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During a study of the abnormal dienone-phenol rearrangement discovered by Marvell and Geiszler, Imel (1960) found that 4-oxo-3,3-dimethyl-3,4-dihydrophenanthrene rearranged slowly to a phenol which was tentatively identified as 3,4-dimethyl-1-phenanthrol; further evidence to support this assignment was deemed essential.

The recent work by Mallory on the photochemical conversion of stilbenes to phenanthrenes suggested a convenient synthesis of 3,4-dimethyl-1-phenanthrol by demethylating the expected product, 1-methoxy-3,4-dimethylphenanthrene, obtained from the ultraviolet irradiation of 2-methoxy-4,5-dimethylstilbene.

This substituted stilbene was synthesized by unequivocal methods and the structure confirmed by spectral methods. Irradiation of the stilbene yielded a different and unexpected product which was identified as 2,3-dimethylphenanthrene (10%), in addition to seven other products. The factors which determine the course of the ring closure step in unsymmetrical cases like that investigated here are not yet clear.

**THE PREPARATION OF 2-METHOXY-4,5-DIMETHYL-  
STILBENE AND ITS PHOTOCHEMISTRY**

by

**HOMER HIN-CHAU TONG**

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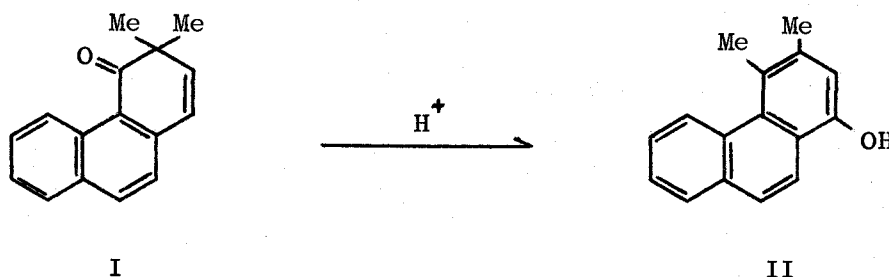
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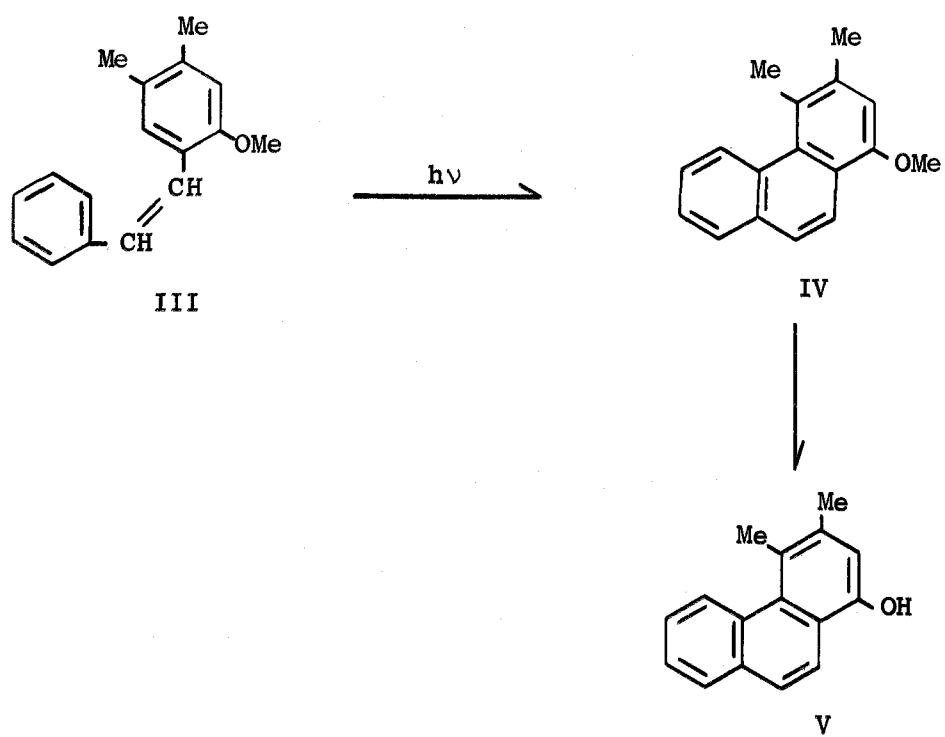
# THE PREPARATION OF 2-METHOXY-4,5-DIMETHYL-STILBENE AND ITS PHOTOCHEMISTRY

## INTRODUCTION

During a study of the abnormal dienone-phenol rearrangement discovered in these laboratories by Marvell and Geiszler (9, p.1-37), Imel (12, p.21-27) found that 4-oxo-3,3-dimethyl-3,4-dihydrophenanthrene (I) rearranged slowly to a phenol which was suggested to be 3,4-dimethyl-1-phenanthrol (II), on the basis of the infrared spectra of the compound and its corresponding phenanthraquinone at different dilutions. The evidence for this product was considered inconclusive and further evidence to support this assignment was deemed essential.



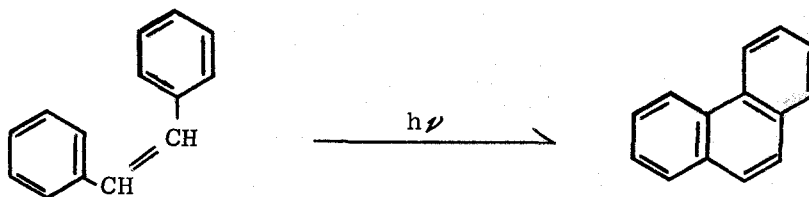
The recent finding of Mallory (15, p.4362) that the photochemical conversion of stilbenes to phenanthrenes can be made a useful synthetic tool suggested a convenient synthesis of 3,4-dimethyl-1-phenanthrol (V), through a completely different but unambiguous route. The scheme involved synthesis of the substituted stilbene (III) which was then to be irradiated (IV) and demethylated (V). An attempt to work out this synthetic scheme is the subject of this thesis.



