SYNTHESIS OF 4-HALOPHENANTHRENES AND 4,5-PHENANTHRYLENEIODONIUM SALTS*†[1]

F. M. Beringer, L. L. Chang, A. N. Fenster and R. R. Rossi

Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York 11201

Abstract—4-Aminophenanthrene, prepared by a new aromatization, has been converted to all four 4-halophenanthrenes: as halogen size increases, NMR spectra show increasing paramagnetic deshielding of the 5-hydrogens, while UV spectra indicate progressively greater molecular non-planarity. Oxidative cyclization of 4-iodophenanthrene gave salts containing the new cyclic 4,5-phenanthryleneiodonium ion.

THE aim of the present work was the synthesis of salts containing the 4,5-phenanthryleneiodonium ion. Cyclic salts are known in which the 2,2′-position of the diphenyliodonium ion are joined directly[2] or are bridged by methylene groups[3] or by nitrogen, oxygen or sulfur.[4] A salt in which the 4,5-positions of phenanthrene are bridged by iodine is previously unreported. 4,5-Phenanthryleneiodonium ions would be of interest for further study because of their predicted unreactivity toward nucleophiles‡ and because of the possible stability of the 1-electron reduction product, 4,5-phenanthryleneiodine.§

Since the projected synthetic route (Chart I) involved 4-aminophenanthrene and 4-iodophenanthrene, it was thought desirable not only to improve the synthesis of the former but also to prepare the 4-halophenanthrenes and examine their spectra for evidence of crowding of the 4,5-substituents and of molecular non-planarity. Indeed, it was uncertain as to whether the large size of iodine would prevent conversion of the 4-diazonium ion to the desired 4-iodophenanthrene.

Synthesis. Because methods of direct substitution give 4-halophenanthrenes in yields below 10%, their preparation is most convenient from 4-aminophenanthrene. The oxime of 4-keto-1,2,3,4-tetrahydrophenanthrene (1)[6-9] was aromatized to 4-aminophenanthrene by hydrogen bromide in acetic acid-acetic anhydride[10] and in comparable yield (60–70%) by a new 3-step procedure (Chart I): diacetylation to N-acetyl-N-acetoxy-4-amino-1,2-dihydrophenanthrene (2), removal of acetic acid to give

---

*This research was supported in part by the Petroleum Research Fund under Grant PRF No. 2334-A1,4.

†This paper is taken from the doctoral dissertation of L. L. Chang and from the master's theses of A. N. Fenster and R. R. Rossi.

‡Joining the two rings of the diphenyliodonium ion through the 2,2′-positions substantially decreased its reactivity toward nucleophiles: J. H. Nachtigal, doctoral dissertation, Polytechnic Institute of Brooklyn, 1967. A tentative explanation involves strain in the tetrahedral transition state as the nucleophile approaches the 2-position.

§Studies of the electroreduction of diaryliodonium salts have indicated the formation of a short-lived diaryliodine free radicals.[5] The rigidity of 4,5-phenanthryleneiodine should increase the lifetime of such a species.

