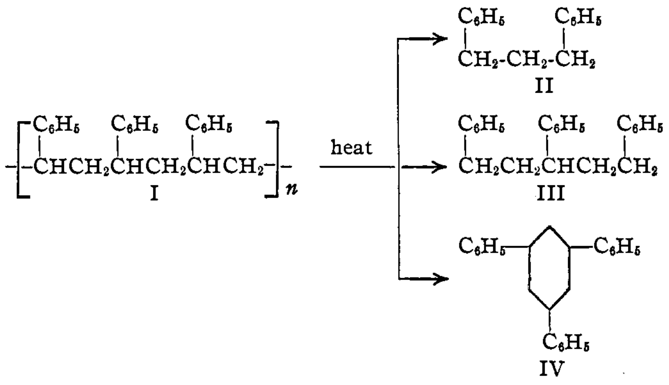
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

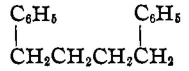
The Structure of Vinyl Polymers. VIII.[1] Polystyrene and Some of its Derivatives

BY C. S. MARVEL AND NEIL S. MOON

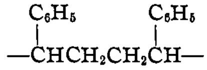
The destructive distillation of polystyrene (I) has been shown by Staudinger and Steinhofer[2] to produce a rather complex mixture of hydrocarbons from which, among other things, 1,3-diphenylpropane (II), 1,3,5-triphenylpentane (III) and 1,3,5-triphenylbenzene (IV) have been isolated and identified. These products furnish excellent evidence that the aryl groups are on alternate carbon atoms in the polymer chain (I).[3]



Midgley, Henne and Leicester[4] found that treatment of styrene with sodium and alcohol yielded 1,4-diphenylbutane (V) and a polymer of styrene which appeared to be identical with that obtained by the polymerization of styrene in the presence of peroxides.

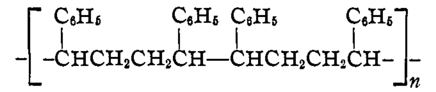

$\overset{C_6H_5}{CH_2}CH_2CH_2\overset{C_6H_5}{CH_2}$

V


$-\overset{C_6H_5}{CH}CH_2CH_2\overset{C_6H_5}{CH}-$

VI

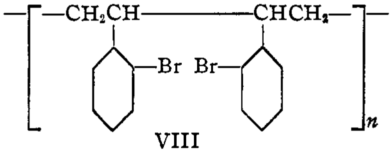
The formation of 1,4-diphenylbutane in this reaction was interpreted as evidence that the biradical (VI) was an intermediate in the polymerization of styrene and that polystyrene might have the "head to head, tail to tail" type of structure (VII).


$-\left[-\overset{C_6H_5}{CH}CH_2CH_2\overset{C_6H_5}{CH}-\overset{C_6H_5}{CH}CH_2CH_2\overset{C_6H_5}{CH}-\right]_n-$

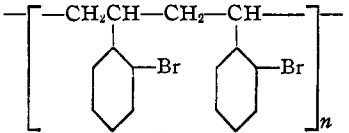
VII

In the present work we have prepared a number of derivatives of styrene containing various functional groups both in the ring and in the side chain with the aim of producing polymers whose chemical reactions would be useful in determining the relative positions of the aryl groups in the polymer chain. Ortho-, meta- and para-bromostyrenes were synthesized and polymerized. Meta- and para-bromostyrenes have been reported previously[5] but the ortho-compound apparently is new. It was prepared readily by dehydration of *o*-bromophenylmethylcarbinol. All three of these bromostyrenes polymerized more readily than styrene itself to give hard, brittle, colorless, transparent products which gradually assumed an amber color on aging for a few months.

