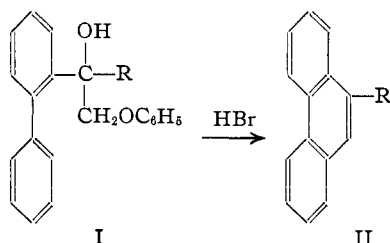


[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ILLINOIS AND DUKE UNIVERSITY]

Synthesis of Phenanthrene Derivatives. III.¹ 9-MethylphenanthreneBY CHARLES K. BRADSHER^{2,3} AND ROY W. H. TESS

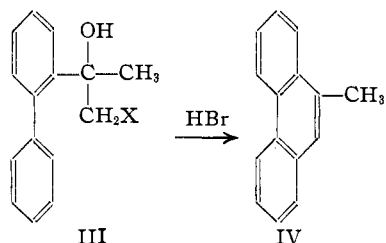
It has been demonstrated that 1-aryl-1-(2-biphenyl)-2-phenoxyethanols (I, R = aryl) readily undergo cyclization to give 9-arylphenanthrenes.⁴



In view of this, it seemed not improbable that the corresponding 1-alkylethanols (I, R = alkyl) might be made to undergo a similar reaction.

We have found that in the case of the methyl-ethanol (I, R = CH₃) such a reaction does take place. When 2-biphenylmagnesium iodide was treated with phenoxyacetone, and the crude carbinol (I, R = CH₃) cyclized by refluxing in a mixture of hydrobromic and acetic acids, 9-methylphenanthrene was obtained in a yield of 32%.

In an effort to find a more satisfactory route to the desired hydrocarbon, the cyclization of a series of carbinols of type III was studied. The



(X = OCH₃, OC₆H₅, OC₁₀H₇(β), N(C₂H₅)₂ or Cl)

methods by which the carbinols were prepared together with the over-all yields of methylphenanthrene (IV) are recorded in Table I.

Although all of the carbinols investigated afforded some methylphenanthrene, the yields varied widely. Since these are the over-all yields for both the Grignard reaction and the cyclization, they may not be interpreted as indicative of the tendency of the several carbinols to cyclize. They

(1) For the preceding paper of this series see *THIS JOURNAL*, **61**, 1524 (1939).

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(4) Bradsher and Schneider, *THIS JOURNAL*, **60**, 2960 (1938); also in unpublished work from this Laboratory.

Carbinol III, X =	Method of preparing Grignard reagent	Method of preparing carbinol Ketone	% yield ^a of hydro- carbon
OCH ₃	CH ₃ MgI	<i>o</i> -C ₁₂ H ₉ COCH ₂ OCH ₃	50
OC ₆ H ₅	<i>o</i> -C ₁₂ H ₉ MgI	CH ₃ COCH ₂ OC ₆ H ₅	32
OC ₁₀ H ₇ (β)	<i>o</i> -C ₁₂ H ₉ MgI	CH ₃ COCH ₂ OC ₁₀ H ₇ (β)	23
N(C ₂ H ₅) ₂	<i>o</i> -C ₁₂ H ₉ MgI	CH ₃ COCH ₂ N(C ₂ H ₅) ₂	10
Cl	<i>o</i> -C ₁₂ H ₉ MgI	CH ₃ COCH ₂ Cl	< 1

^a In each case the percentage yield is calculated from the amount of ketone taken.

do, however, afford us a means for the evaluation of the methods of synthesis studied.

Calculated from the amount of *ketone* used, the route through the methoxyethanol (III, X = OCH₃) gave the highest yield of the desired hydrocarbon. This carbinol, however, was prepared from 2-(*ω*-methoxy)-acetobiphenyl which was itself prepared from 2-iodobiphenyl in a yield of 60%. Thus the average over-all yield from the halide was about 30% whether the route was through the methoxy- or phenoxy-ethanol (III, X = OCH₃ or OC₆H₅) although the latter is more direct. The other routes studied lack the preparative value of these two, but are of interest in illustrating the generality of the cyclization reaction.