CHART I 4-Substituted Phenanthrenes and 4. 5-Phenanthryleneiodonium Salts
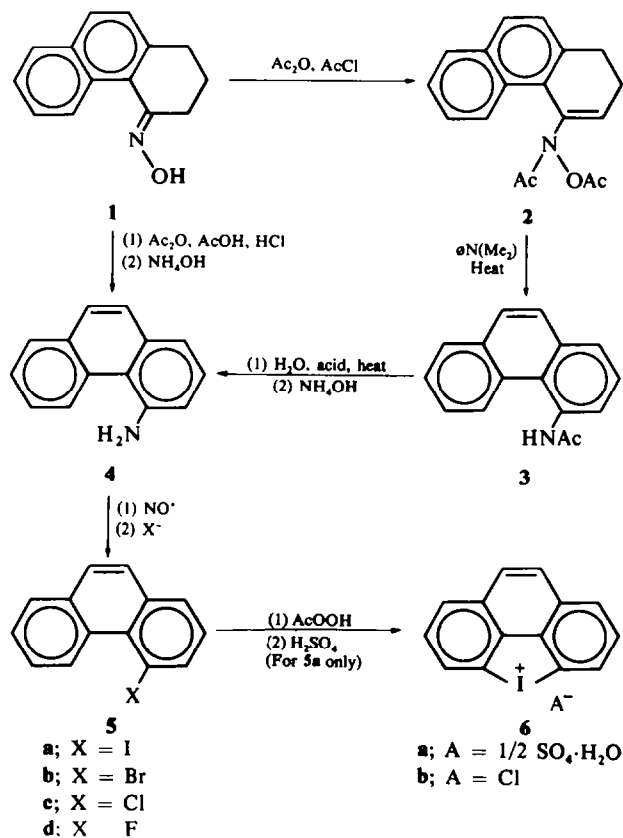
4-acetamidophenanthrene (3), and hydrolysis[11] to 4-aminophenanthrene (4). The isolation of 3 is of interest as its structure is analogous to the N-acetoxydihydroacetanilide postulated as an intermediate in the aromatization of isophorone oxime to mixed trimethylacetanilides under similar conditions.[12] In the present case the loss of the acetoxyl group is inhibited by the nonplanarity of the N-acetoxyamido group with the dihydrophenanthrene ring system; the resulting cation will have full resonance stabilization only when the amide bond lies in the plane of the olefinic bond. Therefore, in the aromatization of the dihydrophenanthrene the loss of the acetoxyl group is slow, and a comparatively high temperature is required.

Our concerns about steric hindrance to the formation of 4-iodophenanthrene proved groundless. Indeed, diazotization was successfully followed either by isolation of the diazonium fluoroborate or by direct conversion of the diazonium solution to the 4-halophenanthrenes.[13, 14]

Finally, under suitable conditions, peroxyacetic acid did not oxidize the 9,10-bond but did oxidize 4-idophenanthrene to the idoso compound;[3] this was not isolated but was cyclized to the 4,5-phenanthryleneiodonium ion (6), obtained as the sulfate hydrate, $(-I^+-)_2 SO_4 \cdot H_2O$, and by metathesis as the chloride.

NMR spectra. The NMR spectrum of phenanthrene was first resolved by Bernstein

et al.[15] The downfield group of intensity 2 at $\tau 1 \cdot 58$ is assigned to the angular 4,5-protons, while the other protons form an envelope around $\tau 2 \cdot 48$. Deshieldings by proximate atoms may be partly steric in origin; i.e. changes in electronic distribution around hydrogen may arise from deviation from normal bonding position of hydrogen and the resulting sterically induced charge polarization of the H—C bond.[16] An additional example is that of the 5-hydrogen in 4-methylphenanthrene: $0 \cdot 28$ ppm downfield from the 4,5-hydrogens in phenanthrene.[17] Deshieldings may also be magnetic, where the magnetic field sensed by hydrogen is affected by movement of electrons in the proximate group.

For the 5-hydrogens in the 4-halophenanthrenes (Table 1), deshielding increases with the size of the halogen* The downfield shift in 4-iodophenanthrene, $1 \cdot 48$ ppm relative to phenanthrene, is believed to be the largest reported to date. These data, however, do not allow separation of the chemical shifts caused by the crowded 4-halogens to be separated into steric and magnetic components, as defined above. Spectra of 4-iodophenanthrene at $100°$ and $-65°$ showed no significant difference from that at room temperature.

TABLE 1. NMR CHEMICAL SHIFTS OF 5-PROTONS IN 4-HALOPHENAN-
THRENES

4-Substituent	τ-Value[a]
Hydrogen	$1 \cdot 56$[b]
Fluorine	$1 \cdot 0$
Chlorine	$0 \cdot 4$
Bromine	$0 \cdot 17$
Iodine	$0 \cdot 1$

[a] In CCl_4 with TMS as internal standard.
[b] Protons 4 and 5.

In a recent paper Dewar *et al.*[19] reported the F-19 NMR spectrum of 4-fluorophenanthrene and commented that strong interaction of 4-fluorine with the 5-protons made the C—F bond more polarized and resulted a paramagnetic shift to lower field. This conclusion is quite compatible with the viewpoint of the present authors.

