Anal. Calcd. for $C_{16}H_{16}O_6S$: C, 57.15; H, 4.76; S, 9.52. Found: C, 57.18; H, 5.00; S, 9.44.

cis-**β-Acetoxystyrene** (I).—*erythro*-α-Hydroxy-β-phenyl-β-toluene-*p*-sulfonyloxypropionic acid (3.5 g., 0.01 mole), acetic anhydride (1.0 g., 0.01 mole), and 10 ml. of anhydrous pyridine were mixed at 10° and allowed to stand at room temperature for 4 hr. The reaction mixture was poured onto 6 ml. of 10% hydrochloric acid and 200 g. of ice and was extracted with two 200-ml. portions of ether. The ether layer was washed with two 200-ml. portions of 5% hydrochloric acid and with 200 ml. of water. Final washing with two 200-ml. portions of 5% sodium bicarbonate solution and 200 ml. of water afforded a yellow ether solution which was dried over anhydrous sodium sulfate. Filtration followed by removal of the solvent under reduced pressure afforded 1.3 g. (78%) of yellow oil. Distillation, b.p. 86–87° (2.0 mm.), yielded a colorless oil which analyzed for *cis*-β-acetoxystrene: ν^{film} 5.7 (C=O), 6.05 (C=C), 6.28, and 6.7 μ (aromatic). Gas chromatography on a 10% silicone gum rubber (SE-30) on Chromosorb W (80–100 mesh) 4 ft. × 0.25 in. column with the column temperature 100°, detector temperature 230°, injection port temperature 300°, inlet pressure of 60 p.s.i., and carrier gas (He) flow rate of 75 ml./min. gave a retention time of 8.5 min.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 73.79; H, 6.19. Found: C, 73.48; H, 6.20.

cis- **and** *trans*-**β-Acetoxystyrene**.[4]—A mixture of 48.0 g. (0.40 mole) of phenylacetaldehyde[26] and 102 g. (1.00 mole) of acetic anhydride was heated in an oil bath to reflux, allowing the distillate boiling at 118° to escape. After a reaction period of 3 hr. the oil bath temperature was increased in order to remove most of the acetic anhydride. The residue was washed several times with water and finally with 5% sodium carbonate solution. The crude oil was distilled employing an 18-in. Vigreux column, affording 9.8 g. (16%) of colorless liquid, b.p. 86–87° (2.0 mm.). Gas chromatography (same conditions as above for *cis*-β-acetoxystyrene) gave retention times for three peaks of 2,[27] 8.5 (*cis*), and 10.2 min. (*trans*).

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 73.79; H, 6.19. Found: C, 73.36; H, 6.11.

α-**Deuterated** *cis*- **and** *trans*-**β-Acetoxystyrene**.—A mixture of 6 g. (0.05 mole) of phenylacetaldehyde, 60 ml. of deuterium oxide, and 10 mg. of anhydrous sodium carbonate was shaken at 30° in a stoppered flask for 4 days. The reaction mixture was extracted with anhydrous ether (250 ml.) and dried over anhydrous sodium sulfate. Filtration followed by removal of ether under reduced pressure afforded a yellow oil. Distillation, b.p. 65–67° (0.45 mm.), afforded 2.09 g. of colorless liquid. The enol acetate was prepared from this methylene-deuterated phenylacetaldehyde by the method described above.

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[26] Aldrich Chemical Co., Milwaukee, Wis.

[27] A trace of phenylacetaldehyde distils with the mixture. G.l.c. indicates that *trans* predominates over *cis* by 61%.

On the Bromopyrenes[1]

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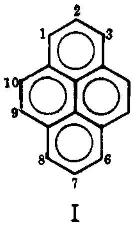
Received July 27, 1964

Treatment of 1-bromopyrene with potassium amide in liquid ammonia gave a mixture of 1-amino- and 2-aminopyrene. Sandmeyer reaction with the latter amine gave 2-bromopyrene in low yield. Bromination of 1,2,3,6,7,8-hexahydropyrene gave the 4-bromo derivative which was dehydrogenated with *o*-chloranil to 4-bromopyrene.

