excess sodium nitrite. The solution was stirred for 1 hr. in the cold and 3.3 g. of mercuric bromide and 4.0 g. of potassium bromide in 20 ml. of water was added with swirling. The mixture was allowed to stand at ice temperature for 1 hr. and the brown precipitate was filtered off, washed well with water, and air dried to yield 1.36 g. (120% based on the formula $C_{16}H_9BrN_2 \cdot HgBr_2$ for the salt) of brown powder.

The dry powder was mixed thoroughly with 4 g. of dry potassium bromide in a 50-ml. flask and the mixture was heated in an oil bath at 120° for 0.5 hr. During the heating, the darkening mass became spongy due to gas evolution. The solid was then digested with hot water and extracted with 200 ml. of hot benzene in five portions. The benzene extracts were washed successively with dilute hydrochloric acid, dilute potassium carbonate, and water, and dried over anhydrous magnesium sulfate. Removal of the solvent yielded a small amount of red oil which was eluted from a 6 × 0.5 in. column of activity I neutral alumina (Woelm) with hexane and benzene–hexane (50:50 v./v.) to give 184 mg. of white solid, m.p. 112–118°.

Anal. Calcd. for $C_{16}H_9Br$: C, 68.33; H, 3.20; Br, 28.47. Found: C, 66.72; H, 3.34; Br, 26.83.

A portion of this material was purified *via* the orange picrate, m.p. 150–155°, to give, after recrystallization from petroleum ether, colorless needles, micro m.p. (K) 132–133°. The polarographic reduction and ultraviolet spectrum were taken on this material but there was insufficient pure sample for a second elemental analysis. The mother liquor of the final crystallization gave white needles on concentration, m.p. 130°.

Anal. Found: C, 67.40; H, 3.4.

A second portion of the original material was recrystallized from petroleum ether to give tan crystals, m.p. 126–131°. Thin layer chromatography on silica gel showed two fluorescent spots. Chromatography on a small silica gel column and elution with cyclohexane and methylene chloride gave a yellow first fraction of wide melting range and a second fraction of white crystals, m.p. 131–132.5°. This product was too small for analysis but thin layer chromatography showed a single fluorescent spot on silica gel.

These experiments suggest the use of successive column chromatography on alumina and on silica gel in subsequent preparations.

A second attempt at preparing this compound under closely similar reaction conditions gave only high-melting yellow solid and failed to yield any material melting below 170° which could be eluted from an alumina column.

The somewhat impure 2-bromopyrene (44 mg., 0.16 mmole), obtained above after chromatography of the reaction mixture, was converted to 2-pyrenyllithium with 1.0 mmole of *n*-butyllithium in ether. Tritiated water (25 μl., 1.4 mmoles, 1 c./ml.) was then added with stirring, followed by 12.0 g. (59.5 mmoles) of pyrene. The ether solution was washed with water and dried over anhydrous magnesium sulfate. The pyrene remaining after removal of the ether was recrystallized from absolute ethanol to give, on two successive recrystallizations, pyrene of specific tritium activity 3.35×10^7 and 3.41×10^7 d.p.m./mmole (calcd. on basis of tritiated water: 5.3×10^7 d.p.m./mmole). The second recrystallization gave 7.70 g. (64%) of white plates, m.p. 149–150°.

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Synthesis of Stilbenes. A Comparative Study[1]

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A number of commonly accepted general methods for the synthesis of *trans-* and *cis*-stilbenes are shown to be of limited use. The best methods of preparing these isomers are *via* the Wittig reaction and the decarboxylation of phenylcinnamic acids, respectively, although neither method gave exclusively one isomer. The structures were confirmed by ultraviolet, infrared, and n.m.r. spectra.

The *trans-* and *cis*-stilbenes form an interesting group of compounds for the study of the transmission of substituent effects from one benzene ring to another through a double bond.[2] A number of methods are commonly reported[3] for the synthesis of stilbenes from compounds containing one benzene ring. These include (A) the condensation of benzaldehydes to benzoins followed by a Clemmensen reduction,[4] (B) the dehydration of 1,2-diarylethanol formed by reaction of benzaldehydes with benzylmagnesium halides,[5] (C) the Meerwein reaction of cinnamic acids with benzenediazonium salts,[6,7] and (D) the decarboxylation of phenylcinnamic acids formed by the reaction of benzaldehydes with phenylacetic acids.[8] Other methods such as the direct condensation of benzaldehydes with toluenes[9] and the oxidative coupling of toluenes[10] are only applicable when the methyl group of the toluene is activated by one or more nitro groups.