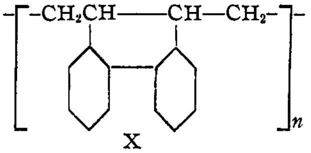
A poly-*o*-bromostyrene which has the 1,2-arrangement (VIII) of the aryl groups along the polymer chain should react with metals to give a dihydrophenanthrene (X) type of polymer in a manner similar to



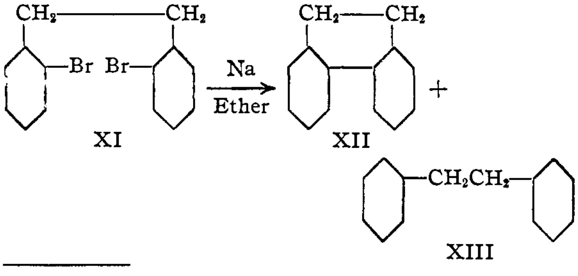
VIII



IX



X



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[1] For the seventh communication in this series, see THIS JOURNAL, 61, 3244 (1939).

[2] Staudinger and Steinhofer, *Ann.*, 517, 35 (1935).

[3] Allen (Gibson Island Conference on Synthetic Resins, July 12, 1939) reported the identification of toluene and isopropenylbenzene as products of the pyrolysis of polystyrene. The formation of isopropenylbenzene is most readily explained on the basis of structure I for this polymer.

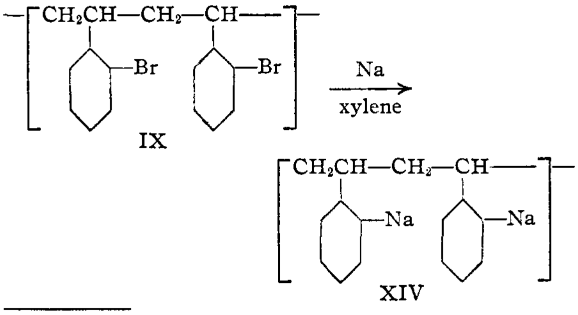
[4] Midgley, Henne and Leicester, THIS JOURNAL, 58, 1961 (1936).

[5] Ziegler and Tiemann, *Ber.*, 55, 3414 (1922); Quelet, *Bull. soc. chim.*, (4) 45, 75 (1929); Brown and Marvel, THIS JOURNAL, 59, 1176 (1937).

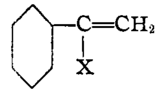
the conversion of 1,2-di-(*o*-bromophenyl)-ethane (XI) to dihydrophenanthrene (XII). Kenner and Wilson[6] have shown that at least a 12% yield of cyclic product results from the action of sodium on 1,2-di-(*o*-bromophenyl)-ethane although debromination to 1,2-diphenylethane (XIII) accounts for most of the product.

When poly-*o*-bromostyrene in dioxane solution was treated with zinc, very little halogen was removed. Neither did copper remove halogen from a nitrobenzene solution of the polymer. Sodium did remove halogen from the hot solution of the polymer in benzene or toluene and when xylene was used as a solvent, the removal of halogen became essentially quantitative. The viscosity of the solution did not change appreciably during this treatment, showing that the polymeric material was not coupling to give a higher molecular weight product and there was no separation from solution as should occur if cross linking of chains had occurred. These facts led to the belief that ring closure must be taking place. However, it was impossible to obtain any evidence of a cyclization reaction. Oxidation of the debrominated polymer gave neither diphenic acid nor a phenanthraquinone derivative. Dehydrogenation and cracking of the polymer over hot selenium gave no phenanthrene derivatives.

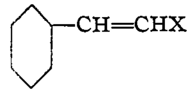
The reaction of poly-*p*-bromostyrene in xylene solution with sodium was next tried. This polymer was as readily debrominated by the treatment as the ortho compound and there was no evidence of cross linking in the reaction. Obviously, then, sodium had reacted with these two polybromostyrenes to give polymeric organometallic materials (XIV) which were hydrolyzed by water during the subsequent steps in the working up of the reaction mixtures. This was confirmed by treating the reaction mixture of poly-*o*-bromostyrene and sodium in xylene with dry carbon dioxide. Some alkali soluble material was produced showing that carbonation had taken place. It seems probable that the *o*-bromophenyl groups are on alternate carbon atoms in the chain (IX) for this formation of the sodium derivative to proceed so smoothly. If the aryl groups are on adjacent carbon atoms (VIII) in the polymer chains some evidence that a Wurtz–Fittig reaction had occurred should have been found.



