Relations between Electronic Absorption Spectra and Spatial Configurations of Conjugated Systems. IX. p-Phenylstilbene, p, p′-Diphenylstilbene, and their Related Compounds

By Hiroshi SUZUKI

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In this part of the series, the results of the measurements of the ultraviolet absorption spectra of *p*-phenylstilbene (1-phenyl-2-*p*-biphenylylethylene), 1-phenyl-2-(2-fluorenyl)-ethylene, *p*,*p*′-diphenylstilbene (1, 2-di-*p*-biphenylylethylene), and its *a*, *a*′-dimethyl derivative (2, 3-di-*p*-biphenylyl-2-butene) are reported, and the calculations based on the simple LCAO molecular orbital method analogous to those for stilbene and related compounds described in the earlier parts[1-4] of this series are applied to these spectra.

In addition, the red-shifts of the conjugation bands observed with these compounds as well as stilbene and related compounds when the solvent is changed from *n*-heptane to benzene are summarized, and the correlation of these shifts with the spatial configurations of the molecules is discussed.

p-Phenylstilbene and 1-Phenyl-2-(2-fluorenyl)-ethylene

The spectra of these compounds (both are probably *trans*) in solutions in benzene and in *n*-heptane are shown in Fig. 1, and the data of the absorption maxima are recorded in Table I. The notation of the bands is analogous to the one in the earlier parts of this series. Thus, the A-band denotes the conjugation band.

These spectra are somewhat similar in shape to that of *trans*-stilbene (cf. Fig. 1 in Part V[1]) of this series). The fine

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[1] H. Suzuki, This Bulletin, 33, 379 (1960).
[2] H. Suzuki, ibid., 33, 389 (1960).
[3] H. Suzuki, ibid., 33, 396 (1960).
[4] H. Suzuki, ibid., 33, 406 (1960).

TABLE I. ABSORPTION MAXIMA

Compound	In benzene A-band		In n-heptane A-band		In n-heptane B- & C-bands	
	λ, mμ	ε	λ, mμ	ε	λ, mμ	ε
p-Phenylstilbene						
	[(343.5)]	22200	[(338)]	23200	225.5	13100
	△327.8	35500	△322.5	36000		
	(317.4)	32900	(311.5)	33200	200.3	31900
1-Phenyl-2-(2-fluorenyl)-ethylene						
	356.5	28450	351.2	29100	258.9	2170
	△341.5	42900	△335.8	43100	230.0	15230
	[(330.5)]	37000	[(327.5)]	37200	223.7	15420
	[(321)]	30800	(318.5)	32450	210.0	26950
	[(307)]	19430	[(303.5)]	21000	204.5	27800
p, p'-Diphenylstilbene						
	[(362)]	31300	[(357)]	0.126*	[(243)]	0.042*
	△343.0	49900	△337.4	0.214*	(220.5)	0.078*
	(332.5)	46200	(327.5)	0.199*	(201.8)	0.254*
p, p'-Diphenyl-α, α'-dimethylstilbene						
	276.2	29000	273.3	0.838*	203	1.826*

Symbol △ denotes the most intense maximum of fine structure. Wavelengths in parentheses denote inflections, and those in double parentheses denote very indistinct inflections.
Symbol * denotes the intensity in absorbance.

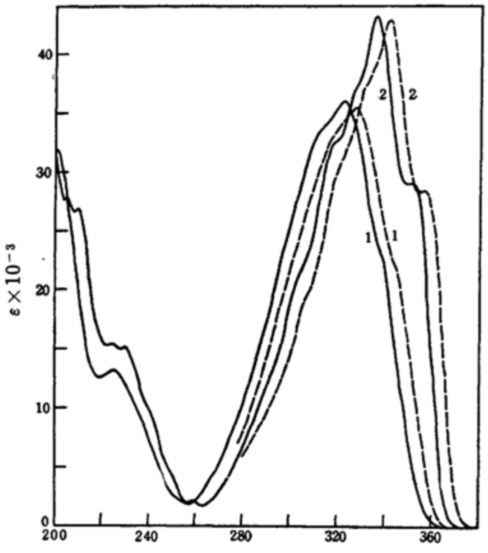

Fig. 1. Ultraviolet absorption spectra: 1, p-phenylstilbene; 2, 1-phenyl-2-(2-fluorenyl)-ethylene: ——, in n-heptane; ----, in benzene.

structure of the conjugation band of p-phenylstilbene is, however, more blurred than that of stilbene. The pattern of the fine structure of the conjugation band of the fluorenyl compound may be said to resemble that of fluorene (cf. Fig. 1 in Part III[5]) of this series).

