manner and the combined residues were distilled through a helix-packed column. The product boiled at 103–104° (6 mm.), n^{20}D 1.5274. The yield of carbinol was 241 g. (1.61 moles) or 86% of the theoretical amount.

3,4-Dimethylstyrene.—The dehydration was carried out as described for the 3,5-isomer. From 256 g. (1.71 moles) of 3,4-dimethylphenylmethylcarbinol there was obtained 137 g. (80% based on the carbinol dehydrated) of 3,4-dimethylstyrene, b. p. 94–96° (26 mm.), n^{20}D 1.5463, d^{25}_{25} 0.909. The recovery of carbinol was 62 g. (24.2%).

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 91.04; H, 9.23.

3,4-Dimethylbenzoic Acid.—This styrene was further characterized by oxidation in the same manner as that described for the preparation of 2,4-dimethylbenzoic acid. The 3,4-dimethylbenzoic acid thus obtained melted at 162–163°. Frey and Horowitz[17] reported a melting point of 163° for this acid.

Polymerization of Isomeric Dimethylstyrenes.—In a Pyrex test-tube was placed 1 g. of the monomer. The test-tube was suspended under an ultraviolet lamp and left there until a hard polymer had been formed (ninety-two hours). The polymer was dissolved in 50 cc. of benzene and precipitated by slowly dropping the solution into 250 cc. of mechanol with methanical stirring. This process was repeated and the powder obtained was dried for five days in a vacuum desiccator. All of these polymers are soluble in benzene.

Table I summarizes the data on these polymers.

TABLE I

Poly-dimethyl-styrene	Approximate mol. wt.[a]	Softening point, °C.	Analyses,[b] % Found C	H
3,5	17,700	148–152	90.76	9.27
2,4	9,000	178–180	90.38	9.27
2,5	18,500	171–176	90.09	9.30
3,4	15,500	163–175	90.94	9.26

[a] These approximate molecular weights were determined by viscosity measurements with the use of an equation developed by Kemp and Peters for the determination of the molecular weight of polystyrene using the *K* value for styrene (Kemp and Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942)). [b] Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15.

Summary

1. The preparations of 3,5-, 2,4-, 2,5- and 3,4-dimethylstyrene are described.

2. The polymers of these monomers have been prepared and characterized.

URBANA, ILL. RECEIVED FEBRUARY 8, 1946

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[17] Frey and Horowitz, *J. prakt. Chem.*, (2) **43**, 113 (1891).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

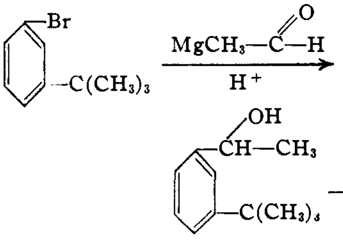
The Preparation and Polymerization of Some Alkyl Styrenes[1,2]

BY C. S. MARVEL, R. E. ALLEN AND C. G. OVERBERGER

In order to investigate the effects of large alkyl groups on the polymerization and copolymerization of styrene derivatives, a study of several branched-chain alkyl substituted styrenes has been carried out in this Laboratory. This paper reports the syntheses of *m-t*-butylstyrene, *m-s*-butylstyrene and *p*-cyclohexylstyrene and gives a brief summary of the properties of their polymers. Data on copolymerization will be reported later.

m-t-Butylstyrene

This monomer was prepared through the following series of reactions.



***m*-Bromo-*t*-butylbenzene.**—This was prepared from 2-bromo-4-*t*-butylaniline by a procedure described in "Organic Syntheses" for the conversion of 3-bromo 4-aminotoluene[3] to *m*-bromotoluene. From 303 g. (1.33 moles) of 2-bromo-4-*t*-butylaniline there was obtained 160 g. (56.2%) of *m*-bromo-*t*-butylbenzene, b. p. 103–106° (17 mm.), n^{20}D 1.5337, d^{4}_{20} 1.251.

Anal.[4] Calcd. for $C_{10}H_{13}Br$: C, 56.35; H, 6.15. Found: C, 56.88; H, 6.21.