## HISTORICAL

The photochemistry of organic compounds is a rapidly developing field today. This rapid development has been the result of recent progress in the understanding of ultraviolet spectroscopy and of the arrival of new microanalytical techniques. Nevertheless, around the turn of the century, it was recognized that light could induce transformations in organic compounds (5, p.385-394 and 18, p.237-250), though useful applications of the various discoveries remained few. In recent years, following the work of Barton, Büchi, Schenk, Schönberg and others, photochemical reactions have been applied with remarkable results, and preparative photochemistry has established its place in organic synthesis.

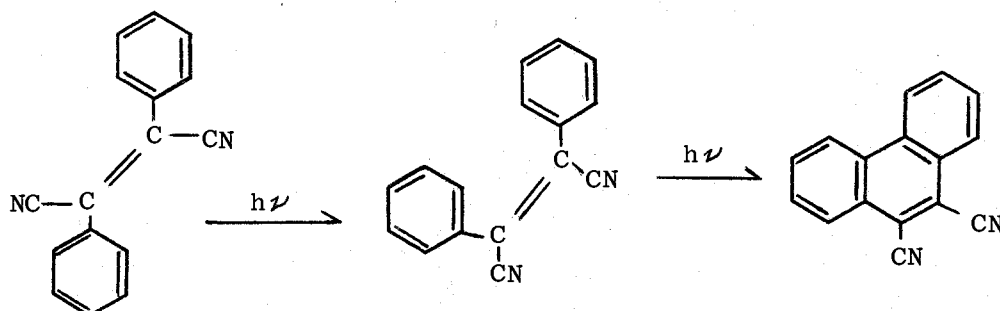
The existence of the stilbene-phenanthrene photosynthesis was first hinted at in 1934 by Smakula (20, p.98). During his investigations on the photochemical isomerization of stilbene, he noticed that irradiation of *cis*-stilbene solutions with ultraviolet light resulted in the formation of a new substance absorbing at 247  $m\mu$ . This observation was confirmed in 1940 by Lewis, Magel and Lipkin (13, p.2976-77), who estimated a 10% yield for the product. It was not



until 1950 when Parker and Spierri (17, p.603), and a few years later



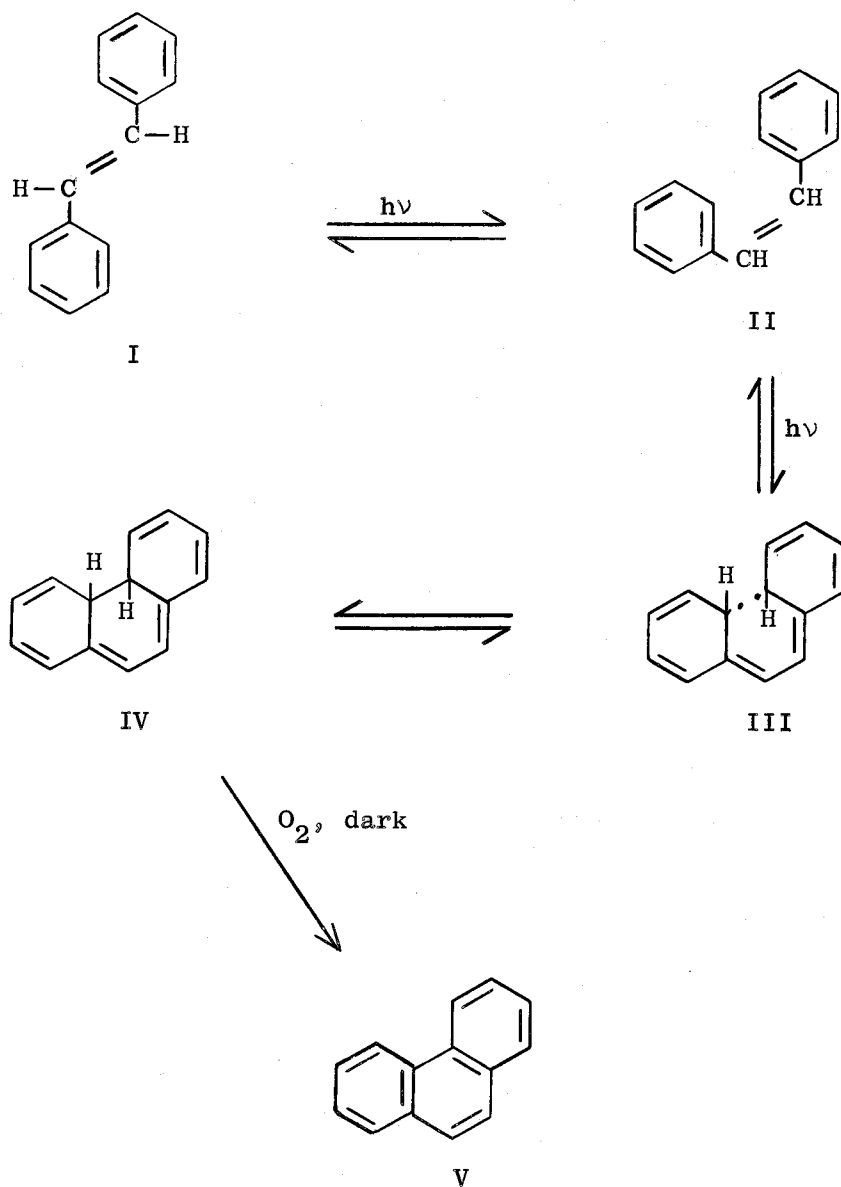
Buckles (4, p.1040), independently identified the product as phenanthrene. Shortly afterwards in 1957, Coe, Garnish and Timmons (6, p.666) reported the formation, in part, of 9, 10-dicyanophenanthrene from prolonged irradiation of trans-dicyanostilbene. These results led to the recognition that the stilbene-phenanthrene photosynthesis



had general applicability. Since then, attention has been directed toward elucidating the mechanism of the reaction and developing the optimum conditions for synthetic purposes.

