spectra showed it to be identical with material prepared by the above method.

Benzylation of 2-Amino-4-thiopteridine.—Into 25 ml. of 28% aqueous ammonium hydroxide were placed 1.0 g. of 2-amino-4-thiopteridine. With vigorous stirring a solution of 0.7 ml. of benzyl chloride in 3 ml. of dioxane was added slowly. Stirring was continued for 1 hr. at room temperature. The precipitate was removed and triturated with 50 ml. of ethanol. The mixture was filtered and water was added to the filtrate until the solution became cloudy. On chilling, a 15% yield of yellow crystalline product with spectral characteristics and melting point identical with those of 2-amino-4-benzylthiopteridine prepared by glyoxal cyclization was obtained.

This product could be prepared conveniently in an over-all yield of 40% by the condensation of the dihydrochloride of II with glyoxal monohydrate, followed by benzylation, without isolation of the intermediate 2-amino-4-thiopteridine.

2-Amino-4-hydroxypteridine.—To a solution of 300 mg. of 2-amino-4-benzylthiopteridine in 25 ml. of absolute ethanol were added 1 g. of sodium hydroxide pellets. The mixture was heated to reflux for 30 min. The reaction mixture was chilled, acidified with 3 *N* hydrochloric acid, and refrigerated for 2 days. The solid product was obtained in 55% yield. Its identity with 2-amino-4-hydroxypteridine obtained by a modification of the method of Cain, Mallette, and Taylor,[15] using solid glyoxal monohydrate rather than glyoxal sodium bisulfite, was established by ultraviolet and infrared spectroscopy and paper chromatography.

4-Hydroxypteridine.—A mixture of 300 mg. of 4-methylthiopteridine and 1.0 g. of sodium hydroxide pellets in 25 ml. of absolute ethanol was heated with stirring to 70° for 30 min. and then evaporated to dryness. The residue was treated with 10 ml. of water and the pH of the mixture was adjusted to 3 with hydrochloric acid. On refrigeration, the product was obtained in 60% yield. Ultraviolet and infrared spectra were identical with those of 4-hydroxypteridine prepared by the method of Albert, *et al.*[30]

2-Amino-4-hydroxylaminopteridine.—A mixture of 4.0 g. of hydroxylamine hydrochloride and 2.0 g. of 2-amino-4-benzylthiopteridine in 100 ml. of ethanol was heated with stirring to reflux for 10 min. and then evaporated to dryness under vacuum. The residue was suspended in 500 ml. of water and the pH was adjusted to 5 with 1 *N* sodium hydroxide solution. On heating, a yellow solution was obtained which was filtered. The filtrate was refrigerated overnight. The yellow, analytically pure precipitate was removed by filtration, washed with water, and dried.

(30) A. Albert, D. J. Brown, and G. Cheeseman, *J. Chem. Soc.*, 474 (1951).

The substance, which was obtained in 75% yield, gave a violet color with ferric chloride and could be converted to 2,4-diaminopteridine upon treatment with boiling aqueous sodium dithionate; ultraviolet spectrum (0.1 *N* HCl): λ_{max} 217 and 340 mμ (ϵ_{max} 23,000 and 9300).

Anal. Calcd. for $C_6H_6N_6O \cdot 3H_2O$: C, 31.00; H, 5.20; N, 36.20; H_2O, 23.34. Found: C, 31.13; H, 5.42; N, 35.90; H_2O, 23.42.

2-Amino-4-hydrazinopteridine. A. From 2-Amino-4-benzylthiopteridine.—A solution of 2.5 g. of 2-amino-4-benzylthiopteridine in 50 ml. of methanol was treated with 2.5 ml. of 85% hydrazine hydrate and heated to reflux for 15 min. with stirring. The solution was refrigerated overnight, the product was removed by filtration and washed with successive portions of water, ethanol, and ether. The residue was recrystallized from hot water and dried over phosphorus pentoxide. A yield of 40% was obtained; ultraviolet spectrum (0.1 *N* HCl): λ_{max} 236, 285, 318 infl., 334, and 347 infl. mμ (ϵ_{max} 12,120, 5000, 7900, 9800, and 8600).

Anal. Calcd. for $C_6H_7N_7 \cdot H_2O$: C, 37.00; H, 4.65; N, 50.25; H_2O, 9.21. Found: C, 37.50; H, 4.93; N, 50.62; H_2O, 8.93.

Reaction with *p*-nitrobenzaldehyde[31] yielded the yellow hydrazone, m.p. 311° dec., which was recrystallized from acetic acid.

Anal. Calcd. for $C_{13}H_{10}N_8O_2 \cdot H_2O$: C, 47.60; H, 3.67. Found: C, 47.48; H, 3.73.

B. From 2,4-Diaminopteridine.—A suspension of 350 mg. of 2,4-diaminopteridine in 25 ml. of 85% hydrazine hydrate was heated with stirring to 140° for 1 hr. On chilling, the product was obtained in 80% yield. Ultraviolet and infrared spectra showed it to be identical with material prepared from 2-amino-4-benzylthiopteridine.