***m-t*-Butylphenylmethylcarbinol.**—Into a 5-liter three-necked, round-bottomed flask fitted with a stirrer, dropping funnel and condenser was placed 49.5 g. (2.04 gram atoms) of magnesium turnings covered with 50 cc. of dry ether. A solution of 434 g. (2.04 moles) of *m*-bromo-*t*-butylbenzene in 1.5 l. of dry ether was added over a period of two hours and the reaction mixture was stirred two hours longer. A solution of 110 g. (2.5 moles) of freshly distilled acetaldehyde dissolved in 1.5 liters of dry ether was added in one hour and the mixture was stirred for an additional two hours.

The reaction mixture was treated in the usual manner, to isolate the product.

After the solvent was removed, the residue was distilled through a helices-packed column. The product boiled at 130–134° (17 mm.), n^{20}D 1.5120, d^{4}_{20} 0.9578. The yield of *m-t*-butylphenylmethylcarbinol was 200 g. (55%).

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.96; H, 9.94.

***m-t*-Butylstyrene.**—The *m-t*-butylphenylmethylcarbinol was dehydrated by two standard procedures.

Procedure A: The general method of Marvel and Brown[5] was used, except that 1 g. of *p-t*-butylcatechol was added to the reaction mixture as an inhibitor. From 377 g. (2.12 moles) of *m-t*-butylphenylmethylcarbinol there was

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[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[2] This is the twenty-third communication on vinyl polymers. For the twenty-second, see Marvel, Saunders and Overberger, THIS JOURNAL, **68**, 1085 (1946).

[3] Bigelow, Johnson and Sandborn, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., second edition, 1941, p. 133.

[4] Microanalyses by Mr. H. S. Clark, Illinois State Geological Survey.

[5] Marvel and Brown, THIS JOURNAL, **59**, 1175 (1937).

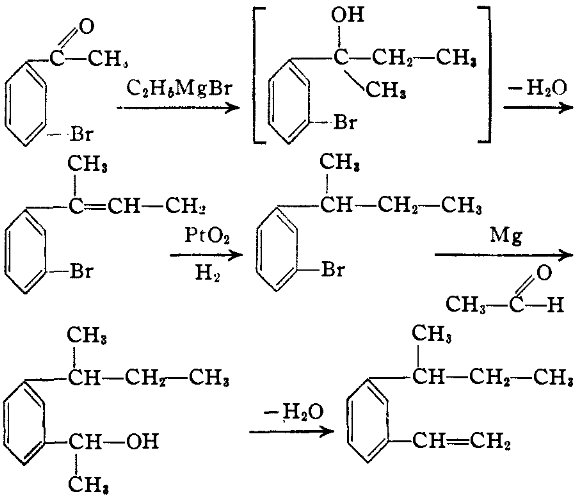
obtained 137 g. (40.4%) of *m-t*-butylstyrene, b. p. 75° (5 mm.), n^{20}_{D} 1.5237, d^{4}_{20} 0.897. A small amount of *p-t*-butylcatechol should always be added to the styrene before final distillation.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.61; H, 9.98.

Procedure B: The general method of Marvel and Shertz[6] was used, except that 1 g. of *p-t*-butylcatechol was added to the carbinol and to the fused potassium acid sulfate. From 212 g. (1.19 moles) of *m-t*-butylphenylmethylcarbinol there was obtained 118 g. (61.4%) of *m-t*-butylstyrene, b. p. 99–100° (17 mm.), n^{20}_{D} 1.5234.

m-s-Butylstyrene

This monomer was prepared by the following series of reactions



m-Bromoacetophenone.—*m*-Nitroacetophenone, prepared according to the directions of "Organic Syntheses"[7] was reduced catalytically in a high-pressure bomb with Raney nickel catalyst. Eleven-hundred and eighty grams (7.15 moles) of *m*-nitroacetophenone was divided into four equal lots of 295 g. each and was reduced catalytically, each in 1100 cc. of absolute ethanol at 50° with one and one-half tablespoons of Raney nickel catalyst. The initial hydrogen pressure was 1950 pounds at 30°. The solvent was removed and each batch was triturated with an excess of concentrated hydrochloric acid after the residue had been diluted with 400 cc. of iced water. The undissolved material after filtration was again triturated with hydrochloric acid. The combined acid-insoluble residues from the four runs (assumed to be *m*-nitroacetophenone) were washed successively with cold water until the washings were no longer acidic. These residues were dried and weighed (173 g.). They were again reduced as before, the solvent was removed, the residue was dissolved in dilute hydrochloric acid and added to the previous four runs. Solid sodium carbonate was added with vigorous stirring to the acid solution until the solution became alkaline to litmus paper. The crude *m*-aminoacetophenone which precipitated was collected on a filter, washed well with cold water, and dried. The solid melted at 92–94°. The yield was 687 g. (71%). Morgan and Moss[8] reported the melting point of *m*-aminoacetophenone as 92–93° while Camps[9] reported it as 96.5°.

