Synthesis of 9,10-Cyclopentenophenanthrene and Its 1′-Methyl Homolog by Cyclialkylation of Tetrahydrophenanthrene[1]

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Indanones have been synthesized[2-5] by cyclizations involving acylation–alkylation. Hart and Tebbe[6] have reported a variation based on a bifunctional condensation of β-chloropropionyl chloride (**1**) with benzene and naphthalene substrates, in which acylation is carried out by aluminum chloride whereas the cyclialkylation is effected by adding concentrated sulfuric acid to the same reaction mixture.

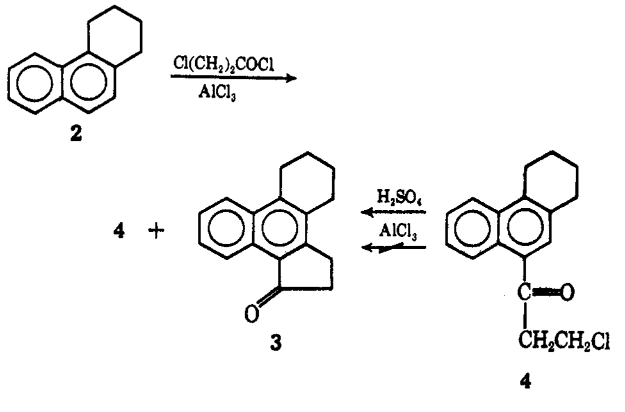
β-Haloaryl ketones obtained as intermediates[7,8] may suffer a partial conversion, by dehydrohalogenation, into α,β-unsaturated ketones.[8] The latter yield the same cyclic ketones by sulfuric acid treatment as those obtained from the halo ketone in the one-step procedure.[6]

The present work describes the bifunctional condensation of 1,2,3,4-tetrahydrophenanthrene (**2**) with **1** in the presence of a little more than 3 equiv of anhydrous aluminum chloride in nitrobenzene to give 1′-keto-1,2,3,4-tetrahydro-9,10-cyclopentenophenanthrene (**3**) (Scheme I).

The sequence of addition of the reagents was critical. Thus, when the acyl chloride **1** was added, as the final reactant, the cyclic ketone **3** was obtained as the predominant product in 25% yield with 6% 9-(1,2,3,4-tetrahydro)phenanthryl-2-chloroethyl ketone (**4**).

However, if the substrate was added last the major product was **4**, obtained in 24% yield with only 6% **3**.

SCHEME I



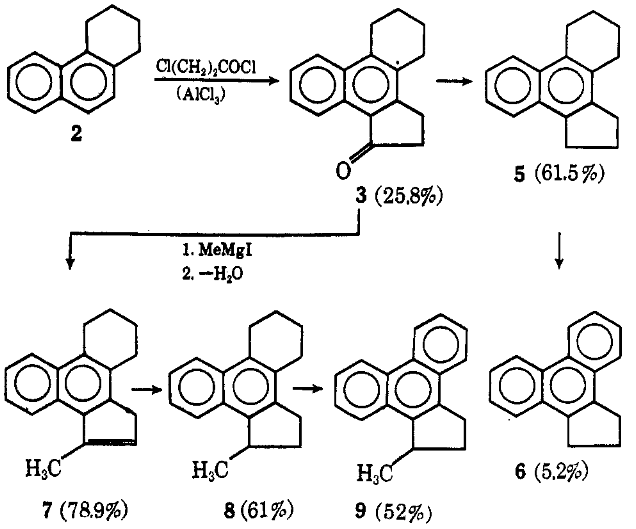
On treatment with concentrated sulfuric acid the halo ketone **4** undergoes an intramolecular ring closure to give **3** in 45% yield. However, **4** is recovered unchanged when treated with aluminum chloride in nitrobenzene.

The formation of the cyclic ketone in the present work, in a direct acylation–cyclialkylation reaction, is unique, comparable with the formation of indanones from aromatic hydrocarbons and α,β-unsaturated acids employing hydrogen fluoride[9] or an excess of aluminum chloride[10] as catalysts.

The conversion of **3** into the corresponding 1,2,3,4-tetrahydro-9,10-cyclopentenophenanthrene (**5**) was carried out both by Clemmensen and Huang-Minlon reductions. The aromatization of **5** to 9,10-cyclopentenophenanthrene (**6**) was accomplished in 52% yield using palladium black. The pure product[11] was obtained by chromatographic decomposition[12] of the trinitrobenzene derivative.

The three-step synthesis shown in Scheme II is the shortest route to **6**.

