_2\cdot\text{CH}_2\text{-}\underset{\text{OH}}{\text{CH}}\text{-CH=CH}_2}$$

$$+ \underset{\text{XV}}{\text{Ph-CH}_2\cdot\text{CH}_2\text{-CH=C=CH}_2}$$

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4) R. N. McDonald and T. W. Campbell, "Organic Syntheses", **40**, 36 (1960); *J. Org. Chem.*, **24**, 1241 (1959).

5) G. F. Woods and H. Sanders, *J. Am. Chem. Soc.*, **69**, 2926 (1947).

6) L. Skattebol, E. R. H. Jones and M. C. Whiting, "Organic Syntheses", **39**, 56 (1959).

7) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen and T. Walker, *J. Chem. Soc.*, **1952**, 1094.

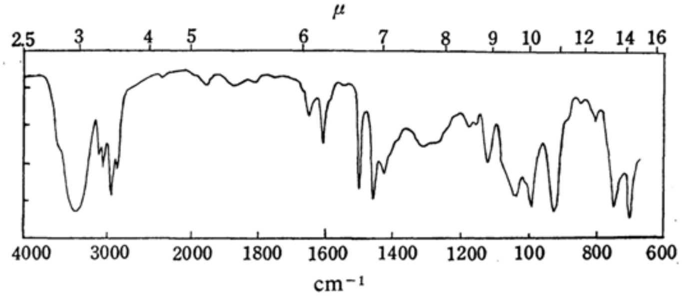


Fig. 1. The infrared spectrum of 5-phenylpent-1-en-3-ol (XIV).

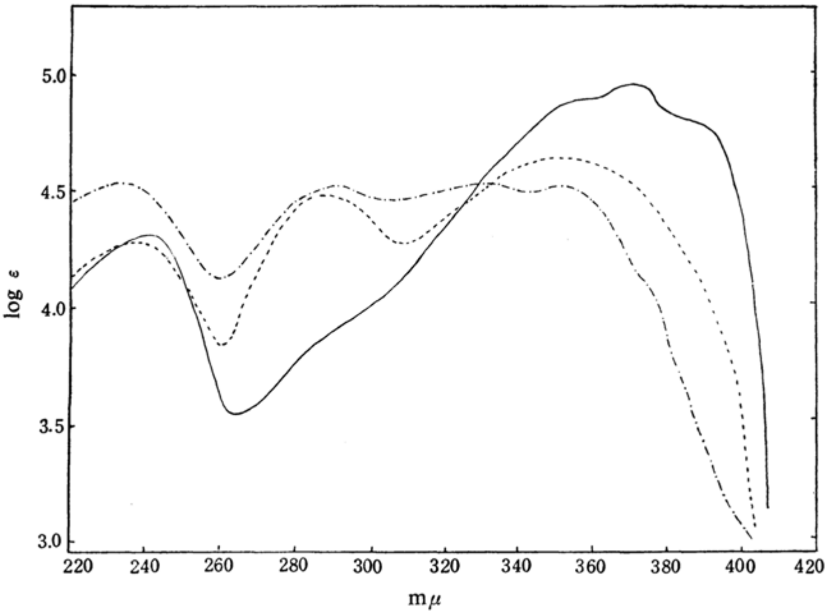
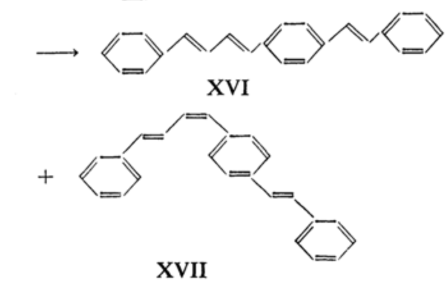


Fig. 2. The electronic spectra of the *p*-styryldiphenylbutadienes (——, all-trans XVI; ------, mono-cis XVII; —·—·—·, Dale's cis compound) (in *n*-hexane).

In addition to the above-mentioned reduction product, a colorless liquid with a lower boiling point was obtained. The formula of an allenic hydrocarbon XV was assigned to this substance on the basis of the absence of hydroxy- and ethynyl-absorptions and the presence of strong peaks of monosubstituted allene in its infrared spectrum.

