The Chemistry of Arene Imines. IV. An Unusual Silver Promoted Transformation of *N*-Chlorophenanthrene 9,10-Imine into 9,10-Phenanthrenequinone Dialkyl Acetals [1]

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Methanolic silver nitrate and perchlorate convert *N*-chlorophenanthrene 9,10-imine (**1**) into 10,10-dimethoxy-9(10*H*)-phenanthrone (**2**) in 60% yield. Substitution of the mthanol by ethanol, 1- and 2-propanol gives phenanthrenequinone diethyl-, di-1-propyl- and di-2-propylacetals (**3-5**), respectively. Silver acetate promotes these transformations only in the presence of a protic acid. The reaction mechanism is assumed to involve the generation of a cyclic nitrenium ion, nucleophilic ring opening by methanol, hydrolysis of the imine function and silver ion promoted oxidation.

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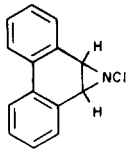
Recently [1-3] we have demonstrated that the chemistry of the highly mutagenic polycyclic arene imines [4] differs in many respects from that of aliphatic aziridines [5]. We now wish to report another unique reaction of an arene imine derivative in which *N*-chlorophenanthrene 9,10-imine (1-chloro-1a,9b-dihydro-1*H*-phenanthro[9,10-*b*]azirine) (**1**) [2] is transferred by alcoholic silver nitrate or perchlorate solutions into nitrogen-free acetals **2-5**.



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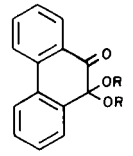
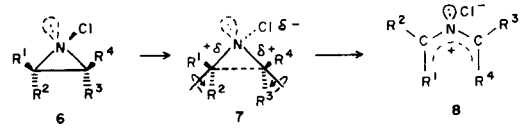
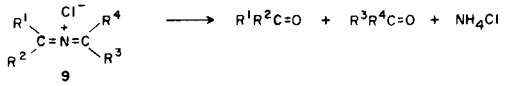


2 R = CH_3 **4** R = $(CH_2)_2CH_3$
3 R = CH_2CH_3 **5** R = $CH(CH_3)_2$

Gassman *et al.* [6] have shown that when simple *N*-chloroethylenimines, that are not fused to aromatic moieties, are solvolyzed by aqueous methanol, the N-Cl bonds undergo heterolytic cleavage accompanied by concerted disrotatory breaking of the aziridine C-C bonds. This process was assumed to involve the intermediary of ionic species such as **8** and **9**, which, under the solvolytic conditions hydrolyze to give ammonium chloride and two carbonyl molecules. The solvolysis was shown to be promoted by silver salts and to be particularly fast if R^2 and R^4 were either alkyl or aryl groups [6].



6 **7** **8**



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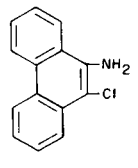
Since the rigid *N*-chlorophenanthrene 9,10-imine cannot undergo such a disrotatory operation it is understandable why **1** does not form 2,2'-diphenaldehyde. Methanolic silver nitrate reacted, however, at reflux with the *N*-chloroarene imine and formed 9,10-phenanthrenequinone dimethyl acetal (10,10-dimethoxy-9(10*H*)-phenanthrone) (**2**) in 60% yield. Similarly silver nitrate solutions of ethanol, 1-, and 2-propanol gave the corresponding acetals **3**, **4** and **5** in 47, 29 and 38% yield, respectively. Since these compounds were slowly hydrolyzed during the work up they were accompanied by varying amounts of 9,10-phenanthrenequinone, but the total yield of acetal and quinone remained constant and reproducible for each alcohol. The major side product in all these transformations was 10-chloro-9-phenanthrenamine (**10**) (compared with the authentic sample prepared from 9-phenanthrenamine) as a result of an aziridine ring cleavage at the low *p*H of methanolic silver salt solution [7], followed by rearrangement of the labile *N*-chloro-9-phenanthrenamine (**11**) intermediate [8]. In fact **10** was shown to be formed upon treatment of 9-phenanthrenamine with *N*-chlorination agents such as *N*-chlorosuccinimide. In the context it should be recalled that solutions of silver nitrate do not necessarily eliminate the nitrogen bound chlorine from chloramines or chlorimines [9].



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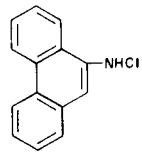

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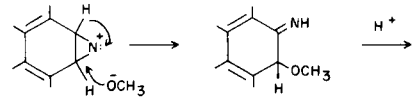
The stuctures of the keto-acetals **2-5** were established by virtue of the elemental analyses, by the indicative ir, pmr and mass spectra given in the Experimental and by their

quantitative hydrolyses by aqueous hydrochloric acid to give 9,10-phenanthrenequinone and the corresponding alcohols.