SCHEME II



The 1′-methyl derivative was synthesized from the cyclic ketone **3**. Butenandt, Dannenberg, and Rahman[11] synthesized **9** by a different route, obtaining the intermediate 3′-methyl-1,2,3,4-tetrahydro-9,10-cyclopentenophenanthrene, an isomer of **8**.

Discussion and Mechanism

The conversion of the β-haloalkylaryl ketone[6-8] into the cyclic ketone in the direct acylation–cyclialkylation process may take place in two possible ways: by an intramolecular alkylation with the haloalkyl group or by the respective α,β-unsaturated ketone from a previous conversion of the halo ketone.

Mayer and Müller[2] postulate the previous conversion of the β-haloalkylaryl ketone into the corresponding unsaturated ketone—by thermal dehydrohalogenation—to explain the cyclization of the former with aluminum chloride, while concentrated sulfuric acid has been supposed to convert both the halo or the

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[1] This paper forms part of the forthcoming Doctoral thesis of B. M. Vuano, Universidad Nacional del Sur, Bahía Blanca.

[2] F. Mayer and P. Müller, *Ber.*, **60**, 2278 (1927).

[3] G. Baddeley and R. Williamson, *J. Chem. Soc.*, 4647 (1956).

[4] R. W. Layer and I. R. MacGregor, *J. Org. Chem.*, **21**, 1120 (1956).

[5] R. T. Arnold and E. Rondesvedt, *J. Amer. Chem. Soc.*, **67**, 1265 (1945).

[6] R. T. Hart and R. F. Tebbe, *ibid.*, **72**, 3286 (1950).

[7] A. Rahman and A. E. Gastaminza, *Rec. Trav. Chim.*, **81**, 645 (1962).

[8] H. Dannenberg and A. Rahman, *Chem. Ber.*, **88**, 1405 (1955).

[9] L. F. Fieser and E. B. Hershberg, *J. Amer. Chem. Soc.*, **61**, 1272 (1939).

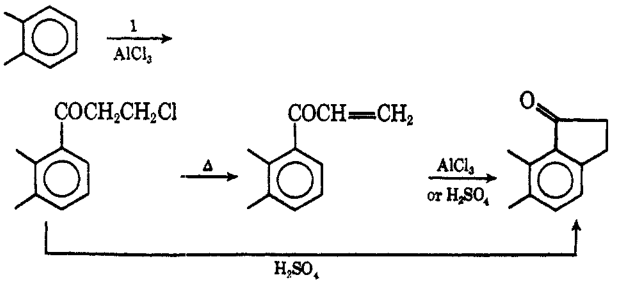
[10] C. F. Koelsch, H. Hochmann, and C. D. Leclaire, *ibid.*, **65**, 59 (1943).

[11] A. Butenandt, H. Dannenberg, and A. Rahman, *Chem. Ber.*, **88**, 1395 (1955).

[12] A. Rahman and O. L. Tombesi, *J. Chromatog.*, **23**, 312 (1966).

unsaturated ketone to the cyclic compound, as formulated in Scheme III.

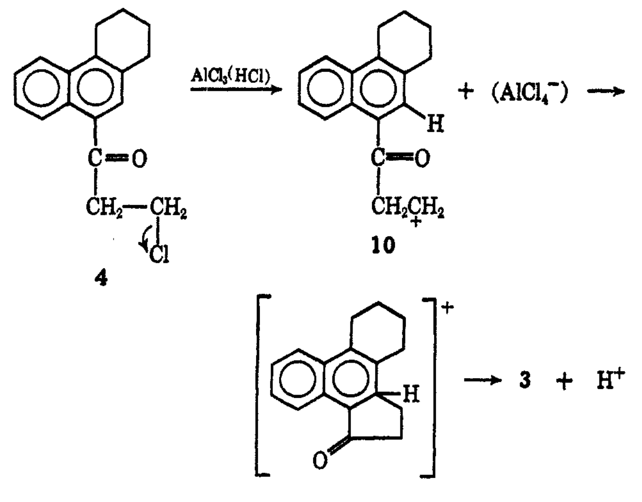
SCHEME III



As to the mechanism of formation of the cyclic ketone **3**, by a bifunctional condensation carried out without the application of heat (which could make possible the conversion of **4** into the corresponding vinyl ketone), one has to take into account three factors: (a) the presence of an excess of aromatic substrate and the metal halide catalyst throughout the reaction, (b) the intermediate formation of chloroketone **4** by an initial acylation liberating hydrogen chloride in the reaction, and (c) nonformation of the cyclic ketone **3** starting from pure **4** in the presence of aluminum chloride but absence of hydrogen chloride. The reaction probably proceeds through the carbonium-ion intermediate **10** involving the ionization of the chlorine atom of the chloro ketone **4**.