Dale⁸⁾ has obtained a minor amount of a cis isomeric compound by the photoisomerization of *p*-styryldiphenylbutadiene. He suggested the structure of XVII to the minor product by the examination of its electronic spectrum, but there remained an uncertainty on account of its small quantity. We have carried out the synthesis of XVII from stilbenealdehyde in order to ascertain his suggestion. The reaction of phosphonium bromide I with stilbenealdehyde at room temperature resulted in the formation of all-trans (XVI) and mono-cis (XVII) isomers of *p*-styryldiphenylbutadiene in a total yield of 75%. The structure of the cis isomer, pale yellow plates with a green fluorescence, was confirmed by the elemental analysis, the examination of electronic and infrared spectra and the transformation into the all-trans isomer (XVI) on exposure to light.



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8) J. Dale, *Acta Chem. Scand.*, **11**, 971 (1957).

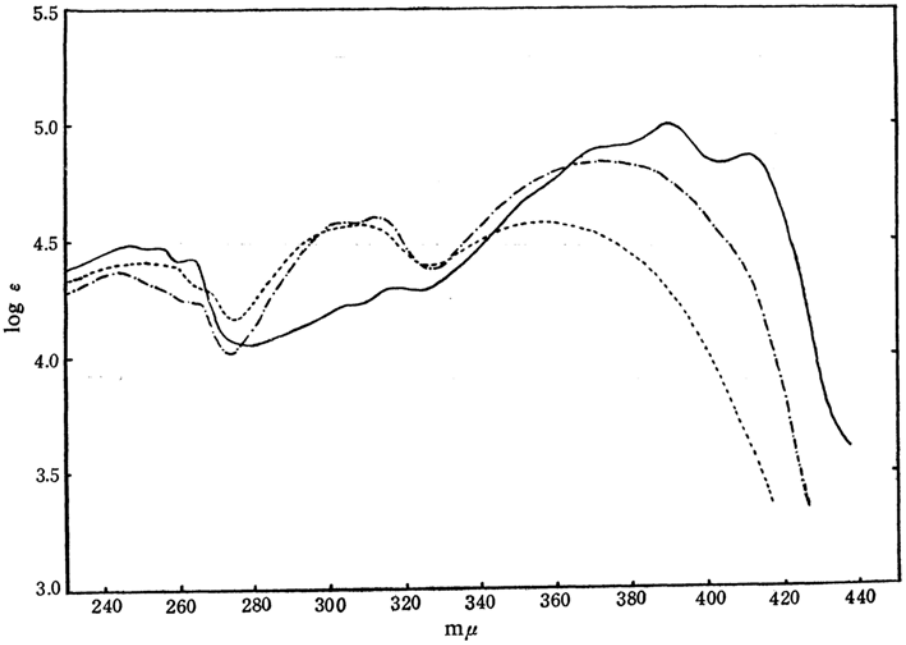
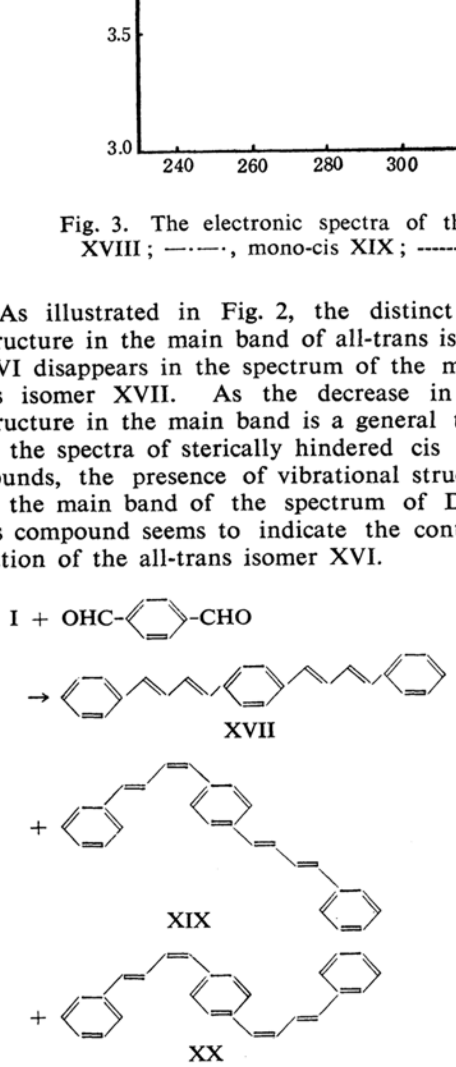


Fig. 3. The electronic spectra of the *p*-bis(phenylbutadienyl)benzenes (——, all-trans XVIII; —·—·, mono-cis XIX; ------, di-cis XX) (in tetrahydrofuran).