The *m*-aminoacetophenone was then converted to *m*-bromoacetophenone by the procedure of Elson, Gibson and Johnson.[10] From 688 g. (5.10 moles) of *m*-aminoacetophenone there was obtained 567 g. (56%) of *m*-bromoacetophenone, b. p. 131–2° (17 mm.), n^{20}_{D} 1.5755. Elson, Gibson and Johnson[10] report the boiling point of *m*-bromoacetophenone as 127.5° (14 mm.), 131° (16 mm.).

1-(m-Bromophenyl)-1,2-dimethylethylene.—Into a 5-liter three-necked, round-bottomed flask equipped with a stirrer, condenser and dropping funnel was placed 69.3 g. (2.85 gram atoms) of magnesium turnings and 50 cc. of dry ether. To this was added with stirring a solution of 350 g. (3.2 moles) of ethyl bromide in 2 liters of dry ether, until all of the magnesium had reacted. A solution of 567 g. (2.85 moles) of *m*-bromoacetophenone in 2 liters of dry ether was added and stirring was continued for an additional eight hours. The reaction mixture was washed in the usual manner. The residue, after removal of the ether solution, was placed in a distilling flask along with 1 cc. of concentrated sulfuric acid and distilled through a helices-packed column under nitrogen until all of the water was removed. Distillation was then continued. The product boiled at 110–112° (17 mm.), n^{20}_{D} 1.5620, d^{4}_{20} 1.2976. The yield was 420 g. (70%).

Anal. Calcd. for $C_{10}H_{11}Br$: C, 56.89; H, 5.25. Found: C, 57.15; H, 5.25.

m-s-Butylbromobenzene.—A solution of 344 g. (1.63 moles) of the substituted ethylene in 800 cc. of absolute ethanol was reduced with hydrogen using 1.7 g. of platinum oxide[11] as catalyst at 25–30°. The reduction was completed in one hour. The ethanol was removed and the residue was distilled through a helices-packed column. The product boiled at 104–107° (15 mm.), n^{20}_{D} 1.5338, d^{4}_{20} 1.2510. The yield was 321 g. (1.505 moles) or 92.3% of the theoretical amount.

Anal. Calcd. for $C_{10}H_{13}Br$: C 56.35; H, 6.15. Found: C, 57.00; H, 6.35.

Attempted reduction of the substituted ethylene over Raney nickel was unsuccessful.

m-s-Butylphenylmethylcarbinol.—Into a 5-liter three-necked, round-bottomed flask equipped with a stirrer, condenser and dropping funnel was placed 36.7 g. (1.51 gram atoms) of magnesium turnings and 50 cc. of dry ether. A solution of 321 g. (1.505 moles) of *m-s*-butylbromobenzene in 800 cc. of dry ether was added over a period of two hours and stirring was continued for an additional two hours. A solution of 75 g. (1.70 moles) of freshly distilled acetaldehyde dissolved in 800 cc. of dry ether was added and stirring was continued for one hour. The reaction mixture was treated in the usual manner. The residue, after the removal of ether, was distilled through a helices-packed column. The product boiled at 133–135° (15 mm.), n^{20}_{D} 1.5105, d^{4}_{20} 0.9553. The yield was 150 g (0.843 mole) or 56% of the theoretical amount.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.86; H, 10.48.

m-s-Butylstyrene.—The procedure was adapted from that of Marvel and Shertz.[6] About 1 g. of *p-t*-butylcatechol was added to the carbinol before dehydration. From 150 g. (0.843 mole) of *m-s*-butylphenylmethylcarbinol, there was obtained 82 g. (61%) of *m-s*-butylstyrene, b. p. 98° (15 mm.), n^{20}_{D} 1.5246, d^{4}_{20} 0.8899. Before final distillation of this styrene, a small amount of *p-t*-butylcatechol was added as an inhibitor.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.55; H, 10.17.

p-Cyclohexylstyrene

When *p*-bromocyclohexylbenzene was allowed to react with magnesium followed by addition of acetaldehyde, none of the expected *p*-cyclohexylphenylmethylcarbinol was isolated. Instead there

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[6] Marvel and Shertz, THIS JOURNAL, **65**, 2054 (1943).