The hypothesis that the conversion of **4** into **3** takes place "in situ" in the presence of hydrogen chloride and excess of aluminum chloride is coherent with the observation that the cyclic ketone is formed predominantly only under those conditions which allow the presence of an excess of the aromatic substrate and the aluminum chloride catalyst. In this way the hydrogen chloride favors the formation of the soluble complex $ArH^+(AlCl_4)^-$ which would permit the dissolution of further amounts of aluminum chloride (Scheme IV).

SCHEME IV



A possible alternative hypothesis that, in the present direct synthesis of the cyclic ketone **3**, intermolecular alkylation may procede intramolecular acylation, as has been reported in a reaction between chlorobenzene and crotonyl chloride,[13] is discarded because in such a case 3′-keto-9,10-cyclopentenophenanthrene,[14] mp 179°, should be formed instead of **3**, mp 212–213°, the ultraviolet spectrum of which corresponds to that of an α-naphthyl ketone.[15]

Experimental Section[16]

A. Reaction between Tetrahydrophenanthrene (2) and β-Chloropropionyl Chloride (1).—To a solution of 25 g (0.184 mol) of anhydrous aluminum chloride in 50 ml of nitrobenzene, cooled to 0°, 10 g (0.054 mol) of **2** was added in one portion and finally a solution of 7.6 g (0.059 mol) of **1** in 25 ml of nitrobenzene was added, in small portions, maintaining the temperature of the reaction mixture at 0°. The mixture was stirred for 4 hr at this temperature, then left at room temperature for 12 hr, and finally hydrolized with ice and hydrochloric acid. After adding about 100 ml of benzene to the reaction mixture, it was washed neutral with water. The solvents were then removed by steam distillation and the reaction product was worked up in benzene. Evaporation of the solvent from the solution dried over anhydrous magnesium sulfate gave 8.6 g of a dark brown semisolid mass, which showed a positive test for halogen. This was chromatographed on neutral alumina. The two fractions eluted with petroleum ether–benzene (3:1 and 1:1) were combined (3.232 g, 25% yield), mp 195–205°, and the mixture was rechromatographed on neutral alumina. This yielded 1.85 g (14%) of the cyclic ketone **3**: mp 212–213.5° [benzene–petroleum ether (bp 60–80°)]; ir ν 5.96 μ (CO), ν_{CH} 13.15 μ (vs); uv λ_{max} 320 mμ (ϵ 6324), 313.5 (8047), 249 (15,859), 242 (16.520), and 222 (27,255).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.11; H, 6.71. Found: C, 86.40; H, 6.82.

The fraction (3.301 g), a dark brown oily liquid, eluted with benzene, was heated with 90 ml of concentrated sulfuric acid, on the water bath, for about 40 min. The reaction product was poured on ice and then extracted with benzene. Evaporation of the solvent gave 1.48 g of a crystalline solid, mp 199–209°, which on recrystallization from benzene–petroleum ether (bp 60–80°) gave mp and mmp 212–213.5° with **3**. The total yield of the pure **3** amounted to 3.33 g (1.85 plus 1.48 g) (25.8%).

Thin layer chromatography (tlc), employing silica gel, was used to confirm the identity of the sample of the cyclic ketone **3**, obtained directly from the petroleum ether–benzene fraction (3:1 and 1:1) with that obtained by treatment of the product obtained from benzene eluate with concentrated sulfuric acid. Benzene–chloroform (1:1), used as solvent and vanilline–H_2SO_4 used as spray reagent, gave hR_f values of 38 and 81, respectively, for **3** and **4**.

One gram of the reaction product, obtained in another experiment, was subjected to adsorption chromatography on silica gel. The first fraction of the benzene–petroleum ether (1:1) eluate gave a solid of mp 109–113°, which on recrystallization from benzene–petroleum ether (bp 60–80°), yielded 0.1 g (*ca.* 6%) of **4**, mp 113–115°.

Anal. Calcd for $C_{17}H_{17}OCl$: C, 74.82; H, 6.28; Cl, 13.00. Found: C, 74.44; H, 6.26; Cl, 12.59.

The second and third fractions of the same eluate, on recrystallization from benzene–petroleum ether, gave **3**, mp and mmp 212–213.5°.

B.—The reaction between **2** and **1** was repeated with the variation that in this case **2** was added as the final reactant. The reaction mixture was worked up as described in A, thus obtaining 8.0 g of an oily product which was taken up in a

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(13) I. G. Farbenindustrie A.G, British Patent 288441 (April 26, 1927); *Chem. Abstr.*, **23**, 606 (1929).