As illustrated in Fig. 2, the distinct fine structure in the main band of all-trans isomer XVI disappears in the spectrum of the mono-cis isomer XVII. As the decrease in fine structure in the main band is a general trend in the spectra of sterically hindered cis compounds, the presence of vibrational structure in the main band of the spectrum of Dale's cis compound seems to indicate the contamination of the all-trans isomer XVI.



XVII

XIX

XX

The reaction of phosphonium bromide I with terephthalaldehyde in place of stilbenealdehyde resulted in the formation of three stereoisomeric *p*-bis(phenylbutadienyl)benzenes. One of these isomers, all-trans form has already been synthesized by different authors, especially Campbell and McDonald used the Wittig reaction of *p*-xylenebisphosphonium chloride with cinnamaldehyde[9]. Each isomer, isolated by chromatography, gave correct analysis and could be transformed into the all-trans form by the photoisomerization. The assignment of their structure was performed on the bases of the electronic and infrared spectroscopic evidences. Also in the series of *p*-bis(phenylbutadienyl)benzene, only the all-trans isomer[9] exhibits a distinct fine structure in the absorption curve. The introduction of cis ethylenic linkage to the system caused blue-shifts (mono-cis, 16 mμ; di-cis, 33 mμ) of the main absorption maxima accompanied with the decrease of their absorption intensities and the appearance of new absorption peaks at the wavelength region of ca. 300 mμ in which the all-trans form has only a slight inflexion (Fig. 3).

The cis forms of the above-mentioned diphenylpolyenes seem to contain much less or no steric strain as compared with the previously discussed hindered cis polystilbenes and the related compounds[1]. But from the above-stated observation, it was revealed that the spectroscopic behavior of the geometrical isomers in these two series of conjugate system was

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[9] G. Drefahl and G. Plotner, *Chem. Ber.*, **91**, 1258 (1958); K. Friedlich and H. Henning, ibid., **92**, 2944 (1959); R. N. McDonald and T. W. Campbell, *J. Org. Chem.*, **24**, 1969 (1959); "Organic Syntheses", **40**, 85 (1960).

similar. This fact indicates that the steric strain in *cis*-polystilbenes are insufficient to exert an influence upon spectroscopic properties.

Experimental*

***trans*, *trans*- and *trans*, *cis*-1, 4-Diphenylbutadiene (II and III).**—To a stirred suspension of triphenylcinnamylphosphonium bromide (I, 6.9 g., 0.015 mol.) and benzaldehyde (1.8 g., 0.017 mol.) in anhydrous ethanol (40 ml.) was added a solution of a slight excess of lithium ethoxide (from 0.15 g. of lithium) in anhydrous ethanol (75 ml.) in a dark room. After stirring for ca. 10 hr., water (70 ml.) was added precipitating a solid. This was separated by filtration (filtrate A), dried and dissolved in cyclohexane. The solution was filtered to remove unchanged phosphonium salt. Concentration of the solution gave colorless needles, m. p. 147∼150°C (1.46 g., 47%), which were recrystallized from cyclohexane yielding trans, trans isomer (II), m. p. 152∼153°C (lit.[4] 152∼153°C).

Filtrate A was extracted with light petroleum (200 ml.) and the extract was washed, dried and chromatographed on alumina. The column (2× 25 cm.) was eluted with light petroleum to give eight 50 ml. fraction. The fractions 3-8 gave the same electronic spectra with that of Zechmeister's trans, cis isomer (UV $\lambda_{\max}$ mμ: 240, 314. $\lambda_{\text{infl.}}$ 247 (in *n*-hexane)) and afforded a colorless liquid, 0.918 g. (30%), which transformed into II, when it was exposed to direct sun light.