The mechanism of the photoconversion of stilbenes to phenanthrenes has been investigated by a number of workers, notably Schaffner, Stegemeyer, Mallory, Moore, and their co-workers. The mechanistic pathway depicted as follows represents the sum of all the pertinent facts known at present.

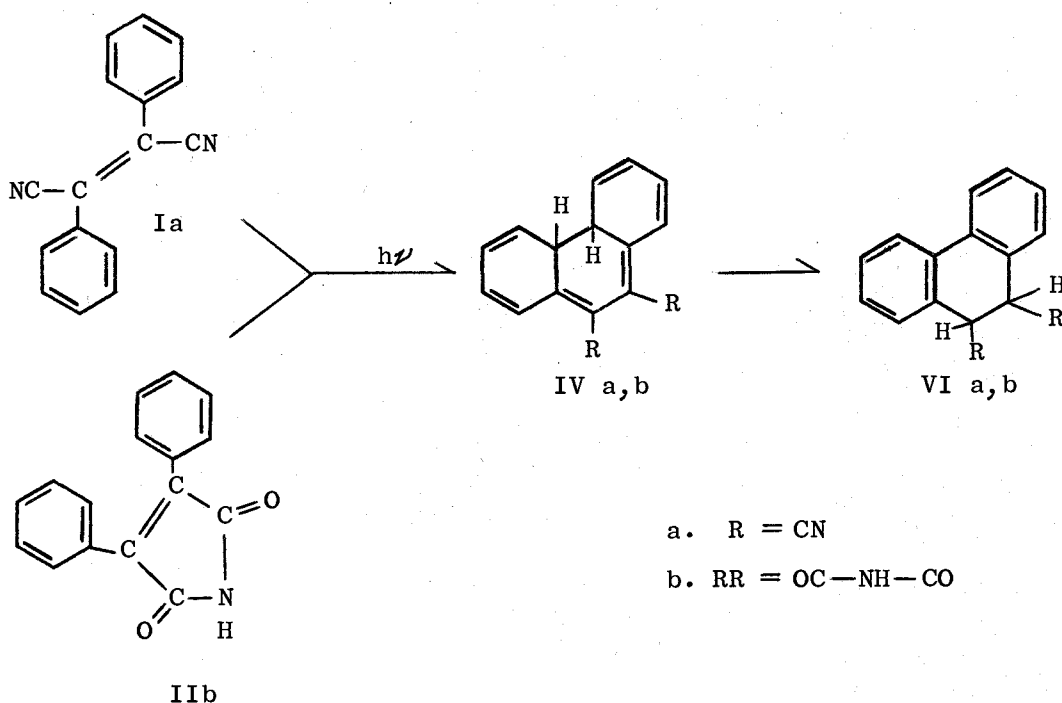
The precursor to photocyclization is cis-stilbene (II) rather than the trans isomer (I). Stegemeyer (23, p.155) reported that the initial rate of formation of phenanthrene was finite when a solution of pure cis-stilbene was irradiated with ultraviolet light; but if trans-stilbene was used instead, the initial rate was zero and phenanthrene began to be formed only as the trans isomer was converted to the cis form by photoisomerization. Moore et al. (16, p.830)



provided further supporting evidence when they obtained only a trace of phenanthrene on photolysis of a  $5 \times 10^{-5}$  M trans-stilbene solution using filtered light of 290-310 m $\mu$ , as compared with normal photolysis using all wavelengths below 310 m $\mu$ ; cis-stilbene shows only weak absorption at 290-310 m $\mu$ .

Interpreting Stegemeyer's results in the previous paragraph and noting that the triplet states reached by inter-system crossing from trans-stilbene singlet and from cis-stilbene singlet are either identical or in rapid equilibrium at room temperature, Mallory (15, p.4382) suggested that the excited state (III) is in the singlet state rather than the triplet. Moore (16, p.830) supported this interpretation. Strong confirmatory evidence was provided by Hammond and co-workers when they failed to observe the formation of the dihydrophenanthrene (IV) in experiments in which stilbene in the triplet-state was produced directly by energy transfer from triplet-state photosensitizer molecules (14, p.3098).

Schaffner first proposed (11, p.1324) that the excited state of stilbene (III) cyclized to form the intermediate dihydrophenanthrene (IV). Moore (16, p.830) showed that irradiation of trans-stilbene in oxygen-free solutions produced a yellow intermediate which absorbed at 447 m $\mu$ . This intermediate yielded phenanthrene when exposed to oxygen but slowly reverted to cis-stilbene in the dark in the absence of oxygen. Sargent and Timmons (19, p.2187) obtained 9,10-dicyano-9,10-dihydrophenanthrene (VIa) and 9,10-dicarboximido-9,10-dihydrophenanthrene (VIb) respectively from irradiation of trans- $\alpha\beta$ -dicyano-stilbene (Ia) and diphenylmaleimide (IIb). They proposed that (VIa)

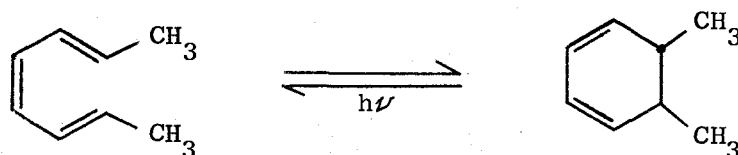


and (VIb) are rearrangement products of the parent dihydrophenanthrene intermediates (IVa) and (IVb).