The maximum of the conjugation band of p-phenylstilbene is at a longer wavelength by about 28.4 mμ relative to the most intense maximum (the γ-band) of fine structure of the conjugation band of stilbene, in accordance with the expectation from the length of the conjugated system. The most intense maximum of fine structure of the conjugation band of the fluorenyl compound is at a still longer wavelength by about 13.3 mμ than that of the biphenylyl compound, a fact which may be considered to correspond to the fact that the most intense maximum of fine structure of the conjugation band of fluorene is at a longer wavelength by about 14.5 mμ than the maximum of the conjugation band of biphenyl[5]).

Now, the calculation method analogous to the one used so far in this series is applied to these compounds. In the calculation the data of the spectra in n-heptane are used as before. The resonance integral for the ethylenic bond is denoted by $\eta\beta$, and as the value of η the value of 1.080, corresponding to the bond length 1.34 Å, is taken. The resonance integral for the bonds connecting the benzene rings to the ethylenic carbon atoms is denoted by $\rho\beta$, and as the value of ρ, the value of 0.908, corresponding to the bond length 1.445 Å, is tentatively taken as in the case of *trans*-stilbene[1]). The resonance integral for the bond

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5) H. Suzuki, ibid., **32** 1357 (1959).

between the two benzene rings in the biphenyl part is denoted by $\mu\beta$.

When as the value of the variable μ the corresponding value for fluorene 1.060 is used, the electronic transition energy ΔE_{A} (the energy difference between the lowest vacant orbital and the highest occupied orbital) is calculated to be 1.018 $(-\beta)$, by the usual procedure of the simple LCAO molecular orbital method. This calculated value of the transition energy, which is referred to as ΔE_{L}, is considered to correspond to the wave number of the most intense maximum of the conjugation band of the fluorenyl compound, 29780 cm^{-1} (335.8 mμ), which is referred to as ν_{L}.

On the other hand, when μ is zero, the value of ΔE_{A} is 1.142 $(-\beta)$, which corresponds conceivably to the wave number of the γ-band of *trans*-stilbene, 34002 cm^{-1} (294.1 mμ)[1]. These values of the calculated and the corresponding observed transition energies are referred to as ΔE_{S} and ν_{S}, respectively.

On the basis of the above determination of the longer-wavelength-side and the shorter-wavelength-side references, the value of ΔE_{A} corresponding to the wave number of the maximum of the conjugation band of the biphenylyl compound, 31008 cm^{-1} (322.5 mμ), is calculated to be 1.054 $(-\beta)$, and the corresponding value of μ is calculated to be 0.877. This calculated value of μ is slightly greater than the corresponding value for biphenyl in solution obtained in Part I[6] of this series. This fact would appear to suggest that the length of the bond concerned is shortened and the angle of twist of the bond is decreased in the biphenylyl compound compared with those in biphenyl in solution, owing to the increase in the extent of conjugation. However, it should not be so asserted, since it may be doubtful whether much reliance can be placed on these numerical values, because of the many assumptions made for simplification in the calculation and especially of the peculiar nature of the parameter μ for fluorene.