2,4-Diaminopteridine.—A solution of 250 mg. of 2-amino-4-benzylthiopteridine in a mixture of 25 ml. of ethanol and 25 ml. of concentrated aqueous ammonium hydroxide was heated in a pressure bottle on a steam bath for 6 hr., cooled to room temperature, and evaporated to dryness under reduced pressure. The residue was recrystallized from 50 ml. of boiling water. A 50% yield of material with infrared and ultraviolet spectra identical with those of 2,4-diaminopteridine prepared by the method of Mallette, Cain, and Taylor[15] was obtained.

Acknowledgment.—We are indebted to Mrs. J. K. Krackov for determining the ultraviolet spectra reported.

(31) R. S. Shriner, R. L. Fuson, and D. Y. Austin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 219.

Photochemistry of Stilbenes. IV. The Preparation of Substituted Phenanthrenes[1a-c]

CLELIA S. WOOD AND FRANK B. MALLORY[1d]

Department of Chemistry, Bryn Mawr College, Bryn Mawr, Pennsylvania

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The synthetic value of the photoconversion of stilbenes to phenanthrenes in solution in the presence of small amounts of iodine and dissolved oxygen is demonstrated by a variety of examples of the preparation of substituted phenanthrenes using this photoreaction.

A general discussion of the scope and mechanism of the photoconversion of stilbenes to phenanthrenes in solution in the presence of oxidants such as iodine and oxygen has been given in an earlier paper in this series.[1a] In the present paper the synthetic value of this photoreaction for the preparation of substituted phenanthrenes will be considered in more detail.

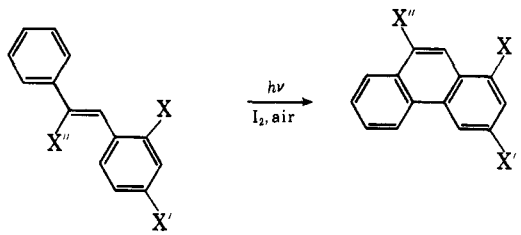
The most satisfactory conditions that have been developed for preparative-scale reactions involve the irradiation with an unfiltered mercury arc of a stirred solution of 0.01 mole of the stilbene derivative and 0.0005 mole of iodine dissolved in 1 l. of cyclohexane or benzene open to the air. The preparative-scale results using this mixture of two oxidants, iodine and dissolved oxygen, are far superior to those achieved using oxygen alone; under the latter conditions the required irradiation times are much longer and the products may be obtained in low yield and low purity.[2,3]

(1) (a) Part III: F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Am. Chem. Soc.*, **86**, 3094 (1964). (b) Taken in part from the Ph.D. Dissertation of C. S. Wood, Bryn Mawr College, 1963. (c) Presented in part before the Organic Division at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961. (d) John Simon Guggenheim Memorial Foundation Fellow, 1963–1964.

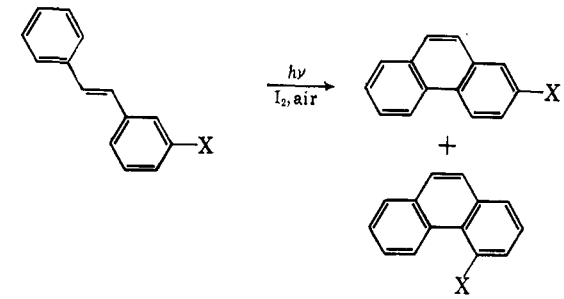
(2) F. B. Mallory, J. T. Gordon, and L. C. Lindquist, Abstracts, 3rd Delaware Valley Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb., 1960.

(3) P. Hugelshofer, J. Kalvoda, and K. Schaffner, *Helv. Chim. Acta*, **43**, 1322 (1960).

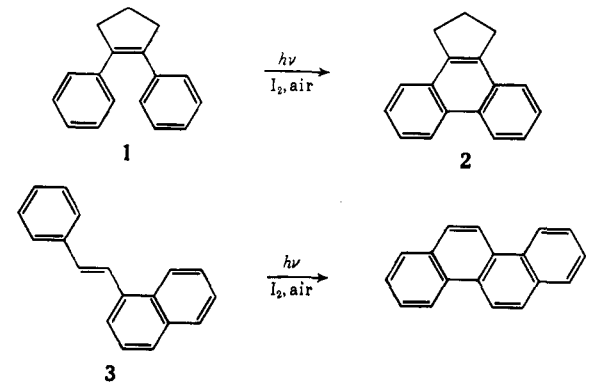
Our results for a variety of examples of this photoreaction are given in Table I. Stilbenes bearing fluoro, chloro, bromo, methoxy, methyl, trifluoromethyl, carboxy, and phenyl substituents have been found to undergo photochemical conversion to the corresponding phenanthrenes. The photoreaction was found to fail, however, with stilbenes having acetyl, dimethylamino, iodo, or nitro substituents, and with 2- and 4-stilbazole and benzalaniline. No rearrangements of substituents have been observed; thus, *o*-, *p*-, or α-substituted stilbenes give 1-, 3-, or 9-substituted phenanthrenes, respectively. *m*-Substituted stilbenes are photoconverted to mixtures of comparable amounts of 2- and 4-substituted phenanthrenes; the difficulty of separating



such mixtures efficiently detracts from the preparative value of the reaction in these cases. However, the 2-substituted isomers, which are generally higher melting than the 4-substituted isomers, can sometimes be separated easily from these mixtures of photoproducts by fractional crystallization; in this manner 2-trifluoromethylphenanthrene[4] and also 2-phenylphenanthrene[5] have been obtained in reasonable yields. *m,m'*-Dimethoxystilbene has been reported[3] to be converted photochemically using dissolved oxygen as the oxidant to a mixture (*ca.* 2:3) of 2,5- and 2,7-dimethoxyphenanthrene; no 4,5-dimethoxyphenanthrene was detected.