The formation of phenanthrene (V) from dihydrophenanthrene (IV) is readily understandable, because of the tertiary and doubly allylic character of the two hydrogens in (IV). These hydrogens should be and are easily removed by a suitable oxidant, such as atmospheric oxygen (11, p.1324) (15, p.4361) and (16, p.830). In the absence of oxygen, however, phenanthrene fails to form at a detectable rate from a stilbene solution; in the vapor phase, oxygen is not required (15, p.4361) (16, p.830) (21, p.1355) and (22, p.580-584).

The only question that remains is the stereochemistry of the two tertiary hydrogens in the yellow intermediate (IV). This may be studied by considering the stilbene-dihydrophenanthrene photocyclization as a special case of the conversion of *cis*-1,3,5-hexatriene to

1,3-cyclohexadiene. Fonken (8, p.550) found that ultraviolet



irradiation of 2,4,6-octatriene in ether solution gave trans-5,6-dimethyl-1,3-cyclohexadiene. This suggests a trans configuration for the intermediate (IV). Furthermore, since the cis-dihydrophenanthrene to phenanthrene conversion was estimated to be exothermic by about 47 Kcal per mole, it should be easily achieved. Thus the absence of such a reaction in an oxygen-free solution indirectly supports a trans-configuration (14, p.3099-3100). On the basis of these data, Mallory tentatively assigned the trans configuration to the intermediate dihydrophenanthrene (IV).

While the mechanistic pathway and the stereochemistry of the stilbene-phenanthrene photosynthesis might need further clarification, the synthetic value of the reaction has definitely been established. Mallory and Wood (24, p.3373-77) have developed and reported in detail a general procedure for the preparation and purification of phenanthrenes (60%-85% yield). Their results are well-summarized and only a few points need be mentioned here. Stilbenes bearing fluoro, chloro, bromo, methoxy, methyl, trifluoromethyl, carboxyl and phenyl substituents undergo photocyclization to the corresponding phenanthrenes while those bearing acetyl, dimethylamino, iodo and nitro substituents failed to react. No rearrangements of substituents have been observed; thus

o-, p- or  $\alpha$ -substituted stilbenes give 1-, 3-, 9-substituted phenanthrenes, while m-substituted stilbenes give mixtures of comparable amounts of 2- and 4-substituted phenanthrenes (24, p.3374).

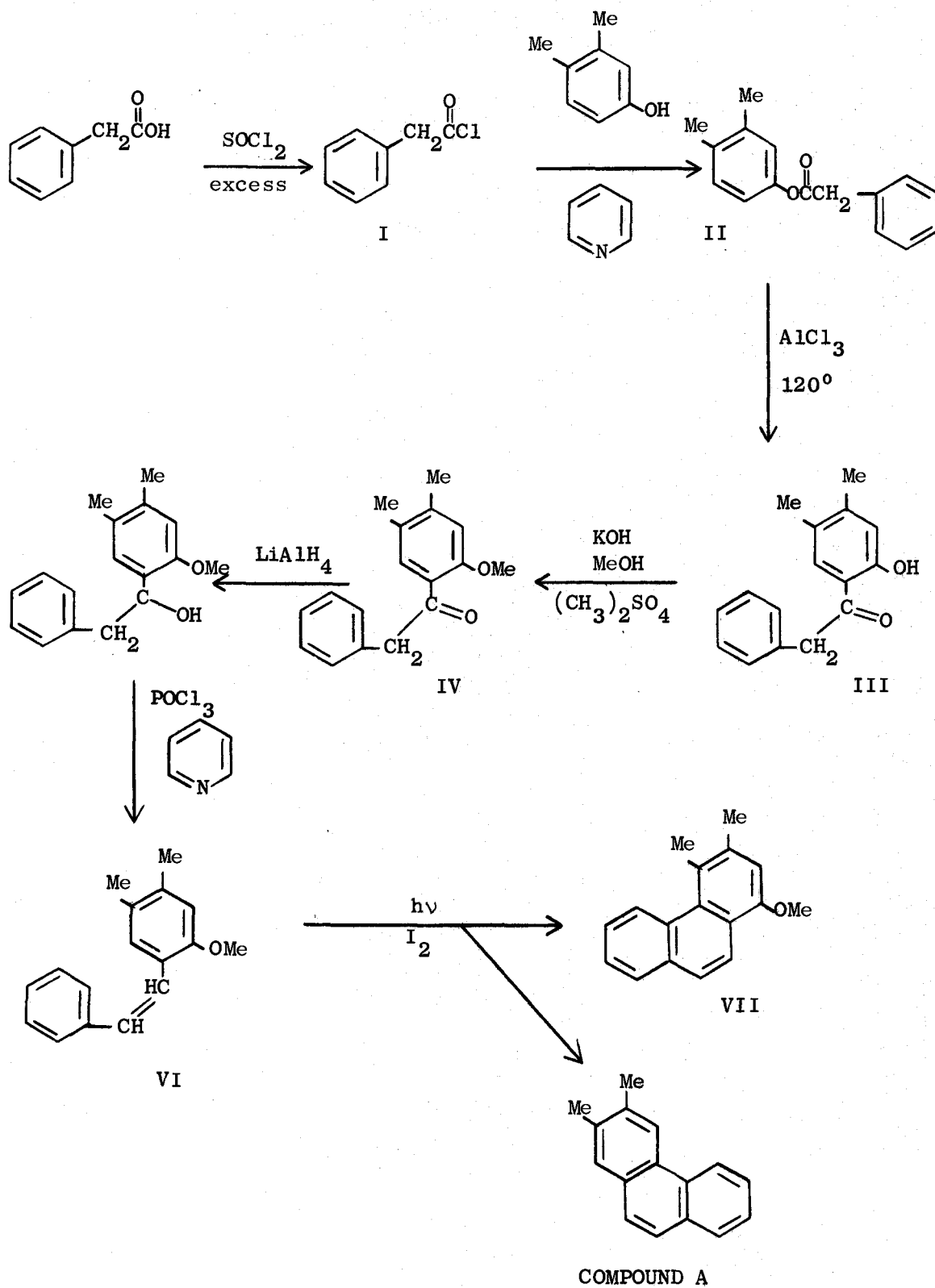
Since substituted stilbenes can readily be prepared, the photochemical method, when applicable, is to be preferred to classical methods like the Pschorr or the Haworth syntheses which involved more steps and lower yields. It is often better than methods involving direct substitution particularly where difficult separations and uncertain structural assignments can be avoided.

