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ATTEMPTS TO PREPARE AROMATIC O-ACYL-HYDROXYLAMINES—II

DEHYDROHALOGENATION OF 1-BROMO-4-ACETYLOXYIMINO-1,2,3,4-TETRAHYDROPHENANTHRENE BY 1,8-DIAZABICYCLO[5.4.0]UNDEC-7-ENE (DBU)

T. R. JUNEJA[a] and H. DANNENBERG*†
Max-Planck-Institut für Biochemie, D-8033 Martinsried bei München, BRD

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Abstract—Dehydrohalogenation of 1-bromo-4-acetyloxyimino-1,2,3,4-tetrahydrophenanthrene by 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) gave a mixture of products. Thirteen of these were identified and together account for 80 per cent of the total yield. The majority are considered to be formed via the labile O-acetylhydroxylamine (**17**); from which it may be concluded that **17** has the following properties under the basic conditions of the reaction. (a) It may rearrange to hydroxamic acid (which gives further products). (b) It may behave as an acetylating agent. (c) Possibly it may generate a nitrenium ion. A further indication that the nitrenium ion is involved, comes from the dehydrobromination reaction when performed in the presence of α-naphthol, α-naphthylamine, 4-hydroxydiphenylamine, and hydrazobenzene. Particular attention is given to the dehydrogenating property of the nitrenium ion.

In the previous communication[1] we investigated the dehydrobromination of 1-bromo-4-acetyloxyimino-1,2,3,4-tetrahydro-phenanthrene (**1**) with tetramethylammonium dimethyl-phosphate. This reaction, however, did not result in the formation of the aromatic O-acetyl-hydroxylamine, but of other products derived by Bamberger rearrangement[2] of the O-acetyl-hydroxylamine (direct or via hydroxamic acid). Because the minimum temperature required for this dehydrobromination was 80° and the final mixture was acidic we wished to carry out the dehydrobromination of **1** under mild and basic conditions. Recently the bicyclic amidine 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) has been reported[3] as being able to dehydrobrominate at room temperature or below. This reagent was used therefore to study the possible formation of O-acetyl-hydroxylamine and its properties.

RESULTS AND DISCUSSION

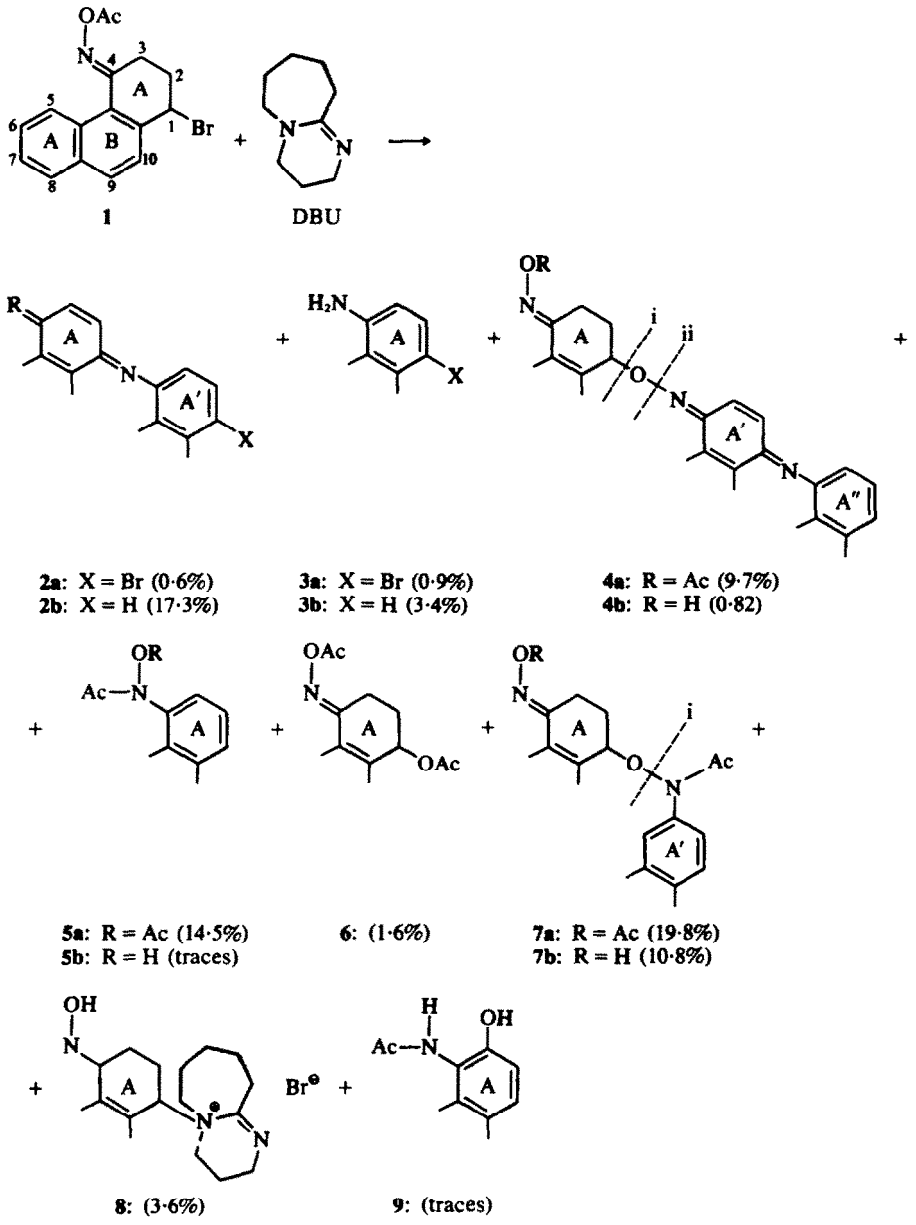
The products obtained (total yield 80%) during the dehydrobromination of **1** with DBU in benzene (room temperature, N_2), were isolated by the combined procedures of column chromatography and preparative TLC, and are given in Scheme 1 (in the sequence of isolation). The reaction was also carried out in presence of α-naphthylamine, α-naphthol, 4-hydroxy-diphenylamine and hydrazobenzene; the isolated products of these compounds are given in Scheme 2.