UV spectra. In phenanthrene itself X-ray studies[20] have shown that the 4,5-hydrogens occupy distorted positions above and below the average plane of the carbon skeleton, which is essentially planar. With increasing size of substituents at 4- or 5-positions, strain increases, and it is likely that the skeleton is progressively deformed from planarity. Thus, the spectrum of 4,5-dimethylphenanthrene[21] was explained as exhibiting a new "ring strain effect",[22, 23] arising from strain distributed over a nucleus by enforced non-planarity of substituents. Other examples include 4,5-dimethylchrysene,[24] 1,12-dimethylbenzophenanthrene,[25] 1-methyl-3-4-benzophenanthrene[26] and bent benzenes.[27]

In the present case of the UV spectra of the 4-halophenanthrenes (Fig. 1), 4-fluorophenanthrene shows a hypsochromic shift from phenanthrene and the same fine structure. As the size of the halogen increases, a bathochromic shift is apparent in

*Cf. similar chemical shifts of the 2'-hydrogens in the 2-halobiphenyls.[18]

the chloro compound, becomes larger in the bromo compound and reaches its limit with 4-iodophenanthrene. A decrease in fine structure is also observed in going from the chloro to the bromo compounds, with 4-iodophenanthrene showing no fine structure. However, these observations lead to no new conclusions regarding the distortions of these molecules from planarity or the strains involved.

Further work. A study of the reactions of the 4,5-phenanthryleneiodonium ion with nucleophiles and with reductants is now planned*
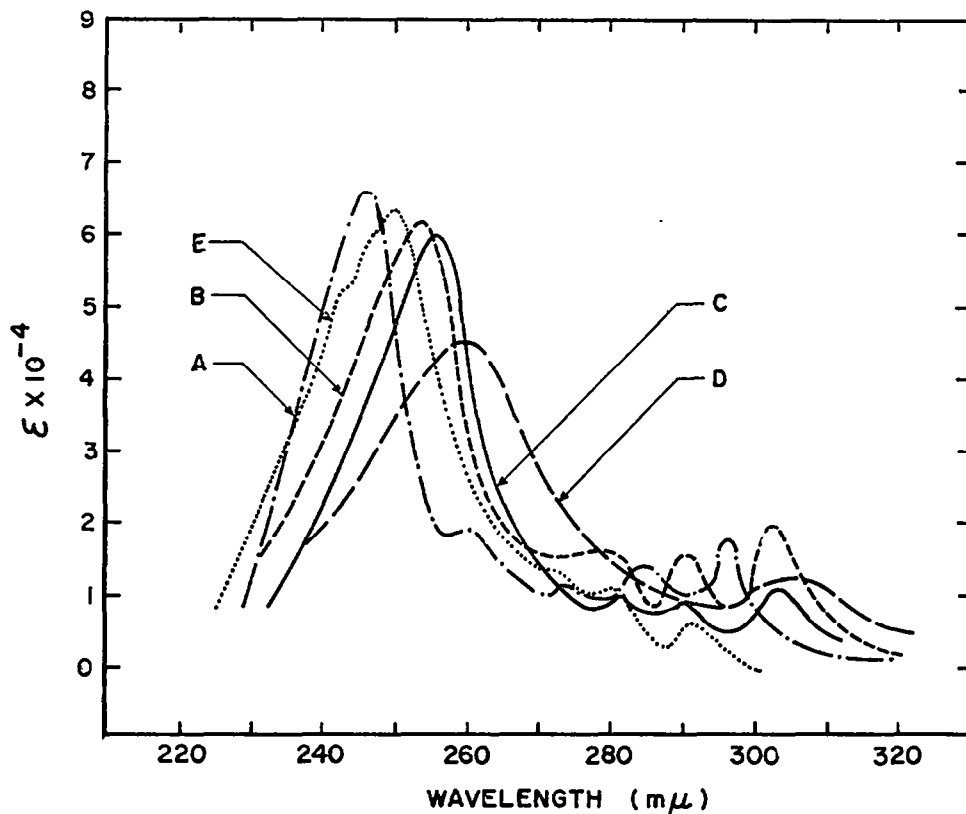

FIGURE 1 UV Spectra: (A) fluorophenanthrene; (B) chlorophenanthrene; (C) bromophenanthrene; (D) iodophenanthrene; (E) phenanthrene.