### I. Synthetic Procedures

The objective of the synthetic scheme was the compound 2-methoxy-4,5-dimethylstilbene (VI) which could be cyclized to the expected 1-methoxy-3,4-dimethylphenanthrene (VIII) by ultraviolet irradiation. The substituted stilbene (VI) was synthesized by the straightforward procedure indicated on page 11. Structures of all the intermediates were readily established as is indicated below by spectral methods, and the elemental analyses were satisfactory.

The Fries reaction, of 3,4-dimethylphenyl phenylacetate (II), can lead theoretically to two products (3, p.342-369). Clearly 2-phenylacetyl-3,4-dimethylphenol is not expected because of the steric hindrance involved in its formation. Treatment of the ester with aluminum chloride gave a hydroxyketone. That this was the expected 2-phenylacetyl-4,5-dimethylphenol (III) was clearly indicated by the infrared spectrum which showed  $\tilde{\nu} = 1645$  (hydrogen bonded carbonyl), and the n.m.r. spectrum which showed singlet aromatic bands (2) for the protons at C<sub>3</sub> and C<sub>6</sub> on the substituted aromatic ring.

Methylation of this hydroxyketone proved unexpectedly difficult, but was finally made to proceed in acceptable yield. Structure of the methylation product (IV) is indicated by the disappearance of the hydroxyl group, elevation of the frequency of the carbonyl (1645 → 1660) and the appearance of a phenolic ether band at 1260 cm.<sup>-1</sup>. Reduction of the carbonyl (V) proceeded without difficulty, and the final elimination reaction yielded the desired product (VI). This substance has the typical ultraviolet spectrum of a stilbene  $\lambda_{\max}$  320, 284, 228 m $\mu$ , and





the expected infrared spectrum. This is the trans isomer as indicated by the  $J_{AB} = 16$  for the coupling of the two olefinic protons, a  $965 \text{ cm.}^{-1}$  in the infrared (2, p.45), and the strong resemblance of the ultraviolet spectrum to that of trans-stilbene. (Figs. 1 and 2)

## II. Ultraviolet Irradiation

### a) Identification of Products

The irradiation was conducted in a cyclohexane solution following closely the procedure given by Mallory (15, p.4362). The progress of the reaction was followed by registering the ultraviolet spectrum of aliquots removed at intervals. After irradiation, the crude product, a brown oil weighing 2.49 g., did not crystallize after being left in the refrigerator for two days. Examination of the oil by thin layer chromatography indicated a mixture of at least eight components. This mixture was chromatographed over alumina and the early fractions yielded a substance, compound A, m.p.  $80^{\circ}$ . After recrystallization, compound A melted sharply at  $79.2-80^{\circ}$  (corr.). The following

Absorptions	Phenanthrene	Compound A
Infrared	1378	1380
(Nujol)	1040	1046
$\text{cm}^{-1}$	872	880
	865	872
	815	805
	732	742
Ultraviolet	293	297
(cyclohexane)	281	284
	274	278
m $\mu$	252	254

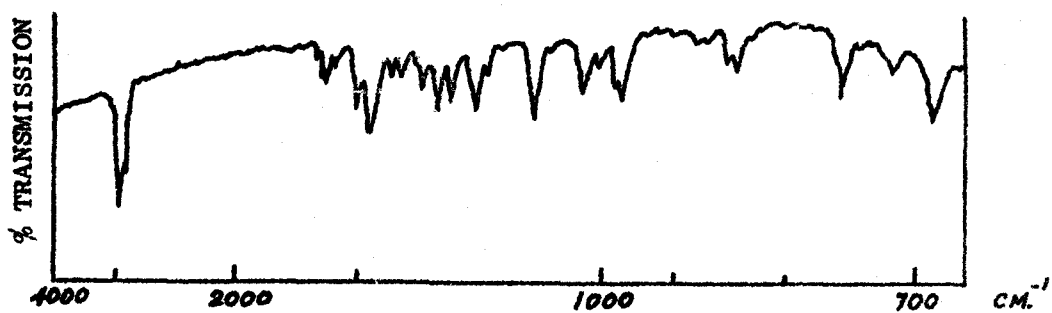


Fig. 1

I. R. SPECTRUM OF 2-METHOXY-4,5-DIMETHYLSTILBENE (VI)

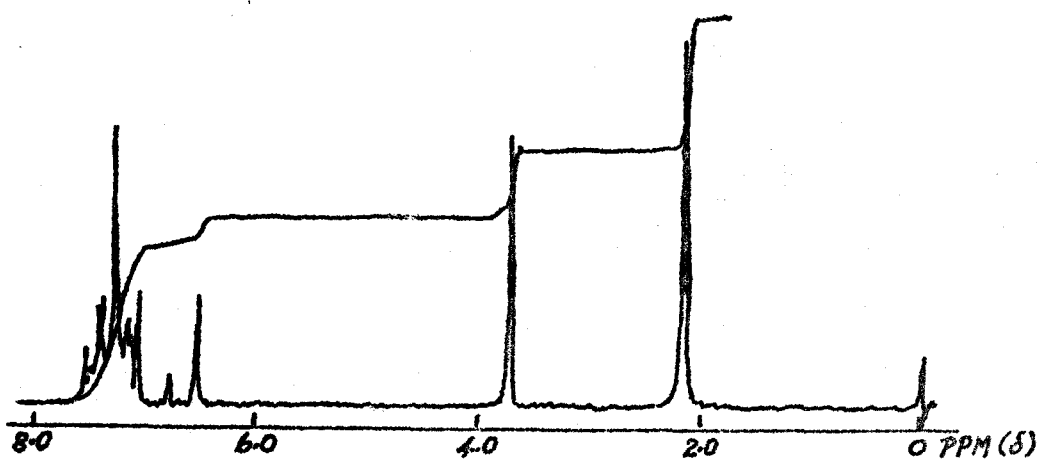


Fig. 2

N.M.R. SPECTRUM OF (VI)