Product analysis. The O-quinoid compounds were reddish violet (**2a**, **2b**, **10**) or red **14** crystalline products. Their mass spectra showed, besides the molecular ion peak, a characteristic fragment of M^+ (CO + H). Their IR spectra had bands in the C=O-range (1640 for **2a** and **2b**, 1650 for **10** and 1645 cm^{-1} for **14**). The NMR spectrum of **2b** showed two characteristic doublets for H-3 and H-2 at δ6·67 and 7·19 ppm respectively (J = 10 Hz). On acid hydrolysis **2b** gives phenanthrene-quinone-1,4[4] and 4-amino-phenanthrene. Similarly **2a** gives phenanthrene-quinone-1,4 and 1-bromo-4-amino-phenanthrene.[1] Acid hydrolysis of **10** gives naphtha-quinone-1,4,[5] and 4-amino phenanthrene. **14** was identified through spectra and mixed m.p. with an authentic sample.[6]

Compounds **4a**, **4b**, **6**, **7a**, **7b**, **8**, **12** and **15** are all 4-hydroxyimino- or 4-acetoxyimino-1,2,3,4-tetra-hydrophenanthrene compounds with different substituents at C-1. The NMR spectra had signals between 1·8–2·7 ppm (H-2, intensity 2), between 2·8 and 3·4 ppm (H-3; intensity 2) and a characteristic signal between 5·2–6·3 ppm (Table 1). Because of the low coupling constant for the signal of H-1 (maximum up to 7 Hz) the substituents at C-1 are probably axial and H equatorial (except **8** in d_4-methanol). In this case the high coupling constant (10 Hz) is only compatible with an axial–axial coupling, which means that the DBU-residue in **8** would be equatorial. The acetoximino-group (in **4a**, **6**, **7a**, **12** and **15**) is characterized by a singlet at 2·27 to 2·33 ppm (intensity 3); these compounds also have a signal at 9·13 to 9·3 ppm (part of an ABCX-system, aromatic H-5).

Compounds **4a** and **4b** were reddish crystalline products. **4a** was assigned the molecular formula $C_{44}H_{31}N_3O_3$ on the basis of elemental analysis and FD-ionisation-masspectrometry (M^+ 649 found and calculated). The

[a]†See footnote Part I.[1]

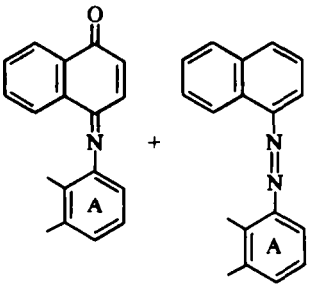


Scheme 1

EI-mass spectrum indicates fragmentation with proton-migration to *m/e* 398 and 251 (fragmentation in **4a** at i) and to *m/e* 382 and 267 (fragmentation in **4a** at ii). The IR-spectrum showed bands characteristic of an acetoxy-imino group (1765, 1200 and 940 cm^{-1}) and the NMR spectrum (Table 1) indicated 23 aromatic H with the following characteristic signals: 2 doublets (J = 10 Hz) for each of the protons H-2′ and H-3′ at δ7·26 and 6·76 ppm respectively, 9·3 ppm (intensity 2) for H-5 and H-5′ and 8·92 ppm (intensity 2) for H-5″ and H-10′. The structure of **4b** was deduced from the UV and NMR spectra; the IR spectrum shows bands characteristic of =N–OH (3280 and 930 cm^{-1}). Finally the relationship between **4b** and **4a** was established by conversion of **4b** to **4a** by acetylation.