Although method B has been widely used to prepare stilbesterol derivatives,[5] it is limited to the use of those benzyl halides which form Grignard derivatives, and to benzaldehydes with substituents that do not react with the Grignard reagent. Method C generally gives very poor yields (<20%).[11] The benzoin and phenylcinnamic acid routes (methods A and D) would seem to be general, and the latter is the only route which leads directly to *cis*-stilbenes. In a modification of this method using piperidine as the condensing reagent, *trans*-stilbenes are reported to be formed directly.[12] This latter method also leads to unsymmetrically substituted stilbenes, which is not the case with the benzoin route.

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Recently a further synthesis has become available in the Wittig reaction (E),[13,14] starting with benzyl bromides. An allied method employing organophosphorus reagents and involving benzyl bromide is *via* a diethyl benzylphosphonate.[15] The former method is reported to give both *cis-* and *trans*-stilbenes[13] and the other exclusively *trans*-stilbene.[14]

This publication reports a comparative study of these various general routes to substituted *trans-* and *cis*-stilbenes, except that employing Grignard reagents.

Method A.—The reaction of 2- and 4-chlorobenzaldehyde with potassium cyanide in methanol was found in the present work to give 2,2′- and 4,4′-dichlorobenzils characterized by their melting points and ultraviolet spectra, and not the corresponding benzoins. No product could be isolated from an attempted benzoin reaction with 2,4-dichlorobenzaldehyde. 4-Cyanobenzaldehyde[16] and 3,5-dimethyl-4-nitrobenzaldehyde[17] have previously been shown to give desoxybenzoins. Here, reduction of the crude benzoin reaction product from 4-chlorobenzaldehyde, however, gave *trans*-4,4′-dichlorostilbene, although no stilbenes were obtained by reducing the reaction products from 2-chloro- and 2,4-dichlorobenzaldehyde.

The reduction of anisoin (4,4′-dimethoxybenzoin) under the normal conditions (amalgamated zinc in hydrochloric acid) was found to give a small yield of 1,2-di(4-methoxyphenyl)ethane, with much unreacted anisoin due to its low solubility. Reduction with zinc amalgam in 50% acetic–hydrochloric acid gave desoxyanisoin, as did reduction with zinc dust in boiling acetic acid.

A recent method[18] of reducing benzoin to *trans*-stilbene involves preparing desyl chloride (PhCHCl·CO·Ph) which is then reduced with sodium borohydride. Here the application of this method to anisoin, however, led to the formation of desoxyanisoin. The reduction of desyl chloride with deteriorated sodium borohydride has been reported[18] to give desoxybenzoin, but fresh samples of hydride gave the same results in the present case with anisoin.

Although the reduction of benzoin is the preferred method of preparing *trans*-stilbene itself, this method seems of limited use in synthesizing substituted *trans*-stilbenes.

Method C.—The reaction of 4-nitrocinnamic acid with diazotized 4-nitroaniline afforded *trans*-4,4-dinitrostilbene in 39% yield. Generally this method gives poorer yields[11] of impure product, as would be expected for a reaction involving free radicals. Moreover, the necessary substituted cinnamic acids must be themselves synthesized from benzaldehydes.

Method D.—The decarboxylation of a phenylcinnamic acid would seem to be the most attractive route to *cis*-stilbenes, which can be isomerized to the *trans* isomer.[11a,19] The direct route to a *trans*-stilbene using piperidine for the condensation and decarboxylation was found in the present work to be limited to the reaction of 4-nitrophenylacetic acid, since phenylacetic acid and 2-nitro-, 4-chloro-, and 2-chlorophenylacetic acid did not react with benzaldehyde, and no reaction occurred between 2-chlorophenylacetic acid and 2-chlorobenzaldehyde. A recent publication[20] has shown that the reaction with 4-nitrophenylacetic acid involves direct decarboxylation of 4-nitrophenyl-*trans*-cinnamic acid to the *trans*-stilbene, by a carbanion mechanism.

