*Alternant Conjugate Systems. II. Syntheses of Stereoisomeric p-Distyrylbenzenes and Related Compounds**

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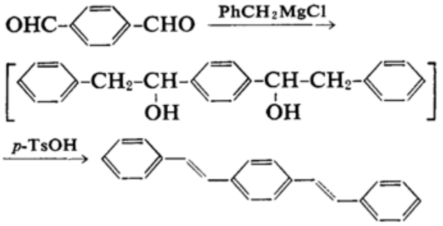
From a study of the ultraviolet absorption spectra of cis-trans isomeric carotenoids, Zechmeister and Pauling¹⁾ have proposed a so-called "cis-peak rule" to correlate the molecular geometry with the spectrum. But the ultraviolet spectra of 1, 18-diphenyl-3, 7, 12, 16-tetramethyl-octadecanonaenes containing one or two sterically hindered cis-double bonds lack the cis-peak²⁾ which would be expected to appear according to the prediction of Zechmeister. Oroshnik³⁾ has also pointed out from his study of the ultraviolet spectra of sterically hindered retrovitamin A methyl ether and analogous compounds that the validity of Zechmeister's rule may be restricted to sterically unhindered cis-polyenes and that the spectra of hindered cis-polyenes cannot be explained by this rule alone.

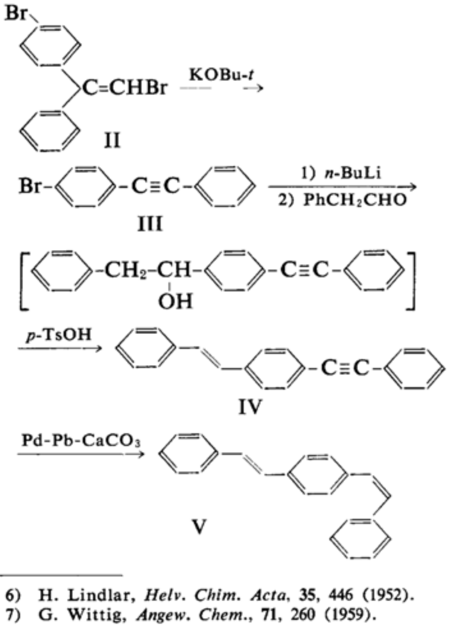
In order to examine the validity of Zechmeister's rule with regard to stilbene derivatives containing hindered cis-double bonds, the authors have carried out the syntheses of three stereoisomers of *p*-distyrylbenzene and related compounds. The present paper deals with the syntheses of these compounds; their spectroscopic properties will be discussed together with those of *p*, *p*′-distyrylstilbenes and related compounds in the following paper of this series.

Among the three possible geometrical isomers of *p*-distyrylbenzene, the trans, trans-isomer was prepared by Kaufmann as early as 1917⁴⁾. Afterward, various methods of preparation of this compound have been proposed⁵⁾. The present authors have synthesized the trans-trans compound I according to the following series of reactions.



I

It is well-known that the ethylenic compound obtained by a dehydrohalogenation or dehydration reaction contains only a small amount of cis-isomer and that the partial hydrogenation of an acetylenic compound over Lindlar's catalyst is regarded as the most practical method obtaining cis-ethylenic compound⁶⁾. More recently, it has been reported in some cases that the Wittig reaction⁷⁾ affords cis-compound together with trans-isomer. The authors have found during the course of the synthetical studies of stilbene homologues that the Wittig reaction is feasible for the synthesis of cis-isomer. Therefore, the second isomer, the *trans, cis-p*-distyrylbenzene (V), was prepared by the above-mentioned two methods.



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* For a preliminary announcement of this study, see This Bulletin, **33**, 711 (1960).

1) L. Zechmeister, L. Pauling et al., *J. Am. Chem. Soc.*, **65**, 1940 (1943); L. Zechmeister, *Chem. Revs.*, **34**, 267 (1944); *Experientia*, **10**, 1 (1954).

2) C. F. Garber, C. H. Eugster and P. Karrer, *Helv. Chim. Acta*, **35**, 1580 (1952); **36**, 562 (1953).

3) W. Oroshnik and A. D. Mebane, *J. Am. Chem. Soc.*, **76**, 5719 (1954).

4) H. Kaufmann, *Ber.*, **50**, 524 (1917).