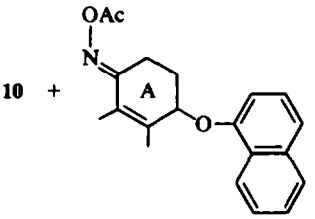
The molecular formula $C_{32}H_{26}N_2O_4$ for **7a** was derived from elemental analysis and its FD-ionisation-mass spectrum (M^+ 502 found and calculated). The EI-mass spectrum showed fragmentation with proton-migration with prominent peaks at *m/e* 267 (loss of ketene, *m/e* 225) and at 235 (loss of ketene, *m/e* 193). The IR spectrum indicated the presence of the acetoxyimino- (1760, 1190 and 920 cm^{-1}) and amide group (1675 cm^{-1}). The NMR

Reaction of 1 with DBU in presence of α-naphthylamine:



10 **11**

Reaction of 1 with DBU in presence of α-naphthol:



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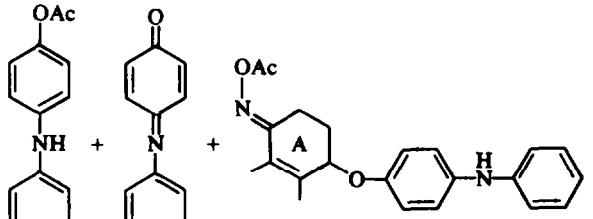
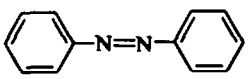
Reaction of 1 with DBU in presence of 4-hydroxy-diphenylamine:



13 **14** **15**

Reaction of 1 with DBU in presence of hydrazobenzene:



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Scheme 2

spectrum (Table 1) indicated 15 aromatic H with H-5 and H-5' having characteristic signals at δ9·13 and 8·89 ppm respectively; beyond the singlet for CH_3 of the acetoxyimino-group at 2·19 ppm (intensity 3) there is a further singlet at 2·03 ppm (intensity 3). The structure of **7a** was confirmed by summating the UV spectra of the 1-hydroxy-4-acetoxyimino-1,2,3,4-tetrahydrophenanthrene and 4-acetamino-phenanthrene which on plotting gave a spectrum identical to that of **7a**. A similar summation of UV spectra confirmed the structure of **7b** (but this showed IR bands characteristic of =N–OH: 3400 and 930 cm^{-1}). The relationship of **7b** to **7a** was established by acetylation of **7b** which then yielded **7a**.

Compound **8** was assigned the molecular formula $C_{23}H_{28}BrN_3O$ on the basis of its elemental analysis and spectral data: IR bands at 3120–3180 and 935 cm^{-1} (=N–OH); the NMR spectrum indicated signals for H-1 (Table 1), for 21 aliphatic and 6 aromatic H (characteristic for H-5 δ9·10 ppm). The UV spectrum was in accordance with the sum of the UV spectra of 4-hydroxyimino-1,2,3,4-tetrahydro-phenanthrene and DBU·HBr.

The molecular formula $C_{26}H_{21}NO_3$ was taken for **12** on

Table 1. NMR signals of H-1 (solvent $CDCl_3$, for **8** d_4-methanol)

Compound	H-1 (δ-values, ppm)
1	5·5 (1) t, J = 3 Hz
4a	5·75 (1) dd, $J_{1,2ax}$ = 5 Hz, $J_{1,2eq}$ = 3·5 Hz
4b	5·73 (1)
6	6·3 (1) t, J = 5 Hz
7a	5·30/5·58 (1)
7b	5·20/5·53 (1)
8	5·62 (1) dd, $J_{1,2ax}$ = 10 Hz, $J_{1,2eq}$ = 5 Hz
12	5·63 (1) dd, $J_{1,2ax}$ = 7 Hz, $J_{1,2eq}$ = 5 Hz
15	5·32 (1) dd, $J_{1,2ax}$ = 6 Hz, $J_{1,2eq}$ = 4 Hz

the basis of the elemental analysis and mass spectrum (395 found and calculated). The latter showed fragmentation at $M^+-C_{10}H_7O$ (*m/e* 252). The NMR spectrum (Table 1) indicated 13 aromatic H with characteristic signal at H-5 (δ9·21 ppm, intensity 1).

Compound **15** was assigned the molecular formula $C_{28}H_{24}N_2O_3$ on the basis of its elemental analysis and mass spectrum (436 found and calculated). The fragment *m/e* 185 (C_6H_5–NH–C_6H_4–$^+$OH) appeared as base peak. The IR spectrum indicated the presence of acetoxyimine (1750, 1200 and 935 cm^{-1}) and N–H (3360 cm^{-1}). The NMR spectrum showed 15 aromatic H (with H-5 at δ9·20 ppm). The signal for NH which appeared at δ5·54 ppm, could be replaced by deuterium.