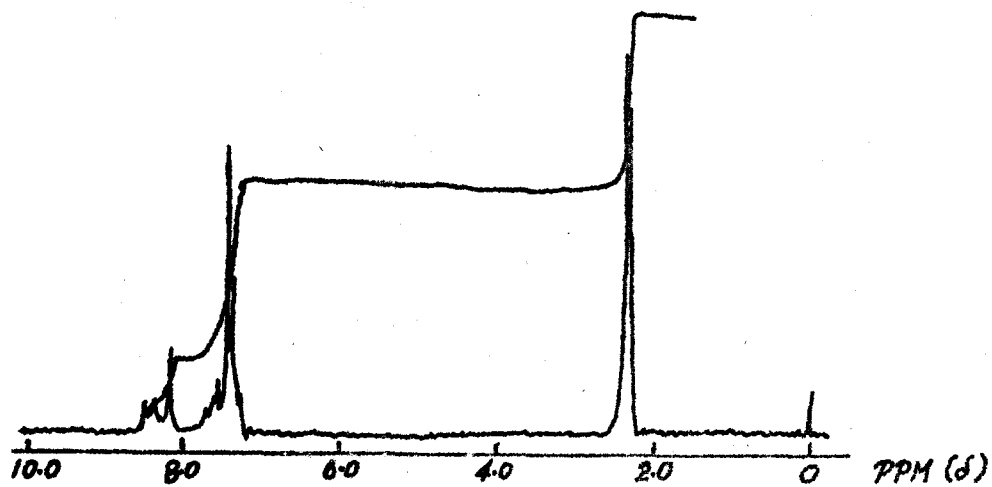


Fig. 3

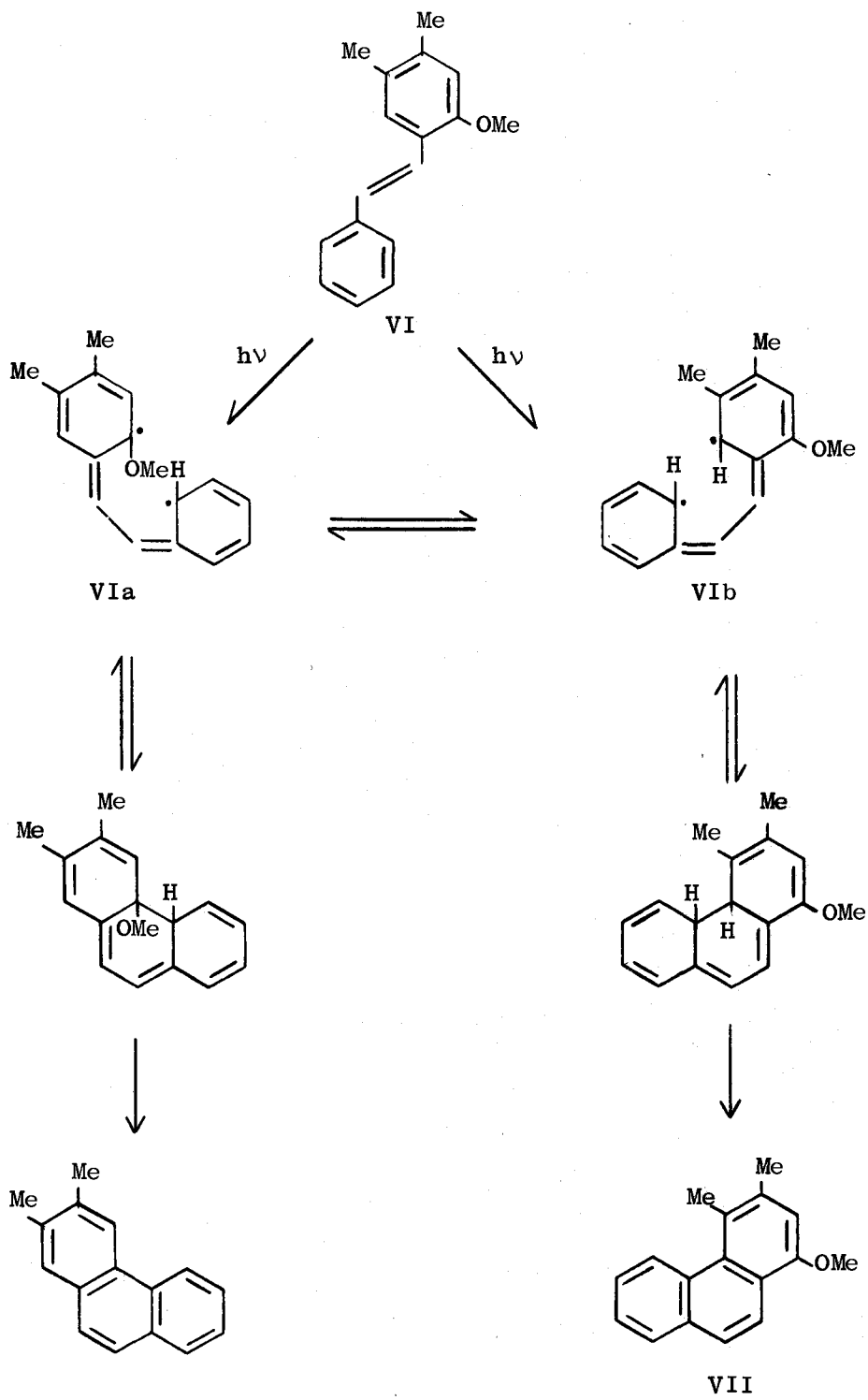
N.M.R. SPECTRUM OF 2,3-DIMETHYLPHENANTHRENE