***trans*, *trans*, *trans*- and *trans*, *cis*, *trans*-1,6-Diphenylhexatriene (IV and V).**—The phosphonium bromide (I, 4.6 g., 0.01 mol.) and cinnamaldehyde (1.3 g., 0.01 mol.) in anhydrous ethanol (20 ml.) were treated with lithium ethoxide (from 0.1 g. of lithium) in 70 ml. of anhydrous ethanol as described in the case of diphenylbutadiene. The reaction mixture was stirred for 8 hr. precipitating leaflets (1.3 g.), which were collected by filtration and had m. p. 192∼194°C. Recrystallization from ethanol-dioxane (1 : 2) gave pure all-trans isomer (IV), 0.7 g. (30%), m. p. 198∼199°C (lit.[3] 203°C). UV $\lambda_{\max}$ mμ (log ε) : 242 (3.98), 336 (4.80), 351.5 (4.93), 371 (4.80) (in *n*-hexane).

Found : C, 93.01 ; H, 6.87. Calcd. for $C_{18}H_{16}$: C, 93.06 ; H, 6.94%.

The above-mentioned mother liquor was diluted with water (100 ml.) precipitating pale yellow crystals. The crude crystals were collected by filtration, dried and chromatographed on alumina (2× 30 cm. column) in a dark place. The column was eluted with light petroleum-benzene (19 : 1, 200 ml. followed by 7 : 3, 600 ml.) to afford ten 50 ml. fractions. The fractions 4-10 gave pale yellow needles, m. p. 103∼109°C, 650 mg. (28%) ; these were recrystallized from water-ethanol (2 : 3) to give central cis isomer (V) as pale yellow long needles, m. p. 109∼110°C (lit.[3] 107°C). UV $\lambda_{\max}$ mμ (log ε) : 260.5 (4.33), 268.5 (4.33), 336 (4.65), 351 (4.73), 369 (4.55) (in *n*-hexane).

Found : C, 93.04 ; H, 6.89. Calcd. for $C_{18}H_{16}$: C, 93.06 ; H, 6.94%.

Reduction of Ethynylstyrylcarbinol (X) with Lithium Aluminum Hydride.—Ethynylstyrylcarbinol (X), colorless needles, m. p. 68∼69°C (66%), was prepared according to Campbell and his coworker[4].

To a suspension of lithium aluminum hydride (3.8 g., 0.1 mol.) in anhydrous ether (400 ml.), a solution of the carbinol (X, 6 g., 0.038 mol.) in anhydrous ether (60 ml.) was added dropwise under stirring and the mixture was refluxed for 30 min. to afford a greenish solution. After cooling, a small amount of ethyl acetate was added into the solution to decompose an excess of the metal hydride and then water (200 ml.) was added. The organic layer was separated by decantation and the residue was washed with two 20 ml. portions of ether. The combined organic layer and washings were washed with water and dried over magnesium sulfate in the presence of a minor amount of hydroquinone. The residual colorless oil obtained by evaporating the solvent was distilled in vacuo to yield 5-phenyl-1-penten-3-ol (XIV), b. p. 73∼74.5°C/0.2 mmHg, 4.8 g. (78%). UV $\lambda_{\max}$ mμ : 254.5, 259, 261.5, 264.5, 268.5 (in *n*-hexane). IR : 3400, 1040 (OH) ; 1650, 993, 925 ($-CH=CH_2$) ; 760, 710 (Ph-) cm^{-1}.

Found : C, 81.12 ; H, 8.84. Calcd. for $C_{11}H_{14}O$: C, 81.44 ; H, 8.70%.