While silver nitrate and silver perchlorate, which are known to generate a high proton concentration in protic solvents [7], promote tranformation **1** → **2** equally well, no **2** was obtained when silver acetate was employed unless a protic acid (*e.g.*, *p*-toluene sulfonic acid) were added. Blank experiments showed, however, that the presence of a silver salt is essential and that in silver-free acids only rearrangement of **1** to **10** takes place.

We assume that in analogy with aliphatic *N*-chloroaziridines [6b], the reaction of silver salts with **2** yields a cyclic nitrenium ion **12**, which can react with methanol to give the ketiminium ion **14**. This highly water sensitive species forms the keto-ether **15** upon hydrolysis.



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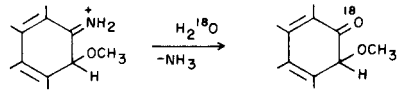

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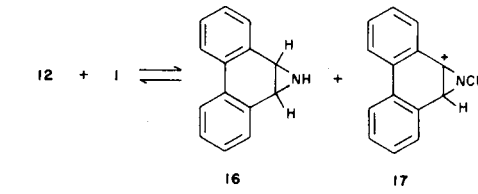
By addition of a small quantity of oxygen-labelled water, $H_2{}^{18}O$ to the reaction mixture, we were able to obtain the keto-acetal in which the carbonyl function contained ^{18}O (Molecular ion 256).

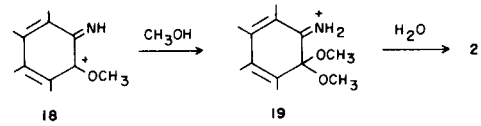
The introduction of the second methoxyl group must be associated with some kind of oxidation. Several oxidants were considered responsible for this process. The possibility of aerial oxidation could be excluded by virture of the identical results obtained in experiments performed under strict exclusion of oxygen (including the work up) and in those carried out under ambient atmosphere. An alternative possibility that the nitrate or perchlorate serves as oxidation agent could also be excluded, since neither nitrites nor chlorates could be detected in the reaction mixtures. A third possibility that the formation of phenanthrenequinone derivatives results from an internal oxidation-reduction process was also shown to be unlikely. The fact that in the numerous runs a constant yield of 60 ± 1% of **2** was obtained, indicates that at most 0.8 molecule of **1** can be reduced per each molecule that is oxidized. Furthermore, if such an oxidation-reduction were involved, the following equilibrium would be the most likely process to take place. However, neither traces of **16** nor of its rearrangement product, 9-phenanthrenamine (free or as the salt) could be detected.



16 17

We assume, therefore, that the oxidation is due to partial reduction of the silver ion, Ag^+, to Ag°. Such oxidations have occasionally been observed during silver-induced skeletal rearrangements of strained cyclic hydrocarbons (See *e.g.*, [10-12]). This assumption is supported by the fact that only part of the calculated silver chloride precipitated in the transformation of **1** and **2**. However, as no deposit of metallic silver has been found, we believe that the reduced silver forms a methanol-soluble complex.

We cannot say at this stage which of the reaction intermediates is actually oxidized. Abstraction of a hydride from either **12** or **13** could lead to **18** that upon reaction with methanol followed by hydrolysis would give **2** and ammonia.



18 19

Finally, we observed that in contrast to **1** the carbocyclic analogue *endo*-1-chlorocyclopropa[l]phenanthrene [13] gives neither **2** nor phenanthrenequinone upon treatment with boiling methanolic silver nitrate solution. It forms, however, a variety of products among which also oxidized compounds are found [14].

EXPERIMENTAL

Reaction of 1-Chloro-1a,9b-dihydro-1*H*-[9,10-*b*]azirine (**1**) with Silver Nitrate in Alcohols.

A solution of 200 mg (0.87 mmole) of **1** [2] and 163 mg (0.96 mmole) of silver nitrate in 20 ml of the appropriate alcohol was refluxed for 30 minutes. The silver chloride was filtered off and the filtrate neutralized with 5% aqueous sodium bicarbonate. After removal of the alcohol under reduced pressure, the residue was taken into dichloromethane, dried (magnesium sulfate) and chromatographed on silica gel (a 1:3 mixture of ether and petroleum ether served as eluent). By this procedure the following ketals were obtained.

10,10-Dimethoxy-9(10*H*)-phenanthrone (**2**).