fractions yielded a component suspected of being the trans and cis isomers of the substituted stilbene (VI). This mixture was fluorescent, had an  $R_f$  value similar to that of the original stilbene, and showed a similar infrared spectrum. Further fractions were not identified. A comparison of the spectral data of compound A with that of phenanthrene showed a striking similarity and suggested that compound A should have the phenanthrene skeleton. Finally, its n.m.r. spectrum (Fig. 13) did not show the presence of the methoxy group. Consequently the substituted stilbene (VI) was assumed to have lost its methoxy group during cyclization to form the phenanthrene ring. Comparison of the properties of compound A and some of its derivatives with some dimethylphenanthrenes and their derivatives (7, p.2196 and 10, p.457-8) suggested that compound A was 2,3-dimethylphenanthrene.

	1,3-dimethyl- phenanthrene	2,3-dimethyl- phenanthrene	Compound A
m.p.	76-7°	79-80°	79.2-80° (Corr.)
picrate	153-5°	146-7°	149-50°
styphnate	165-6°	147-8°	151-151.5°

#### b) Rationale

Though the formation of 2,3-dimethylphenanthrene in the irradiation of 2-methoxy-4,5-dimethylstilbene was unexpected, the process can readily be rationalized (p.15). It has been reported that irradiation of m-substituted stilbenes gives mixtures of 2- and 4-substituted phenanthrenes (15, p.4362). Similarly (VI) can react via either (VIa)



or (VIb) to give 2,3-dimethylphenanthrene or 1-methoxy-3,4-dimethylphenanthrene (VIII). It was assumed originally that the 2-methoxy substituent could serve as a blocking group so that (VII) would be the predominant product. It is possible that the 5-methyl substituent is bulky enough to offer steric hindrance so that the methoxy group is expelled instead to produce a less strained structure. Furthermore, the recent report (24, p.3373-4) that a small amount of phenanthrene was formed along with 1-methoxyphenanthrene when a highly diluted solution of o-methoxystilbene was irradiated suggests that the o-methoxy group on a substituted stilbene maybe somewhat labile relative to other o-substituents. These considerations provide at least a partial explanation for the unexpected result obtained.

## EXPERIMENTAL

Phenylacetyl Chloride.--A solution containing 100 g. (0.735 mole) of phenylacetic acid in four molar equivalents of thionyl chloride was heated slowly to boiling and then refluxed for 3 hours. Excess thionyl chloride was removed in vacuo, at 144 mm. and 38°. The light reddish phenylacetyl chloride, b.p. 95° (13 mm.) weighed 109 g. (96%) [reported 96° (14 mm.)] (1, p.2277).

3,4-Dimethylphenyl Phenylacetate.--Phenylacetyl chloride, 105 g. (0.68 mole), was added dropwise to a solution of 83.1 g. (0.68 mole) of 3,4-dimethylphenol in 80.5 ml. (1 mole) of pyridine under anhydrous conditions and with constant stirring. The resulting mixture warmed up slightly, and after being shaken occasionally for an hour, it was left standing at room temperature overnight. The semi-solid mass was washed with 150 ml. of water and 5% NaHCO<sub>3</sub> respectively. The crude product was recrystallized from 95% alcohol, yielding 93.1 g. (57%), m.p. 53-54°, of the desired product.

Anal. Calcd. for C<sub>16</sub>H<sub>16</sub>O<sub>2</sub>: C, 79.97; H, 6.71. Found: C, 79.76; H, 6.55.

2-Phenylacetyl-4,5-dimethylphenol.--A mixture of 91.3 g. (0.38 mole) of 3,4-dimethylphenyl phenylacetate and 69.0 g. (0.52 mole) of powdered anhydrous AlCl<sub>3</sub> in a 1-l. flask was immersed in an oil bath preheated to 90°. The mixture was heated rapidly to 120-125° and maintained there for 25 minutes while being stirred vigorously. After standing overnight, the reaction mixture was decomposed with 95% EtOH.

The crude product was taken up in petroleum ether and the solution extracted with Claisen's alkali. The alkaline layer was carefully acidified with 2N HCl, and the solid product recrystallized from EtOH, m.p. 70-71°, 39.5 g. (43%),  $\bar{\nu}$  = ca. 3100 broad (chelate OH), 1645 (hydrogen-bonded CO), 1270 (phenol) and 1380 (Me)  $\text{cm.}^{-1}$ .

Anal. Calcd. for  $\text{C}_{16}\text{H}_{16}\text{O}_2$ : C, 79.97; H, 6.71. Found: C, 80.12; H, 6.65.

2-Phenylacetyl-4,5-dimethylanisole.---To a mixture of 36 g. (0.15 mole) of 2-phenylacetyl-4,5-dimethylphenol in 10 ml. of  $\text{CH}_3\text{OH}$  was added excess Claisen's alkali (57 ml., containing 0.265 mole of KOH) and 27.6 ml. (36.8 g. or 0.292 mole) of dimethylsulfate, alternately in small portions; the solution was stirred vigorously and kept at 70°. After the addition, the solution (alkaline) was refluxed for 2 hours, allowed to cool to room temperature and extracted with pentane. The pentane solution was washed with Claisen's alkali, 5%  $\text{NaHCO}_3$  and water respectively. The solvent was removed by evaporation and the crude product was recrystallized from  $\text{CH}_3\text{OH}$ . The yield was 30 g. (80%), m.p. 54-55°,  $\bar{\nu}$  = 1660 (unbonded CO) and 1260 (ether)  $\text{cm.}^{-1}$ .

