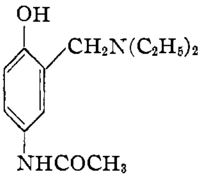
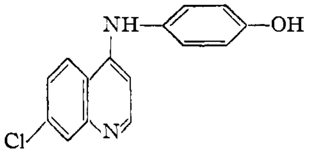

II


III

III and formaldehyde and a nine-fold excess of diethylamine, which may be recycled, over-all yields as high as 80% have been realized from 4,7-dichloroquinoline and *p*-aminophenol hydrochloride. It is of interest to note that this yield is much higher than that obtained when a primary amine—ethylamine—was used in the process.[5]

Experimental

7-Chloro-4-(4-hydroxyanilino)-quinoline (III).—Yields of the previously prepared hydrochloride[6] of III from 4,7-dichloroquinoline and *p*-aminophenol hydrochloride were virtually quantitative when the heated reaction mixture was stirred. To obtain the free base, the salt was suspended in an excess of ammonia and the mixture stirred vigorously. The free base (III) was collected and dried to constant weight; yield 128–135 g. (95–100%); m. p. 254–256°. Recrystallization from alcohol did not significantly affect the melting point.

Anal. Calcd. for $C_{15}H_{11}ClN_2O$: C, 66.54; H, 4.10. Found: C, 66.52; H, 4.18.

4-(7-Chloro-4-quinolylamino)-α-diethylamino-*o*-cresol (Camoquin, I).—A mixture of 27 g. (0.1 mole) of 7-chloro-4-(4-hydroxyanilino)-quinoline (III), 3.4 g. (0.11 mole) of 95% paraformaldehyde, 100 ml. (0.98 mole) of diethylamine and 100 ml. of isopropyl alcohol was stirred and heated under reflux for eight hours. Complete solution was effected within an hour. At the end of the reflux period, the mixture was well cooled and then filtered. The crystalline product, a light cream in color, was sucked dry; yield 29.8 g. (84% yield); m. p. 200–205° (dec.). Mixed m. p. determination with a sample prepared by the original process[7] showed no depression.

The filtrate was saved for subsequent runs. Before the second cycle, the diethylamine was replenished by washing the product prior to its removal from the funnel with 10 ml. (0.1 mole) of the amine. To the combined filtrates was added 0.1 mole of III, and the reaction was repeated. For six recycles the over-all yield was about 80%.

Camoquin Dihydrochloride.—A mixture of 25 g. (0.07 mole) of Camoquin base and 20 ml. of hot concentrated hydrochloric acid readily formed a solution. Upon cooling, the mass quickly began to crystallize. At this time 75 ml. of acetone was added and the mixture vigorously stirred and cooled. The product, a yellow crystalline monohydrate, was collected on a Buchner funnel and dried; yield 95–99%; m. p. 179–183°.[7]

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(5) *Cf.* ref. 4, p. 1367.

(6) *Cf.* ref. 4, p. 1373.

(7) *Cf.* ref. 4, p. 1366.

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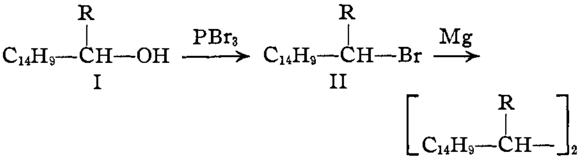
RECEIVED AUGUST 22, 1949

Some New Bis-9-phenanthryl Derivatives

BY CHARLES K. BRADSHER AND RICHARD S. KITTILA[1]

As a continuation of our study of phenanthrene derivatives having substituents at the 9 position, we have now prepared some new bis-9-phenanthryl compounds. The two hydrocarbons prepared (III, R = CH_3 and R = C_2H_5) may be

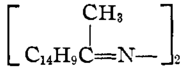


$$\underset{\text{I}}{C_{14}H_9\text{—}\overset{\overset{\large R}{|}}{C}H\text{—}OH} \xrightarrow{PBr_3} \underset{\text{II}}{C_{14}H_9\text{—}\overset{\overset{\large R}{|}}{C}H\text{—}Br} \xrightarrow{Mg} \underset{\text{III}}{\left[C_{14}H_9\text{—}\overset{\overset{\large R}{|}}{C}H\text{—}\right]_2}$$

III

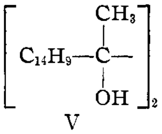
considered as members of a series in which the 1,2-bis-(9-phenanthryl)-ethane (III, R = H) of Tarbell and Wystrach[2] is the simplest member.

The two new hydrocarbons were prepared by treatment of the appropriate halide (II) in ether with one-half gram atom of magnesium. Seeking alternate approaches to the synthesis of the bis-phenanthrylbutane (III, R = CH_3), it was found that the phenanthrylbromoethane (II, R = CH_3) did not undergo the Wurtz reaction, and that the azine (IV) of 9-acetophenanthrene (IV) was not



$$\left[C_{14}H_9\overset{\overset{\large CH_3}{|}}{C}\text{=N—}\right]_2$$

IV



$$\left[C_{14}H_9\text{—}\underset{\underset{\large OH}{|}}{\overset{\overset{\large CH_3}{|}}{C}}\text{—}\right]_2$$

V

reduced to the tetrahydroazine under the conditions employed by Baker[3] in the synthesis of hexestrol derivatives.