This compound was obtained as colorless crystals, mp 98-100° (from ether-petroleum ether) [15], yield 60%; ir (Nujol): 1705 cm^{-1} (C=O); 300 MHz pmr (deuteriochloroform): δ 3.351 (s, 6H, OCH_3), 7.384 (t, 2H, $J_{1,2} = J_{2,3} = J_{5,6} = J_{6,7} = 7.6$ Hz, H2, H6), 7.460 (dt, 1H, $J_{1,3} = 1.6$ Hz, $J_{2,3} = J_{3,4} = 7.6$ Hz, H3), 7.621 (dt, 1H, $J_{5,7} = 1.6$ Hz, $J_{6,7} = J_{7,8} = 7.6$ Hz, H7), 7.790 (dd, 1H, $J_{1,2} = 7.6$ Hz, $J_{1,3} = 1.6$ Hz, H1), 7.861 (d, 2H, $J_{3,4} = J_{7,8} = 7.6$ Hz, H4, H8), 7.926 (dd, 1H, $J_{5,6} = 7.6$ Hz, $J_{5,7} = 1.6$ Hz, H5); EI ms: (70 eV, 70°) m/e (relative intensity) 254 ($M^{+\cdot}$, 4), 224 ($C_{15}H_{12}O_2^{+\cdot}$, 23), 223 ($C_{15}H_{11}O_2^+$, 7), 195 ($C_{14}H_{11}O^+$, 100), 165 ($C_{13}H_9^+$, 7), 152 ($C_{12}H_8^{+\cdot}$, 17).

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.59; H, 5.51; Found: C, 75.61; H, 5.76.

10,10-Diethoxy-9(10*H*)-phenanthrone (**3**).

This compound was obtained as colorless crystals, mp 67-70° (from ether), yield 32% (in addition to 15% of 9,10-phenanthrenequinone and 11% of 10-chloro-9-phenanthrenamine (**10**) that was identical with the authentic sample described below); ir (Nujol): 1715 cm^{-1} (C=O); 300 MHz pmr (deuteriochloroform): δ (t, 6H, J = 7.0 Hz, CH_2CH_3), 3.575 (two ABq, 4H, J_{AB} = 7.0 Hz, CH_2CH_3), 7.382 (t, 2H, $J_{1,2} = J_{2,3} = J_{5,6} = J_{6,7}$ = 7.4 Hz, H2, H6), 7.448 (t, 1H, $J_{2,3} = J_{3,4}$ = 7.4 Hz, H3), 7.620 (t, 1H, $J_{6,7} = J_{7,8}$ = 7.4 Hz, H7), 7.822-7.882 (m, 3H, H1, H4, H8), 7.937 (d, 1H, $J_{5,6}$ = 7.4 Hz, H6); CI ms: (isobutane) 237 $(MH-C_2H_5OH)^+$.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.60; H, 6.38. Found: C,76.43; H, 6.43.

10,10-Bis(1-propoxy)-9(10*H*)-phenanthrone (**4**).

This compound was obtained as a pale yellow viscous oil, yield 29%, ir (neat): 1710 cm^{-1} (C=O); 300 MHz pmr (deuteriochloroform): δ 0.839 (t, 6H, J = 7.4 Hz, CH_3), 1.556 (sextet, 4H, J = 7.0 Hz, CH_3CH_2), 3.446 and 3.518 (2 × dt, 4H, J_1 = 6.7 Hz, J_2 = 2.3 Hz, CH_2O), 7.375 (t, 2H, $J_{1,2} = J_{2,3} = J_{5,6} = J_{6,7}$ = 7.4 Hz, H2, H6), 7.445 (dt, 1H, $J_{1,3}$ = 1.6 Hz, $J_{2,3} = J_{3,4}$ = 7.4 Hz, H3), 7.610 (dt, 1H, $J_{5,7}$ = 1.2 Hz, $J_{6,7}$ = 7.4 Hz, H7), 7.835, 7.846 and 7.858 (3 × d, 3H, $J_a = J_b = J_c$ 7.4 Hz, H1, H4, H8), 7.925 (dd, 1H, $J_{5,6}$ = 7.4 Hz, $J_{5,7}$ = 1.2 Hz, H5); EI ms: (70 eV, 80°) m/e (relative intensity) 266 $[(M-C_3H_8)^+, 2]$, 253 $(C_{17}H_{17}O_2^+, 6)$, 252 $(C_{17}H_{16}O^{+\cdot}, 31)$, 223 $(C_{15}H_{11}O_2^+, 33)$, 209 $(C_{14}H_9O_2^+, 19)$, 182 $(C_{13}H_{10}O^{+\cdot}, 15)$, 181 $(C_{13}H_9O^+, 100)$, 180 $(C_{13}H_8O^{+\cdot}, 15)$, 152 $(C_{12}H_8^{+\cdot}, 20)$.