The mass spectrum of **5a** gave molecular weight M^+ 293 with successive loss of two ketenes (*m/e* 251 and 209). The IR spectrum showed bands characteristic of –NO·CO·CH_3 (1793 cm^{-1})[7] and amide I (1690 cm^{-1}). Absence of the amide II-band indicated that the acetyloxy and acetyl groups were attached to the same N. The NMR spectrum gave two singlets each of 3H (δ1·85 and 2·27 ppm). All the remaining 9H were aromatic with a characteristic signal for H-5 (δ8·96 ppm). The structure of the hydroxamic acid **5b** is derived from the positive test obtained with ferric chloride and its mass spectrum (M^- 251 found and calculated and M^+-ketene). As only very small quantities of **5b** were available other spectra could not be obtained.

Mass spectrometry of compound **11**, a red crystalline product, gave in addition to a molecular ion peak (M^+ 332) characteristic fragments at $M^+-C_{10}H_7$ and $M^+-C_{14}H_9$ (*m/e* 235 and 185 respectively).

The molecular formula $C_{14}H_{13}NO_2$ for **13** was derived from its elemental analysis and mass spectrum (M^+ 227). The IR spectrum showed characteristic ester (1735 and 1225) and NH (3390 cm^{-1}) bands. Its identity was confirmed by synthesis from 4-hydroxydiphenylamine and acetic anhydride in the presence of DBU. Products **3a**, **3b** and **9** were identified as described in Part I of this series.[1] The structure of **16** was confirmed by comparison of its spectra with that obtained from an authentic sample and by mixed m.p.[8]

Mechanism. The mechanism proposed here is an attempt to explain the formation of the majority of the products of the dehydrobromination of **1** with DBU in purely ionic terms. Further evidence is required in some instances since the possibility that free radicals also participate in some of the reactions cannot be excluded.

Some products (**4a**, **6**, **7a**, **8** and also **12** and **15**) may be formed by nucleophilic replacement of bromine in **1** by various ions present in the mixture. An initial step in this type of reaction would be the hydrolysis of **1** to **1a**, but alternatively the hydroxyimino compounds (**4b**, **7b**, **8**) may be formed from the acetoxyimino compounds by hydrolysis during the course of the reaction.

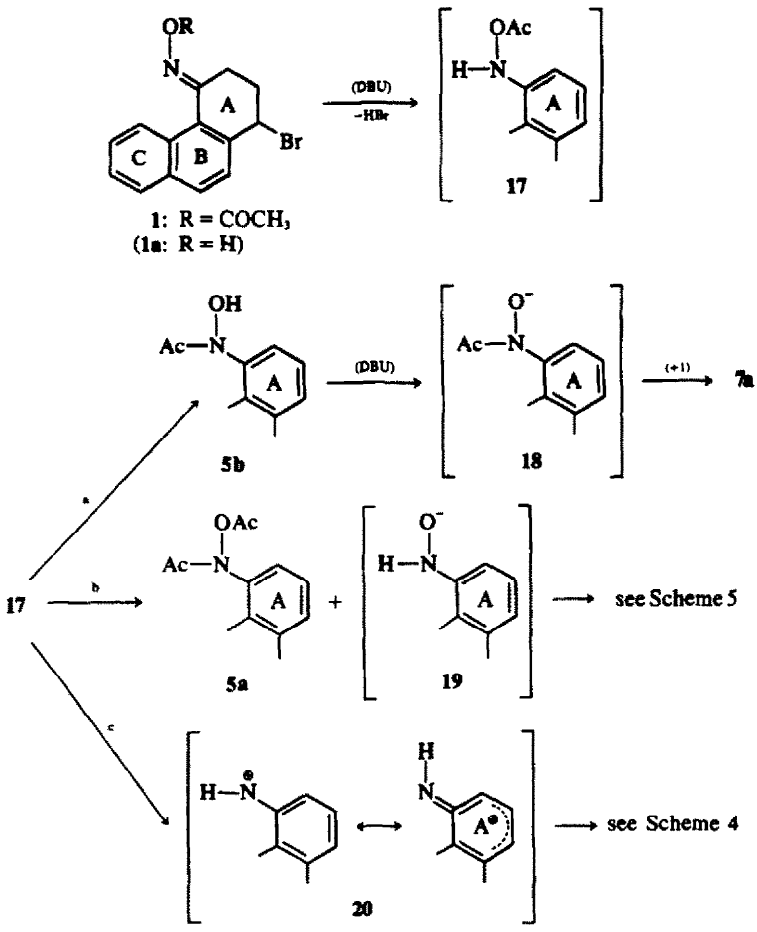
The origin of the products with aromatic ring A (and these represent the majority of the reaction products) may be explained as arising from the aromatic O-acetylhydroxylamine **17** as intermediate, in a number of ways: (a) rearrangement, (b) transacetylation, (c) generation of nitrenium ion.

Path a: The formation of hydroxamic acids (**5b**) from O-acylhydroxylamines is known. **5b** was isolated together with **9** from the aqueous washings of the mixture after careful acidification in ice and extraction with ether. The formation of **9** is considered as occuring by Bamberger rearrangement[2] of **5b** during the acidification of the aqueous washings. Compound **5b** may be converted to its ionic form (**18**) because of the basic nature of the mixture, and as such generate **7a** by nucleophilic replacement of the Br atom in **1** (see above for **7b**).