***p,p'*-Diphenylstilbene and its *α,α'*-Dimethyl Derivative**

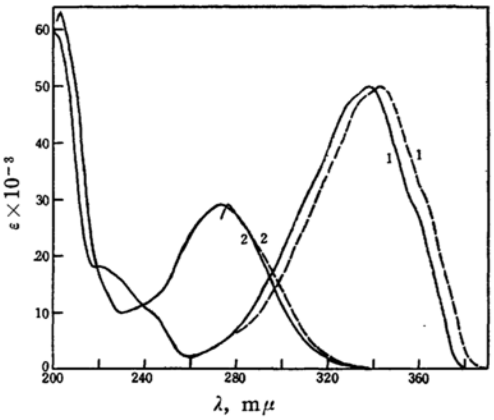

Fig. 2. Ultraviolet absorption spectra: 1, *p,p'*-diphenylstilbene; 2, *p,p'*-diphenyl-*α,α'*-dimethylstilbene: ——, in *n*-heptane; ----, in benzene.

The spectra of these compounds (both are probably the *trans* isomers) in solutions in benzene and in *n*-heptane are shown in Fig. 2, and the data of the absorption maxima are summarized in Table I. The solubilities of these compounds in *n*-heptane are so low that the concentrations of the solutions in *n*-heptane and hence the molecular extinction coefficients of the spectra could not be determined. Accordingly, in Table I the intensities of the absorption bands of these compounds in *n*-heptane are represented in absorbance (the solution of the parent compound used is an almost saturated solution, and the solution of the dimethyl derivative is a solution of very roughly quarter the concentration of the saturated solution; the cell path length is 1 cm.). In Fig. 2, the extinction of the main band of each compound in *n*-heptane has been arbitrarily set to be equal to its extinction in benzene. From these data, it is evident that the solubility of the *α,α'*-dimethyl compound is considerably higher than that of the parent compound. In addition, the melting point of the dimethyl compound (about 240~245°C) is considerably lower than that of the parent compound (about 303~305°C). These facts are very similar to those observed in the comparison between *trans*-stilbene and its *α,α'*-dimethyl derivative[3].

The fine structure of the conjugation band of the diphenylstilbene is further more blurred when compared with that of the phenylstilbene, and the maximum of the former is shifted further toward the longer wavelength than that of the latter. On the other hand, the conjugation band of the dimethyl derivative is almost structureless, and is at a considerably shorter wavelength and of lower intensity than that of the parent compound. This situation is also very similar to that

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[6] H. Suzuki, ibid., **32**, 1340 (1959).

observed in the comparison between *trans*-stilbene and its α,α'-dimethyl derivative[3], and is undoubtedly explained in terms of the steric effect of the methyl substituents.

Similarly to the treatment in the preceding section, the resonance integral for the ethylenic bond is denoted by $\eta\beta$, and the value of η is assumed to be 1.080. The resonance integral for the "single" bond between the two benzene rings in each biphenyl part is denoted by $\mu\beta$, and the value of μ is assumed to be 0.780, being equal to the corresponding value for biphenyl in solution[6]. (This choice of the value is not conclusive, but it is believed that a small change of this value does not alter significantly the final result of the present calculation). The resonance integral for each "single" bond in the stilbene part of the molecule is denoted by $\rho\beta$, in which ρ is the variable in the present calculation.

When as the value of ρ the corresponding value for planar *trans*-stilbene, 0.9084, is taken, the energy of the allowed transition from the highest occupied orbital to the lowest vacant orbital, ΔE_A, is calculated to be 1.0181 $(-\beta)$. This value is ΔE_L in the present treatment, and is considered to correspond to the wave number of the maximum of the conjugation band of p,p'-diphenylstilbene, 29638 cm^{-1} (337.4 mμ). This compound should be more conjugated than *trans*-stilbene as well as biphenyl, and consequently, the lengths of the "single" bonds, the angles of twist of the bonds, and hence the values of ρ and μ are possibly different from the corresponding ones in *trans*-stilbene and in biphenyl. In spite of this, since it is believed that small changes of the values of ρ and μ will not significantly alter the final result, on the analogy of the calculation for terphenyls described in Part IV[7] of this series, the calculation is carried out on the basis of the above assumptions.

When ρ is zero, the value of ΔE_A is 1.523 $(-\beta)$. This value is ΔE_S in the present calculation, and corresponds to the wave number of the maximum of the conjugation band of biphenyl in *n*-heptane, 40486 cm^{-1} (247.0 mμ)[6].