α-Chlorostyrene (XV, $X = Cl$) was prepared by the method of Dufraisse and Viel[7] and attempts



XV



XVI

were made to polymerize it with heat, ultraviolet light, benzoyl peroxide, ascaridole, stannic chloride and the boron fluoride complex with ethyl acetate. No polymer was obtained although the boron fluoride catalyst did convert α-chlorostyrene into 1,3,5-triphenylbenzene (IV).

α-Methoxystyrene[8] (XV, $X = OCH_3$), β-bromostyrene (XVI, $X = Br$), α-acetoxystyrene (XV, $X = OCOCH_3$) and β-acetoxystyrene[9] (XVI, $X = OCOCH_3$) failed to give polymers with peroxide catalysts or under the influence of ultraviolet light. β-Nitrostyrene (XVI, $X = NO_2$) was polymerized by the method of Vorländer and Herrmann[10] but the polymer was too insoluble to permit the attack of any reagents.

Experimental

***o*-Bromophenylmethylcarbinol.**—A suspension of methylmagnesium chloride was prepared by passing commercial methyl chloride, dried by passing through a calcium chloride tower, into ice cold anhydrous ether covering 100 g. of magnesium turnings. When the ether was saturated with methyl chloride the cooling bath was removed and the temperature of the mixture allowed to rise to room temperature. Usually the reaction between methyl chloride and the magnesium started readily when this was done. Occasionally it was necessary to repeat the cooling and saturating with methyl chloride. Once the reaction had started another 500 cc. of dry ether was added and methyl chloride was slowly passed into the mixture until the magnesium had dissolved. A grayish precipitate separated during the reaction. If the loss of ether became too great more was added to the reaction mixture.

When the formation of the Grignard reagent was complete, a solution of 600 g. of *o*-bromobenzaldehyde in 1200 cc. of dry ether was added slowly to the cooled solution. After all of the aldehyde had been added, the reaction mixture was warmed slowly and finally refluxed gently for

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[6] Kenner and Wilson, *J. Chem. Soc.*, 1108 (1927).

[7] Dufraisse and Viel, *Bull. soc. chim.*, (4) **37**, 874 (1925).

[8] Lauer and Spielman, This Journal, **55**, 4923 (1933).

[9] V. Auwers and Eisenlohr, *J. prakt. Chem.*, (2) **82**, 100 (1910).

[10] Vorländer and Herrmann, *Abhandlung der Naturforschenden Gesellschaft zu Halle*, **21**, 251 (1899); *Chem. Centr.*, **70**, I, 730 (1899).

about an hour. Usually the addition product separated from solution at this stage but if it did not appear the reaction mixture was allowed to stand until it did separate. The reaction mixture was then worked up in the usual manner. The yield was 568 g. (87%) of a colorless, viscous liquid boiling at 91–98° (2 mm.). A sample was redistilled for analysis. It boiled at 108.5° (6.5 mm.); d^{27}_{27} 1.470; n^{20}_{D} 1.5702; n^{25}_{D} 1.5678.

Anal. Calcd. for C_8H_9OBr: C, 47.76; H, 4.51. Found: C, 47.39, 47.99; H, 4.40, 4.51.

When methylmagnesium iodide was used in place of methylmagnesium chloride, the product was red and it seemed impossible to remove iodine completely even by washing with sodium bisulfite, as the red color always reappeared when the product was heated.