The decarboxylation of phenylcinnamic acid is usually carried out in quinoline (b.p. 230°) in the presence of copper chromite,[8a] when *cis*-stilbene is the only product. In our hands it proved difficult to remove the last traces of quinoline from the product, particularly when small amounts of material were involved, and other solvents were investigated. No decarboxylation occurred in dimethylaniline (b.p. 192°), and reaction in dimethyl sulfoxide (b.p. 120°) gave about equal amounts of *cis-* and *trans*-stilbene in low yield. However, decarboxylation in collidine (b.p. 175°) gave largely *trans*-stilbenes (85%) with some *cis*-stilbene (15%). That the *trans*-stilbene was not formed by isomerization of the *cis* isomer was shown by the fact that the *cis*-stilbene was recovered unchanged (in 90% yield) on refluxing with copper chromite in collidine for 16 hr.

A number of substituted *cis*-α,β-diphenylacrylic acids (*trans*-α-phenylcinnamic acids) were then prepared by condensation of the appropriate phenylacetic acid and benzaldehyde (see Table I). Decarboxylation was carried out in quinoline with the copper chromite catalyst. The α-4-methyl, α-4-fluoro, and α-2-methoxy acids gave exclusively the 4-substituted *cis*-stilbenes (see Table II). However, α-4-methoxyphenylcinnamic acid gave predominately the *trans*-4-methoxystilbene and the isomeric β-4-methoxy acid gave exclusively this isomer. α-4-Chlorophenylcinnamic acid afforded a low yield (5%) of *cis*-stilbene; it has been

TABLE I

PHYSICAL CONSTANTS OF DIPHENYLACRYLIC ACIDS

Compd.	M.p.,[a] °C.	λ_{max},[b] mμ (ϵ)
α,β-Diphenylacrylic acid	172 (172[c])	277 (10,950) [274 (14,000)[d]]
α-4-Methyl-	168 (173[e])	276 (14,200) [282 (16,200)[e]]
α-4-Methoxy-	156–158 (158–159[f])	270 (13,000) [272 (13,680)[e]]
α-4-Fluoro-	167–168[g]	277 (13,700)
α-4-Chloro-	182–183 (180–181[d])	282 (15,600) [282 (13,500)[d]]
α-2-Methoxy-	136–137[h]	273 (16,000)
α-2-Chloro-	165–168[i]	275 (19,150)
α,β-4,4′-Dichloro-	153–155[j]	286 (19,000)
α-2,4-Dichloro-	155–156[k]	280 (13,700)

[a] Literature values in parenthesis. [b] Literature values in brackets. Data refer to 95% ethanol solution. [c] Ref. 33. [d] Ref. 21. [e] Ref. 11a. [f] C. D. Gutsche, E. F. Jason, R. S. Coffey, and H. E. Johnson, *J. Am. Chem. Soc.*, **80**, 5726 (1958). [g] *Anal.* Calcd. for $C_{15}H_{11}FO_2$: C, 74.38; H, 4.55. Found: C, 74.26; H, 4.65. [h] *Anal.* Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.28; H, 5.41. [i] *Anal.* Calcd. for $C_{15}H_{11}ClO_2$: C, 69.64; H, 4.29. Found: C, 69.92; H, 4.45. [j] *Anal.* Calcd. for $C_{15}H_{10}Cl_2O_2$: C, 61.64; H, 3.42. Found: C, 61.91; H, 3.76. [k] *Anal.* Calcd. for $C_{15}H_{10}Cl_2O_2$: C, 61.64; H, 3.42. Found: C, 61.69; H, 3.38.

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TABLE II

PHYSICAL CONSTANTS OF *cis*-STILBENES

Compd.	B.p.,[a] °C. (mm.)	λ_{max},[b] mμ (ε)	Δλ[c]	Infrared, cm.$^{-1}$
Stilbene	105–110 (2) [134 (10)][d]	278 (10,200)	. . .	694, 916
4-Methyl-	110–112 (2) [108–112 (12)[e]]	278 (13,000) [281 (12,000)[e]]	. . .	695
4-Methoxy-	98–100 (2) [145 (15)[f]]	276 (11,700) [286 (14,000)[e]]	−2	699
4-Fluoro-	110–112 (2)[g]	280 (10,600)	+2	703, 913
2-Methoxy-	185–192 (2) [138–140 (0.1)[h]]	280 (10,500)	+2	696
2-Chloro-	120–122 (2) [118–120 (1.5)[d]]	276 (11,100)	−2	704
2,4-Dichloro-	140–150 (3)[i]	290 (7,500)	+12	693