Despite the interest generated in polynuclear aromatic hydrocarbons in recent years as the result of advances in the theories of π-electron systems, relatively little progress has been made in the chemistry of these compounds, especially with respect to the introduction of substituents at relatively unreactive sites in the parent hydrocarbon. An important case in point is that of pyrene (I). The isomeric tritiated pyrenes were required for our studies of the rates of acid- and base-catalyzed isotope exchange in aromatic hydrocarbons[3]; the labeled hydrocarbons are generally readily available from the corresponding bromides but only 1-bromopyrene is described in the literature.[4]



I

1-Substituted pyrenes are readily available by direct electrophilic substitution. The usual approach to substituents in the 2- and 4-positions of pyrene follows the lines of the early work of Vollmann[5] who started with the carboxylic acids. Synthesis of the acids themselves, however, often involves unpredictable yields and tedious separation of isomers.[6] Furthermore, this approach is cumbersome for the introduction of halogens in that the acid is converted to the amine which must then be converted to the halide by the Sandmeyer reaction or a variation thereof, a reaction which often goes in low yield with polynuclear aromatic amines.

In an effort to circumvent some of these difficulties, two additional approaches to the problem have been employed: (a) use of partially hydrogenated pyrene to effect specific directivity in bromination, followed by dehydrogenation and (b) use of *cine* substitution *via* a 1,2-dehydropyrene intermediate to convert 1-bromopyrene to a mixture of 1- and 2-aminopyrene, separation of the amines and conversion to the halide. Neither of these approaches is without precedent in polynuclear aromatic compounds, though neither has to our knowledge been employed in the pyrene series. Method a, for example, has been used to prepare 3-bromofluoranthene from 1,2,3,10b-tetrahydrofluoranthene in excellent yield.[7] An analogous approach has also been reported recently in the synthesis of the

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[1] This research was supported in part by The Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant No. M4 (965) 62/64-554.

[2] National Science Foundation Predoctoral Fellow, 1960–1963; Eastman Kodak Science Award in Chemistry, 1962.

[3] A. Streitwieser, Jr., and R. G. Lawler, *J. Am. Chem. Soc.*, **85**, 2854 (1963); A. Streitwieser, Jr., and I. Schwager, unpublished results.

[4] G. Lock, *Ber.*, **70**, 926 (1937).

[5] H. Vollmann, H. Becker, N. Corell, and H. Streeck, *Ann.*, **531**, 1 (1937).

[6] A. Berg, *Acta Chem. Scand.*, **10**, 1362 (1956).

[7] R. Tobler, T. Holbro, P. Sutler, and W. Kern, *Helv. Chim. Acta*, **24**, 100E (1941).

hexanoyl derivatives of perylene.[8] Likewise, method b is well known in the conversion of 1-bromonaphthalene to a 1:2 mixture of 1- and 2-naphthylamine and in other reactions involving aryne intermediates.[9] It has also been reported that 1-bromopyrene forms the 1,2-dehydropyrene intermediate with lithium piperidide in ether,[10a] although no products were identified.

Results and Discussion

By slow addition of 1 mole of bromine to 1,2,3,6,7,8-hexahydropyrene in acetic acid at room temperature, it is possible to obtain a good yield of 4-bromo-1,2,3,-6,7,8-hexahydropyrene. Use of carbon disulfide or carbon tetrachloride as solvents for the bromination of 1,2,3,6,7,8-hexahydropyrene, a more rapid rate of addition of bromine, or bromination at elevated temperatures gives a product which appears to be contaminated by an impurity unstable in the presence of air and moisture which renders purification extremely difficult. Catalytic dehydrogenation of the bromo compound with palladium on charcoal at 176° leads to replacement of bromine by hydrogen. Chloranil has no effect, but *o*-chloranil at 70° effects dehydrogenation to give 4-bromopyrene.