Two special cases of the photoreaction are given in Table I: the conversion of 1,2-diphenylcyclopentene (**1**) to 9,10-cyclopentenophenanthrene (**2**), and the conversion of α-styrylnaphthalene (**3**) to chrysene.



As can be seen in Table I, the products of these photo reactions were generally obtained in yields of 60–85%. The yields of 1-substituted phenanthrenes from *o*-substituted stilbenes were somewhat lower, however. *o*-Chlorostilbene and *o*-methylstilbene were shown not to be photoconverted to any significant extent to phenanthrene itself (by formal loss of the elements of HX instead of H_2) since phenanthrene was neither isolated nor detected spectrally as a product of these photoreactions. However, when *o*-methoxystilbene was irradiated at high dilution (*ca.* 4×10^{-5} *M*) with dissolved oxygen as the oxidant, a small amount of phenanthrene was formed along with 1-methoxyphenanthrene as indicated by ultraviolet spectroscopy. Although no phenanthrene was isolated from the preparative-scale reaction of *o*-methoxystilbene described in Table I, the infrared spectrum of the crude product suggested that a small amount of phenanthrene was present.[6] Except for those phenanthrenes with methoxy substituents, the products listed in Table I were found to be quite stable under the irradiation conditions employed.

The use of concentrations of the stilbene greater than about 0.02 *M* was avoided in order to minimize the side reaction of photodimerization to give a tetraarylcyclobutane. Also, reactions carried out starting with more than 0.01 mole of the stilbene were found to give slightly lower yields of less pure products than reactions carried out under the conditions given in Table I. Thus, for the photoconversion of larger amounts of a stilbene it is preferable to carry out the irradiation using separate portions of 0.01 mole or less of the starting material;

(4) (a) The mixture of 2- and 4-trifluoromethylphenanthrene (*ca.* 1:1 as indicated by infrared spectra) that was obtained in 89% yield from the photoreaction of *m*-trifluoromethylstilbene was separated to give one isomer as a solid, m.p. 112.9–113.3°, and the other isomer as a liquid, slightly contaminated by the first isomer; both samples gave satisfactory elemental analyses. Structure assignments were possible for these two products on the basis of their proton n.m.r. spectra,[4b] since the n.m.r. signals for protons at the 4- and 5-positions of phenanthrenes are characteristically shifted downfield compared with the signals for the protons at the remaining positions.[4c] Thus, the isomer melting at 112.9–113.3° is assigned the 2-trifluoromethylphenanthrene structure since its spectrum exhibited a low-field multiplet of at least five lines at δ 8.50–8.82 with area corresponding to two protons. attributed to the protons at the 4- and 5-positions; the spectrum also exhibited a broad singlet at δ 8.05–8.17 with area corresponding to one proton, attributed possibly to the proton at the 1-position shifted slightly downfield by the adjacent electron-attracting trifluoromethyl group, and a multiplet of at least nine lines at δ 7.55–7.90 with area corresponding to the remaining six protons. The isomer obtained as a liquid is assigned the 4-trifluoromethylphenanthrene structure since its spectrum exhibited a low-field multiplet of at least seven lines at δ 8.42–8.90 with area corresponding to one proton, attributed to the proton at the 5-position; the rest of the spectrum consisted of a multiplet of at least twenty lines at δ 7.10–8.13 attributed to the remaining eight protons. For comparison purposes, the spectrum of 3-trifluoromethylphenanthrene was obtained. This spectrum exhibited a broad singlet at δ 8.75–8.83 with area corresponding to one proton, attributed to the proton at the 4-position shifted slightly downfield by the adjacent trifluoromethyl group; a multiplet of at least four lines at δ 8.38–8.75 with area corresponding to one proton, attributed to the proton at the 5-position; and a multiplet at δ 7.42–7.88 with area corresponding to the remaining seven protons. (b) The authors are grateful to Dr. S. L. Manatt, Jet Propulsion Laboratory, California Institute of Technology, for obtaining these spectra. (c) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 248–253.

(5) The photoreaction of *m*-phenylstilbene was carried out in the laboratories of Professor S. C. Dickerman at New York University and the results were communicated privately to us by Professor Dickerman.

(6) Another example of a stilbene photocyclization that involves the loss of an *o*-methoxy group, the photoconversion, in part, of 2-methoxy-4,5-dimethylstilbene to 2,3-dimethylphenanthrene, has been found and communicated privately to us by Professor E. N. Marvell at Oregon State University.