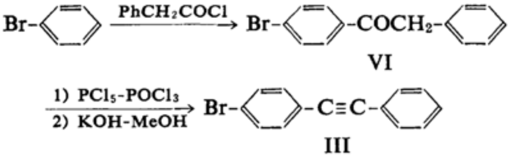
5) a) G. Drefahl and G. Plötner, *Chem. Ber.*, **91**, 1274 (1958); b) J. Dale, *Acta Chem. Scand.*, **11**, 971 (1957); c) K. Friedrich and H. G. Henning, *Chem Ber.*, **92**, 2944 (1959); T. W. Campbell and R. N. McDonald, *J. Org. Chem.*, **24**, 1246 (1959).

6) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

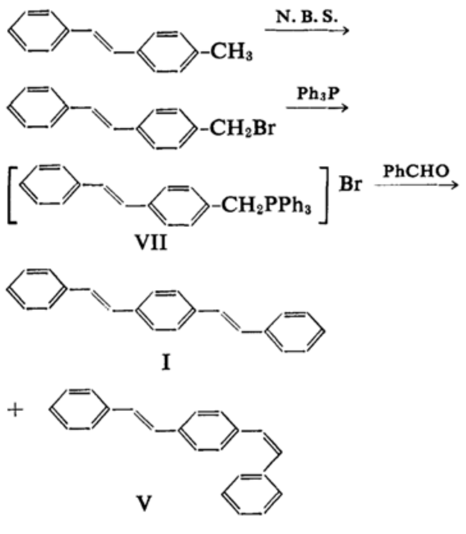
7) G. Wittig, *Angew. Chem.*, **71**, 260 (1959).

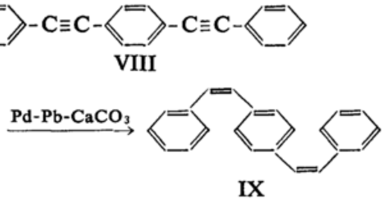
The corresponding acetylenic analogue, *p*-styryltolan (IV), was synthesized according to the following scheme from *p*-bromotolan (III), which is prepared by means of a Fritsch-Buttenberg-Wiechell rearrangement[8] of *α*-*p*-bromophenyl-*β*-bromostyrene (II).

p-Bromotolan (III) was also obtained by a dehydrochlorination of the ketodichloride of *p*-bromodesoxybenzoin (VI). This method has, however, been found to be less advantageous owing to the low yield of the Friedel-Crafts reaction for the preparation of VI.

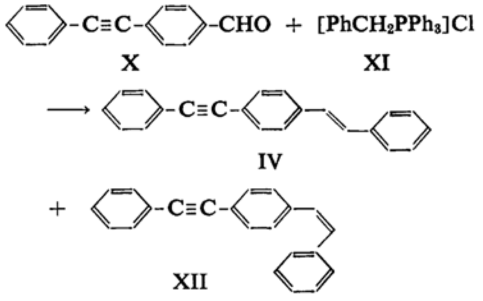


p-Bromomethylstilbene which was derived from *p*-methylstilbene was converted to phosphonium salt VII. The reaction of the salt VII with benzaldehyde yielded *trans*, *trans*-distyrylbenzene and *trans*, *cis*-distyrylbenzene (V) in about the same yield. The trans, cis-isomer V thus obtained was found to be identical with the trans, cis-isomer derived from acetylenic analogue by partial hydrogenation.





The third isomer, *cis*, *cis*-*p*-distyrylbenzene (IX), was prepared by the double partial hydrogenation of *p*-bisphenylethynyl-benzene (VIII)[9] over Lindlar's catalyst*.



The reaction of tolanaldehyde (X)[10] with benzyltriphenylphosphonium chloride (XI) also gave *trans*-*p*-styryltolan (IV) and *cis*-*p*-styryltolan (XII) in about equal yields. The formation of an equal amount of cis-isomer was also observed in the Wittig reaction of other stilbene homologues, which experiments will be reported on in a following paper. The formation of a four-membered cycle in an intermediate stage of Wittig reaction is generally accepted, and the formation of cis- and trans-isomers in an almost equal yield seems to be rather peculiar on the basis of this hypothesis, since the intermediate of the cis-isomer is

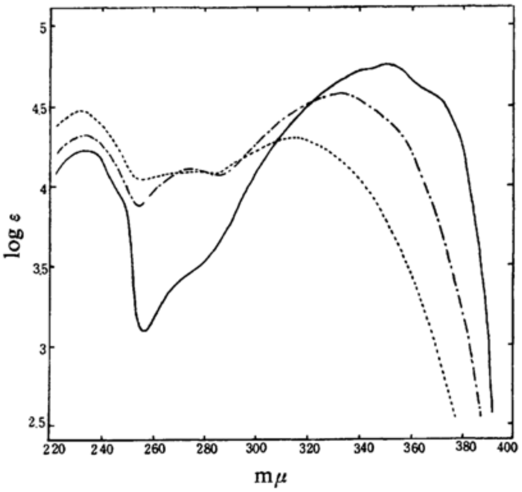


Fig. 1. The ultraviolet spectra of *p*-distyrylbenzenes in *n*-hexane.
trans, *trans*, ——; *trans*, *cis*, —·—·; *cis*, *cis*, ----