Our methods for the synthesis of 9-methylphenanthrene, though more convenient than those of Windaus⁵ and of Haworth,⁶ cannot compare with the method of Bachmann⁷ which involves only the action of methyl iodide on 9-phenanthrylmagnesium bromide. If our synthesis finds application, it will be in the preparation of derivatives rather than of the hydrocarbon itself.

One further observation of interest is that 1-methyl-1-(2-biphenyl)-2-phenoxyethanol-1 (III, X = OC₆H₅) can be cyclized to 9-methylphenanthrene in 10% yield by the action of aluminum chloride. This constitutes a new type of Friedel and Crafts reaction.

Experimental

Phenoxyacetone.⁸—This ketone was prepared by a modification of the general procedure of Bradsher and

(5) Windaus, *Ann.*, **439**, 59 (1924).

(6) Haworth and Mavin, *J. Chem. Soc.*, 2720 (1932).

(7) Bachmann, *THIS JOURNAL*, **56**, 1383 (1934).

(8) Previously prepared in unstated yields by the addition of sodium to a phenol solution of chloroacetone, Stoermer, *Ber.*, **23**, 1253 (1895). Since the completion of this problem, a more satisfactory method has been reported using bromoacetone, Calaway and Henze, *THIS JOURNAL*, **61**, 1355 (1939).

Rosher¹ for the preparation of α -phenoxy ketones. Phenol (51.7 g.), anhydrous potassium carbonate (76 g.) and acetone (300 cc.) were placed in a 3-necked flask and mechanically stirred while a solution of chloroacetone (46.8 g.) in acetone (50 cc.) was added slowly over the period of a half hour. Sufficient heat was evolved to cause refluxing of the acetone. Stirring was continued for twenty-four hours. The inorganic salts were then filtered off, the solution concentrated, poured into water and extracted with ether. The ethereal solution was washed with dilute alkali, dried, concentrated and the residue distilled under reduced pressure. The product was a nearly colorless liquid, b. p. 117–124° (19 mm.); yield 17.7 g. (23%). If the mixture is refluxed for three hours instead of being stirred at room temperature for twenty-four hours, the yield is 21%.

1-Methyl-1-(2-biphenyl)-2-phenoxyethanol-1 (III, X = OC₆H₅).—A Grignard reagent was prepared from 20 g. of 2-iodobiphenyl. To this was added a solution of 10 g. of phenoxyacetone in dry ether. After refluxing for forty-five minutes, the mixture was decomposed with a 20% solution of ammonium chloride. Upon concentration of the ethereal extract, the carbinol was obtained as a brown oil. This was not purified further.

Cyclization of 1-Methyl-1-(2-biphenyl)-2-phenoxyethanol-1.—The crude carbinol obtained above was dissolved in 110 cc. of acetic acid, and 60 cc. of 40% hydrobromic acid added. The mixture was refluxed for twenty-four hours. It was then neutralized, steam-distilled from some tarry material and the product collected by filtration. Once recrystallized from methanol, this product gave 3.1 g. (32%) of 9-methylphenanthrene as white needles, m. p. 91–92.5°. An analytical sample obtained by repeated crystallization melted at 91.5–92.5°.

Anal. Calcd. for C₁₈H₁₂: C, 93.69; H, 6.31. Found: C, 93.68; H, 6.31.

The picrate, recrystallized from alcohol, was obtained as fine orange needles, m. p. 153–154°.

1-Methyl-1-(2-biphenyl)-2-methoxyethanol-1 (III, X = OCH₃).—A Grignard reagent was prepared from 2.8 g. of methyl iodide and an ether solution of 2.1 g. of 2-(ω -methoxy)-acetobiphenyl⁴ was added. The mixture was decomposed with ammonium chloride solution, and the crude carbinol obtained by evaporation of the ethereal solution.

Cyclization of 1-Methyl-1-(2-biphenyl)-2-methoxyethanol-1.—The crude carbinol obtained above was refluxed for twenty-four hours with a mixture of 20 cc. of acetic acid and 10 cc. of 40% hydrobromic acid. There was little evidence of tar formation, and upon cooling the 9-methylphenanthrene crystallized from the solution. Twice crystallized from methanol, the hydrocarbon was obtained in a yield of 1.78 g. (50%); m. p. 88–91°.