TABLE I

THE PHOTOCONVERSION OF STILBENES TO PHENANTHRENES[a]

Stilbene	Amt., g.	Irr. time, hr.	Phenanthrene	Recrystn. solvent	Yield, %	M.p., °C.	Lit. m.p., °C.
Parent	1.80	7	Parent	95% EtOH[b]	73	98.0–99.4	99.0–99.5[c]
p-F	1.98	10	3-F	MeOH	76	88.2–89.0	84[d]
p-Cl	2.15	6	3-Cl	MeOH	76	79.6–80.2	80.5–81.5[e]
p-Br	2.59	16[f]	3-Br	95% EtOH	76	81.2–82.8	83–84[e]
p-CH_3O	1.05[g]	20[f]	3-CH_3O	MeOH	42	52.0–56.4[h]	59[i]
p-CH_3	1.94	10	3-CH_3	MeOH	67	61.5–62.9	62–63[j]
p-CF_3	2.48	14	3-CF_3	MeOH	60	54.0–56.4	...[k]
o-Cl	2.15	20[f]	1-Cl	95% EtOH	57	115.2–119.0[l]	120.0–120.5[e]
o-CH_3O	2.10	10	1-CH_3O	MeOH	46	98.5–102.0[m]	105[n]
o-CH_3	1.94	8	1-CH_3	MeOH	57	117.6–119.6[o]	118,[j] 123[p]
m-CF_3	2.48	8	2-, 4-CF_3	...	89	Liquid[q]	...[q]
α-CO_2H	2.24[r]	12	9-CO_2H	95% EtOH	72	255.0–256.0[s]	259.2–260.0[t]
α-C_6H_5	2.56	5	9-C_6H_5	95% EtOH	85	103.4–104.4	104–105[u]
1	2.20	3	**2**	95% EtOH[v]	71	147.3–150.0[w]	150, 154[x]
3	2.30	4	Chrysene	C_6H_6[y]	77	253.5–254.5	255–256[z]

[a] The photoconversions were carried out starting with 0.01 mole of the stilbene and 5 mole % of iodine in 1 l. of cyclohexane unless otherwise noted. The crude products were purified by chromatography on alumina prior to recrystallization. [b] The product was purified by reduced-pressure sublimation prior to recrystallization. [c] C. C. Price, C. E. Arntzen, and C. Weaver, *J. Am. Chem. Soc.*, **60**, 2837 (1938). [d] P. M. G. Bavin and M. J. S. Dewar, *J. Chem. Soc.*, 4486 (1955); we believe that this melting point is in error; after several additional recrystallizations from 95% ethanol our sample of 3-fluorophenanthrene had constant m.p. 89.3–90.3°. *Anal.* Calcd. for $C_{14}H_{11}F$: C, 85.69; H, 4.62; F, 9.68. Found: C, 85.52; H, 4.57; F, 9.70. [e] W. E. Bachmann and C. H. Boatner, *J. Am. Chem. Soc.*, **58**, 2194 (1936). [f] A Hanovia water-cooled 19433 Vycor immersion well was used with a General Electric H100A4/T mercury lamp. [g] 0.005 mole. [h] Two subsequent recrystallizations from 95% ethanol gave material melting at 57–58°. [i] R. Pschorr, *Ber.*, **34**, 3998 (1901). [j] R. D. Haworth, *J. Chem. Soc.*, 1125 (1932). [k] Two additional recrystallizations from methanol gave a sample of 3-trifluoromethylphenanthrene as transparent cubes, m.p. 56.4–57.6°. *Anal.* Calcd. for $C_{15}H_9F_3$: C, 73.17; H, 3.68. Found: C, 72.96; H, 3.83. [l] An additional recrystallization from 95% ethanol gave material melting at 118.0–119.4°. [m] An additional recrystallization from methanol gave material melting at 102.0–103.2°. [n] L. F. Fieser, *J. Am. Chem. Soc.*, **51**, 2460 (1929). [o] Subsequent recrystallization from dilute ethanol gave material melting at 120.0–121.1°. [p] R. Pschorr, *Ber.*, **39**, 3106 (1906). [q] See Experimental section. [r] The reaction was run in 1 l. of reagent grade, thiophene-free benzene. [s] Recrystallization of the 1.60 g. of 9-phenanthroic acid that was collected from the chilled reaction mixture by suction filtration gave 1.22 g. (55%) of material melting at 257.5–259.0°. [t] J. A. Dixon and D. D. Neiswender, Jr., *J. Org. Chem.*, **25**, 499 (1960). [u] C. K. Bradsher and A. K. Schneider, *J. Am. Chem. Soc.*, **60**, 2960 (1938). A sample of 9-phenylphenanthrene that had been exhaustively purified by zone refining and by recrystallization from 95% ethanol melted at 104.1–104.7°. [v] The product was sublimed at reduced pressure after recrystallization. [w] Two additional recrystallizations from 95% ethanol gave 9,10-cyclopentenophenanthrene with m.p. 152.5–153.5°. [x] G. M. Badger, W. Carruthers, J. W. Cook, and R. Schoental, *J. Chem. Soc.*, 169 (1949); C. Weizmann, E. Bergmann, and T. Berlin, *J. Am. Chem. Soc.*, **60**, 1331 (1938). [y] The usual chromatography was omitted; the crude product was sublimed prior to recrystallization. [z] A. Magnus, H. Hartmann, and F. Becker, *Z. physik. Chem.* (Leipzig), **197**, 75 (1951).

the total irradiation time required for complete conversion of a large amount of a stilbene will not be affected significantly by dividing the reactant into smaller batches, and the irradiated batches can be combined for work-up. In some cases it was found advantageous to use a water-cooled probe to avoid high temperatures in that small portion of the reaction mixture immediately surrounding the light source in which the photoreaction occurs.[1a]