[7] Corson and Hazen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., second edition, 1943, p. 434.

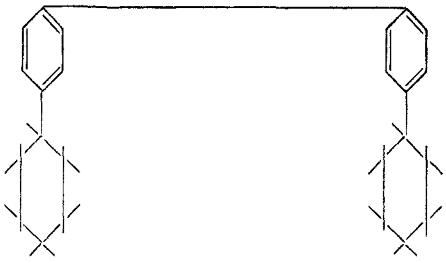
[8] Morgan and Moss, *J. Soc. Chem. Ind.*, **42**, [2] 462T (1923).

[9] Camps, *Arch. Pharm.*, **240**, 1 (1902).

[10] Elson, Gibson and Johnson, *J. Chem. Soc.*, 1128 (1930)

[11] Adams, Voorhees and Shriner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., second edition 1941, p. 463.

was obtained a complex mixture consisting of the derived styrene and some polymer, the hydrocarbon (I) derived from the coupling reaction and *p*-cyclohexylacetophenone.



I

From 2 to 3% of the reaction product consisted of the coupling product (I). A small quantity of *p*-cyclohexylacetophenone was isolated and characterized by its 2,4-dinitrophenylhydrazone derivative. This ketone could have resulted from the oxidation of the methyl carbinol by the acetaldehyde or oxidation by the air introduced in the vacuum distillation of the reaction products. After repeated fractional distillation of the reaction products, 18% of pure *p*-cyclohexylstyrene was isolated.

This method of preparation is not very satisfactory as the yield of *p*-cyclohexylstyrene is low and the fractional distillations required for its isolation are very tedious.

***p*-Bromocyclohexylbenzene.**—The bromination of cyclohexylbenzene was carried out according to directions given by Marvel and Himel.[12]

Reaction of *p*-Bromocyclohexylbenzene with Magnesium with Subsequent Addition of Acetaldehyde.—Into a 5-liter three-necked, round-bottomed flask equipped with stirrer, dropping funnel and condenser were placed 58.4 g. (2.4 gram atoms) of magnesium turnings covered with 50 cc. of dry ether. To this, with stirring, was added 574 g. (2.4 moles) of *p*-bromocyclohexylbenzene dissolved in 2 liters of dry ether. The Grignard reaction started easily after the addition of a small crystal of iodine. The formation of a fine precipitate which coated the magnesium retarded the reaction. Excessive stirring did not seem to help but lack of stirring permitted the fine precipitate to settle and left some of the uncoated magnesium free to react. After all the *p*-bromocyclohexylbenzene had been added, the reaction mixture was gently refluxed for one hour and allowed to stir for an additional six hours. At the end of this time, 120 g. (2.73 moles) of freshly prepared acetaldehyde dissolved in 2 liters of ether was added with stirring over a period of three hours. The reaction mixture was then allowed to stir an additional three hours. The reaction mixture was decomposed with iced dilute hydrochloric acid and the ether layer was separated. The aqueous layer was extracted with a small portion of ether and the total ether solution was divided into two 1.75-liter portions and each portion was washed with 600 cc. of a 10% sodium bicarbonate solution and then twice with 600-cc. portions of water. The ether solution was dried over anhydrous magnesium sulfate, the drying agent and ether were removed and the residue was distilled through a sixteen-inch helices-packed column.

TABLE I

Fraction no.	Weight, g.	Boiling point, (4-5 mm.) °C.	n^{20}D
1	10	< 90	
2	81	90-93	1.5268
3	75	93-100	1.5268
4	15	100-110	1.5323
5	40	110-120	1.5490
6	60	120-130	1.5501
7	2	130-150	

white solid, m. p. 63-66°

A large polymeric residue did not distil. A sample of fraction 6 indicated a pure hydrocarbon upon analysis and reacted with bromine dissolved in carbon tetrachloride. Fractions 5 and 6 were combined for redistillation through a fourteen-inch helices-packed column. A forerun of 5 g. was discarded, b. p. 95-115° (3 mm.). The main product boiled at 120-122° (3-4 mm.); n^{20}D 1.5501. The yield was 80 g. or 18% of the theoretical amount based on the *p*-bromocyclohexylbenzene. This was carefully refractionated through the same column to obtain a sample for analysis. The pure *p*-cyclohexylstyrene boiled at 110° (2 mm.), n^{20}D 1.5520, d^{25}_{25} 0.952.