1-(2-Naphthoxy)-acetone⁹ was prepared by refluxing a mixture of 46.8 g. of chloroacetone, 79.2 g. of β -naphthol, and 76 g. of anhydrous potassium carbonate in 500 cc. of acetone. The product was worked up as in the case of phenoxyacetone except that the crude material was purified by crystallization from methanol rather than by distillation. Twice crystallized, the product was obtained as small irregular white crystals, m. p. 69–72°; yield 21 g. (21%).

(9) This ketone has been prepared previously in unstated yields by Stoermer, *Ann.*, **312**, 237 (1900).

1-Methyl-1-(2-biphenyl)-2-(2-naphthoxy)-ethanol-1 (III, X = OC₁₀H₇(β)).—A Grignard reagent was prepared from 15.4 g. of 2-iodobiphenyl and to it was added a solution of 10 g. of 1-(2-naphthoxy)-acetone in 50 cc. of dry benzene. The crude carbinol was isolated as in the case of the corresponding phenoxy carbinol (III, X = OC₆H₅).

Cyclization of 1-Methyl-1-(2-biphenyl)-2-(2-naphthoxy)-ethanol-1.—The crude carbinol was cyclized by refluxing for sixteen hours in a mixture containing 50 cc. of acetic acid and 50 cc. of 34% hydrobromic acid. The product was worked up as in the cyclization of the phenoxy carbinol (III, X = OC₆H₅). The yield was 2.24 g. (32%); m. p. 91–92°.

1-Methyl-1-(2-biphenyl)-2-diethylaminoethanol-1 (III, X = N(C₂H₅)₂).—A Grignard reagent was prepared from 28 g. of 2-iodobiphenyl and 12.9 g. of diethylaminoacetone¹⁰ added in ether solution. The mixture was refluxed for thirty minutes and then decomposed with ammonium chloride solution. The crude carbinol was obtained in ether solution.

Cyclization of 1-Methyl-1-(2-biphenyl)-2-diethylaminoethanol-1.—The ether solution obtained above was extracted with 2 N hydrochloric acid and the acid extract concentrated to a small volume under reduced pressure. To the residue was added 125 cc. of 34% hydrobromic acid and the mixture refluxed for forty-eight hours. The solution was extracted with ether, the ether evaporated and the residue crystallized from methyl alcohol; yield 2.0 g. (10%), m. p. 92–93°.

1-Methyl-1-(2-biphenyl)-2-chloroethanol-1 (III, X = Cl) was prepared in a manner analogous to that employed in the synthesis of the corresponding phenoxyethanol (III, X = OC₆H₅). A Grignard reagent was prepared from 19.9 g. of 2-iodobiphenyl and treated with 6.55 g. of chloroacetone. The crude carbinol, obtained as in the preceding cases, was a viscous brown liquid.

Cyclization of 1-Methyl-1-(2-biphenyl)-2-chloroethanol-1.—The crude carbinol obtained above was cyclized as in the case of the corresponding phenoxyethanol. The resinous product, after vacuum distillation, yielded a few crystals of 9-methylphenanthrene, m. p. 90–92°. Attempts to cyclize the carbinol with 85% sulfuric acid or aluminum chloride were unsuccessful.

Cyclization of 1-Methyl-1-(2-biphenyl)-2-phenoxyethanol-1 by the Action of Aluminum Chloride.—The crude carbinol, obtained from 10 g. of phenoxyacetone by the method previously described, was dissolved in 240 cc. of carbon bisulfide and 10 g. of aluminum chloride added. The reaction was allowed to proceed overnight. The mixture was treated in the usual way and the 9-methylphenanthrene isolated as the picrate, yield 2.8 g. (10%).

Summary

The new type of ring closure has been extended to the synthesis of 9-methylphenanthrene. Several variations of the ring closure have been studied.

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(10) Stoermer and Dzinski, *Ber.*, **28B**, 2220 (1895).