EXPERIMENTAL

Spectra were taken as follows: IR, on Perkin–Elmer Spectrometers (137 Infracord and Model 521, Grating); UV, on Perkin–Elmer 202 UV-Visible Spectrophotometer; NMR, on Varian A-60 Spectrometer. M.ps., taken on a Hershberg apparatus, are corrected; the procedure for melting-decomposition points of iodonium salts was that previously described.[28]

4-*Keto*-1,2,3,4-*tetrahydrophenanthrene oxime* (1). γ-2-Naphthylbutyric acid was prepared by succinoylation of naphthalene[6] (ca. 50%), followed by Clemmensen-Martin[7] reduction (ca. 65%). Cyclization of this acid with HF[8] gave 4-keto-1,2,3,4-tetrahydrophenanthrene (ca. 85%), which was converted to 1[9] in 85-95% yield by hot basic ethanolic hydroxylamine.

4-*Aminophenanthrene* (4). Langenbeck's procedure[10] for the dehydration and aromatization of 1 was improved, in part by the substitution of HBr for HCl. Anhyd HBr was bubbled into a stirred soln of 16·88 g of 1 (80 mmol) in 75 ml Ac_2O and 5 ml AcOH until saturation (ca. 1 hr). After one day of stirring,

* See footnote § on page 001.

the resulting dark soln gave a yellow ppt of 4-aminophenanthrene hydrobromide, which was collected, washed thoroughly with ether, neutralized and sublimed to give **4**, m.p. 64–65°; reported m.p. 62·5–63·5°,[11] 65–66°[29] and 55°.[10] Resaturation with HBr of the mother liquor gave after a week a second crop of the amine hydrobromide, also converted to **4**. The combined yield of **4** was 9·65 g (50 mmol, 62·5%). From the second AcOH-Ac$_2$O mother liquor there was obtained by neutralization with NH$_4$OH, extraction with ether, removal of solvent, trituration with 5% EtOH in hexane, and crystallization from hexane 10% of 4-acetamidophenanthrene, m.p. 194–195°; reported m.p. 196°.[11]

N-*Acetyl*-N-*acetoxyl-4-amino*-1,2-*dihydrophenanthrene* (**2**). A mixture of **1** (0·8 g, 3·8 mmol) and 25 ml Ac$_2$O was stirred at about 75° for 45–50 hr, treated with 3·5 ml (0·45 mmol) AcCl in 5·5 ml Ac$_2$O and heated at 100° for 10–12 hr. After water and hexane had been added slowly with stirring to the cooled reaction mixture, the ppt that separated between the two layers was collected and recrystallized twice from cyclohexane to give tan crystals, m.p. 135–137°. The crystals were then sublimed at 185°/1 mmHg to give 0·95 g (3·2 mmol, 84%) of **2**, m.p. 137·5–138°; IR (KBr) 3060, 3020, 1760 (acetoxy C = O), 1,650 1300 to 1160 (acetate), and 820 cm^{-1}. (Found: C, 72·95; H, 5·59; N, 4·52. C$_{18}$H$_{17}$NO$_1$ requires: C, 73·22; H, 5·76; N, 4·74%).