Anal. Calcd. for  $\text{C}_{17}\text{H}_{18}\text{O}_2$ : C, 80.28; H, 7.13. Found: C, 79.73; H, 6.92.

2-Methoxy-4,5-dimethylphenylbenzylcarbinol.---A solution of 25.43 g. (0.1 mole) of 2-phenylacetyl-4,5-dimethylanisole in 125 ml. of anhydrous ether was added dropwise to an equal volume of ether containing 1.15 g. (0.028 mole) of 95% pure  $\text{LiAlH}_4$ . The reaction mixture was protected from atmospheric moisture by  $\text{CaCl}_2$  tubes and

addition was made at such a rate that a gentle reflux was maintained. After the addition, the solution was stirred for an hour and then 5 ml. of water and 60 ml. of 3N  $\text{NH}_4\text{Cl}$  were added cautiously to decompose the hydride. The resulting aqueous layer was extracted with two 30 ml. portions of ether, the ether solutions combined and washed with two 50 ml. portions of water. Evaporation of the ether gave a crude product which was recrystallized from 400 ml. of 3:1 methanol-water mixture. This gave a white solid, 24.3 g. (95%), m.p. 90-92.5°. Further recrystallization from ligroin (70-90° fraction) gave crystals, m.p. 90-91.5°,  $\bar{\nu}^{\text{Nujol}} = 3280$  (bonded OH) and  $\bar{\nu}^{\text{CCl}_4} = 3530$  (free OH)  $\text{cm.}^{-1}$ .

Anal. Calcd. for  $\text{C}_{17}\text{H}_{20}\text{O}_2$ : C, 79.65; H, 7.86. Found: C, 79.80; H, 7.51.

2-Methoxy-4,5-dimethylstilbene.—To a solution of 3 ml. (0.02 mole) of phosphorus oxychloride in 3 ml. of dry pyridine was added dropwise with stirring 12.42 g. (0.048 mole) of 2-methoxy-4,5-dimethylphenylbenzylcarbinol in 12 ml. of dry pyridine. The solution warmed up during the addition which took 70 minutes. An additional 1 ml. of  $\text{POCl}_3$  in 2 ml. of dry pyridine was introduced, and the solution was kept at reflux temperature in an oil bath overnight. After cooling, it was poured into 250 g. of cracked-ice with vigorous stirring. The mixture was extracted with three 200 ml. portions of pentane, the pentane solution washed with three 200 ml. portions of water and dried over anhydrous  $\text{MgSO}_4$ . The solvent was evaporated, giving 10.77 g. (93%), m.p. 50-54° of white crystals. An analytical sample was prepared by recrystallization from isopropanol, m.p. 55-56°,  $\bar{\nu}^{\text{Nujol}} = 1626, 1609, 1595,$



1502, 1280, 1252 (ether), 965 (trans double bond)  $\text{cm.}^{-1}$ ,  $\lambda_{\text{max}}$  (cyclohexane) 320, 284, 228  $\text{m}\mu$ . The n.m.r. spectrum ( $\text{CCl}_4$ ) showed three singlets, (6H) at  $\tau$ 7.87, (3H) at  $\tau$ 6.29, (1H) at  $\tau$ 3.50; AB pattern (2H) ( $J = 16$  cps) at  $\tau$ 2.66 and  $\tau$ 3.03; and multiplet (6H) between 426-450 cps.

Anal. Calcd. for  $\text{C}_{17}\text{H}_{18}\text{O}$ : C, 85.67; H, 7.61. Found: C, 85.85; H, 7.33.

Irradiation of 2-Methoxy-4,5-dimethylstilbene.---A solution of 2.38 g. (0.01 mole) of 2-methoxy-4,5-dimethylstilbene in 1 l. of cyclohexane containing 50.8 mg. (0.2 mmole) of iodine was irradiated for 15 hours using a 450 watt medium pressure Hanovia ultraviolet lamp. As the reaction proceeded the initially pink solution turned yellow and a precipitate appeared. The solution was filtered, washed with 0.01M sodium thiosulfate solution and dried over anhydrous  $\text{MgSO}_4$ . Evaporation of the solvent left 2.49 g. of brown oil. This was chromatographed over alumina (75 g. Merck) using cyclohexane as eluant. The early fractions contained 220 mg (10.8%) of 2,3-dimethylphenanthrene, m.p. 79-81°. After recrystallization from  $\text{CH}_3\text{OH}$  containing a trace of water, the product melted at 79.2-80°,  $\tilde{\nu} = 1380, 1046, 880-872$  doublet, 805 and 742  $\text{cm.}^{-1}$ ,  $\lambda_{\text{max}}$  297, 284, 278, 254  $\text{m}\mu$ . The n.m.r. spectrum showed two singlets at  $\tau$ 7.67 and  $\tau$ 7.71 and a series of peaks between 438-520 cps. The ratio of the areas under the latter to the former was 1.4 (calculated for 2,3-dimethylphenanthrene = 1.3). 2,3-Dimethylphenanthrene has been reported to melt at 79-80° (7, p.2196). Further elution using cyclohexane-benzene mixtures gave no pure materials.

### SUMMARY

The synthesis of 2-methoxy-4,5-dimethylstilbene has been achieved by unequivocal methods and the structure confirmed by spectral methods. Irradiation of the substituted stilbene employing the method recently developed by Mallory gave unexpected results. Instead of the expected product, 1-methoxy-3,4-dimethylphenanthrene, a different phenanthrene was obtained and was identified as 2,3-dimethylphenanthrene (10%). At least seven other products, two of which were tentatively identified as the trans and cis isomers of the substituted stilbene, were present in the irradiation product.

Clearly ring closure to a dihydrophenanthrene bearing angular substituents can occur. When these can be conveniently eliminated under the reaction conditions, formation of a phenanthrene with loss of a substituent is to be expected. The factors which determine the course of the ring closure step in unsymmetrical cases like that investigated here are not yet clear.

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