[a] Literature values are in brackets. [b] Values determined in 95% ethanol. [c] Displacement from *cis*-stilbene. [d] Ref. 34. [e] G Riezebos and E. Havinga, *Rec. trav. chim.*, **80**, 446 (1961). [f] W. H. Brunner and J. Kustatcher, *Monatsh.*, **82**, 100 (1951). [g] *Anal* Calcd. for $C_{14}H_{11}F$: C, 84.85; H, 5.55. Found: C, 84.91; H, 5.85. [h] Ref. 7a. [i] *Anal.* Calcd. for $C_{14}H_{10}Cl_2$: C, 67.74; H, 4.06 Found: C, 68.06; H, 4.28.

previously reported to give traces of this olefin.[21] α-4-Chlorophenyl-4-chlorocinnamic acid gave only *trans*-4,4′-dichlorostilbene, whereas α-2-chlorophenylcinnamic acid formed about equal amounts of the *cis*- and *trans*-stilbenes. These differences in the courses of the decarboxylation of the substituted phenylcinnamic acids have been shown[20] to be due to the ready isomerization of the reactive *cis*-stilbenes under the conditions of the reaction.

Method E.—The Wittig reaction of the yield from benzyltriphenylphosphonium chloride with benzaldehyde in the presence of sodium ethoxide in ethanol has been reported to give nearly equal amounts of *cis* and *trans* isomers (see Table III), and this was confirmed in the present work. The use of potassium *t*-butoxide in *t*-butyl alcohol, however, reduced the proportion of *cis*-stilbene to 25%. A recent publication[14b] indicates that the addition of lithium bromide to a solution of sodium ethoxide in dimethylformamide–benzene increases the proportion of *cis* isomer (to 81%). However, when lithium bromide, dissolved in dimethylformamide and not prepared *in situ*, was used here, the increase was small (to 53%).

TABLE III

SYNTHESIS OF STILBENES *via* WITTIG REACTION

Phosphorane	Benzaldehyde	Base	% *cis*[a]
H	H	BuLi–C_6H_6	29[b]
H	H	*t*-BuOK	25[c]
H	H	EtONa	54,[b] 45[c]
H	H	DMF–EtONa–LiBr	81,[b] 53[c]
H	4-MeO, 2-Cl	EtONa	0[c]
H	2,4-Cl_2, 4-Cl	*t*-BuOK	0[c]
H	4-MeO, 4-NO_2	DMF, etc.	0[c]
H	4-MeO, 4-HO, 3-HO	EtONa	0[d]
4-Me, 4-NO_2, 3-Br	H	EtONa	0[d]
4-NO_2	4-MeO	BuLi–C_6H_6	0[e]
4-MeO	4-NO_2	BuLi–C_6H_6	48[e]

[a] Normalized to 100%. [b] Ref. 14. [c] Present work. [d] Ref. 21. [e] Ref. 23.

In our hands the Wittig reaction with 4-methoxy- and 2-chlorobenzaldehydes using sodium ethoxide gave only *trans*-stilbene, as did the reaction employing 4-methoxy- and 4-nitrobenzaldehydes with sodium ethoxide and lithium bromide in dimethylformamide. Reaction of 4-chloro- and 2,4-dichlorobenzaldehyde in *t*-butyl alcohol also gave exclusively *trans*-stilbene. It has been reported that the reactions of 4-methoxy- and 3- and 4-hydroxybenzaldehydes with phenylmethylenetriphenylphosphorane, and of 4-methyl-, 4-nitro-, and 3-bromophenylmethylenetriphenylphosphorane with benzaldehyde and sodium ethoxide give only *trans*-stilbenes.[22] However, the over-all yields reported were low in many cases, and the mother liquors were not distilled to isolate any liquid *cis*-stilbenes, as was done in the present work. A recent publication[23] reports that the reaction of 4-nitrobenzaldehyde with 4-methoxyphenylmethylenetriphenylphosphorane gives 48% *cis*-4-nitro-4′-methoxystilbene, whereas only the *trans* isomer is formed from 4-methoxybenzaldehyde and 4-nitrophenylmethylenetriphenylphosphorane. The base used in these reactions was butyllithium, which gives the lowest percentage of *cis*-stilbene in the case of the unsubstituted components (see Table III).