Path b: The formation of **5a** (which could be an ultimate carcinogen) may be explained by transacetylation of **17** by **17** with the simultaneous formation of **19** (see below); but this point needs further clarification. Another instance of transacetylation has been found in the reaction of **1**, in the presence of 4-hydroxydiphenylamine, where **13** was produced. In an attempt to increase the yield of **5a**, the dehydrobromination of **1** with DBU was carried out in presence of acetic anhydrive in order to acetylate **17**, but the major product isolated was **6** together with N,N,O-triacetyl-4-amino-3-phenanthrol.

Path c: Nitrenium ions generated in acidic medium are reported[2] to undergo nucleophilic substitution or electrophilic attack on nucleophiles present. Miller *et al.*[9,10] have proposed that under physiological conditions aromatic O-acylhydroxylamines can generate the nitrenium ion. The reaction of **1** with DBU also provides us with evidence of the origin of the nitrenium ion.

The best evidence of the properties of the nitrenium ion **20** in our reaction comes from the reaction of **1** with DBU carried out in the presence of α-naphthylamine which resulted in the formation of **10** and **11** (although these compounds are only obtainable in low yield). In the first step of the reaction naphthylamine would undergo electrophilic attack by **20** at the *para*-position (with respect to the amino group) or at the amino group itself. In the next step the intermediate compounds are dehydrogenated: (a) to an unidentified iminoquinone that gives **10** after hydrolysis during chromatographic isolation on silica gel (see below), (b) to the azo-compound **11**. Compound **10** is also formed if the reaction *cf* **1** with DBU is carried out in presence of α-naphthol instead of α-naphthylamine. Dehydrogenating activity in the mixture has also been observed in the presence of 4-hydroxy-



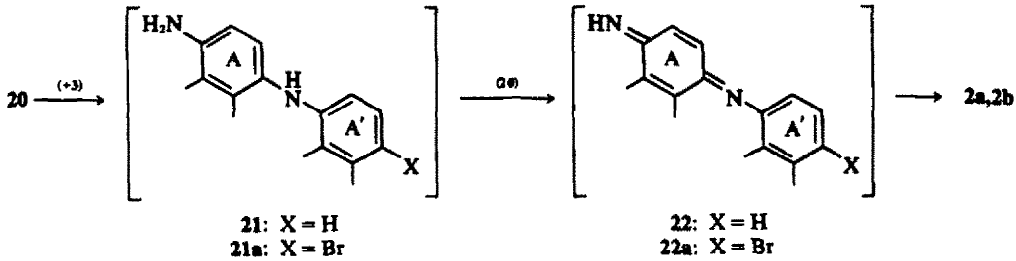
Scheme 3

diphenylamine where compound **14** is formed, but is best observed when the reaction contains hydrazobenzene.

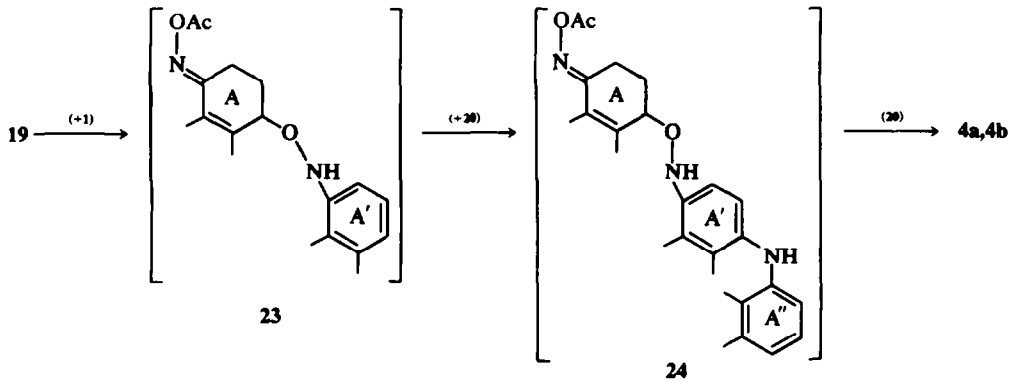
The mixture containing hydrazobenzene was intensively yellow (normally reddish brown) on completion of the reaction, and TLC indicated the absence of products **2a**, **2b**, **4a** and **4b** (products that require **20**), but compounds **3**, **5**, **6** and **7** were detected. The UV spectrum of this mixture in the range of 420–560 nm was similar to azobenzene (**16**) having a common λ_{max} at 447 nm.

The dehydrogenation of hydrazobenzene to azobenzene, in a mixture containing standard amounts of compound **1**, hydrazobenzene and DBU in benzene under N_2, was followed in a quantitative manner by measuring the extinction at 447 nm. A control reaction from which compound **1** was omitted, but otherwise identical to the preceding reaction, was also set up. Only 12·2% of hydrazobenzene was dehydrogenated to azobenzene in the control, compared to 68% in the experimental reaction.