Attempts to apply the same approach to the synthesis of 2-bromopyrene failed when all brominations of 4,5,9,10-tetrahydropyrene gave only amorphous, high-melting solid[10b]; hence, recourse was had to method b. Treatment of 1-bromopyrene with potassium amide in liquid ammonia affords a 50% yield of an approximately 1:1 mixture of 1- and 2-aminopyrene which can be easily separated by fractional crystallization. In one experiment, 2-aminopyrene was converted in low yield to 2-bromopyrene by means of the Schwechten modification of the Sandmeyer reaction,[11] but a second attempt failed to give any product.

The crude product from the successful preparation was partially purified by column chromatography on alumina but satisfactory analyses were not obtained. One sample was purified *via* the picrate and gave product, m.p. 132–133°. The ultraviolet spectrum and dropping mercury polarogram were run on this sample. A second sample from the original chromatogram showed two spots by thin layer chromatography on silica gel. After column chromatography on silica gel, the product had m.p. 131–132.5° and showed a single spot on thin layer chromatography. In both cases the amount of purified material obtained was insufficient for microanalysis; nevertheless, the melting point of 133° would appear to pertain to 2-bromopyrene of reasonable purity.

The ultraviolet spectra of the three bromopyrenes are compared in Table I. These spectra differ only slightly and resemble that for pyrene itself. The polarograms in dimethylformamide containing tetrabutylammonium iodide as supporting electrolyte gave three reduction waves.[12] Half-wave potentials for the first waves are recorded in Table I. The second and third waves gave the same half-wave potentials for all three bromides and correspond to the two waves of pyrene.

TABLE I

COMPARISON OF THE PROPERTIES OF PYRENE AND THE MONOBROMOPYRENES

Substituent	M.p., °C.	Picrate, m.p., °C.	λ_{max}, mμ (log ϵ)[a]	$-E_{1/2}$, v. *vs.* Hg pool[b]
H	152.2–152.9[c]	220–222[d]	229 (4.58), 239 (4.88), 260 (4.26), 271 (4.69), 302 (4.00), 318 (4.40), 333 (4.75)[e]	. . .
1-Br	95–96.5	172[f]	233 (4.59), 242 (4.80), 265 (4.39), 276 (4.67), 313 (4.06), 326 (4.46), 343 (4.67)	1.17
2-Br	132–133[g]	150–155	239 (4.75), 248 (5.01), 266 (4.44), 277 (4.64), 306 (4.08), 320 (4.51), 335 (4.75)	1.23
4-Br	148–150[g]	177–181	232 (4.53), 241 (4.80), 264 (4.29), 275 (4.52), 308 (3.97), 322 (4.36), 338 (4.58)	1.20

[a] In isooctane. [b] Half-wave potentials for 2–3 × 10^{-4} *M* solutions in DMF 0.1 *M* in tetrabutylammonium iodide. Ref. 12. [c] R. C. Jones and M. B. Neuworth, *J. Am. Chem. Soc.*, **66**, 1497 (1944). [d] L. Small, *J. Org. Chem.*, **7**, 158 (1942). [e] In *n*-heptane. H. Fromherz, L. Thaler, and G. Wolf, *Z. Electrochem.*, **49**, 387 (1943). [f] Ref. 4. [g] Micro melting point.

Further evidence that the two hitherto unreported bromides are bromopyrenes was shown by conversion to tritiated pyrene by halogen–metal exchange with *n*-butyllithium followed by quenching with tritiated water. The tritiated pyrenes thus produced undergo acid- and base-catalyzed hydrogen isotope exchange at rates different from each other and from 1-tritiopyrene synthesized from 1-bromopyrene.[3]

The procedures outlined here for the preparation of the bromopyrenes may well be applicable with little modification to synthesis of the other halopyrenes and thus make them more readily available as intermediates for syntheses in the pyrene series. In extending these methods to other polynuclear aromatics, however, two stumbling blocks present themselves: bromination of a partially hydrogenated arene and conversion of a polynuclear aromatic amine to the corresponding halide. Both of these reactions seem to be very sensitive to the reaction conditions employed, with optimum conditions varying from compound to compound. It is possible that the first of these reactions is complicated by side-chain bromination,[13] possibly followed by polymerization which would account for unstable and high-melting by-products. The failure of the Sandmeyer reaction in many cases with amines of the higher arenes, however, has not as yet been explained satisfactorily, although it is known that aromatic amines may undergo a wide variety

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(8) H. E. Zieger, Ph.D. Dissertation, Pennsylvania State University, 1961; *Dissertation Abstr.*, **22**, 84 (1962).