Method F.—Wadsworth and Emmons[15] employed sodium hydride in ethylene glycol dimethyl ether (b.p. 83°) for the reaction of diethyl benzylphosphonate with benzaldehyde and found that *trans*-stilbene was formed exclusively. They suggested that the reaction may involve a direct route leading to *trans*-stilbene and also proceed *via* a cyclic intermediate, similar to that originally postulated[13] for the Wittig reaction, leading to both *cis*- and *trans*-stilbenes. The absence of the *cis* isomer in the product was explained as due to its isomerization to the *trans* product at the relatively high temperature (85°) of the reaction. In the present work, using sodium hydride in dimethylformamide–benzene (b.p. *ca.* 125°) only *trans*-stilbene was again formed, and moreover, *cis*-stilbene was found not to isomerize to the *trans* isomer under these conditions. Thus, it appears that the reaction proceeds by the direct mechanism.

The reaction with 2-chloro- and 4-methoxybenzaldehyde was also found to afford the corresponding *trans*-stilbenes.

In summary it appears that the best general method for preparing *cis*-stilbenes is by the decarboxylation of phenylcinnamic acids in quinoline. However, the Wittig reaction or the benzylphosphonate route offer the best methods of directly preparing *trans*-stilbenes.

Spectra. The structures of the *cis*- and *trans*-stilbenes were confirmed by the determination of their spectra. The *cis*-stilbenes (Table II) all showed a sharp n.m.r. peak at τ 6.50 ± 0.1 (in carbon tetrachloride).[24]

The *trans*-stilbenes (Table IV) gave a strong characteristic infrared peak at 948–971 cm.$^{-1}$ (de Tar and Carpino[19] report 963.4 cm.$^{-1}$). The *cis*-stilbenes (Table II) gave a peak of medium intensity at 694–704

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TABLE IV

PHYSICAL CONSTANTS OF *trans*-STILBENES

Compd.	M.p.,[a] °C.	λ_{max},[b] mμ (ε)	Δλ[c]	Infrared, cm.$^{-1}$
Stilbene	124 (124[d])	296 (28,100), 305 (26,700)	...	952
4-Methyl-	119 (120[e])	300 (28,900), 310 (27,800)	+4	959
4-Methoxy-	136 (136–137[f])	306 (29,000), 310 (27,500)	+10	959
4-Chloro-	129 (129[g])	348 (27,400)	+4	954
4-Nitro-	155 (155[h])	348 (27,300)	+52	*i*
2-Chloro-	39–40 (39–40[j])	295 (19,300)	−1	961
2,4-Dichloro-	76 (71[h])	330 (18,100)	+34	952
4,4′-Dichloro-	176 (177[h])	305 (33,700), 315 (32,900)	+9	952
4,4′-Dinitro-	282 (282[k])	303 (18,610)	+7	971

[a] Literature values are in parenthesis. [b] Values determined in 95% ethanol. [c] Displacement from 296-mμ band of *trans*-stilbene. [d] Ref. 4a. [e] F. Sacardiglia and T. D. Roberts, *Tetrahedron*, **3**, 197 (1958). [f] Ref. 34. [g] R. Anschutz, *Ber.*, **60B**, 1320 (1927). [h] Ref. 32. [i] Insoluble in carbon disulfide. [j] Ref. 36. [k] Ref. 20.

cm.$^{-1}$ (lit.[19] 780 cm.$^{-1}$). A peak at *ca.* 920 cm.$^{-1}$ [19,25] was found to be less characteristic.

The *trans*-stilbenes showed maxima at 300–350 mμ[2] (ε 20,000–30,000), and in the cases of stilbene and 4-methoxy-, 4-chloro-, and 4-methylstilbene the maxima appeared as a doublet (Table IV). The *cis*-stilbene absorbed at lower wave lengths (270–290 mμ) and with a lower intensity (10,000–13,000). This *cis*- and *trans*-azobenzenes also show such differences,[26] which are attributable to steric hindrance to coplanarity in the *cis* compounds. The *trans-o*-stilbenes absorbed with lower intensities than their *para* isomers and this is also due to the same effect.[27] Comparison of the intensities of the pairs of *para*- and *ortho*-substituted *trans*-methoxy- and chlorostilbenes gave an angle of deformation (θ) to coplanarity in the *ortho* isomer of 18 and 34°, respectively (from $\cos^2 \theta = \epsilon\ ortho/\epsilon\ para$[26]). The corresponding *trans*-chloroazobenzenes gave $\theta = 35°$.[26]