Triphenyl-5-phenyl-2, 4-pentadienylphosphonium Bromide (VI).—The hydrogenation of the ethynylcarbinol (X, 23.6 g., 0.15 mol.) in anhydrous tetrahydrofuran (200 ml.) over Lindlar's catalyst (1 g.) resulted in the uptake of ca. 1.1 mol. of hydrogen. After removal of the catalyst and the solvent, the residue was distilled in vacuo, yielding styrylvinylcarbinol (XI) as colorless oil, b. p. 91∼94°C/0.1 mmHg, 21.8 g. (90.8%). A solution of the vinylcarbinol (XI, 21 g.) in aqueous dioxane (70%, 300 ml.) was treated with concentrated sulfuric acid (5 ml.) at 40∼50°C for 2 hr. The reaction mixture was poured into water (1 l.) and extracted with ether. The ethereal extract was washed successively with aqueous potassium carbonate and water and dried over magnesium sulfate. The colorless solid obtained by evaporation of ether was recrystallized three times from light petroleum to give 5-phenyl-2, 4-pentadienol (XII), m. p. 73∼78°C, 5 g. (24%).

To a solution of the crude pentadienol (XII, 3.2 g.) in chloroform (100 ml.) was added dropwise a solution of phosphorus tribromide (2 g.) in chloroform (30 ml.), and the crude bromide XIII was isolated according to the usual method. A solution of triphenylphosphine (10 g.) in toluene (80 ml.) was added to a solution of the crude bromide in toluene (20 ml.), precipitaing a white phosphonium salt. The reaction was allowed to proceed overnight without external heating and the reaction mixture was then stirred at 40∼50°C for 6 hr. After cooling, the light brown oil deposited was immediately crystallized. The crude crystals were filtered and washed with toluene containing a small amount of ethanol to yield slightly brownish white crystals of phosphonium bromide VI, m. p. ca. 236∼240°C, in a yield of 5.8 g.

***trans*, *trans*, *trans*- and *trans*, *trans*, *cis*-1, 6-Diphenylhexatriene (IV and VII).**—A solution of lithium ethoxide in anhydrous ethanol (from 0.05 g. of lithium in 50 ml. of anhydrous ethanol) was

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* All melting points are not corrected.

added dropwise to a stirred suspension of the phosphonium bromide (VI, 3 g., 6.2 mmol.) and benzaldehyde (0.8 g., 7.5 mmol.) in anhydrous ethanol (20 ml.) in a dark place. After stirring for 7 hr. at room temperature, a deposition of brownish plates was observed. The reaction mixture was diluted with water and extracted with a mixture of benzene-light petroleum. The crystals, precipitated on standing the mixture, were collected by filtration (filtrate A) and recrystallized from aqueous dioxane yielding all-trans isomer (IV) as yellow plates, m. p. 194~198°C, in a yield of 0.2 g. (14%).

Filtrate A was chromatographed on alumina from benzene-light petroleum (b. p. 60~70°C) (9 : 1 followed by 4 : 1) to afford six 50 ml. fractions. The fractions 4–6 afforded colorless oil, 241 mg. (17%), which exhibited the same electronic spectra with that of Zechmeister's *trans, trans, cis*-1, 6-diphenylhexatriene (VII). UV $\lambda_{\max}$ mμ : 256, 263, 338 (in *n*-hexane).

All-*trans*- and *trans, cis, trans, trans*-1, 8-Diphenyloctatetraene (VIII and IX).—A stirred suspension of phosphonium bromide (VI, 2.5 g., 5.15 mmol.) and cinnamaldehyde (0.8 g., 16 mmol.) in anhydrous ethanol (20 ml.) was mixed with a solution of a small excess of lithium ethoxide in ethanol and stirred at room temperature for 10 hr. After standing overnight, the mixture was diluted with water precipitating a crystalline solid. This solid was separated, dried and digested with a small amount of chloroform. The insoluble part was recrystallized from the same solvent yielding all-trans isomer (VIII) as brownish yellow plates, m. p. 229~233°C, 0.3 g. (23%). This was recrystallized twice from the same solvent to give an analytical sample, m. p. 235~236.5°C (lit.[3] 235°C). UV $\lambda_{\max}$ mμ (log ε): 242 (4.06), 354 (4.89), 372.5 (5.04), 394.5 (4.95) (in *n*-hexane).

Found : C, 92.66 ; H, 6.59. Calcd. for $C_{20}H_{18}$: C, 92.98 ; H, 7.02%.