It was found that 9-acetophenanthrene could be reduced to the corresponding pinacol (V) by the action of zinc and alkali or, less satisfactorily, by zinc and acetic acid.

Experimental

1-Bromo-1-(9-phenanthryl)-ethane (II, R = CH_3).—A solution of 4 g. of 1-(9-phenanthryl)-ethanol-1[4] in 30 ml. of dry ether was cooled and 1.2 ml. of phosphorus tribromide was added with shaking. After the solution had been allowed to stand for two hours in an ice-bath, the ether was removed under vacuum, and the residue triturated with 8 ml. of cold methanol. The resulting solid (5.1 g.) was collected, taken up in benzene and the benzene solution washed and dried. Upon concentration of the solution and addition of petroleum ether, the bromide was obtained as white crystals, m. p. 85.5–87.5°, yield 3.2 g. (62%). Recrystallization yielded a product, m. p. 86.5–89°, which was not improved by further recrystallization.

Anal.[5] Calcd. for $C_{16}H_{13}Br$: C, 67.38; H, 4.59. Found: C, 67.72; H, 4.60.

2,3-Bis-(9-phenanthryl)-butane (III, R = CH_3).—A solution containing 5.7 g. of the above bromide in 15 ml. of dry benzene was added slowly with mechanical stirring to 0.25 g. of magnesium and 15 ml. of dry ether. The mixture was refluxed on the steam-bath for six hours and the solid collected, m. p. 281.5–282.5°; yield 1.1 g. (27%). Recrystallization from benzene yielded a fine white powder, m. p. 283.5–284°.

Anal. Calcd. for $C_{32}H_{26}$: C, 93.61; H, 6.39; molecular weight, 411. Found[5]: C, 93.66; H, 6.13; molecular weight 388 (ebulliometric in chloroform).

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[1] U. S. Public Health Service Fellow (1948–1949).

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

(3) Baker, *ibid.*, **65**, 1572 (1943).

(4) Bachmann, *ibid.*, **56**, 1366 (1934).

(5) Analyses by Microanalytical Laboratory, University of Pittsburgh.

9-Acetophenanthreneazine.—A solution containing 10 g. of 9-acetophenanthrene[6] in 10 ml. of ethanol and 3 ml. of acetic acid was heated to boiling. Hydrazine hydrate (1.8 ml.) in 3 ml. of ethanol was added slowly and the mixture refluxed for a half-hour. On cooling, a tacky material separated, but on reheating, this material crystallized yielding 8.2 g. (83%) of a yellow pulpy solid, m. p. 139–149°. Recrystallization from chloroform gave 3.9 g. (39%), m. p. 149–150°. The analytical sample was pale yellow, m. p. 149.5–150°.

Anal. Calcd. for $C_{32}H_{24}N_2$: C, 88.04; H, 5.54. Found[7]: C, 88.28; H, 5.25.

9-(Phenanthryl)-ethylcarbinol (**I**, R = C_2H_5).—To a solution of 9-phenanthrylmagnesium bromide,[4] prepared from 13 g. of 9-bromophenanthrene, a solution of 3 g. of propionaldehyde in 10 ml. of dry benzene was added dropwise. The reaction mixture was kept cold for two and one-half hours and then stirred at room temperature for three hours. Worked up in the usual way, the carbinol crystallized from benzene as fine white needles, 7.1 g. (79%), m. p. 102–103°. The same melting point was observed for an analytical sample obtained by repeated recrystallization.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found[8]: C, 86.23; H, 6.56.

1-Bromo-1-(9-**phenanthryl**)-**propane** (**II**, R = C_2H_5) was prepared by the same procedure used in the preparation of the homolog (II, R = CH_3). From 24 g. of the carbinol above, 23.7 g. (78%) of crystallized material, m. p. 62–68° was obtained. In recrystallizing the product from ligroin (60–90°) care must be exercised to prevent heating the solution too long. The purest product obtained was gotten by saturating ligroin at room temperature and allowing spontaneous evaporation to occur until the product started to crystallize. In this way, a sample m. p. 69–70° was obtained as white needles which darkened on standing. Even this material was not analytically pure since it gave a high value for carbon.