We believe that the dehydrogenating activity in all the above mentioned reactions is due principally to the nitrenium ion **20**, which is itself hydrogenated to



Scheme 4



Scheme 5

4-amino-phenanthrene (**3b**; isolated or identified in all reactions). The nitrenium ion-mediated dehydrogenation may take place via its triplet state, but the possibility that nitrene[11] is also involved cannot be excluded.

With the knowledge that nitrenium ion **20** can act as an electrophilic reagent and can also possess dehydrogenating properties we return to the possible mechanism of the formation of the reaction products **2a**, **2b** (Scheme 4) and **4a** (**4b**) (Scheme 5).

The nitrenium ion **20** may engage in electrophilic attack on **3b** or **3a** (or conversely **3b** or **3a** may carry out nucleophilic attack on **20**) to give the (not isolated) intermediate **21** (**21a**), which is itself possibly dehydrogenated by **20** to another intermediate **22** (**22a**) (also not isolated). Hydrolysis of **22** (**22a**) during chromatographic isolation on silica gel* would then give **2b** (**2a**).

The possible origin of the products **4a** and **4b** is illustrated by Scheme 5. Firstly, a nucleophilic replacement of bromine in **1** by the ion **19** (path b) may take place; secondly electrophilic attack by **20** on the (not isolated) intermediate **23** gives the (not isolated) intermediate **24**; and thirdly the dehydrogenation of **24** by **20** gives **4a**.

In summary, it may be concluded, from the results of the dehydrobromination of **1** with tetramethylammonium dimethylphosphate[1] and with DBU, that aromatic O-acylhydroxylamines can, depending on the conditions, participate in a variety of reactions. Knowledge of these reactions may contribute to a better understanding of the action of ultimate forms of carcinogenic amines on macromolecules in the cell.

*Indirect evidence of the possible formation of **2b** (**2a**) from **22** (**22a**) was obtained through UV studies of the mixture with and without the addition of a drop of HCl (the original reddish brown colour of the mixture changes to violet brown in presence of HCl; this violet colour was characteristic of **2a** and **2b**). The UV spectrum of the reaction mixture in presence of HCl was similar to the UV spectrum of **2b**. It was also observed that on subjecting the mixture to TLC a red-violet streak was produced (R_f 0·47 to 0·6; benzene–EtOAc 85:15). When this streak was eluted and rechromatographed in the same system it was then found to travel as a circular spot with an R_f corresponding to pure samples of **2a** or **2b**. The presence of this streak in the original TLC separation may be due to slow hydrolysis of $\rangle C{=}NH$ (**22**) to $\rangle C{=}O$ (**2b**) (see above for the formation of **10**).

EXPERIMENTAL

Instruments and materials are given in Part I.[1] Molecular weights of **4a**, **7a**, **7b** were determined by FD-ionisation with masspectrometer SM 731 from Varian MAT-GmbH, Bremen.

Dehydrobromination of 1-bromo-4-acetoxyimino-1,2,3,4-tetrahydrophenanthrene (**1**) *with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).* To a soln of **1** in dry benzene (2·0 g in 100 ml) 2·5 mole equiv DBU in 10 ml benzene was added dropwise under N_2 and the mixture was allowed to stand at room temp. for about 20 hr. The crystalline product was filtered off and retained for the isolation of **8** (see below). The basic filtrate (litmus paper) was neutralised by washing with distilled water. The aqueous washings were retained for the isolation of **5b** and **9** (see below). The organic layer was dried, and on TLC gave spots with R_f 0·11 (**7a**, **7b**), 0·25 (**5a**), 0·29 (**6**), 0·47 (**3a**, **3b**), 0·53 (mixture) and 0·6 (mixture) and also a reddish-violet streak from R_f 0·47–0·6 (solvent: benzene–EtOAc 85:15). Expected products are given in parenthesis.

After TLC the benzene layer was concentrated and chromatographed on a silica gel column (150 g). The column was eluted with benzene-EtOAc (90:10) and 15 ml fractions collected (140 fractions in total). Fractions with the same TLC-R_f were pooled. These were fractions 21–34; 37–40; 41–70 and 71–140. Fractions 21–34: The reddish-violet residue was dissolved in benzene and on TLC gave 4 spots, R_f 0·41 (**2b**), 0·36 (**3a**), 0·30 (**3b**) and 0·14 (**4a**, **4b**), with benzene as solvent. The soln was chromatographed on a silica gel column (150 g) with benzene as eluent; 60 fractions ( )', each of 15 ml were collected.

Fractions (1–5)': *1'-Bromo-N-(4-phenanthryl)-1,4-phenanthrene-quinone-1-imine* (**2a**). The residue from MeOH gave reddish violet crystals (8 mg, 0·6%), m.p. 210–213°; IR (cm^{-1}) 1640 ($\rangle C{=}O$); MS: M^+ 461/463. M^+–CO–H (432/434).