For those cases in which the photochemical method is applicable, it is preferable to classical methods for preparing substituted phenanthrenes. Fewer steps are involved than in the Pschorr or the Haworth syntheses. Also, the photochemical method (except for the reactions of *m*-substituted stilbenes) has two advantages over methods involving direct substitution on a phenanthrene: the tedious and difficult separation of a mixture of isomeric substituted phenanthrenes is avoided, and the structure of the photochemical product apparently (on the basis of the results presented in Table I) can be assigned safely from knowledge of the structure of the reactant stilbene. Substituted stilbenes are readily available by a variety of methods as indicated below.[7]

$$ArCH_2Cl + Ar'CHO \xrightarrow[(2)\ -H_2O]{(1)\ \text{Grignard}} Ar{-}CH{=}CH{-}Ar'$$

$$ArBr + Ar'CH_2CHO \xrightarrow[(2)\ -H_2O]{(1)\ \text{Grignard}} Ar{-}CH{=}CH{-}Ar'$$

$$ArCH_2CO_2H + Ar'CHO \xrightarrow[(2)\ -CO_2]{(1)\ Et_3N,\ Ac_2O} Ar{-}CH{=}CH{-}Ar'$$

$$ArNH_2 + Ar'CH{=}CHCO_2H \xrightarrow{\text{diazotization}} Ar{-}CH{=}CH{-}Ar'$$

$$ArCHO \xrightarrow{KCN} Ar{-}\overset{O}{\overset{\|}{C}}{-}\overset{OH}{\overset{|}{C}}H{-}Ar \xrightarrow[(2)\ NaBH_4\ (3)\ Zn]{(1)\ SOCl_2} Ar{-}CH{=}CH{-}Ar$$

Experimental[8]

Preparation of Stilbenes.—For all those cases described below in which the stilbenes are capable of exhibiting *cis–trans* isomerism, the products were shown to have the *trans* configuration, expected by the method of synthesis, by the presence in their in-

(7) (a) H. Adkins and W. Zartman, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 606; (b) R. E. Buckles and K. Bremer, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p. 777; R. E. Buckles and N. G. Wheeler, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p. 857; (c) C. S. Rondestvedt, Jr., *Org. Reactions*, **11**, 189 (1960); (d) L. F. Fieser, *J. Chem. Educ.*, **31**, 291 (1954).

(8) Melting points are corrected. Boiling points are uncorrected. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Sublimations were carried out at a pressure of about 0.03 mm. using equipment described elsewhere.[9] N.m.r. spectra were obtained at 60 Mc. in deoxygenated deuteriochloroform solution with tetramethylsilane as an internal standard using a Varian Associates A-60 spectrometer.

(9) F. B. Mallory, *J. Chem. Educ.*, **39**, 261 (1962).

frared spectra of an intense absorption peak in the 961–967-cm.$^{-1}$ region.[10]

trans-**Stilbene.**—Eastman grade *trans*-stilbene was recrystallized from 95% ethanol (20 ml./g.) to give a 92% recovery of material with m.p. 123.6–124.2° (lit.[11] m.p. 125°).

trans-p-**Fluorostilbene.**—A mixture of 6.0 g. (0.25 g.-atom) of magnesium turnings, an iodine crystal, and 30 ml. of dry tetrahydrofuran was stirred mechanically during the addition over 15 min. of a solution of 43.0 g. (0.25 mole) of *p*-bromofluorobenzene in 120 ml. of tetrahydrofuran. The reaction mixture was heated for an additional 40 min. after which there was added with good stirring 23.0 g. (0.19 mole) of phenylacetaldehyde in 30 ml. of tetrahydrofuran over a period of 10 min. The reaction mixture was maintained at reflux for an additional 40 min. and was then poured onto ice and dilute sulfuric acid. The organic layer was separated and evaporated to dryness using a water aspirator and a rotary evaporator. The residue was heated at reflux for 2 hr. with 100 ml. of 50% sulfuric acid. The resulting dark solid was collected by suction filtration, washed with water, recrystallized from 95% ethanol, sublimed, and finally recrystallized again from 95% ethanol to give 19.5 g. (52%) of white crystalline *trans-p*-fluorostilbene, m.p. 123.6–124.6°. A sample purified by three additional recrystallizations from 95% ethanol melted at 124.4–125.0°.

Anal. Calcd. for $C_{14}H_{11}F$: C, 84.82; H, 5.59; F, 9.58. Found: C, 84.82; H, 5.68; F, 9.58.

A small sample of this material was treated with pyridinium bromide perbromide in acetic acid solution[12] and the resulting solid was collected by suction filtration and recrystallized from methanol rapidly (to avoid extensive dehydrobromination). *meso-p*-**Fluorostilbene dibromide** was obtained as white plates, m.p. 214.5–214.8° dec.