Experimental

Benzoin Method (A).—Benzoin was prepared from benzaldehyde and potassium cyanide in methanol[28] in 80% yield. Similar reaction with 2- and 4-chlorobenzaldehyde gave 2,2′- (60%) and 4,4′-dichlorobenzil (55%), which were chromatographed on alumina from benzene–hexane: m.p. 128 and 198°, respectively (lit. m.p. 128°[29] and 195–196°,[30] respectively); light absorption, λ_{max} 258 mμ (ε 3100) and λ_{max} 272 (25,900), respectively; no infrared hydroxyl band. No pure compound could be isolated from the reaction with 2,4-dichlorobenzaldehyde.

Reduction of Benzoin.—The reduction of benzoin with amalgamated zinc powder and hydrochloric acid[4] gave *trans*-stilbene, m.p. 116–121° (lit.[4a] m.p. 124°). This melting point could not be raised by recrystallization or chromatography on alumina from benzene–hexane.

Reduction of the crude product of the condensation of 4-chlorobenzaldehyde with potassium cyanide gave *trans*-4,4′-dichlorostilbene, m.p. 175° (lit.[30] m.p. 175–176°). No product could be isolated from the reduction of the crude reaction products from 2-chloro- and 2,4-dichlorobenzaldehyde.

The reduction of anisoin (4,4′-dimethoxybenzoin) with amalgamated zinc and hydrochloric acid gave a small yield of 4,4′-dimethoxydiphenylethane, m.p. 121° (lit.[31] m.p. 125°).

Reduction of anisoin with zinc amalgam in 1:1 acetic acid hydrochloric acid, maintaining the temperature below 15° for 2 hr. gave desoxyanisoin: m.p. 108–109° (lit.[31] m.p. 109°); λ_{max} 225 mμ (ε 22,100), 277 (16,200).

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.64; H, 6.30.

The same product was obtained by reducing anisoin with zinc dust in boiling acetic acid.

Following the modified method of Fieser,[18] anisoin (5.2 g.) was warmed on a steam bath, and thionyl chloride (4 ml.) was added. After heating for 5 min. the excess thionyl chloride was distilled *in vacuo*. Petroleum ether (10 ml.) was added and the sample again was evaporated *in vacuo*. The remaining oil was dissolved in ethanol (40 ml.) and sodium borohydride (0.36 g.) was added. After 10 min. zinc dust (2 g.) and acetic acid (4 ml.) were added, and the mixture was refluxed for 1 hr. The product (2.8 g.) was recovered by ether extraction and recrystallized from ethanol, m.p. 109–110°, no depression in mixture melting point with desoxyanisoin.

Direct Phenylacetic Acid Route (D). *trans*-**4-Nitrostilbene.**—4-Nitrophenylacetic acid (4.0 g.) and benzaldehyde (2 g.) were refluxed with piperidine (1 ml.) for 3 hr.[12] giving the product (3.0 g.), m.p. 155° from ethanol (lit.[32] m.p. 154–155°).

No stilbenes could be isolated from similar reactions of benzaldehyde with phenylacetic acid or 2-nitro-, 4-chloro-, and 2-chlorophenylacetic acid, or of 2-chlorobenzaldehyde with 2-chlorophenylacetic acid.

Via **Phenylcinnamic Acids.** *cis*-**Stilbene.**—Phenylcinnamic acid (9 g.) was heated at 210–220° for 1.25 hr. with copper chromite[28] (4 g.) in practical grade quinoline (56 ml.).[8a] The mixture was immediately cooled, poured into 10% hydrochloric acid (200 ml.), and extracted with ether. The ether was washed several times with 10% hydrochloric acid, then with 20% hydrochloric acid, water, and 10% sodium carbonate, and dried. Distillation gave *cis*-stilbene (3 g.), b.p. 108–110° at 2 mm. (lit.[7a] b.p. 134° at 10 mm.), and *trans*-stilbene (1 g.), m.p. 124° (lit.[4a] m.p. 124°).

Decarboxylation of phenylcinnamic acid (9 g.) in collidine with copper chromite at 175° for 18 hr. gave *trans*-stilbene (3.4 g.), m.p. 124°, and *cis*-stilbene (0.8 g.), b.p. 110–112° at 2 mm. No decarboxylation resulted in N,N-dimethylaniline (b.p. 192°) for 20 hr.