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8) W. P. Buttenberg, *Ann.*, **279**, 327 (1894); P. Lipp, *Ber.*, **56**, 570 (1923); G. H. Coleman et al., *J. Am. Chem. Soc.*, **56**, 132 (1934); **58**, 2310 (1936); M. Bouis, *Ann. Chim.*, [10] **9**, 402 (1928); A. A. Bothner-By, *J. Am. Chem. Soc.*, **77**, 3293 (1955).

9) S. Misumi, This Bulletin, **34**, 1827 (1961).

* Dale[5a] assigned the configuration of *trans*, *cis*-distyrylbenzene to a compound of m. p. about 95°C., which was isolated from the products of the photoisomerization of trans, trans-isomer. However, the ultraviolet spectra of pure trans, cis- and cis, cis-compounds indicate that the compound of m. p. about 95°C is possibly a mixture of trans, cis- and cis, cis-isomers.

10) G. Drefahl and G. Plötner, *Chem. Ber.*, **93**, 990 (1960).

TABLE I. PROPERTIES OF *p*-DISTYRYLBENZENES AND RELATED COMPOUNDS

	M. p., °C	UV spectrum, $\lambda_{max}(\varepsilon_{max})$, m$\mu$			
t—*t*	266 ~267	232 (16200)		350 (57000)	
t—*c*	114 ~114.5	232 (20000)	273 (12200)	331 (36500)	
c—*c*	86.5~ 87.5	232 (27600)	270 (10900)	314 (17700)	
A—A	181.5~182	222 (20800)		318 (45400)	337 (27000)
A—*t*	211 ~211.5	230 (26600)		333 (55300)	
A—*c*	78 ~ 78.5	227 (26800)	271 (17700)	312 (32900)	

t, *c* and A denote *cis*-ethylenic, *trans*-ethylenic and acetylenic linkage, respectively.

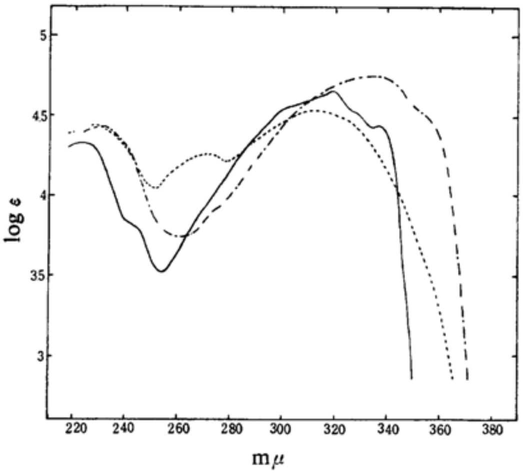

Fig. 2. The ultraviolet spectra of *p*-styryltolans (IV, *trans*, —·—· ; XII, *cis*, ----) and distolan (VIII, ——) in *n*-hexane.

probably less stable than that of the trans-isomer owing to the steric interaction of two phenyl groups.

The ultraviolet spectra of the above-mentioned three stereoisomeric *p*-distyrylbenzenes and two *p*-styryltolans are presented in Figs. 1 and 2. The spectroscopic and physical properties of these compounds are summarized in Table I.

The shifts of the wavelength, where the absorption maxima of these compounds at the longest wavelength appear, represent an interesting feature. The introduction of a cis-double bond or an acetylenic bond instead of a trans-double bond caused a blue shift of ca. 18 and 16 mμ respectively. The absorption intensities of λ_{max} at the longest wavelength of *trans-trans*, *trans*-acetylene and acetylene-acetylene compounds diminish with the increase in the amount of acetylenic linkage. Usually the absorption intensity of polyyne compound was found to be 2.6 fold as large as that of polyene compound. This phenomenon has been explained in terms of the larger number of π-electrons in triple bond and the linear geometry of polyyne compound[11]. As stated above, this is not valid for the absorption intensities of an alternant conjugate system of the styryltolan type. The decrease of absorption intensity by the introduction of aceylenic linkage seems to be attributable to an enhancement of the free rotation of the *p*-phenylene group, which may decrease the probability of transition of the full conjugate system.

The photoisomerizations and the discussions concerning the cis-peak of these compounds will be reported in the following paper together with those of the compounds of the distyrylstilbene series.