The soluble part obtained by evaporating chloroform was resolved in benzene-light petroleum (b. p. 60~70°C) (1 : 9) and chromatographed on alumina (2×30 cm.). The column was eluted with benzene-light petroleum (1 : 9, 1 : 4 and 1 : 1, successively) and subsequently with benzene to divide into twenty 50 ml. fractions. The fractions 5–14 gave yellow crystals, m. p. 129~136°C, 292 mg. (22%), which was recrystallized from light petroleum (b. p. 60~70°C) yielding pure *trans, cis, trans, trans*-1, 8-diphenyloctatetraene (IX) as yellow needles, m. p. 132.5~133.5°C (lit.[3] 139~141°C). UV $\lambda_{\max}$ mμ (log ε) : 236 (4.09), 246.5 (4.06), 274.5 (4.34), 284 (4.39), 353 (4.65), 371 (4.76), 392 (4.61) (in *n*-hexane).

Found : C, 93.00 ; H, 6.83. Calcd. for $C_{20}H_{18}$: C, 92.98 ; H, 7.02%.

All-*trans*- and Mono-*cis*-*p*-styryl-1, 4-diphenylbutadiene (XVI and XVII).—A stirred suspension of *p*-stilbenealdehyde (2.1 g., 0.01 mol.) and the phosphonium bromide (I, 4.6 g., 0.01 mol.) in absolute ethanol (30 ml.) was treated with a solution of lithium ethoxide (from 0.1 g. of lithium) in anhydrous ethanol (70 ml.) and the mixture was stirred at room temperature for 18 hr. After standing overnight, the crystals deposited were separated by filtration and digested with benzene (120 ml.). The insoluble product was combined with the other crop which was obtained by the chromatography described below, and recrystallized from chlorobenzene to give all-trans isomer (XVI), m. p. 258~259°C, 1.42 g. (46.1%).

Found : C, 93.41 ; H, 6.58. Calcd. for $C_{24}H_{20}$: C, 93.46 ; H, 6.54%.

The above-mentioned soluble part in benzene was chromatographed on alumina (2×30 cm.) and there was obtained a solid, 0.88 g. (28.6%), m. p. 108~115°C, recrystallization of which from aqueous ethanol (90%) gave mono-cis isomer (XVII), m. p. 115~116°C as light yellow plates with a green fluorescence.

Found : C, 93.07 ; H, 6.50. Calcd. for $C_{24}H_{20}$: C, 93.46 ; H, 6.54%.

All-*trans*-, Mono-*cis*- and Di-*cis*-*p*-bisphenylbutadienylbenzene (XVIII, XIX and XX).—To a suspension of the phosphonium bromide (VI, 1.8 g., 0.037 mol.) and terephthalaldehyde (2.4 g., 0.018 mol.) in anhydrous ethanol (70 ml.) was added a solution of lithium ethoxide (from 0.3 g. of lithium) in anhydrous ethanol (75 ml.) under stirring at room temperature. After stirring for 3 hr., the mixture was allowed to stand overnight, and then stirred at 40~50°C for 30 min., cooled and diluted with water (150 ml.). The yellow solid precipitated was collected, dried, digested with benzene and filtered (filtrate A). The insoluble solid was recrystallized from chlorobenzene yielding all-trans isomer (XVIII) as yellow plates, m. p. 278~279.5°C, 1.15 g. (18%).

Found : C, 93.06 ; H, 6.64. Calcd. for $C_{25}H_{22}$: C, 93.37 ; H, 6.63%.

Filtrate A was chromatographed on alumina. Elution was carried out with light petroleum (b. p. 60~70°C), benzene-light petroleum (b. p. 60~70°C) and finally with benzene. The crude material obtained from the light petroleum eluate (150 ml.) was recrystallized three times from the same solvent to yield di-cis isomer (XX) as pale yellow fine needles, m. p. 120.5~121°C, 0.5 g. (8%).

Found : C, 93.06 ; H, 6.65. Calcd. for $C_{26}H_{22}$: C, 93.37 ; H, 6.63%.

Later fractions gave, on recrystallization from benzene-light petroleum, pure mono-cis isomer (XIX), as light yellow plates, m. p. 153~154°C, 1.2 g. (19%).

Found : C, 93.31 ; H, 6.83. Calcd. for $C_{26}H_{22}$: C, 93.37 ; H, 6.63%.

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