Anal. Calcd. for $C_{14}H_{11}Br_2F$: Br, 44.64. Found: Br, 44.82.

trans-p-**Chlorostilbene.**[13]—The procedure was based on general methods previously described.[7b] Condensation of *p*-chlorobenzaldehyde with phenylacetic acid in the presence of triethylamine and acetic anhydride gave *p*-**chloro-α-phenylcinnamic acid**, m.p. 202–203° (lit.[14] m.p. 202–203°). This acid was decarboxylated by heating with copper chromite catalyst in quinoline. The crude product was heated with a trace of iodine to effect isomerization of the *cis* to the *trans* isomer. After recrystallization from 95% ethanol there was obtained *trans-p*-chlorostilbene, m.p. 129.2–129.6° (lit.[15] m.p. 127°).

trans-p-**Bromostilbene.**—From the Grignard reaction of *p*-dibromobenzene and phenylacetaldehyde in ether there was obtained after dehydration *trans-p*-bromostilbene, m.p. 136.0–137.6° (lit.[16] m.p. 139.5–140.0°).

trans-p-**Methoxystilbene.**[13]—The procedure was similar to that described above for *trans-p*-chlorostilbene. Condensation of *p*-anisaldehyde with phenylacetic acid gave *p*-**methoxy-α-phenylcinnamic acid**, m.p. 189–190° (lit.[16] m.p. 193–194°). Decarboxylation and *cis* → *trans* isomerization followed by recrystallization from absolute ethanol and sublimation gave *trans-p*-methoxystilbene, m.p. 136.2–137.0° (lit.[17] m.p. 135–136°).

trans-p-**Methylstilbene.**[13]—The procedure was similar to that described above for *trans-p*-chlorostilbene. Condensation of *p*-tolualdehyde with phenylacetic acid gave *p*-**methyl-α-phenylcinnamic acid**, m.p. 168–171° (lit.[16] m.p. 168°). Decarboxylation and *cis* → *trans* isomerization followed by recrystallization from 95% ethanol gave *trans-p*-methylstilbene, m.p. 119.2–119.8° (lit.[17] m.p. 119.5–120.0°).

trans-p-**Trifluoromethylstilbene.**—*p*-Trifluoromethylphenylmagnesium bromide was prepared from 22.5 g. (0.10 mole) of *p*-bromobenzotrifluoride, 5.0 g. (0.21 g.-atom) of magnesium turnings, and 0.5 g. of iodine in 100 ml. of dry ether by a method previously described.[18] To the well-stirred solution of the Grignard reagent was added over 30 min. 12.0 g. (0.12 mole) of phenylacetaldehyde in 40 ml. of ether. The mixture was heated at reflux for an additional 15 min. and then was poured onto ice and dilute hydrochloric acid. The two-phase mixture was extracted with ether and the ether extract was evaporated using a water aspirator and a rotary evaporator. The residue was heated at reflux for 30 min. with 200 ml. of 50% sulfuric acid. This mixture was extracted with ether and the ether extract was dried over anhydrous sodium sulfate and evaporated to dryness on a steam bath. The residue was sublimed to give 16.0 g. (65%) of material that was subsequently recrystallized from 95% ethanol to give 12.3 g. (50%) of *trans-p*-trifluoromethylstilbene, m.p. 132.6–133.6°. A small sample purified by three additional recrystallizations from 95% ethanol melted at 133.3–133.6°.

Anal. Calcd. for $C_{15}H_{11}F_3$: C, 72.57; H, 4.47; F, 22.96. Found: C, 72.65; H, 4.43; F, 22.95.

trans-o-**Chlorostilbene.**—From the Grignard reaction of *o*-chlorobenzyl chloride and benzaldehyde in ether there was obtained after dehydration *trans-o*-chlorostilbene, m.p. 38–39° (lit.[19] m.p. 39–40°).

trans-o-**Methoxystilbene.**—Using the previously described procedure[20] involving the Grignard reaction of benzyl chloride and *o*-anisaldehyde and subsequent dehydration there was obtained *trans-o*-methoxystilbene, m.p. 58.6–59.5° (lit.[20] m.p. 59°).

trans-o-**Methylstilbene.**—The Grignard reaction of *o*-bromotoluene and phenylacetaldehyde in ether gave after dehydration *trans-o*-methylstilbene, b.p. 108° (0.1 mm.) [lit.[21] b.p. 120–125° (0.15 mm.)]. A sample was purified by three recrystallizations from 95% ethanol to give *trans-o*-methylstilbene as white needles, m.p. 33.8–34.3°.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.89; H, 7.36.

A small sample of this material was treated with pyridinium bromide perbromide in acetic acid solution[12] and the resulting solid was collected by suction filtration and recrystallized from isopropyl alcohol to give *meso-o*-**methylstilbene dibromide**, m.p. 160.2–160.8° dec. (lit.[21] m.p. 158–159°).

trans-m-**Trifluoromethylstilbene.**—The procedure was similar to that described above for *trans-p*-trifluoromethylstilbene. From *m*-bromobenzotrifluoride and phenylacetaldehyde there was obtained after recrystallization from 95% ethanol *trans-m*-trifluoromethylstilbene, m.p. 65.8–66.6°. A small sample purified by four additional recrystallizations from 95% ethanol melted at 66.6–67.0°.

Anal. Calcd. for $C_{15}H_{11}F_3$: C, 72.57; H, 4.47. Found: C, 72.73; H, 4.24.

α-**Phenylcinnamic Acid.**—Condensation of benzaldehyde with phenylacetic acid by a previously described method[7b] gave after recrystallization from 95% ethanol α-phenylcinnamic acid, m.p. 174.8–175.6° (lit.[7d] m.p. 174–175°).

1,2-Diphenylcyclopentene (1).—Previously described procedures[22] were used. The Grignard reaction of bromobenzene and methyl cyclobutanecarboxylate gave cyclobutyldiphenylmethanol that was refluxed with 90% formic acid to give, after recrystallization from methanol, 1,2-diphenylcyclopentene, m.p. 58.1–60.0° (lit.[22c] m.p. 59°).