On the basis of the above references, from the wave numer of the conjugation band of the α,α'-dimethyl derivative in *n*-heptane, 36590 cm^{-1} (273.3 mμ), the corresponding value of ΔE_A is calculated to be 1.342 $(-\beta)$, and then the following corresponding values are obtained by the usual procedure: ρ, 0.461; θ, 57°; R, 1.488 Å. The calculated value of the interplanar angle θ between the benzene ring and the ethylenic bond, 57°, for this compound coincides almost completely with the value for *trans*-α,α'-dimethylstilbene, 58°[3].

In this connection, it was planned originally to apply a similar method also to 1,2-di-(2-fluorenyl)-ethylene and its 1,2-dimethyl derivative. However, the attempts to prepare these compounds regrettably resulted in failure.

Lastly in this section, the spectra of ketazines may be briefly referred to. Compounds which are probably *p*-biphenylyl methyl ketazine and 2-fluorenyl methyl ketazine were obtained as by-products in the processes of preparation, or in attempts at preparation, of the corresponding dimethylstilbenes, as will be described in the experimental part. The spectra of these ketazines are shown in Fig. 3. These compounds are only very slightly soluble in *n*-heptane, so that the concentrations of the solutions used could not be determined. Consequently, the intensities of absorption are expressed in absorbance (for very roughly saturated solutions; the cell path length, 1 cm.).

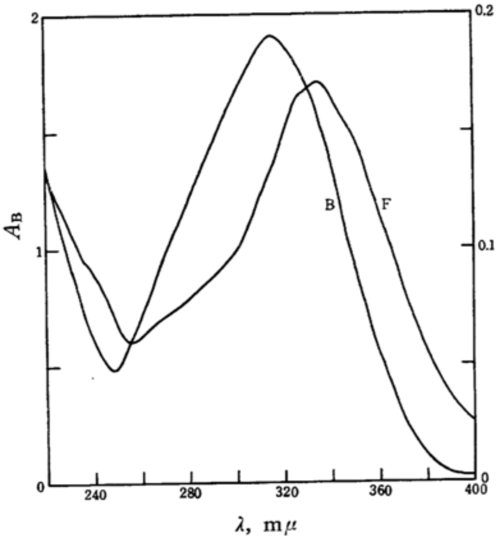

Fig. 3. Ultraviolet absorption spectra: B, *p*-biphenylyl methyl ketazine; F, 2-fluorenyl methyl ketazine. Note separate ordinates for the compounds.

Also in this case, the absorption maximum of the fluorenyl compound (335 mμ) is at a longer wavelength than that of the

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[7] H. Suzuki, ibid., **33**, 109 (1960).

TABLE II. THE SOLVENT EFFECT OF BENZENE ON THE ULTRAVIOLET ABSORPTION SPECTRA. —The red-shifts of the conjugation bands associated with the change of the solvent from n-heptane to benzene.

Compound	Absorption max. (in n-heptane)		$\Delta\lambda$ mμ	$\Delta\nu$ cm^{-1}	Molecular configuration
	λ, mμ	ε			
p-Nitrostilbene	345.0	23820	+5.5	−455	planar
p, *p'*-Diphenylstilbene	337.4	49900$^{b)}$	+5.6	−483	planar
1-Phenyl-2-(2-fluorenyl)-ethylene	335.8	43100	+5.7	−497	planar
p-Phenylstilbene	322.5	36000	+5.3	−502	planar
Tetraphenylethylene	308.7	15300	+2.5	−260	nonplanar
p-Methoxystilbene	302.7	28950	+5.0	−537	planar
Triphenylethylene	298.5	18220	+3.3	−366	nonplanar
trans-Stilbene	294.1	27950	+4.7	−535	planar
p, *p'*-Diphenyl-α, α'-dimethylstilbene	273.3	29000$^{b)}$	+2.9	−384	nonplanar

The values of ε denoted by symbol b represent the values for benzene solutions.

corresponding biphenylyl compound (315 mμ). If these compounds were planar, they would be expected to show the conjugation bands at considerably longer wavelengths than *p*,*p'*-diphenylstilbene. In fact, however, it is not so. This fact is considered to indicate that these ketazines are conceivably nonplanar.