Anal. Calcd. for $C_{20}H_{22}O_3$: C, 77.42; H, 7.10. Found: C, 77.16; H, 7.28.

10,10-Bis(2-propoxy)-9(10*H*)-phenanthrone (**5**).

This compound was obtained as colorless crystals of the hemihydrate, mp 104-106° (from ether), yield 11% (in addition to 21% of 10-chloro-9-phenanthrenamine (**10**) and 27% of 9,10-phenanthrenequinone); ir (Nujol): 1725 cm^{-1} (C=O); 300 MHz pmr (deuteriochloroform): δ 1.057 (dd, 6H, J_1 = 6.3 Hz, J_2 = 1.8 Hz, $CH(CH_3)_2$), 4.197 (heptet, 2H, J = 6.3 Hz, $CH(CH_3)_2$), 7.394 (t, 2H, $J_{1,2} = J_{2,3} = J_{5,6} = J_{6,7}$ = 7.8 Hz, H2, H6), 7.438 (dt, 1H, $J_{1,3}$ = 1.6 Hz, $J_{2,3} = J_{3,4}$ = 7.8 Hz, H3), 7.631 (dt, 1H, $J_{5,7}$ = 1.6 Hz, $J_{6,7} = J_{7,8}$ = 7.8 Hz, H7), 7.860-7.925 (m, 3H, H1, H4, H8), 8.035 (dd, 1H, $J_{5,6}$ = 7.8 Hz, $J_{5,7}$ = 1.6 Hz, H5); EI ms: (70 eV, 150°) m/e (relative intensity) 310 ($M^{+\cdot}$, 4), 251 $(C_{17}H_{15}O_2^+, 100)$, 223 $(C_{15}H_{11}O_2^+, 13)$, 209 $(C_{14}H_9O_2^+, 26)$, 181 $(C_{13}H_9O^+, 17)$.

Anal. Calcd. for $C_{20}H_{22}O_3 \cdot \frac{1}{2}H_2O$: C, 75.24; H, 7.21. Found: C, 75.50; H, 7.26.

10-Chloro-9-phenanthrenamine (**10**).

A solution of 300 mg (1.55 mmoles) of 9-phenanthrenamine (freshly prepared by lithium aluminium hydride reduction of 9-azidophenanthrene [16]) and 228 mg (1.71 mmoles) of *N*-chlorosuccinimide in 25 ml of dichloromethane was refluxed for 10 minutes. The mixture was cooled, washed (3 ×) with water, dried and the solvent removed under reduced pressure. Recrystallization of the residue from ether afforded 300.5 mg (85%) of **10** as colorless crystals that darkened upon exposure to air for several days, mp 113-115°; ir (Nujol), 3385, 3480 cm^{-1} (NH_2); 300 MHz pmr (deuteriochloroform): δ 7.41 (dt, 1H, J = 8.2 Hz, J = 1.2 Hz, H3 or H6), 7.592-7.692 (m, 3H, H2, H7 and H3 or H6), 7.867 (dd, 1H, $J_{6,8}$ = 2.3 Hz, $J_{7,8}$ = 7.4 Hz, H8), 8.178 (d, 1H, $J_{1,2}$ = 8.2 Hz, H1), 8.571 (d, 1H, J = 8.2 Hz, H4 or H5), 8.670 (dd, 1H, J = 7.4 Hz, J = 2.3 Hz, H4 or H5); CI ms: (isobutane) 230, 228 (MH^+); EI ms: (70 eV, 50°) m/e (relative intensity) 229, 227 ($M^{+\cdot}$, 100), 201, 199 $(C_{13}H_8Cl^+, 8)$, 165 $(C_{13}H_9^+, 24)$.

Anal. Calcd. for $C_{14}H_{10}ClN$: C, 73.85; H, 4,43; Cl, 15.57; N, 6.15. Found: C, 74.14; H, 4.59; Cl, 15.52; N, 6.29.

Compound **10** was also obtained in 32% yield by refluxing equimolar amounts of **1** and silver perchlorate in dichloromethane for 30 minutes.

When a mixture of one equivalent of **10** and 1.5 equivalents of sodium nitrite was treated at 0° with excess 10% hydrochloric acid followed by heating with ethanol at 40°, the neutralized product gave after chromatography on alumina, 9-chlorophenanthrene of mp 54° (identical with an authentic sample prepared from 9-phenanthroyl chloride [17]) as the sole product.

Acknowledgement.

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