4-*Acetamidophenanthrene* (**3**). Compound **2** (65 mg, 0·22 mmol) in 12.5 ml of N,N-dimethylaniline was heated under reflux for about 48 hr. To the stirred, cooled dark soln about 8 ml MeI was added. After 1 hr this entire mixture was treated with 100 ml warm water and stirred overnight. The ppt was crystallized from 80% EtOH to give 45 mg (0·18 mmol, 85%) of **3**, m.p. 194–195°; reported m.p. 196°.[11] Compound **3** was then converted to **4** by the method of Krueger and Mosettig.[11]

4-*Fluorophenanthrene* (**5d**). The cold (0°) diazonium chloride soln, prepared by adding 1 g NaNO$_2$ in 5 ml water to a mixture of 3·0 ml conc HCl, 35 ml water and 840 mg (4·36 mmol) 4-aminophenanthrene in 5 ml dioxan, was treated with 3·5 ml of 48% of fluoroboric acid, stirred for 30 min at 0–5° and held at 5° overnight. The ppt of 4-phenanthrenediazonium fluoroborate was collected, washed with ice-cold water and dried over P$_2$O$_5$. (The fluoroborate could not be washed with alcohol or with ether, and it decomposed on standing.) A suspension of the dry diazonium fluoroborate in 100 ml hexane was decomposed by refluxing for ½ hr. The residue from concentration of the soln was chromatographed on florisil with hexane to give 344 mg (1·76 mmol, 41 %) of **5d**, m.p. 47°; reported m.p. 47°;[13] IR (KBr) 3050, 1605, 1585, 1530, 1500, 1000, 822, 728, 715 cm^{-1}; UV max (MeOH) 246·5 mµ (ε 6·63 × 10^4); NMR (CCl$_4$) τ1·0 (m, 1) and 2.56 ppm (m, 8).

4-*Chlorophenanthrene* (**5**). To a suspension of 1·0 g (4·4 mmol) 4-phenanthrylamine hydrochloride in 20 ml water and 2 ml conc HCl there was added dropwise 1·0 gNaNO$_2$ in water. Vigorous stirring for 1 hr gave a suspension of a yellow diazonium salt, which was added slowly to a cooled and stirred soln of 1·1 g CuCl in 14 ml conc HCl. Stirring was continued until the mixture reached room temp. The mixture was then warmed gently on a steam bath until all the N$_2$ was evolved. The CH$_2$Cl$_2$ extract of the cooled mixture was dried and chromatographed on florisil with hexane, giving 400 mg (1·88 mmol, 43·5%) crude 4-chlorophenanthrene. Sublimation under 0·5 mmHg and drying gave 270 mg (1·27 mmol, 29·5%) 4-chlorophenanthrene, m.p. 57° (reported m.p. 58·5–59°[14]); IR (KBr) 3040, 1560, 1575, 1490, 820, 730, 715, 700, 641 cm^{-1}; UV max (MeOH) 254 mµ (ε 6·16 × 10^4); NMR (CCl$_4$) τ 0·4 (m, 1) and 2·5 ppm (m, 8). (Found: C, 79·25; H, 4·20; Cl, 16·58%. C$_{14}$H$_9$Cl requires: C, 79·06; H, 4·23; Cl, 16·71%).

4-*Bromophenanthrene* (**5b**). With the foregoing procedure and using 1·6 g CuBr in 15 ml 48% HBr, 1·42 g (5·2 mmol) 4-phenanthrylamine hydrobromide were converted to 4-bromophenanthrene. Chromatography on florisil using hexane afforded 200 mg (0·78 mmol, 14·4%) 4-bromophenanthrene. The compound had a m.p. of 52·5–53°, IR (KBr) 3040, 1560, 1500, 1490, 814, 735, 700, 590 cm^{-1}; UV max 256 mµ (ε 6·0 × 10^4); NMR (CCl$_4$) τ 0·17 (m, 1) and 2·66 ppm (m, 8). (Found: C, 65·36; H, 3·45; Br, 31·17 C$_{14}$H$_9$Br requires: C, 65·39; H, 3·52; Br, 31·07%).