Acid hydrolysis. 4 mg **2a** in 2 ml dioxane with 2 drops of HCl aq was heated in boiling water, till the soln was colourless. Solvent was removed under vacuum and the residue suspended in distilled water. This suspension, which was acidic, was then extracted with ether. The ethereal layer was dried and the solvent removed. The yellow residue obtained was identified as phenanthrene-quinone-1,4.[4] The aqueous layer was made basic with Na_2CO_3 and extracted with ether. The product obtained from the ether extract was 1-bromo-4-amino-phenanthrene.

Fractions (6–10)': N-(4-*Phenanthryl*)-1,4-*phenanthrene-quinone*-1-*imine* (**2b**). The residue from MeOH gave reddish-violet crystals (200 mg, 17·3%), m.p. 157°; λ_{max} (EtOH): 226 (ε 70,000), 253 (49,000), 285·5 (39,000), 296·5 (40,000), 362 (8000) and 514 nm (4000); IR (cm^{-1}): 1640 (>C=O); NMR: 17 aromatic H, therefrom H-5 9·76 (1) (part of ABCX-system), H-5' 8·9 (1) (part of ABCX-system), H-9 8·26 (1) d, J = 9 Hz and H-10 8·9 (1) d, J = 9 Hz, H-2 7·21 (1) d, J = 10 Hz and H-3 6·62 (1) d, J = 10 Hz, H-3' 6·82 (1) dd J = 2 Hz and 8 Hz, as also 10 H between 7·35–8 ppm, MS: M^+ 383, M^+–CO–H (354) (Found: C, 87·01; H, 4·33; N, 3·13; $C_{18}H_{17}NO$ requires: C, 87·73; H, 4·44; N, 3·13%).

Acid hydrolysis. 20 mg **2b** was hydrolysed by the same method as described for **2a** and the products isolated were identified as phenanthrene quinone-1,4 and 4-amino-phenanthrene.[12]

Fractions (11–16)': 1-*Bromo*-4-*amino*-*phenanthrene* (**3a**). Isolated and identified as described in Part I': 15 mg (0·9%).

Fractions (21–30)': 4-*Amino*-*phenanthrene* (**3b**). Isolated and identified as described in Part I': 40 mg (3·4%).

Fractions (38–60)': N⁴-[4-*Acetoxyimino*)-1,2,3,4-*tetrahydro*-1-*phenanthryloxy*] -N¹'- (4-*phenanthryl*)-1,4-*phenanthrene*-*quinone*-*diimine* (**4a**) *and* N⁴-[4-*hydroxyimino*-1,2,3,4-*tetrahydro*-1-*phenanthryloxy*] -N¹'- (4-*phenanthryl*)-1,4-*phenanthrene*-*quinone*-*diimine* (**4b**). The fraction gave a reddish-brown residue. **4a** (R_f 0·62) and **4b** (R_f 0·51) were separated by PTLC ($CHCl_3$-EtOH 200:1). **4a** (corresponding to R_f 0·62), from benzene-light petroleum mixture gave reddish crystals (100 mg, 7·7%), m.p. 187–190°, λ_{max} (dioxane): 225 (ε 100,000), 300 (44,000), 331 (30,000), 388 (8000) and 459 nm (4000); IR (cm^{-1}): 1765, 1200 and 940 (=N–O'CO'CH_3); NMR: 23 aromatic H, therefrom H-5 and H-5' 9·3 (2) (part of ABCX-system), H-10' and H-5'' 8·92 (2) (part of ABCX-system), H-3' 6·76 (1) d, J = 10 Hz, H-2' 7·26 (1) d, J = 10 Hz, as also 17 H between 7·3–8·2 ppm; H-1 (s. Table 1), H-2 2·4–2·7 (2), H-3 3·0–3·4 (2), CH_3–CO– 2·27 ppm (1) s; MS (FD-ionisation): M^+ 649. (Found N, 6·55; $C_{44}H_{31}N_3O_3$ requires: N, 6·47%).

Compound **4b**, corresponding to the PTLC-R_f 0·51, gave reddish crystals from benzene (10 mg, 0·8%), m.p. 208–210°; λ_{max} (dioxane) 228 (ε 98,000), 300 (44,000), 335 (26,000), 388 (9000) and 458 nm (4700); IR (cm^{-1}): 3280 (OH), 930 (N–O); NMR: 23 aromatic H, therefrom H-5 9·40 (1) (part of ABCX-system), H-10, H-5', H-5'', 9·0 (3), H-3' 6·76 (1) d, J = 10 Hz, H-2' 7·45 (1) d, J = 10 Hz as also 17 H between 7·3–8·1 ppm; H-1 (s. Table 1), H-2 1·8–2·0 (2), H-3 3·0–3·3 ppm (2). **4b** was converted to **4a** by treating it with acetic anhydride.