***o*-Bromostyrene.**—In a 50-cc. Claisen flask were placed 30 g. of *o*-bromophenylmethylcarbinol, 5 g. of freshly fused and powdered potassium acid sulfate and 0.3 g. of hydroquinone. The mixture was heated under a pressure of 21–30 mm. in an oil-bath at 155–160°. To the distillate was added a little hydroquinone and ether, the water was separated, the ether dried and the mixture distilled. The yield was 9 g. (33%) of product of b. p. 60–65° (3 mm.); 65° (4 mm.); d^{27}_{27} 1.468; n^{25}_{D} 1.5893.

Anal. Calcd. for C_8H_7Br: C, 52.47; H, 3.86. Found: C, 52.75; H, 4.22.

The product was slightly lachrymatory and polymerized on standing even in the presence of hydroquinone.

***o*-Bromo-α-chloroethylbenzene.**—This was prepared by adding dropwise 201 g. of *o*-bromophenylmethylcarbinol to 292 g. of thionyl chloride in the cold. After the evolution of hydrogen chloride and sulfur dioxide had slowed down, the reaction mixture was warmed to 50° for about an hour. Distillation gave 183 g. (83%) of a product boiling at 63–65° (2 mm.). A sample purified by redistillation had the following constants: d^{20}_{20} 1.499; n^{20}_{D} 1.5693.

Anal. Calcd. for C_8H_8BrCl: C, 43.77; H, 3.67. Found: C, 43.70; H, 3.77.

Attempts to remove hydrogen chloride from this product by treatment with quinoline were ineffective.

Poly-*o*-bromostyrene.—*o*-Bromostyrene containing 1–2% of hydroquinone polymerized slowly and a solid product was obtained in a matter of months. Heating alone or especially in the presence of peroxides such as benzoyl peroxide greatly accelerated the polymerization. Freshly distilled *o*-bromostyrene was polymerized in three to five minutes at 175°, whereas at 160° several hours were required to produce the same result.

Most of the polymer used in these experiments was produced by adding 0.2% of benzoyl peroxide to *o*-bromostyrene and heating the mixture to about 140–150° in an oil-bath. The reaction was exothermic and once started proceeded rapidly. It was complete in a few minutes. The end-point could be detected by noting the cessation of the evolution of bubbles. The product as first formed was a hard, brittle, colorless transparent mass. Even if the *o*-bromostyrene used was yellow, the polymer was colorless. On standing, however, an amber color developed in the polymer in a few months.

The polymer was soluble in benzene, toluene, xylene, dioxane and nitrobenzene. It was insoluble in ether, ethyl and methyl alcohols, ethyl acetate, glacial acetic acid and acetone. By dissolving the polymer in benzene or dioxane and pouring this solution into a large excess of ether or methyl alcohol, a colorless amorphous powder was obtained.

A sample of polymer prepared at 140–150° in the presence of benzoyl peroxide had an approximate molecular weight of 24,000 as indicated by viscosity measurements[11]; n^{25}_{D} 1.6333 ± 0.003.[12]

Anal. Calcd. for $(C_8H_7Br)_x$: Br, 43.67. Found: Br, 43.35, 43.73.

Poly-*m*- and *p*-Bromostyrenes.—These products were prepared in the same general manner and their properties were essentially the same as recorded for poly-*o*-bromostyrene. Dr. H. R. Moulton of the American Optical Company has kindly determined the refractive indices of these two polymers for us. The meta isomer has a refractive index of 1.63 and the para isomer 1.62.

Reaction of Poly-*o*-bromostyrene with Metals.—A solution of 1 g. of poly-*o*-bromostyrene in 500 cc. of dioxane was refluxed for seven days with 5 g. of activated zinc.[13] The solution took on an orange-yellow color. About half of the dioxane was removed by distillation and the remaining solution was filtered to remove the zinc. The polymer was precipitated as a buff powder by pouring this solution into water. Analysis of the polymer showed 35.54 and 35.37% bromine remaining.