4-*Iodophenanthrene* (**5a**). NaNO$_2$ (1 g) was added slowly to a cold soln of 7·5 ml water and 15 ml conc H$_2$SO$_4$; warming to 70° with stirring gave a clear soln of nitrosyl sulfuric acid. This was cooled to 0·°, and 0·950 g (4·9 mmol) 4-aminophenanthrene in 5 ml pyridine was added dropwise over 1 hr. The cold soln was stirred for 1·5 hr more, diluted with water to 250 ml, giving a brown-red ppt, treated with a soln of 1·5 g KI in water, and stirred for 15 min, with foaming and appearance of a red tar. A CH$_2$Cl$_2$ extract of the mixture was washed twice with Na$_2$S$_2$O$_3$ aq, dried, concentrated and chromatographed twice on florisil with hexane. The second eluate was concentrated and dried to give 625 mg (2·1 mmol, 43%) 4-iodophenanthrene, m.p. 44·5–45·0°; IR (KBr) 3040, 1650, 1585, 1530, 1500, 820, 735, 715, 700, 632 cm^{-1}; UV max (MeOH) 260 mµ (ε 3·2 × 10^4); NMR (CCl$_4$) τ 0·1 (m, 1) and 1·68–3·16 ppm (m, 8).

(Found: C, 55·45; H, 3·20; I, 41·69. $C_{14}H_9I$ requires: C, 55·26; H, 2·96; I, 41·78%).

To a slurry of 4-phenanthrenediazonium fluoroborate prepared from 0·95 g (4·95 mmol) of **4** in 200 ml cold water a soln of 1·5 g KI in 10 ml water was added and gave 0·6 g (1·97 mmol, 40%) of **5a** after usual workup and chromatography.

4,5-Phenanthryleneodonium sulfate hydrate (**6a**). A soln of peroxyacetic acid was prepared as suggested by Sandin.[3] After 50 ml 30% H_2O_2 was added slowly to 200 ml cold Ac_2O, the mixture was kept at 0° until it became homogeneous, whereupon it was stored in a refrigerator. (The commercially available peroxyacetic acid diluted with glacial AcOH was also effective in the following oxidative cyclization.)

A soln of 760 mg (2·5 mmol) 4-iodophenanthrene in 25 ml Ac_2O was added slowly to 25 ml peroxyacetic acid soln and allowed to stand at room temp overnight. The mixture, which was now believed to contain the iodoso compound, was cooled in ice. To the cold stirred soln there was then added dropwise over a period of 1 hr 10 ml conc H_2SO_4. After the reaction had been stirred for 3 hr. at room temp, it was diluted to 150 ml with ice. The ppt that formed was collected, washed with acetone and with ether and crystallized twice from hot water. The white crystals were collected, washed with anhyd ether and dried over P_2O_5 under vacuum, yielding 300 mg (0·75 mmol, 30%) 4,5-phenanthryleniodonium sulfate hydrate, m.p. of 266–268° (dec); IR (KBr) 3600–3500 (OH), 3030 (C—H) 1620, 1600, 1550 (aromatic skeletal), 1200–1050 (water absorption), 825, 750 (aromatic substitution pattern) and 695 cm^{-1} (C-I). (Found: C, 46·35; H, 2·50; I, 34·83; s, 4·10. $C_{28}H_{18}I_2SO_5$ requires: C, 46·65; H, 2·50; I, 35·37; S, 4·45%).

4,5-Phenanthryleneiodonium chloride (**6b**). The iodoso compound was prepared as described for the bisulfate. The reaction mixture was cooled in an ice-water bath, and to the cold soln there was added dropwise with stirring 30 ml of conc H_2SO_4. After standing at room temp overnight, the reaction mixture was treated with a NaCl aq, with formation of a flocculent ppt. The ppt was allowed to age overnight, collected and washed with water, EtOH, acetone and ether. The iodonium chloride was found insoluble to any appreciable extent in all solvents tested. The white crystals after drying gave 650 mg (1·9 mmol, 76%) 4,5-phenanthryleneiodonium chloride, m.p. 287–289° (dec); IR (KBr) 3030, 1630, 1600, 1550, 825, 750, and 695 cm^{-1}. (Found: C, 49 49; H, 2·48; Cl, 10·08; I, 37·25. $C_{14}H_8ICl$ requires: C, 49·70; H, 2·37; Cl, 10·50; I, 37·43%).

REFERENCES

[1] Preceeding paper: F. M. Beringer and R. A. Nathan, *J. Org. Chem.* **34**, 685 (1969).