Decarboxylation of 7 g. of acid occurred in refluxing dimethyl sulfoxide (b.p. 120°) for 20 hr. Water was added, and the product was extracted with ether. Chromatography on alumina from heptane and heptane–benzene gave *trans*-stilbene (1.1 g.), m.p. 122–123°, and latter oily fractions which were distilled to give *cis*-stilbene (1.2 g.), b.p. 170–180° at 15 mm. *cis*-Stilbene (2.0 g.) was recovered unchanged (by infrared spectrum) (1.8 g.) after refluxing for 16 hr. in collidine with copper chromite.

A number of *trans*-α-phenylcinnamic acids were prepared by condensation of commercially available phenylacetic acids and benzaldehydes in acetic anhydride and triethylamine,[33] and were recrystallized from benzene and hexane. The decarboxylation in quinoline with copper chromite of α-4-methyl-, α-4-fluoro-, and α-2-methoxyphenylcinnamic acids gave only the corresponding *cis*-stilbenes (see Table II).

Decarboxylation of α-4-methoxyphenylcinnamic acid (3 g.) in collidine (19 ml.) with copper chromite (1.2 g.) for 18 hr. gave *trans*-4-methoxystilbene (1.8 g., 69%), m.p. 136° (lit.[34] m.p. 136–137°), and *cis*-4-methoxystilbene (0.3 g., 10%), b.p. 98° at 2 mm. (lit.[35] b.p. 145° at 15 mm.).

α-2-Chlorophenylcinnamic acid (3 g.) similarly gave *trans*-2-chlorostilbene (0.8 g., 32%), m.p. 39–40° (lit.[36] m.p. 39–40°), and *cis*-2-chlorostilbene (1.0 g., 40%), b.p. 120–122° at 2 mm., (lit.[36] b.p. 118–120° at 1.5 mm.). α-4-Chlorophenylcinnamic acid similarly afforded *trans*-4-chlorostilbene (70%), m.p. 128° (lit.[34] m.p. 129°), and *cis*-4-chlorostilbene (5%), b.p. (bath) 90° at 0.05 mm. α-4-Chlorophenyl-4-chlorocinnamic acid gave *trans*-4,4′-di-chlorostilbene (70%), m.p. 175–176° (lit.[30] m.p. 175–176°). α-2,4-Dichlorophenylcinnamic acid, however, gave only *cis*-2,4-dichlorostilbene.

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Via **Meerwein Reaction**. ***trans*-4,4′-Dinitrostilbene**.—4-Nitroaniline (0.6 g.) was diazotized in 25% hydrochloric acid (11 ml.) and ice (10 g.) at 5° with sodium acetate (0.25 g.) in water (3 ml.) and poured into 4-nitrocinnamic acid (0.8 g.) and anhydrous sodium acetate (0.08 g.) in acetone (40 ml.). An aqueous solution of 0.15 *M* cupric chloride (2 ml.) was added, and the mixture was kept at 14–17° for 1.5 hr. Evaporation of the acetone gave *trans*-4,4′-dinitrostilbene (0.4 g., 39%), m.p. 282° (from acetic acid) (lit.[37] m.p. 282°).

Via **Wittig Reaction**.—Benzyltriphenylphosphonium chloride, m.p. 315° (lit.[38] m.p. 317–318°), was prepared in nearly theoretical yield from benzyl chloride and triphenylphosphine.

cis- **and** ***trans*-Stilbene**.—Benzyltriphenylphosphonium chloride (9 g.) was added to a solution of sodium (0.46 g.) in anhydrous ethanol (50 ml.) in a nitrogen atmosphere. The resulting orange solution was treated with benzaldehyde (2.5 ml.) and stirred for 50 hr.[13b] The solution was poured into 25% hydrobromic acid (50 ml.), precipitating *trans*-stilbene, m.p. 123–124° (2.1 g., 55% yield.) The filtrate was evaporated at reduced pressure and extracted with ether. The ether extract was washed with 5% sodium bisulfite solution and evaporated. The residue was treated with petroleum ether to precipitate triphenylphosphine oxide (4 g.), m.p. 151–152° (lit.[39] m.p. 155°). Evaporation of the organic solution and distillation of the residue gave *cis*-stilbene, 1.8 g. (45%), b.p. 105–110° at 2 mm. (lit.[8a] b.p. 134° at 10 mm.).