An attempt to carry out an Ullmann reaction by treating 1 g. of poly-*o*-bromostyrene in 500 cc. of nitrobenzene with 3 g. of copper bronze produced a black, tarry intractable material.

Boiling a solution of 5 g. of poly-*o*-bromostyrene in 2 liters of dry benzene with an excess of clean sodium shavings for fifty hours gave a polymer which contained 37.59–36.99% bromine. After three days of treatment in boiling toluene a polymer was formed containing 34.62–35.54% bromine. Using boiling xylene with sodium, almost complete removal of bromine resulted in 300 to 400 hours. The details of such an experiment follow.

A solution of 2 g. of poly-*o*-bromostyrene in 1 liter of dry technical xylene (which had been purified by refluxing with sodium followed by distillation) was refluxed in an all-glass apparatus with about 7 g. of freshly sliced, clean sodium. The reaction mixture turned yellow in about an hour and gradually assumed an orange color and became somewhat opaque. After about three hundred hours of boiling, part of the xylene was distilled and water was added carefully to destroy the excess sodium. The mixture was then steam distilled to remove the remaining xylene. The polymer which remained was a white or gray, porous, brittle mass. It was dissolved in dioxane and precipitated by pouring the solution into water. The polymer was analyzed for bromine and all of the solutions were saved and analyzed for bromide ion. Many experiments were performed before the time necessary for the removal of bromine was found. In three hundred

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(11) Staudinger, "Die hochmolekularen organischen Verbindungen," J. Springer, Berlin, 1932.

(12) This determination was made by Dr. M. L. Willard to whom we are indebted for permission to include it in this publication.

(13) Marvel, Sample and Roy, THIS JOURNAL, **61**, 3241 (1939).

hours 97% removal of bromine was obtained and in a four hundred and fifty hour run 100% of the bromine was removed.

Carbonation of the Reaction Product of Sodium and Poly-*o*-bromostyrene.—A solution of 15 g. of poly-*o*-bromostyrene in 1 liter of xylene was heated under a reflux condenser for twenty days with 50 g. of sodium. Solid carbon dioxide was then introduced into the reaction mixture. The excess sodium was removed mechanically, the xylene by steam distillation and the insoluble polymer by filtration. The water layer (about 1.5 liters) on acidification gave about 0.23 g. of acidic material. The water layer was then made alkaline, concentrated to about 300 cc. and again acidified. About 1.5 g. of acidic material was obtained. This fraction was a very complex mixture and melted over the range of 90–225°. There was some crystalline material which must have been formed by degradation of the polymer. The neutral equivalent was 76–78.

Anal. Found: C, 69.54; H, 5.87; Br, none.

No definite products were isolated but the experiment did establish the fact that an alkali metal derivative was formed by the reaction of sodium and the poly-*o*-bromostyrene.

Attempts to Oxidize the Debrominated Polymer.—The debrominated polymer was treated with hot chromic acid in glacial acetic acid, with hot nitric acid and with potassium dichromate in dilute sulfuric acid but none of these procedures gave products which could be characterized.

Heating 2 g. of the debrominated polymer with 6 g. of selenium to 400° for twenty hours gave no crystalline products but only gummy solids and brownish powders.

Action of Sodium on Poly-*p*-bromostyrene.—A reaction mixture containing 2.5 g. of poly-*p*-bromostyrene, 1 liter of xylene and 4.7 g. of sodium was heated under a reflux condenser for about five hundred and fifty hours as described for the ortho isomer. Analysis of the water solution showed that 99% of the bromine was removed. The polymer remaining was soluble in xylene and dioxane.

α-Chlorostyrene and Boron Trifluoride–Ethyl Acetate Complex.—A reaction mixture containing 2 cc. of α-chlorostyrene, 3 drops of boron trifluoride–ethyl acetate complex[14] and 2 cc. of ethyl alcohol was sealed and set aside. After two years a mass of long plate-like crystals had separated. The tube was opened and these crystals were recrystallized from absolute alcohol. They melted at 171.5–173.5° whereas the 1,3,5-triphenylbenzene is reported to melt at 172°.[15]

Anal. Calcd. for $C_{24}H_{18}$: C, 94.07; H, 5.93. Found: C, 93.90; H, 6.01.