[2] L. Mascarelli and G. Benati, *Gazz. Chim. Ital.* **38**, II, 624 (1908); N. E. Scarle and R. Adams, *J. Am. Chem. Soc.* **55**, 1649 (1933).

[3] J. Collette, D. McGreer, R. Crawford, F. Chubb and R. B. Sandin, *Ibid.*, **78**, 3819 (1956).

[4] F. M. Beringer, L. Kravetz and G. B. Topliss, *J. Org. Chem.* **30**, 1141 (1965); W. K. Hwang, *Sci. Sinica, (Peking)* **6**, 123 (1957): *Chem. Abstr.* **51**, 16476 (1957): W. K. Hwang. *Hua Hsueh Pao*, 23. 438 (1957); *Chem. Abstr.* **52**, 16356 (1958); W. K. Hwang, C. H. Wang, and S. Y. Chen, *K'o Hsueh T'ung Pao*, No. 2, 49 (1957); *Chem. Abstr.* **53**, 4280 (1959).

[5] H. E. Bachofner, F. M. Beringer and L. Meites, *J. Am. Chem. Soc.* **80**, 4269, 4274 (1958).

[6] R. D. Haworht, *J. Chem. Soc.* 1127 (1932).

[7] E. L. Martin, *Organic Syntheses*, (Edited by A. H. Blatt), Coll. Vol. II: p. 499. J. Wiley, New York (1943).

[8] W. S. Johnson, in *Organic Reactions*, R. Adams, Ed., Vol. II, John Wiley and Sons. Inc., New York, 1944. p. 157.

[9] G. Schroeter, H. Muller and J. Y. S. Huang, *Ber. Dtsch. Chem. Ges.* **62**, 654 (1929).

[10] W. Langenbeck and K. Weissenborn, *Ibid.* **72**, 724 (1939).

[11] J. W. Krueger and E. Mosettig, *J. Org. Chem.* **3**, 345 (1938).

[12] F. M. Beringer and I. Ugelow, *J. Am. Chem. Soc.* **75**, 2635 (1953).

[13] For 4-fluorophenanthrene: P. M. G. Bavin and M. J. S. Dewar, *J. Chem. Soc.* 4486 (1955).

[14] Another route to 4-chlorophenanthrene: P. B. D. De La Mare, E. A. Johnson and J. S. Lomas, *Ibid.* 5973 (1963).

[15] H. J. Bernstein, W. G. Schneider and J. A. Pople, *Proc. Roy. Soc.* **236A**, 515 (1956).

[16] B. V. Cheney, *J. Am. Chem. Soc.* **90**, 5386 (1968).

[17] R. H. Martin, N. Defay, F. Geerts-Evrard and H. Figeys, *Bull. Soc. Chim. Belges* **73**, 199 (1964).
[18] S. Brownstein, *J. Am. Chem. Soc.* **80**, 2300 (1958).
[19] M. J. S. Dewar, R. C. Fehey and P. J. Grisdale, *Tetrahedron Letters*, 343 (1963).
[20] R. Mason, *J. Mol. Phys.* **4**, 413 (1961).
[21] G. M. Badger, J. E. Campbell, J. W. Cook, R. A. Raphael and I. Scott, *J. Chem. Soc.* 2326 (1950).
[22] R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds* p. 23. Wiley, New York (1951).
[23] L. L. Ingraham, *Steric Effects in Organic Chemistry* (Edited by M. S. Newman). Chap 11. Wiley, New York (1956).
[24] R. N. Jones, *J. Am. Chem. Soc.* **63**, 313 (1941).
[25] M. S. Newman and M. Wolf, *Ibid.* **74**, 3225 (1952).
[26] G. M. Badger and I. S. Walker, *J. Chem. Soc.* 3238 (1954).
[27] D. J. Cram, N. L. Allinger and H. Steinberg, *J. Am. Chem. Soc.* **76**, 6132 (1954).
[28] F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner and E. Sommer, *Ibid.* **81**, 342 (1959).
[29] K. G. Rutherford and M. S. Newman, *Ibid.* **79**, 213 (1957).