α-**Styrylnaphthalene (3).**—Using the previously described procedure[23] involving the Grignard reaction of benzyl chloride and α-naphthaldehyde and subsequent dehydration there was obtained α-styrylnaphthalene, m.p. 71–72° (lit.[23] m.p. 70.0–70.5°).

Preparation of the Light Source.—A 100-w. General Electric H100A4/T mercury lamp was modified by cutting away the outer glass envelope and also by detaching the inner quartz bulb from the screw base on which it was mounted. The two electrical leads from the lamp were then connected by means of insulated wire to a General Electric 9T64Y-3518 or 9T64Y-1019 transformer. The modified mercury lamp was inserted in a 17-mm.-i.d. quartz tube that was about 30 cm. long and sealed on one end.

Photoconversion of Stilbenes to Phenanthrenes.—The general procedure used for the photoconversion of stilbenes to the corresponding phenanthrenes is as follows. A mixture of 0.01 mole of the stilbene and 0.127 g. (0.0005 mole) of iodine was dissolved

(10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen and Co., Ltd., London, 1958, p. 34.

(11) W. Schlenk and E. Bergmann, *Ann.*, **463**, 116 (1928).

(12) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1955, p. 181.

(13) We are indebted to Lois C. Lindquist for carrying out these preparations.

(14) J. F. Codington and E. Mosettig, *J. Org. Chem.*, **9**, 408 (1944).

(15) R. Von Walther and W. Raetze, *J. prakt. Chem.*, [6] **65**, 258 (1902).

(16) J. I. G. Cadogan, E. G. Duell, and P. W. Inward, *J. Chem. Soc.*, 4164 (1962).

(17) L. Zechmeister and W. H. McNeely, *J. Am. Chem. Soc.*, **64**, 1919 (1942).

(18) R. G. Jones, *ibid.*, **69**, 2346 (1947).

(19) F. Bergmann, J. Weizman, and D. Schapiro, *J. Org. Chem.*, **9**, 408 (1944).

(20) G. A. R. Kon and R. G. W. Spickett, *J. Chem. Soc.*, 2724 (1949).

(21) F. Bergmann and D. Schapiro, *J. Org. Chem.*, **12**, 57 (1947).

(22) (a) G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 1804 (1948); (b) S. H. Graham and A. J. S. Williams, *ibid.*, 4066 (1959); (c) R. Criegee, A. Kerckow, and H. Zinke, *Ber.*, **88**, 1878 (1955).

(23) J. L. Everett and G. A. R. Kon, *J. Chem. Soc.*, 1601 (1948).

in 1 l. of cyclohexane (Eastman practical grade, redistilled) in a 1-l. erlenmeyer flask. The flask was placed in a cold-water bath consisting of a 10-qt. polyethylene bucket having a drain inserted through the wall of the bucket near the top; the reaction mixture was maintained at 22–23° by running a stream of tap water into the bath. The quartz tube containing the mercury lamp was immersed in the magnetically stirred cyclohexane solution and the solution was irradiated until the reaction was completed.

The irradiation time required in each case was determined by following the progress of the reaction by infrared spectroscopy. After an appropriate interval of irradiation a 5-ml. aliquot was withdrawn from the reaction mixture and evaporated to dryness under reduced pressure; then the residue was dissolved in 0.2 ml. of carbon tetrachloride or chloroform and the infrared spectrum was obtained using 0.1-mm. sodium chloride cells. To ensure completion of the reaction the irradiation was generally continued for 1–2 hr. after the appropriate absorption peaks characteristic of the starting material were no longer detectable in the spectrum obtained in this way.

A typical procedure for isolation of the product is as follows. The reaction mixture was transferred to a 2-l., round-bottomed flask and evaporated to dryness using a water aspirator and a rotary evaporator. The residue was dissolved (except for a small amount of resinous material that adhered to the flask) in 50 ml. of warm cyclohexane and this solution was poured onto a column of alumina (Merck 71707) 1.8 cm. in diameter and 6–8 cm. in length. The round-bottomed flask was rinsed quickly with three portions of 10 ml. of cyclohexane and these rinsings were poured onto the column. Finally, the column was eluted with additional cyclohexane (50–150 ml.) until no further amount of the desired product was obtained in the eluate but before a significant amount of the yellow byproducts were removed from the column. The total eluate was evaporated to dryness using a water aspirator and a rotary evaporator and the residue was purified by sublimation and/or recrystallization. Further details are given in Table I.

Most of the phenanthrenes were characterized in part by oxidation to the known phenanthrenequinone derivatives (see Table II). In a typical oxidation of this sort 1.0 g. of chromium trioxide was added to a solution of 0.5 g. of the phenanthrene in 20 ml. of glacial acetic acid. The resulting mixture was warmed gently until no material remained undissolved and then the solution was heated at reflux for 1 hr. before being cooled and diluted with 100 ml. of water. The yellow-orange solid was collected by suction filtration, washed with 50 ml. of water, dried, and purified by sublimation and/or recrystallization.