(14) G. M. Badger, W. Carruthers, and J. W. Cook, *J. Chem. Soc.*, 2044 (1949).

(15) H. Dannenberg and D. Dannenberg von Dresler, *Liebigs Ann.*, **585**, 1 (1954).

(16) Melting points were determined on Kofler hot stage and are uncorrected. Infrared (ir) spectra were run in Nujol mulls on a Perkin–Elmer Model 137-B spectrophotometer and ultraviolet (uv) spectra on a Beckman spectrophotometer Model DB, in 95% ethanol.

minimum quantity of benzene and precipitated with ether. The solid obtained on filtration and washing with benzene–petroleum ether, on crystallization from the latter, gave 3.6 g (24%) of **4**, mp 113–115°, which was found to be identical with the sample of the same obtained in A (mixture melting point and tlc).

The filtrate from the above, on evaporation of the solvent, gave a semisolid product (4.2 g), which on alumina chromatography as described before, gave from the benzene–petroleum ether (1:1) eluate 0.72 g (5.6%) of the cyclic ketone **3**, mp and mmp 212–213.5° (benzene–petroleum ether).

C. Intramolecular Cyclization of the Chloro Ketone 3.—The chloro ketone **3** (0.6 g) was heated for 40 min with 20 ml of concentrated sulfuric acid on the water bath. After cooling, the reaction mixture was hydrolyzed with ice, neutralized with sodium carbonate, and worked up with benzene. The yield of **4** so obtained was 0.24 g (45.2%); after purification by alumina chromatography and crystallization from benzene–petroleum ether it melted at 212–213.5°. An attempt to cyclize **3** by using a 3 *M* proportion of aluminum chloride in nitrobenzene resulted in its recovery.

D. 9,10-Cyclopenteno-1,2,3,4-tetrahydrophenanthrene (5). **Clemmensen Reduction of 3.**—A mixture of 0.45 g of **5**, 15.0 g of amalgamated zinc, 10 ml of concentrated hydrochloric acid, and 5 ml of toluene was refluxed for 24 hr and 3 ml of concentrated hydrochloric acid was added every 6 hr over this period. The toluene layer was separated and the aqueous layer was extracted with ether. The ether–toluene solution, worked up as usual, gave 0.31 g of an oily liquid which was purified by neutral alumina chromatography. The product obtained from the petroleum ether (bp 60–80°) eluate (0.12 g, mp 50–56°), on a second alumina chromatography, gave **5** as colorless crystals: mp 60–62° (acetone); ν_{CH} 13.25 μ; uv $\lambda_{\max}$ 322 mμ (ε 932), 293 (5239), 282 (4795), 270 (3330), 256 (2131), *237* (55,926), and 216 (25,885).

Anal. Calcd for $C_{17}H_{18}$: C, 91.85; H, 8.16. Found: C, 91.82; H, 8.24.

Huang-Minlon reduction of **3** (0.7 g), using 0.6 g of potassium hydroxide, 30 ml of diethylene glycol, and 1.5 ml of 85% hydrazine hydrate, by the usual procedure, gave 0.4 g (61.5%) of an oily product, which on purification by alumina chromatography, gave 0.3 g (46.1%) of the pure hydrocarbon **5**, mp 60–62° (acetone) (lit.[14] mp 65°), which was not depressed on admixture with the sample obtained by Clemmensen reduction. A thin layer chromatogram, using silica gel G as adsorbent, petroleum ether (bp 60–80°) as solvent, and 1% chloroform solution of $SbCl_3$ as spray reagent, gave an hR_f value of 55 for the hydrocarbon **5**.

E. 9,10-Cyclopentenphenanthrene (6).—**5** (200 mg) was aromatized by heating with 48 mg of palladium black for 50 min at 260–70° under a nitrogen atmosphere. The reaction product, on working up in petroleum ether (bp 40–60°) gave 100 mg (52%) of **6**, which after neutral alumina chromatography melted at 134–139°. Repeated crystallization in ethanol raised the melting point to 136–140°. The pure product was obtained by the method of chromatographic decomposition[12] of the trinitrobenzolate, on basic alumina (Woelm): mp and mmp 147–149.5°; ir ν_{CH} 13.25 and 13.80 μ; uv $\lambda_{\max}$ 354 mμ (ε 610), 339 (741), 300 (5711), 289 (4817), 280 (5406), 270 (7608), *254* (22,672), 245 (18,617), 239 (15,805), 220 (11,406), and 213 (14,780).