(9) See, for example, R. Huisgen in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960.

(10) (a) R. Huisgen, W. Mack, K. Herbig, N. Ott, and E. Anneser, *Chem. Ber.*, **93**, 412 (1960). (b) NOTE ADDED IN PROOF.—R. Bolton [*J. Chem. Soc.*, 4637 (1964)] has prepared 2-pyrene derivatives *via* nitration of 4,5,9,10-tetrahydropyrene.

(11) (a) H. W. Schwechten, *Ber.*, **65**, 1606 (1932); (b) W. E. Bachmann and C. H. Boatner, *J. Am. Chem. Soc.*, **58**, 2194 (1936).

(12) I. Schwager, details to be published separately.

(13) E. Baciocchi and G. Illuminati, *Tetrahedron Letters*, **No. 15**, 637 (1962), and references cited therein.

of side reactions under diazotizing conditions.[14] Because of the uncertainties concerning the nature of side reactions encountered with the higher aromatics, therefore, at present, an almost purely empirical approach must be used in finding the optimum reaction conditions for a given compound.

Experimental

General.—Elemental analyses were performed by the Microanalytical Laboratories of the University of California. Ultraviolet spectra were obtained with a Perkin-Elmer Model 202 recording spectrophotometer. Tritium counting was accomplished using a Nuclear Chicago Model 723 ambient temperature liquid scintillation counter and polarography was carried out in dimethylformamide with tetra-*n*-butylammonium iodide as supporting electrolyte using a Sargent Model XV polarograph with Hg-pool electrode. N.m.r. spectra were obtained with a Varian A-60. Melting points are uncorrected and in some cases were determined with a Kofler micro hot stage (K).

4-Bromo-1,2,3,6,7,8-hexahydropyrene.—To a solution of 4.0 g. (0.019 mole) of 1,2,3,6,7,8-hexahydropyrene (Rugerswerke) in 50 ml. of glacial acetic acid was added with stirring 3.2 g. (0.020 mole) of bromine in 50 ml. of glacial acetic acid over a period of 1 hr. at room temperature. As the addition proceeded, product precipitated from the solution. After the bromine addition was complete, the acetic acid was warmed to dissolve the solid which was then allowed to recrystallize, giving 4.5 g. (81%) of light yellow needles, m.p. 127–130° (lit.[5] m.p. 130–131°).

Attempted Catalytic Dehydrogenation of 4-Bromo-1,2,3,6,7,8-hexahydropyrene.—4-Bromo-1,2,3,6,7,8-hexahydropyrene (1.0 g.) and 0.23 g. of 5% palladium on charcoal were refluxed in 100 ml. of *p*-cymene with a sweep of dry carbon dioxide for 9.5 hr. The *p*-cymene was distilled off under high vacuum leaving 1.2 g. of brown residue. Recrystallization of the residue from absolute ethanol gave 0.42 g. of white needles, m.p. 104.8–106.1°, in three crops.

Polarographic reduction of a sample of the first crop gave waves with $-E_{1/2}$ (Hg pool) = 1.77 ± 0.01 and 2.24 ± 0.01 v. with a diffusion current ratio of 224:163. Assuming the first wave to be a two-electron wave due to C–Br bond reduction and the second due to addition of an electron to the aromatic π-electron systems associated with both brominated and unbrominated hexahydropyrene, the relative amounts of 4-bromo-1,2,3,6,7,8-hexahydropyrene and 1,2,3,6,7,8-hexahydropyrene in the sample can be estimated to be 61 and 39%, respectively. Note that the analysis differs substantially from that calculated for a simple 2:1 mixture.