Correlation of Solvent Effects of Benzene with Spatial Configurations of Aromatic Solute Molecules

It was previously reported that the conjugation bands of *trans*-stilbene and some related componds are shifted toward considerably longer wavelengths when the solvent is changed from n-heptane to benzene[1,2]. A similar phenomenon is observed also with the compounds treated in the present paper. In Table II, the data of the red-shifts observed hitherto are summarized, in which symbols $\Delta\lambda$ and $\Delta\nu$ denote the magnitude of the displacement of the band in wavelength (mμ) and that in wave number, respectively, associated with the change of the solvent from n-heptane to benzene. In this table, solely the data on the most intense maximum of the conjugation band of each compound are assembled, the data on the inflections or vestigial bands being excluded.

It is to be noted here that whether or not the apparent absorption maximum of *p*,*p'*-diphenyl-α, α'-dimethylstilbene in benzene at 276.2 mμ is the true maximum may be somewhat doubtful, because the apparent maximum is so near the shorter-wavelength-side limit (about 270 mμ) of the range in which the measurement of the spectra by using benzene as the solvent is possible. If it is not so, the intrinsic absorption maximum of this compound must be at a shorter wavelength than the apparent maximum. Accordingly, the value of $\Delta\lambda$ for this compound listed in Table II may be considered rather as the upper limit.

Because of inevitable uncertainty in determination of the positions of the absorption maxima, the numerical values of $\Delta\lambda$ as well as $\Delta\nu$ may not be decisive. With such a reservation, however, it seems that the following generalization can be drawn from Table II: whereas the red-shifts for the planar molecules are about 5 mμ, the red-shifts for the probably nonplanar molecules are about 3 mμ and considerably smaller than the values for the planar molecules.

According to Bayliss[8], the magnitude (in cm^{-1}) of the red-shift of an absorption band of a nonpolar solute by a nonpolar solvent depends directly on the oscillator strength of the band, inversely on the frequency of the band, therefore, directly on the wavelength of the band, and is related to the refractive index n of the solvent at the frequency concerned, depending directly on $(n^2-1)/(2n^2+1)$. Thus, the band is shifted toward lower frequencies and therefore toward longer wavelengths with the increasing refractivity of the solvent.

The refractive index of benzene is greater than that of n-heptane. It seems, however, that the great bathochromic effect of benzene relative to n-heptane observed here can not be attributed wholly to the difference of refractivity. For

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[8] N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).

example, by the use of Eq. 12 in Bayliss' paper, the magnitude of the red-shift of the conjugation band of *trans*-stilbene associated with the change of solvent from *n*-heptane to benzene is roughly calculated to be only about 60 cm^{-1}. This calculated value is by far smaller than the observed value.

In general, the intensity of the conjugation band of a non-planar compound is considerably smaller than that of the corresponding planar compound. Hence it would be expected that the difference of the magnitude of the red-shift between the planar compounds and the nonplanar compounds might be rather related to the difference of the intensity of the band. This is, however, unlikely, in view of the fact that the conjugation band of *p,p'*-diphenyl-α,α'-dimethylstilbene, which is undoubtedly nonplanar, shows a relatively small red-shift in spite of considerably high intensity. Further, as will be evidently seen in Table II, there is no regular relation between the magnitudes of the red-shifts and the wavelengths of the bands.

Therefore, it seems most natural after all to correlate the magnitude of the red-shift with the spatial configuration of the solute molecule, and this correlation seems to suggest, as already mentioned in Part V[1], the presence of a special interaction between the π-orbitals (or π-electrons) of the solute molecule and those of benzene.

Experimental

Measurements of Spectra.—The ultraviolet absorption spectra of the olefins were measured with a Cary recording spectrophotometer Model 14 M-50. The spectra of the ketazines were measured with a Beckman type spectrophotometer.