Separation of 2-Trifluoromethylphenanthrene (4) and 4-Trifluoromethylphenanthrene (5).—The 2.18-g. mixture of **4** and **5** that was obtained from the irradiation of *m*-trifluoromethylstilbene (see Table I) was dissolved in 75 ml. of boiling, 30–40° petroleum ether. The solution was concentrated to about 25 ml., cooled in ice, and filtered to give 0.80 g. of crude **4**, m.p. 107.0–111.7°. The filtrate was chromatographed on alumina using additional 30–40° petroleum ether as eluent. The first fraction yielded 1.06 g. of crude **5** as a colorless liquid; the second fraction yielded an additional 0.23 g. of crude **4** that was combined with the 0.80 g. obtained earlier. Crude **4** was purified by one recrystallization from methanol, three recrystallizations from 95% ethanol, and two sublimations to give 2-trifluoromethylphenanthrene melting at 112.9–113.3°.

Anal. Calcd. for $C_{15}H_9F_3$: C, 73.19; H, 3.68. Found: C, 73.43; H, 3.72.

Crude **5** was purified by chromatography on silicic acid using 30–40° petroleum ether as eluent and by molecular distillation to give 4-trifluoromethylphenanthrene as a liquid containing *ca.* 5–10% of the other isomer **4** as indicated by infrared spectra.

Anal. Found: C, 72.99; H, 3.81.

TABLE II
PHENANTHRENEQUINONE DERIVATIVES

Phenanthrene-quinone	Recrystn. solvent	M.p., °C.	Lit. m.p., °C.
Parent	95% EtOH[a]	209.0–210.0	208–209.5[b]
3-F	Acetone[a]	248.5–249.5	. . .[c]
3-Cl	Sublimed	262.5–263.5	261[d]
3-Br	HOAc	272.0–272.5	268[e]
3-CH_3O[f]	95% EtOH[a]	209.0–209.5	208[h]
3-CH_3[i]	95% EtOH[a]	212.5–214.5	205–206[j]
3-CF_3	Acetone[a]	229.5–230.5	. . .[k]
1-Cl	95% EtOH	229.0–229.5	228–230[l]
1-CH_3	95% EtOH	195.8–196.5	191[j] 196[m]
2-CF_3	Acetone[a]	249.3–250.0	. . .[n]

[a] The crude product was purified by reduced-pressure sublimation prior to recrystallization. [b] G. M. Jaffe and A. R. Day, *J. Org. Chem.*, **8**, 43 (1943). [c] *Anal.* Calcd. for $C_{14}H_7FO_2$: C, 74.34; H, 3.12. Found: C, 74.34; H, 3.22. [d] H. Sandquist and A. Hagelin, *Ber.*, **51**, 1515 (1918). [e] J. Schmidt and O. Spoun, *ibid.*, **43**, 1802 (1910). [f] The picrate derivative, prepared from 3-methoxyphenanthrene and picric acid in 95% ethanol solution, melted at 123.5–124.0° (lit.[g] m.p. 124–125°). [g] R. Pschorr, *Ber.*, **34**, 3998 (1901). [h] R. Pschorr, O. Wolfes, and W. Buckow, *ibid.*, **33**, 162 (1900). [i] The picrate derivative, prepared from 3-methylphenanthrene and picric acid in 95% ethanol solution, melted at 138.4–139.4° (lit.[j] m.p. 137–138°). [j] R. D. Haworth, *J. Chem. Soc.*, 1125 (1932). [k] *Anal.* Calcd. for $C_{15}H_7F_3O_2$: C, 65.23; H, 2.55. Found: C, 65.19; H, 2.77. [l] G. G. Smith and D. G. Ott, *J. Am. Chem. Soc.*, **77**, 2342 (1955). [m] R. Pschorr, *Ber.*, **39**, 3106 (1906). [n] *Anal.* Calcd. for $C_{15}H_7F_3O_2$: C, 65.23; H, 2.55. Found: C, 65.48; H, 2.50.

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A Preparation of β-Sitosterol[1a]

G. I. FUJIMOTO AND A. E. JACOBSON[1b]

Albert Einstein College of Medicine, Yeshiva University, New York 61, New York

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β-Sitosterol from tall oil has been converted to partially synthetic β-sitosterol by the following series of reactions: oxidation to sitostenone (IIa), ring opening to the keto acid IIIa, lactonization through the chloro lactone IVa to the enol lactone Va, Grignard addition to VIa, rearrangement to sitostenone, enol acetylation, and reduction to β-sitosterol. Purification at each stage afforded samples which are compared spectrally with corresponding cholesterol series compounds. β-Sitosterol-4-C^{14} has been prepared by this method.

Although β-sitosterol (Ia) has been isolated from most plant sources, it has rarely been carefully purified.[2] The classical methods of fractional crystallization and of regenerating from derivatives do not eliminate closely related plant sterols from β-sitosterol. Close structural similarities and mixed crystal formation appear to render purification difficult. There is also the probable pres-

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(2) For recently reported methods, see (a) H. Werbin, I. L. Chaikoff, and M. R. Imada, *Arch. Biochem. Biophys.*, **89**, 213 (1960); (b) J. A. Steele and E. Mosettig, *J. Org. Chem.*, **28**, 571 (1963); (c) M. J. Thompson, W. E. Robbins, and G. L. Baker, *Steroids*, **2**, 505 (1963). A review of previous methods is given in "Elsevier's Encyclopedia of Organic Chemistry," Vol. 14S, Suppl. 3, Elsevier Publishing Co., 1954, p. 1809S.