Experimental*

***trans*, *trans*-*p*-Distyrylbenzene (I).** — *a) From Terephthalaldehyde*.—To a stirred solution of benzylmagnesium chloride (from magnesium, 3.75 g. and benzyl chloride, 20.0 g., 0.158 mol.) in dry ether (100 ml.) was added dropwise terephthalaldehyde[12] (10.0 g., 0.075 mol.) in dry tetrahydrofuran (150 ml.); this mixture was refluxed for 3 hr. A saturated aqueous solution of ammonium chloride was added to the cooled mixture and the organic layer separated by decantation. The inorganic residue was extracted with ether and the extract combined with the organic layer. The solvent was distilled from the combined solution to give the crude glycol (27 g.). A solution of the crude glycol (25 g.) in dry toluene (220 ml.) containing *p*-toluenesulfonic acid (0.8 g.) was refluxed for 2 hr. The crystals deposited from the cooled reaction mixture were filtered and recrystallized from chlorobenzene, yielding *trans*, *trans*-*p*-distyrylbenzene (I), on light greenish yellow plates, m. p. 261~262.5°C. The viscous tarry material obtained by concentration of the mother liquor was treated with chlorobenzene, yielding a second crop of I. The crude material was repeatedly recrystallized from chlorobenzene to give I. The total yield was found to be 4.3 g. (22%). Further recrystallization from the same solvent afforded pure I, m. p. 266~267°C.

Found: C, 93.59; H, 6.76. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43%.

b) From p-Styrylbenzyl-triphenylphosphonium Bromide (VII).—I was obtained from VII together with *trans*, *cis*-*p*-distyrylbenzene (V). The details will be described in section b) on the preparation of V.

***p*-Bromotolan (III).**—The bromostyrene (II) was prepared from *p*-bromoacetophenone[13] via three

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[11] F. Bohlmann, *Angew. Chem.*, 65, 385 (1953).

* All melting points are uncorrected.

[12] J. M. Snell and A. Weissberger, "Org. Synth.", Col. Vol. I (1948), p. 109.

[13] R. Adams and C. R. Noller, ibid., (1955), p. 788.

steps according to the method of Bothner-By[8] in a yield of 26%, trans-form, m. p. 105.5~106.5°C. A solution of potassium *tert*-butoxide in *tert*-butyl alcohol (from potassium, 3 g. and *tert*-butyl alcohol, 40 ml.) was stirred with the finely powdered *p*-bromostyrene (II, 17 g., 0.05 mol.), and the mixture was refluxed for 3 days. To the cooled reaction mixture, *tert*-butyl alcohol (180 ml.) and water (360 ml.) were added, precipitating a colorless solid. The solid was filtered, washed with water and dried. The recrystallization of solid from light petroleum yielded III, in the form of colorless plates, m. p. 82~83°C, 10.5 g. (83%).

Found: C, 65.81; H, 3.54; Br, 30.73. Calcd. for $C_{14}H_9Br$: C, 65.39; H, 3.53; Br, 31.07%.

***trans-p*-Styryltolan (IV).** — *a) From p-Bromotolan (III).*—A little excess of *n*-butyllithium in ether (prepared from *n*-butyl chloride and lithium, the concentration being estimated by titration with 0.1 N hydrochloric acid) was slowly stirred into a solution of *p*-bromotolan (10.3 g., 0.04 mol.) in dry ether (100 ml.) in an atmosphere of pure nitrogen, and the mixture was refluxed for 2.5 hr. To the resultant orange yellow solution of tolan-lithium was added phenylacetaldehyde (6 g., 0.05 mol., freshly prepared from the dimethylacetal) in dry ether (65 ml.) at room temperature. A gradual change of the orange yellow color of the mixture to a white suspension was observed. Then the mixture was refluxed for 3 hr. to complete the reaction. A slow stream of pure nitrogen was introduced continuously into the reaction flask throughout these operations. A saturated aqueous solution of ammonium chloride (5.5 g.) and water were successively added to the cooled reaction mixture. The organic layer was separated. The organic layer and the ethereal extract were combined, washed with water and dried. The orange-colored oily residue obtained on evaporating the solvent was dissolved in dry toluene (150 ml.) containing *p*-toluenesulfonic acid (0.5 g.). The solution was refluxed, and the water formed was removed continuously by means of a water-separator. The crystals deposited on cooling the mixture were filtered and the mother liquor concentrated, resulting in the deposition of a second crop of crystals. The combined crystals were recrystallized twice from benzene, yielding *trans-p*-styryltolan, in the form of colorless leaflets, m. p. 211~211.5°C, 3.5 g. (31%).