***p*-Phenylstilbene.** — This compound was prepared by the Meerwein reaction. The diazonium salt of *p*-aminobiphenyl was prepared by adding dropwise with stirring a solution of 27 g. of sodium nitrite in 45 ml. of water to a mixture of 300 ml. of 25 % hydrochloric acid, 63.4 g. of *p*-aminobiphenyl, and 300 g. of ice. An ice bath was placed around the reaction flask and 235 g. of crystalline sodium acetate was added. A solution of 55.5 g. of cinnamic acid in 900 ml. of acetone was added and the ice bath was removed. Five minutes later a solution of 40.6 g. of cupric chloride in 90 ml. of water was dropwise added and the mixture was stirred for about three hours at room temperature. After being left to stand overnight, the copious green precipitate was collected on a filter and dissolved in a large amount of benzene. The benzene solution was washed in turn with a dilute solution of sodium carbonate, with water, with dilute hydrochloric acid, and then with water, dried on calcium chloride, and treated with activated charcoal. On concentrating the solution by evaporation, pale orange-yellow crystals separated. The crystals were repeatedly recrystallized from benzene. Thus, about 34.5 g. of *p*-phenylstilbene, colorless crystals melting at 220.0~220.5°C, was obtained (about 36% of the theoretical amount). A solution of this compound in benzene shows violet fluorescence.

p-Aminobiphenyl was prepared after the procedure described by Schlenk[9] by reducing *p*-nitrobiphenyl in ethanol with stannous chloride and concentrated hydrochloric acid. From 77 g. of *p*-nitrobiphenyl, 64.5 g. of *p*-aminobiphenyl, pale brown-yellow leaflets melting at 53~55°C, was obtained after recrystallization from ethanol (98.6% of the theoretical amount).

p-Nitrobiphenyl was prepared, according to the directions of Maki and his coworker[10], by nitration of biphenyl in acetic acid. From 154.2 g. of biphenyl, 91 g. of *p*-nitrobiphenyl, pale yellow needles melting at 114.5~115.3°C, was obtained after recrystallization from ethanol.

1-Phenyl-2-(2-fluorenyl)-ethylene. — This compound was prepared by the Meerwein reaction, quite analogously to the preparation of *p*-methoxystilbene described in Part V[1] of this series. From 22.8 g. of 2-aminofluorene, 5.1 g. of the product was obtained after a series of purification processes by treatment with activated charcoal and by repeated recrystallization from benzene; colorless needles melting at 219.5~221.0°C (15.1% of the theoretical amount).

Found: C, 94.04; H, 6.17. Calcd. for $C_{21}H_{16}$: C, 93.99; H, 6.01%.

2-Aminofluorene was prepared by the method described in Organic Syntheses[11], by reducing 2-nitrofluorene in ethanol with zinc dust together with calcium chloride. From 106.3 g. of 2-nitrofluorene, 66.3 g. of 2-aminofluorene, orange-brown needles melting at 125~126.5°C, was obtained (72.7% of the theoretical amount).

2-Nitrofluorene was prepared according to the directions described in Organic Syntheses[11] by nitration of fluorene. From 120 g. of fluorene, 108 g. of the probably somewhat crude product, yellow needles melting at 151~154°C, was obtained (about 71% of the theoretical amount).

***p,p'*-Diphenylstilbene.**—This compound was prepared, after the procedures of preparation of some symmetrical diarylethylenes described by Wood and his coworkers[12] and also the procedures of preparation of 1,2-dimesitylethylene described by Fuson and Best[13], by heating polythio-*p*-phenylbenzaldehyde with copper powder.

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[9] W. Schlenk, *Ann.*, **368**, 303 (1909).

[10] T. Maki and K. Ōbayashi, *J. Chem. Soc., Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **54**, 375 (1951).

[11] W. H. Carothers (Editor-in-Chief), "Organic Syntheses", Vol. XIII, John Wiley & Sons, Inc., New York (1933) p. 74.

[12] J. H. Wood, J. A. Bacon, A. W. Meibohm, W. H. Throckmorton and G. P. Turner, *J. Am. Chem. Soc.*, **63**, 1334 (1941).

[13] R. C. Fuson and C. E. Best, ibid., **67**, 155 (1945).