Other attempts to polymerize α-chlorostyrene with ultraviolet light, benzoyl peroxide, ascaridole, anhydrous stannic chloride and large amounts of the boron trifluoride–ethyl acetate complex[14] gave colored products but no definite polymeric compounds. In one experiment α-chlorostyrene was heated to 130–140° with ascaridole and an impure 1,3,5-triphenylbenzene was obtained.

α-Acetoxystyrene.—Several attempts to add acetic acid to phenylacetylene under various conditions failed to give this product. It was then prepared from styrene bromohydrin obtained by the method of Read and Reid.[16] To 181 g. of styrene bromohydrin was added in small portions 141 g. of acetyl chloride.[17] Heat was evolved during the addition. The reaction mixture was refluxed for ten hours after the addition was complete and then allowed to stand overnight. The excess acetyl chloride was destroyed by pouring the mixture on cracked ice. The organic layer was collected in ether, separated, washed with sodium bicarbonate solution, dried and distilled. The yield was 199.5 g. (91%) of a product of b. p. 105–107° (3 mm.); d^{20}_{20} 1.386; n^{20}_D 1.5380.

Anal. Calcd. for $C_{10}H_{11}O_2Br$: C, 49.40; H, 4.56. Found: C, 49.59; H, 4.63.

A mixture of 48.6 g. of α-acetoxy-β-bromoethylbenzene, 51.5 g. of quinoline and 0.2 g. of hydroquinone was heated to 145–155° for one hour and then distilled under reduced pressure. The yield of product boiling at 80–90° (2 mm.) was 49 g. The quinoline was removed by washing with dilute hydrochloric acid and the product was then fractionated several times through a modified Widmer column. Some decomposition occurred during distillation and analysis of the product showed it to be slightly impure. The yield of product was about 11 g. (34%) boiling at 87.5–89.5° (3.5 mm.); 57.5–58° (0.5 mm.); d^{20}_{20} 1.074; n^{20}_D 1.5533.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.04; H, 6.21. Found: C, 72.84; H, 6.41.

The dibromide was prepared by treating a sample of the above product with bromine in dry carbon tetrachloride. After recrystallization from 95% ethyl alcohol the dibromide melted at 93.5–94.5°.

Anal. Calcd. for $C_{10}H_{10}O_2Br_2$: C, 37.20; H, 3.13. Found: C, 37.23; H, 3.20.

Attempts to Polymerize Various α- and β-Substituted Styrenes.—A variety of catalysts under different conditions were used with α- and β-acetoxystyrene, β-bromostyrene and α-methoxystyrene but no true polymers were obtained. Details of the experiments are therefore not recorded.

Summary

1. Poly-*o*-bromostyrene prepared by peroxide polymerization reacted with sodium in boiling xylene to give replacement of bromine by sodium and no evidence for a Wurtz–Fittig reaction was obtained. This indicates a 1,3-structure for the polymer.

2. Poly-*p*-bromostyrene also reacted with sodium in xylene to give complete removal of halogen without cross linking the polymer chains.

3. α-Chlorostyrene under the influence of boron trifluoride was slowly converted to 1,3,5-triphenylbenzene.

4. α-Acetoxystyrene has been prepared from

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[14] Morgan and Taylor, *Chemistry and Industry*, **50**, 869 (1931).

[15] Odell and Hines, THIS JOURNAL, **35**, 81 (1913).

[16] Read and Reid, *J. Chem. Soc.*, 1488 (1928).

[17] The authors are indebted to the Bakelite Corporation for generous samples of styrene.

styrene bromohydrin by acetylation and dehydrohalogenation.