Found: C, 94.09; H, 5.83. Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75%.

b) From p-Tolanaldehyde (X) by Wittig Reaction. —The reactions described below were carried out in a dark place. *p*-Tolanaldehyde[10] (1 g., 4.85 mmol.) and benzyltriphenylphosphonium chloride (2 g., 5.15 mmol., m. p. 313~315°C) were mixed with absolute ethanol (25 ml.). To the stirred suspension was added an excess of lithium ethoxide in absolute ethanol. After stirring for 8.5 hr. at room temperature, the deposited pale yellow solid (0.7 g., a mixture of *trans-p*-styryltolan and phosphonium salt) was filtered. The solid was dissolved in benzene and the solution passed through a column of alumina to remove the phosphonium salt. The crude crystals obtained on evaporating the filtrate were recrystallized from benzene, yielding *trans-p*-styryltolan, in the form of colorless leaflets, m. p. 210~211°C, 0.5 g. (35.7%); this was found to be identical with the specimen obtained by the above-mentioned method a) by mixed melting point determination.

***cis-p*-Styryltolan (XII).** — The following operations were carried out in a dark place. The above-mentioned mother liquor of the Wittig reaction was diluted with water, precipitating a mixture of a solid and a brown oily material. The precipitate was dissolved in light petroleum. The solution was passed through a column of alumina and eluted with the same solvent. A colorless solid (m. p. 76~78°C) obtained from the eluate was recrystallized from aqueous ethanol, giving *cis-p*-styryltolan (XII), m. p. 78~78.5°C, colorless needles, 0.6 g. (49.2%).

Found: C, 93.88; H, 5.69. Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75%.

***trans, cis-p*-Distyrylbenzene (V).** — *a) Partial Reduction of trans-p-Styryltolan (IV).*—The following operations were carried out in a dark place. Hydrogenation of the styryltolan (IV, 0.1 g.) in tetrahydrofuran (20 ml.) over Lindlar's catalyst resulted in the uptake of ca. 1 mol. of hydrogen. After removal of the catalyst, the solvent was evaporated under a reduced pressure. The residue was mixed with hot ethanol. The hot mixture was filtered to remove a small amount of insoluble trans, trans-isomer. The crystals separated on cooling the filtrate were filtered promptly. The crystals were found to be pure trans, cis-isomer V, in the form of colorless plates, m. p. 114~114.5°C.

Found: C, 93.58; H, 6.44. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43%.

b) From p-Styrylbenzyl-triphenylphosphonium Bromide (VII).—The following reactions and operations were carried out in a dark place. The phosphonium salt (VII, 2 g., 3.74 mmol.) was added to a solution of benzaldehyde (0.4 g., 3.77 mmol.) in absolute ethanol (60 ml.). Into this suspension was stirred an excess of a solution of lithium ethoxide in absolute ethanol. The mixture was stirred for 3 hr. at room temperature, and the solid was filtered (filtrate A). The solid was digested with boiling ethanol (30 ml.) and the insoluble material (solid B) filtered. The filtrate was cooled to yield trans, cis-isomer (V), m. p. 113.5~114.5°C. This was combined with the second crop, which was obtained on diluting the filtrate A with water and recrystallized from ethanol, yielding pure trans, cis-isomer (V), in the form of colorless plates, m. p. 113.5~114.5°C, 340 mg. (32.3%). This substance showed no depression of the melting point on admixture with the specimen derived by the above-mentioned method a).

Recrystallization of the solid B from chlorobenzene yielded trans, trans-isomer I, in the form of light greenish yellow plates, m. p. 253°C, 370 mg. (35.1%). The mixed melting point determination of this substance with the specimen derived from terephthalaldehyde proved the identity.

Exposure of the mother liquor of recrystallization of trans, cis-isomer to direct sunlight resulted in a deposition of crystals. This crystals were found to be identical with trans, trans-isomer I, m. p. 255°C, 44 mg. (4%).

The total yield of the Wittig reaction was found to be 754 mg. (71.5%).

***cis, cis-p*-Distyrylbenzene (IX)**.—Two moles of hydrogen were absorbed in a period of 18 min. on the hydrogenation of a solution of *p*-bis(phenylethynyl)benzene (VIII, 80 mg.) in tetrahydrofuran (20 ml.) over Lindlar's catalyst. After removal of the catalyst, the solvent was distilled under reduced pressure, yielding crystals. Repeated recrystallization of the crystals from light petroleum afforded cis, cis-isomer IX, in the form of colorless leaflets, m. p. 86.5~87.5°C.

Found: C, 93.79; H, 6.60. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43%.

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