Anal. Calcd. for $C_{14}H_{18}$: C, 90.26; H, 9.73. Found: C, 90.38; H, 9.67.

Fraction 7 (Table I) was recrystallized from aqueous ethanol with the use of Norite; m. p. 64-67°. Successive recrystallizations from aqueous ethanol gave a white solid melting at 66-68°.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.96. Found: C, 83.03; H, 8.85.

A 2,4-dinitrophenylhydrazone was prepared by a conventional method.[13] Several recrystallizations from ethyl acetate gave orange crystals melting at 201-203°.

Anal. Calcd. for $C_{20}H_{22}O_4N_4$: N, 14.65. Found: N, 14.70.

The distillation residue (130 g.) was heated, transferred to a 1-liter Erlenmeyer flask, 800 cc. of absolute alcohol was added and the solution was refluxed for one hour. The alcohol was decanted from the viscous insoluble polymer and cooled. Crystals which melted at 120-140° and were very sticky and impure separated. A second recrystallization from absolute ethanol raised their melting point to 180-200°. Repeated recrystallizations from ethyl acetate raised the melting point to 198-199°. The yield of *p,p'*-dicyclohexylbiphenyl was 20 g. or 2.6% of the theoretical amount. Bodroux and Thomassin[14] have reported a melting point of 202-203° for *p,p'*-dicyclohexylbiphenyl.

No other crystalline products were isolated from the distillation residue.

Polymerization of *m-t*-Butylstyrene, *m-s*-Butylstyrene and *p*-Cyclohexylstyrene.—In a Pyrex test-tube was placed 1 g. of the monomer. The test-tube was suspended under an ultraviolet lamp and left there until a hard polymer had been formed (twenty-four hours). The polymer was dissolved in 50 cc. of benzene or chloroform and precipitated by slowly dropping the solution into 300 cc. of methanol with vigorous mechanical stirring. This process was repeated and the powder obtained was dried for one week in a vacuum desiccator. All of the polymers obtained were benzene soluble.

Poly-*m-t*-butylstyrene: mol. wt.[15] about 12,800; softening point 123-165°. *Anal.* Calcd. for $(C_{12}H_{16})_x$: C, 89.94; H, 10.06. Found: C, 89.00; H, 9.99; ash, 1.3.

Poly-*m-s*-butylstyrene: mol. wt.[15] about 32,400; softening point 150-165°. *Anal.* Calcd. for $(C_{12}H_{16})_x$: C, 89.94; H, 10.06. Found: C, 89.46; H, 9.90; ash, 0.2.

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[12] Marvel and Himel, THIS JOURNAL 62, 1550 (1940).

[13] Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., second edition, 1940, p. 143.

[14] Bodroux and Thomassin, *Compt. rend.*, **205**, 991 (1937).

[15] These approximate molecular weights were determined by viscosity measurements with the use of an equation developed by Kemp and Peters for the determination of the molecular weight of polystyrene using the K value for styrene (Kemp and Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942)).

Poly-*p*-cyclohexylstyrene: mol. wt.[15] about 28,000; softening point 186–230°. *Anal.* Calcd. for $(C_{14}H_{18})_x$: C, 90.26; H, 9.73. Found: C, 89.97; H, 9.67.

Summary

1. The preparations of *m*-*t*-butylstyrene, *m*-*s*-butylstyrene and *p*-cyclohexylstyrene are described.
2. The polymers of these monomers have been prepared and characterized.