Anal. Calcd for $C_{17}H_{14}$: C, 93.53; H, 6.46. Found: C, 93.21; H, 6.71.

The thin layer chromatogram gave an hR_f value of 46 for the sample of **6** obtained as above and for the authentic sample.[11]

F. $\Delta^{1'}$-1′-Methyl-9,10-cyclopentadieno-1,2,3,4-tetrahydrophenanthrene (7).—A benzene solution of 0.95 g of the cyclic ketone **3** was added, under cooling and mechanical stirring, to a solution of the Grignard reagent prepared from 0.42 g of magnesium and 1.2 ml of methyl iodide. The reaction mixture was heated under reflux for 2.5 hr, then decomposed with an ice–ammonium chloride mixture, and extracted with ether. The ethereal solution, on working up as usual, gave 0.9 g of the corresponding carbinol, which was directly dehydrated in 30 ml of pyridine by careful treatment with 0.3 ml of phosphorus oxychloride. The reaction mixture was heated on the steam bath for 20 min and finally hydrolyzed with ice and hydrochloric acid. The ethereal extract of the reaction product, on working up as usual, gave 0.74 g (78.9%) of **7** as an oily product, which was purified by neutral alumina chromatography. The product from the petroleum ether (bp 60–80°) eluate, on two crystallizations from the same solvent, gave **7**: mp 82–84°; ir ν_{CH} 13.32 μ (s); uv $\lambda_{\max}$ 331 mμ (ε 10,202), 326 (10,576), 314 (13,244), 247 (67,532), *241* (68,702), 220 (37,252), and 202 (35,053).

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.01; H, 7.82.

G. 1′-Methyl-1,2,3,4-tetrahydro-9,10-cyclopentenophenanthrene (8).—A methanolic solution of 0.4 g of **7** was reduced catalytically employing 80 mg of palladium black at atmospheric pressure, obtaining thereby 0.245 g (61%) of **8** as a colorless liquid which, on purification by alumina chromatography, in which almost all the compound passed in the petroleum ether (bp 60–80°) eluate, was directly aromatized to **9**: ir ν_{CH} 13.25 μ (vs); uv $\lambda_{\max}$ 355 mμ (ε 2177), 329 (8558), 326 (7866), *237* (80,805), and 218 (36,815).

Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.76; H, 8.34.

H. 1′-Methyl-9,10-cyclopentenophenanthrene (9).—**8** (200 mg) was heated with 40 mg of platinum black, at 290–300° for about 40 min. The reaction product was taken up in dry petroleum ether (bp 40–60°) and directly passed through a column of neutral alumina (Woelm). The total petroleum ether eluate yielded 103 mg (52.2%) of **9** as a crystalline solid, which on repeated crystallization from ethanol gave mp and mmp 89–91° with an authentic sample[11] of 1′-methyl-9,10-cyclopentenophenanthrene: ir ν_{CH} 13.30 and 13.75 μ; uv $\lambda_{\max}$ 354 mμ (ε 1160), 338 (1113), 302 (12,156), 289 (10,115), 278 (11,368), 270 (17,075), *254* (52,195), 246 (42,734), 222 (21,576), and 212 (29,464).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.97; H, 6.71.

Registry No.—**2**, 1013-08-7; **3**, 18910-39-9; **4**, 18910-40-2; **5**, 18910-41-3; **6**, 723-98-8; **7**, 18910-43-5; **8**, 18910-44-6; **9**, 18910-45-7.

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Trapping of 3,4-Pyridyne by Methylmercaptide Ion in Ammonia

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Compelling evidence for the intermediacy of 3,4-pyridyne (I) in the reactions of 3- and 4-halopyridines with nitrogen bases has been obtained.[1] Competition experiments involving the addition of pairs of nucleophiles to this intermediate generally have employed mixed nitrogen bases in an ether solvent.[2] There is also a report of a competition involving a nitrogen and a carbon nucleophile in ammonia but only the 4-

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(1) For reviews of hetaryne chemistry, see (a) T. Kauffmann, *Angew. Chem. Intern. Ed. Engl.*, **4**, 543 (1965); (b) H. J. den Hertog and H. C. van der Plas, *Advan. Heterocycl. Chem.*, **4**, 121 (1965); (c) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967.

(2) Th. Kauffmann and R. Nürnberg, *Chem. Ber.*, **100**, 3427 (1967); Th. Kauffmann, H. Fischer, R. Nürnberg, M. Vestweber, and R. Wirthwein, *Tetrahedron Lett.*, 2911, 2917 (1967).