3,4-Bis-(9-phenanthryl)-hexane (**III**, R = C_2H_5).—A mixture of 0.6 g. of magnesium, a crystal of iodine and 30 ml. of dry ether was heated for ten minutes and then a solution of 13 g. of the halide above (II, R = C_2H_5) in 30 ml. of benzene was added with stirring over the period of one hour. The mixture was refluxed for twenty hours, decomposed in the usual way, and the organic layer separated, washed and dried. Upon concentration of the solvent 4 g. of crystals, m. p. 210–223°, was obtained. By repeated fractional recrystallization from chloroform-ethanol, this was separated into a less soluble material (unidentified), which, on analysis, did not appear to be a hydrocarbon, and a more soluble material, m. p. 241–241.5°, which was obtained as white rectangular plates having approximately the expected composition.

Anal. Calcd. for $C_{34}H_{30}$: C, 93.10; H, 6.90. Found[8]: C, 92.77; H, 7.11.

2,3-Bis-(9-phenanthryl)-butandiol-2,3 by Reduction of 9-Acetophenanthrene.—(a) In basic solution: To a solution of 5 g. of potassium hydroxide in 50 ml. of 80% ethanol, 0.5 g. of 9-acetophenanthrene and 2 g. of powdered zinc were added. The mixture was refluxed with stirring for one week during which time 1 g. of powdered zinc was added daily for the first three days and once again after two more days. The solid product was collected and the zinc removed by the action of hydrochloric acid. The residue was dissolved in chloroform, filtered and allowed to crystallize. The white crystals weighed 0.2 g. (40%), m. p. 292.5–293.5°. An analytical sample was prepared by repeated recrystallization from chloroform, m. p. 294–296°.

(b) In acid solution: A solution of 2 g. of 9-acetophenanthrene in 35 ml. of ethanol was diluted with 5 ml. of water and 5 ml. of acetic acid. The mixture was stirred on the steam-bath while 5.6 g. of granulated zinc was added in small portions. The mixture was refluxed, 2 ml. of acetic acid being added every twelve hours for the first two days and one ml. of acetic acid added every twelve hours for six days thereafter. The material was treated with hydrochloric acid, dissolved in chloroform, filtered and allowed to crystallize; yield 0.2 g., m. p. 291–292°.

Anal. Calcd. for $C_{37}H_{26}O_2$: C, 86.85; H, 5.92; molecular weight, 443. Found[8]: C, 86.48; H, 6.18; molecular weight, 447 (ebulliometric, chloroform).

The pinacol was unaffected when treated with hydrogen at 1500 lb./sq. in. at 157–163° in the presence of copper chromite. It was recovered unchanged after refluxing for three hours with either acetyl chloride or acetic anhydride.

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RECEIVED AUGUST 16, 1949

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[6] Bachmann and Boatner, THIS JOURNAL, **58**, 2098 (1936).

[7] Analysis by Micro-Tech Laboratories.

[8] Analysis by Clark Microanalytical Laboratory.

Reaction of Phenylmagnesium Bromide with Basically Substituted Nitriles

BY DAVID E. CLARK[1] AND HARRY S. MOSHER

The recent publication by Hauser, *et al.*,[2] on the reaction of γ-diethylaminobutyronitrile with various aryl Grignard reagents to give γ-diethylaminopropyl aryl ketones has prompted the report of the following related work at this time. In the course of other investigations, it was necessary to synthesize γ-, δ- and ϵ-piperidinoalkyl phenyl ketones. These compounds were prepared in satisfactory yields by the reaction of phenylmagnesium bromide with the corresponding basic nitrile. Such nitriles were readily obtained from the α,ω-dihalogen alkanes by conversion to the halonitriles with potassium cyanide, followed by substitution of the remaining halogen atom with the basic group.[3,4,5,6]

The preparation of γ-piperidinobutyrophenone has been previously reported by Petit[7]; however, in a review of this work, we found that hydrolysis with dilute hydrochloric acid of the reaction complex formed from phenylmagnesium chloride and γ-piperidinobutyronitrile gave rise to a white precipitate, which could be recrystallized from methyl alcohol, m. p. 214–220°. This phenomenon was not reported by Petit, since he hydrolyzed the complex with water and immediately rendered the solution basic. The formation of this solid was unexpected, since the basic ketone should have been soluble in the acid solution. A Volhard determination gave a value

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[1] Taken in part from the thesis presented to Stanford University, August, 1948, by David E. Clark in partial fulfillment of the requirements for the M.S. degree.

[2] Humphlett, Weiss and Hauser, THIS JOURNAL, **70**, 4020 (1948).

[3] Utermohlen and Hamilton, *ibid.*, **63**, 156 (1941).

[4] Strukov, *Khim. Farm. Prom.*, 332 (1933); *Chem. Abst.*, **28**, 3714 (1934).

[5] Whitmore, Mosher, *et al.*, THIS JOURNAL, **66**, 730 (1944).

[6] This is the reverse of the sequence employed in ref. 2 and leads to slightly better yields in the case of the trimethylene derivatives. See ref. 5 for an improvement of the "Organic Syntheses" preparation of γ-chlorobutyronitrile.

[7] F. Petit, *Bull. sci. acad. roy. Belg., Classe de sci.*, **12**, 775 (1926).