A similar reaction with benzyltriphenylphosphonium chloride (9 g.) and 4-methoxybenzaldehyde (4.1 g.) gave only *trans*-4-methoxystilbene (4.1 g.), m.p. 136° (lit.[40] m.p. 136–137°); evaporation of the petroleum ether extract gave no liquid fraction.

Reaction of benzyltriphenylphosphonium chloride (9 g.) with 2-chlorobenzaldehyde (3.2 g.) also gave only *trans*-2-chlorostilbene (3.6 g.), m.p. 39–40° (lit.[36] m.p. 39–40°).

***trans*-Stilbene**.—Benzyltriphenylphosphonium chloride (9 g.) was added to potassium (0.85 g.) in anhydrous *t*-butyl alcohol (80 ml.) in a nitrogen atmosphere. Benzaldehyde (2.5 ml.) was added, the reaction was stirred for 54 hr., and worked up as above, giving *trans*-stilbene (3.0 g., 75%), m.p. 124°, and *cis*-stilbene, b.p. 110–115° at 2 mm. (1.0 g., 25%).

Reaction of benzyltriphenylphosphonium chloride (9 g.) with 2,4-dichlorobenzaldehyde (3.0 g.) under the same conditions gave *trans*-2,4-dichlorostilbene (4.6 g.), m.p. 76° (lit.[7b] m.p. 71°).

A similar reaction with 4-chlorobenzaldehyde (2.8 g.) gave *trans*-4-chlorostilbene (4.0 g.), m.p. 129° (lit.[41] m.p. 129°).

With Lithium Bromide.—Reaction of benzyltriphenylphosphonium chloride (10 g.) in anhydrous ethanol (55 ml.) containing sodium (0.51 g.) in the presence of lithium bromide (2.2 g.)[14b] added in N,N-dimethylformamide (7 ml.), with benzaldehyde (3.4 g.) as above, gave *trans*-stilbene, m.p. 124° (2.3 g., 45%), and *cis*-stilbene, b.p. 108–114° at 2 mm. (2.8 g., 50%).

The reaction of benzyltriphenylphosphonium chloride (9 g.) with 4-methoxybenzaldehyde (3.2 g.) under these conditions gave *trans*-4-methoxystilbene (3.9 g.), m.p. 136° (lit.[40] m.p. 136–137°), and with 4-nitrobenzaldehyde (3.8 g.) gave *trans*-4-nitrostilbene (4.5 g.), m.p. 155° (lit.[32] m.p. 155°).

Diethyl Benzylphosphonate.—Triethylphosphite (40 g.) and benzyl chloride (30 g.) were refluxed for 24 hr., giving diethyl benzylphosphonate[42] (50 g.), b.p. 170–174° at 15 mm. (lit.[42] b.p. 153–154° at 11 mm.).

***trans*-Stilbene**.—Diethyl benzylphosphite (14 ml.) and benzaldehyde (7.5 ml.) was added to a solution of sodium hydride (4 g., 25% in mineral oil)[15] in N,N-dimethylformamide (40 ml.) and benzene (80 ml.). The solution was refluxed for 1 hr., and then cooled and diluted with water. The organic layer was separated, the aqueous phase was extracted with ether, and the combined organic extracts were dried and evaporated, giving *trans*-stilbene (10.2 g., 90%), m.p. 122°, raised to m.p. 124° on recrystallization from ethanol (lit.[4a] m.p. 124°).

cis-Stilbene (1.5 g.) was refluxed with sodium hydride in dimethylformamide–benzene for 1 hr. and was recovered unchanged (by infrared) in 87% yield.

Diethyl benzylphosphonate (5 ml.) and 2-chlorobenzaldehyde (3 g.) treated as above gave *trans*-2-chlorostilbene (3.8 g.), m.p. 39–40° (lit.[36] m.p. 39–40°), and reaction with 4-methoxybenzaldehyde (3 g.) gave *trans*-4-methoxystilbene (4.0 g.), m.p. 136° (lit.[40] m.p. 136°).

Spectra.—The ultraviolet spectra were determined in solution of purified 95% ethanol using a Beckman D. U. spectrometer. The infrared spectra were determined in solutions of Spectrograde carbon tetrachloride and carbon disulfide using a Baird-Atomic, Model KM-1, spectrometer with a sodium chloride prism. The nuclear magnetic resonance spectra were determined in solution of carbon tetrachloride using a Varian A-60 spectrometer.

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