A solution of 9.1 g. of *p*-phenylbenzaldehyde in 340 ml. of absolute ethanol was saturated with dry hydrogen chloride. Hydrogen chloride and hydrogen sulfide were then passed into the solution for two and one-half hours at −3∼0°C. The almost white (or pale pink) powder produced in this way was isolated, washed several times with absolute ethanol, and dried in a vacuum desiccator; m. p. 80∼88°C; yield, 9 g. A mixture of 9 g. of the crude thioaldehyde and 26 g. of copper-bronze powder was heated for thirty minutes in a small flask by means of a sand bath at 260∼310°C. The copper powders turned black, and white crystals separated on the surface of the mixture. After cooling, the ethylenic compound was repeatedly extracted with large quantities of boiling xylene. The xylene solution was concentrated to bring about crystallization. Repeated recrystallization from xylene and treatment with activated charcoal gave 0.7 g. of pure *p,p'*-diphenylstilbene, colorless thin plates melting at 301.5∼304.5°C (8.4% of the theoretical amount from the aldehyde). This compound proved to be only slightly soluble in benzene and in xylene, and hardly soluble at all in *n*-heptane and in ethanol. A dilute solution in xylene, benzene, as well as *n*-heptane shows intense violet fluorescence.

Found: C, 94.02; H, 6.28. Calcd. for $C_{26}H_{20}$: C, 93.94; H, 6.06%.

The preparation of *p*-phenylbenzaldehyde, white thin plates melting at 60∼61°C, will be reported in the succeeding part of this series.

The author attempted also to prepare *p,p'*-diphenylstilbene by reducing *p,p'*-diphenylbenzoin with zinc amalgam and hydrochloric acid after the procedures to prepare *trans*-stilbene from benzoin described in Organic Syntheses[14], and also by the method analogous to the one to prepare *trans*-stilbene described by Fieser[15], which involves three steps: replacement of the hydroxyl group of benzoin by chlorine (with thionyl chloride), reduction of the carbonyl group with sodium borohydride to give the chlorohydrin, and elimination of the elements of hypochlorous acid with zinc and acetic acid. These attempts resulted in failure. Thus, by either method, solely an unidentified product, colorless thin plates melting at 227.0∼227.5°C, was obtained in good yield. The ultraviolet absorption spectrum of this compound in *n*-heptane shows a structureless band with the maximum at 275 mμ.

p,p'-Diphenylbenzoin was prepared, according to the directions of Gomberg and Natta[16], by the benzoin condensation of *p*-phenylbenzaldehyde. From 42.5 g. of *p*-phenylbenzaldehyde, 25.9 g. of the product purified by repeated recrystallization from xylene and by treatment with activated charcoal, almost colorless or faint yellow crystals melting at 166∼169.5°C, was obtained (61% of the theoretical amount). As a by-product, about 2 g. of *p*-phenylbenzoic acid, colorless needles melting at 219.5∼222°C, was obtained.

***p,p'*-Diphenyl-α,α'-dimethylstilbene.**—This compound was prepared from *p*-phenylacetophenone (*p*-biphenylyl methyl ketone) after the Vargha Kovács' method[17]. A mixture of 10 g. of *p*-phenylacetophenone, 100 ml. of isopropyl alcohol, and 25 g. of 80% hydrazine hydrate was refluxed for about 30 hr. A thick white precipitate of the hydrazone was collected and dried in a vacuum desiccator. The hydrazone proved to be soluble with difficulty in petroleum ether. To a solution of the crude hydrazone in about 500 ml. of benzene, 18.1 g. of yellow mercuric oxide was added, and the mixture was stirred for about 9 hr. at room temperature. After filtration, into the pale red-orange solution sulfur dioxide was passed for thirty minutes. After removal of the solvent, the yellow residual solid was extracted with petroleum ether (b.p. 80∼100°C). Repeated recrystallization of the residue from xylene gave 5.8 g. of a compound, yellow, bright, thin plates melting at 274.5°C, which is probably *p*-biphenylyl methyl ketazine. On the other hand, the petroleum ether extract solution was filtered through a chromatographic column of alumina, and then concentrated to bring about crystallization. Fractional recrystallization of the crystals from petroleum ether gave very small quantities of colorless prisms melting at 240∼245°C and small quantities of pale yellow needles melting at about 260∼290°C. Although both the quantities were far too small for complete identification, the former compound (the colorless prisms) is considered probably to be the desired compound. On the other hand, the ultraviolet absorption spectrum of the latter in *n*-heptane shows a band with maxima at 289 and 313.5 mμ, and the spectrum in benzene shows a structureless band at 300 mμ.