Anal. Calcd. for $C_{16}H_9Br$: C, 68.33; H, 3.20; Br, 28.47. Calcd. for 61% $C_{16}H_{15}Br$ and 39% $C_{16}H_{16}$: C, 76.8; H, 6.2; Br, 17.0. Calcd. for 66.7% $C_{16}H_{15}Br$ and 33.3% $C_{16}H_{16}$: C, 75.3; H, 7.0; Br, 18.5. Found for first crop: C, 77.62; H, 6.47; Br, 15.78. Found for second crop: C, 76.34; H, 6.01; Br, 17.66.

The melting point of a synthetic mixture of 3 moles of 4-bromo-1,2,3,6,7,8-hexahydropyrene and 2 moles of 1,2,3,6,7,8-hexahydropyrene thoroughly ground together was 104–105.8°.

From the polarographic and analytical data and the sharp melting point, it would appear that the product of the attempted dehydrogenation consisted of a 3:2 compound of 4-bromo-1,2,3,6,7,8-hexahydropyrene with 1,2,3,6,7,8-hexahydropyrene.

Quinone Dehydrogenation of 4-Bromo-1,2,3,6,7,8-hexahydropyrene.—4-Bromo-1,2,3,6,7,8-hexahydropyrene (5 g., 0.017 mole) and 14.0 g. (0.057 mole) of tetrachloro-*o*-benzoquinone (Chemical Procurement Laboratories) were refluxed together under nitrogen for 76 hr. in 125 ml. of sodium-dried benzene. The red-brown benzene solution was passed through an 8 × 1.5 in. column of activity I neutral alumina. The first 100 ml. of eluate yielded 1.23 g. of light yellow plates, m.p. 138–147°. A second fraction of 300 ml. obtained by further elution with benzene gave a red solid. This solid was taken up in benzene and rechromatographed on a similar column. The first 250 ml. of benzene eluate yielded 2.04 g. of light yellow plates.

The two crops of crystals were combined and the n.m.r. spectrum was taken of a 4 mole % solution in carbon tetrachloride. Complex absorption occurred below τ 2.25. A barely detectable absorption occurred at τ 6.95, presumably due to a trace of undehydrogenated 4-bromo-1,2,3,6,7,8-hexahydropyrene. This slightly impure material formed a bright orange picrate, m.p. 177–181°. Decomposition of the picrate with ammonia and recrystallization of the free bromo compound from cyclohexane gave light yellow cubes, micro m.p. (K) 148.2–150.2°.

Anal. Calcd. for $C_{16}H_9Br$: C, 68.33; H, 3.20; Br, 28.47. Found: C, 68.23; H, 3.23; Br, 28.62.

A 48-mg. sample of 4-bromopyrene was stirred with 1 mmole of *n*-butyllithium in ether for 15 min. at room temperature. Twenty-five microliters (1.4 mmole) of tritiated water (100 mc./ml.) was added followed by 3.00 g. (14.8 mmoles) of pyrene (Rutgerswerke) in ether. The ether was removed and the residual pyrene was recrystallized from absolute ethanol. Material of specific tritium activity 1.21 × 10^7 d.p.m./mmole was obtained from the first recrystallization. A picrate was formed from this material and decomposed with ammonia. The pyrene thus obtained was recrystallized from absolute ethanol to give 1.6 g. (53%) of white prisms, m.p. 149.3–150° (lit.[15] m.p. 152.2–152.9°), specific activity 1.18 × 10^7 d.p.m./mmole (calculated on basis of tritiated water used: 2.3 × 10^7 d.p.m./mmole).

Refluxing 1 g. of 4-bromo-1,2,3,6,7,8-hexahydropyrene with 3 g. of chloranil in 25 ml. of dry toluene for 19 hr. gave only unreacted chloranil after work-up.