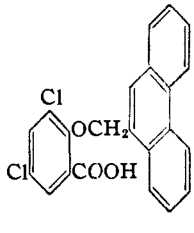
URBANA, ILL. RECEIVED FEBRUARY 20, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

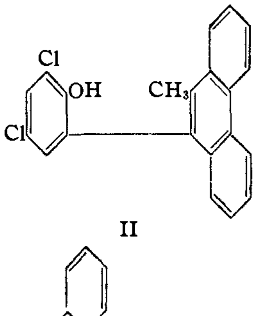
The Synthesis of 9-Phenanthrylmethyldichlorophenol and Related Compounds

BY D. S. TARBELL AND YOSHIO SATO

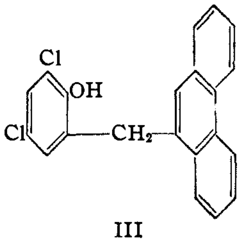
In a study of the effect of heat on benzyl, β-naphthylmethyl and 9-phenanthrylmethyl ethers of dichlorosalicylic acid,[1] it was found that the phenanthrene derivative I differed from the other two in its behavior. When heated at 230°, it evolved carbon dioxide in 75% yield and formed a phenolic rearrangement product of the composition corresponding to 2-(9-methyl-10-phenanthryl)-4,6-dichlorophenol (II) or 2-(9-phenanthrylmethyl)-4,6-dichlorophenol (III). The structure of the rearrangement product was not established by Wystrach, but it is shown in the present paper to be III, by the synthesis of both II and III.



I

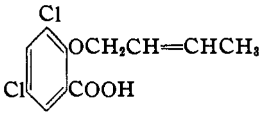


II

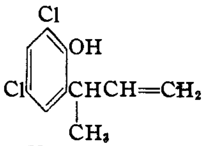


III

It was considered at the outset that the most likely structure for the product was II, since this corresponds to a rearrangement with attachment of the γ-carbon atom (inversion) of the pseudo-allyl group in I. It was shown previously[2] that the rearrangement of O-crotyl-3,5-dichlorosalicylic acid (IV) led to V, by inversion, and I can be regarded as a γ-substituted allyl ether similar to IV.

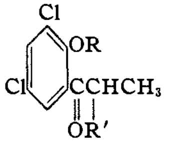


IV

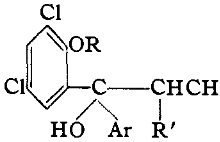


V

The absorption spectrum of the rearrangement product did not point unambiguously to either structure II or III. The most direct method of synthesis of II is the method of Bradsher and Schneider,[3] in which a 2-xenylphenylphenoxyethylcarbinol is cyclized to a 9-arylphenanthrene. The intermediates we employed for the synthesis are indicated below and the reactions proceeded well, following the general procedures of Bradsher and co-workers. The phenoxypropiophenone IX yielded the carbinol X when treated with 2-xenylmagnesium iodide, and this was cyclized to a compound, m. p. 128–129°, not, however, identical with the rearrangement product, which melts at 137.5–138.5°. The cyclization product was shown to be II by the similarity of its absorption curve to that of 9-methyl-10-phenylphenanthrene (Fig. 1). Further, on vigorous oxidation with chromic acid, it yielded what was probably phenanthrenequinone, although the small amount available prevented complete identification.[4]



VI, R = H, R′ = H
VII, R = CH_3, R′ = H
VIII, R = CH_3, R′ = Br
IX, R = CH_3, R′ = OC_6H_5



X, R = CH_3,
R′ = OC_6H_5,
Ar = 2-xenyl

As an alternative synthesis of II, the olefin oxide method[5] was investigated at the same time. The carbinol X was prepared by the action of 2-

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(1) Tarbell and Wystrach, THIS JOURNAL, **65**, 2149 (1943).

(2) Tarbell and Wilson, *ibid.*, **64**, 607 (1942).

(3) Bradsher and Schneider, *ibid.*, **60**, 2960 (1938).

(4) One point in the synthesis of II may be mentioned. The bromination of the acylphenol VI to give the α-bromoketone was slow and unsatisfactory, whereas bromination of the methyl ether VII went smoothly, yielding VIII. A somewhat analogous situation was observed by Shriner and Witte (THIS JOURNAL, **61**, 2328 (1939)). The reason for the slow rate of substitution of the α-hydrogens in the *o*-acylphenol VI is probably the hydrogen bonding between the carbonyl group and the phenolic hydroxyl. This suggests that some interesting information might be gained by comparing rates of bromination of *o*-acylphenols and the amount of hydrogen bond formation as shown by infrared studies.

(5) Bradsher, THIS JOURNAL, **61**, 3131 (1939), and later papers.