The poorness of the yield of the desired compound in the above experiment is considered to originate in imperfection of the oxidation of the hydrazone. The author attempted to oxidize the hydrazone by using lead dioxide instead of mercuric oxide, and also by using petroleum ether as solvent (suspension). However, these attempts resulted in failure, the only isolated product in each experiment being the ketazine.

The author attempted to prepare this dimethyl compound also after the procedures described by Cline and his coworkers[18] to prepare α,α'-dimethylstilbene by heating trithioacetophenone with Raney nickel in xylene in an atmosphere of nitrogen. From 6.3 g. of *p*-phenylacetophenone, about 4 g. of the corresponding thio compound, pale grayish yellow powder, was obtained after the procedures of the preparation of trithioacetophenone described by Baumann and Fromm[19].

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[14] L. I. Smith (Editor-in-Chief), "Organic Syntheses", Vol. 23, John Wiley & Sons, Inc., New York (1943), p. 86.

[15] L. F. Fieser, "Experiments in Organic Chemistry", 3rd. Ed., D. C. Heath and Company, New York (1955), p. 179—180.

[16] M. Gomberg and F. J. Van Natta, *J. Am. Chem. Soc.*, **51**, 2238 (1929).

[17] L. v. Vargha and E. Kovács, *Ber.*, **75B**, 794 (1942).

[18] J. K. Cline, E. Campaign and J. W. Spies, *J. Am. Chem. Soc.*, **66**, 1136 (1944).

[19] E. Baumann and E. Fromm, *Ber.*, **28**, 895 (1895).

However, the final product obtained by heating the thio compound with Raney nickel was yellow, bright crystals melting at 328.5~330.0°C and soluble with difficulty in usual organic solvents. The ultraviolet absorption spectrum of this product in benzene showed a structureless band with the maximum at 354 mμ.

The preparation of *p*-phenylacetophenone, m.p. 119~121.5°C, will be described in the succeeding part of this series.

Unsuccessful Attempts to Prepare 1,2-Di-(2-fluorenyl)-ethylene. — Preparation of this compound by heating polythio-2-formylfluorene with copper powder after the preparation of *p,p'*-diphenylstilbene described above was attempted. However, the only product isolated was pale yellow needles melting at 289~290.5°C, whose spectrum in *n*-heptane resembles the spectum of 2-formylfluorene as well as that of 2-acetylfluorene (cf. the succeeding part of this series), showing a band with well-resolved fine structure, the most intense maximum of which is at about 310.5 mμ. This product is probably not the desired compound, as was revealed by the spectrum.

The preparation of 2-formylfluorene, faint yellow needles melting at 85.5~86.5°C, will be described in the succeeding part of this series.

Unsuccessful Attempts to Prepare 2,3-Di-(2-fluorenyl)-2-butene. — Preparation of this compound by the Vargha and Kovács' method analogously to the preparation of 2,3-di-*p*-biphenylyl-2-butene (*p,p'*-diphenyl-α,α'-dimethylstilbene) described above was attempted. However, the attempts to oxidize the hydrazone of 2-fluorenyl methyl ketone (2-acetylfluorene) with mercuric oxide and with lead dioxide were unsuccessful, and the only isolated product was an orange-yellow crystalline compound melting at 301~302°C, which is considered to be 2-fluorenyl methyl ketazine.

The preparation of 2-acetylfluorene, colorless crystals melting at 127.5~128°C, will be described in the succeeding part of this series.

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Department of Chemistry
College of General Education
The University of Tokyo
Meguro-ku, Tokyo