2-Aminopyrene.—A solution of potassium amide in liquid ammonia was prepared by standard techniques[16] from 6 g. (0.15 g.-atom) of potassium metal and 500 ml. of liquid ammonia. Solid 1-bromopyrene[4] (10.0 g., 0.035 mole) was added in small portions over 15 min. The solution was stirred for 1 additional hr. and excess amide was destroyed with ammonium chloride. Evaporation of the ammonia yielded a brown residue which was digested with several portions of hot benzene. Cold, concentrated hydrochloric acid was added to the benzene extract to precipitate the amine hydrochloride which was insoluble in concentrated HCl. The crude hydrochloride was digested with concentrated ammonium hydroxide solution on a steam bath for 0.5 hr. and the amine was extracted into ether giving 5.1 g. of crude brown solid after removal of the solvent. Recrystallization of the crude material from toluene gave 2.25 g. (29%) of greenish tan metallic plates of 2-aminopyrene: m.p. 190–210° dec. (lit.[5] m.p. 207°); $\lambda_{\max}^{\text{cyclohexane}}$ 264 mμ (log ϵ 4.81), 283 (4.23), 296 (4.00), 309 (3.91), 323 (4.26), 338 (4.61), 372 (s), 377 (3.53), 391 (s), and 399 (3.54); lit.[17] $\lambda_{\max}^{\text{hexane}}$ 262 mμ (log ϵ 4.88) 282 (4.30), 294 (4.19), 309.5 (4.16), 322.5 (4.48), 338 (4.71), 370 (2.91), 378.5 (3.12), 392 (3.16), and 400 (3.32).

Anal. Calcd. for $C_{16}H_{11}N$: C, 88.48; H, 5.07; N, 6.45. Found: C, 88.28; H, 5.17; N, 6.67.

A 15-mg. sample of this compound was refluxed for 3 min. with 0.2 ml. of acetic anhydride and allowed to crystallize from the solvent to give yellow needles, micro m.p. (K) 227.5–229° (lit.[5] m.p. 229° for N-acetyl-2-aminopyrene).

Removal of the toluene from the mother liquors gave 2.11 g. of yellow solid, m.p. 100–110° (lit.[5] m.p. 117–118° for 1 aminopyrene). Purification by recrystallization from methanol or cyclohexane was not successful. The ultraviolet spectrum of the material in cyclohexane showed strong absorption at 242 mμ (log ϵ 4.58) but only a small shoulder at 264 mμ [lit.[17] $\lambda_{\max}^{\text{hexane}}$ 242 mμ (log ϵ 4.74) for 1-aminopyrene]. On the basis of melting point and ultraviolet spectrum, it appears that the mother liquors consisted of an approximately 27% yield of impure 1-aminopyrene.

2-Bromopyrene.—A solution of nitrosylsulfuric acid was prepared by warming 1.5 g. of sodium nitrite, 15 ml. of cold, concentrated sulfuric acid, and 7.5 ml. of water for 15 min. on the steam bath. The solution was cooled in an ice bath and 485 mg. (1.72 mmoles) of 2-aminopyrene in 15 ml. of pyridine was added with stirring over 45 min. After 1 additional hr. of stirring in the cold, the mixture was diluted to 125 ml. with ice and water and 1.2 g. of urea in 25 ml. of water was added to decompose the

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[14] See, for example, K. H. Saunders, "The Aromatic Diazo Compounds and Their Technical Applications," 2nd Ed., Edward Arnold and Co., London, 1949; H. H. Hodgson, *Chem. Rev.*, **40**, 251 (1947). NOTE ADDED IN PROOF.—In other cases we found the ordinary Sandmeyer reaction to be superior to the Schwechter modification; *cf.* ref. 10b.

[15] R. C. Jones and M. B. Neuworth, *J. Am. Chem. Soc.*, **66**, 1497 (1944).

[16] C. R. Hauser and W. R. Dunnavant, *Org. Syn.*, **39**, 73 (1959).

[17] G. Förster and J. Wagner, *Z. Physik. Chem.* (Leipzig), **B37**, 353 (1937).

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

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

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

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

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

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

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

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

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

Acknowledgment.—We are indebted to Dr. Irving Schwager for the polarographic measurements.

Synthesis of Stilbenes. A Comparative Study[1]

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Received September 8, 1964

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

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

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

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(1) The Puerto Rico Nuclear Center is operated under Contract No. AT-(40-1)-1833 by the University of Puerto Rico for the Atomic Energy Commission.

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