5. Attempts to polymerize a variety of α- and β-substituted styrenes have been unsuccessful.

URBANA, ILLINOIS RECEIVED NOVEMBER 13, 1939

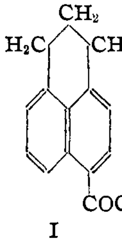
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Further Observations on the Use of Hydrogen Fluoride in Acylations and Cyclizations

BY LOUIS F. FIESER AND E. B. HERSHBERG[1]

In a first paper[2] on this subject it was reported that acenaphthene can be acylated smoothly by reaction with various free acids, acid anhydrides and acid chlorides in the presence of liquid anhydrous hydrogen fluoride at room temperature. Under the same conditions, entirely negative results were obtained with benzene, naphthalene, phenanthrene, anthracene and 1,2-benzanthracene. These observations have now been extended, partly in the hope of casting further light on the remarkable specificity of acenaphthene in the reaction, and partly to see if any additional examples could be found of unusual orientations of practical synthetic value, as encountered in the acetylation of the above hydrocarbon by the hydrogen fluoride method.[2] We may state at the outset that no such applications have been discovered and that the theoretical interpretation still seems obscure.

Two other aromatic hydrocarbons which, like acenaphthene, contain an alicyclic side ring, have been found amenable to acylation under the above conditions. Perinaphthane reacted fairly readily with either acetic acid or acetic anhydride to give as the chief product a substance identified as the 4-aceto derivative I by oxidative degradation.



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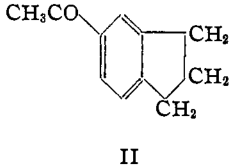

II

The orientation is thus the same as in the benzoylation of the hydrocarbon by the Friedel and Crafts (Perrier) method.[3] Satisfactory condensation also occurred in the presence of hydrogen fluoride between hydrindene and either acetic acid or benzoyl chloride, and again substitution took the normal course and gave the 5-derivatives, such as II. The direct substitution of an α-naphthoyl group in the 4-position of hydrindene would give a known ketone[4] which is easily convertible into cholanthrene, but the total ketonic reaction product obtained with α-naphthoic acid and hydrogen fluoride yielded no hydrocarbon on pyrolysis and afforded on purification a crystalline substance which evidently is the 5-derivative.

It was next found that certain of the hydrocarbons which do not react at room temperature and atmospheric pressure can be acylated by conducting the condensation in an iron pressure vessel under reflux at temperatures up to that of the steam-bath. The acetylation of acenaphthene under these conditions was investigated for comparison and because of the usefulness in syntheses of the 1-aceto compound made available by this reaction. The condensation proceeded smoothly and 1-acetoacenaphthene was obtained in even better yield (37%) than at room temperature. The ketone was converted through the acid to the new 1-acenaphthaldehyde by the Rosenmund reaction. Using the pressure apparatus naphthalene and acetic anhydride gave a mixture of the α- and β-aceto compounds somewhat richer in the β-isomer than that obtained by the Friedel and Crafts method in carbon bisulfide solution[5]; the hydrocarbon did not react with succinic anhydride at moderate temperatures and tar formation occurred on attempting to push the reaction. At 50–55° phenanthrene and acetic anhydride gave a mixture from which the 2- and 3-acetyl compounds were isolated, as with aluminum chloride.[6] A condensation of the hydrocarbon with crotonic acid was also effected giving an oil which appears to be a mixture of isomeric methylketo-

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[1] Research Fellow on funds from the National Cancer Institute and the Eli Lilly Company.

[2] Fieser and Hershberg, THIS JOURNAL, **61**, 1272 (1939).

[3] Fieser and Hershberg, *ibid.*, **60**, 1658 (1938).

[4] Fieser and Seligman, *ibid.*, **57**, 2174 (1935).

[5] Fieser, Holmes and Newman, *ibid.*, **58**, 1055 (1936).

[6] Mosettig and van de Kamp, *ibid.*, **52**, 3704 (1930).