Fractions 37–40: 1-*Acetoxy*-4-*acetoxyimino*-1,2,3,4-*tetrahydrophenanthrene* (**6**). The residue was a colourless crystalline product which gave **6** from light petroleum (30 mg, 1·6%), m.p. 121–123°, λ_{max} (EtOH): 224·5 (ε 39,000), 239 (29,000) and 309·5 nm (9000); IR (cm^{-1}): 1765, 1190 and 935 (=N–O'CO'CH_3), 1720, 1240 (–O'CO'CH_3); NMR: 6 aromatic H, therefrom H-5 9·13 (1) (part of ABCX-system) as also 5 H between 7·5–8·1 ppm; H-1 (Table 1), H-2 2·0–2·4 (2), H-3 3·0–3·2 (2), CH_3CO– 2·06 (3), s, and 2·28 ppm (3), s. MS: M^+ 311, M^+-ketene (269), M–CH_3'COOH (251) (Found: C, 70·40; H, 5·82; N, 4·28; $C_{18}H_{17}NO_4$ requires: C, 69·45; H, 5·46; N, 4·5%).

Fractions 41–70: N-*Acetoxy*-4-*acetamido*-*phenanthrene* (**5a**). **5a** was purified by repeated PTLC for spectral analysis. It was initially obtained as an oily mass which solidified on standing (250 mg, 14·5%); λ_{max} (dioxane): 253·5 (ε 47,000), 299 (9600), 337 (1200) and 353·5 nm (1400); IR (cm^{-1}): 1793 (–N–OCOCH$_3$) and 1690 (amide); NMR: 9 aromatic H, therefrom H-5 8·96 (1) (part of ABCX-system) as also 8 H between 7·4–8 ppm; CH_3'CO– 1·85 (3), s, and 2·22 ppm (3), s; MS: M^+ 293, M^+-ketene (251) and *m/e* 251-ketene (209).

Fractions 71–140: N-[4-(*Acetoxyimino*)-1,2,3,4-*tetrahydro*-1-*phenanthryl*-*oxy*]-N-(4-*phenanthryl*)-*acetamide* (**7a**) *and* N-[4-(*hydroxyimino*)-1,2,3,4-*tetrahydro*-1-*phenanthryloxy*]-N-(4-*phenanthryl*)-*acetamide* (**7b**): **7a** (R_f 0·20) and **7b** (R_f 0·07) ($CHCl_3$-MeOH 200:1) were separated by PTLC using this solvent.

Compound **7a** gave colourless crystals from benzene (300 mg; 19·8%), m.p. 177–178°; λ_{max}(EtOH): 220 (ε 59,000), 247 (60,000), and 301 nm (19,000); IR(cm^{-1}): 1760, 1190 and 922 (=N'CO'CH_3), 1675 (amide); NMR: 15 aromatic H, therefrom H-5 9·13 (1) (part of ABCX-system), H-5' 8·89 (1) (part of ABCX-system) as also 1 H between 7·2–8 ppm; H-1 (s. Table 1), H-2 1·8–2·0 (2), H-3 2·8–3·1 (2), CH_3CO– 2·04 (3), s, and 2·19 ppm (3), s; (probably two isomers with H-1 axial and equatorial); MS (FD-ionisation) M^+ 502, (EI-ionisation) *m/e* 267, 267-ketene (225), *m/e* 235, 235-ketene (193) (Found: C, 76·00; H, 5·23; N, 4·92; $C_{32}H_{26}N_2O_4$ requires: C, 76·49; H, 5·18; N, 5·27%).

Compound **7b** (R_f 0·07) gave colourless crystals from benzene-light petroleum (150 mg, 10·8%), m.p. 181–182°; λ_{max} (EtOH): 215 (ε 47,000), 238 (62,000) and 300 nm (17,000); IR (cm^{-1}): 3400, 930 (=N–OH), 1660 (amide); NMR: 15 aromatic H, therefrom H-5 and H-5' 8·9 (2) (part of ABCX-system) as also 13 H between 7·3–8 ppm; H-1 (see Table 1), H-2 1·8–2·1 (2), H-3 2·8–3·1 (2), CH_3'CO–2·0 ppm (3), s; (probably two isomers with H-1 axial and equatorial); MS (FD-ionisation) M^+ 460, (EI-ionisation) *m/e* 235, 235-ketene (183), *m/e* 225. **7b** was converted to **7a** on treatment with acetic anhydride.

N-(4-*Phenanthryl*)-*acetohydroxamic acid* (**5b**), *and* 4-*acetamido*-3-*phenanthrol* (**9**). The aqueous washings of the filtrate of the reaction mixture, were carefully acidified in presence of ice and ether. The ethereal layer was dried and the solvent removed. Separation of **5b** and **9** was achieved by fractional crystallisation from benzene-petrol ether.

Compound **5b** (few crystals), m.p. 132°, gave characteristic reddish-violet colour with ferric chloride; MS: M^+ 251, M^+-ketene (209). **9** (traces), gave a positive test for phenol and was identified as described in Part I.[1]

Although **5b** and **9** both had the same M^+ (251), they were differentiated through mass spectra. **9** gave a fragment at *m/e* 233 as a base peak probably through loss of H_2O and easy cyclization to oxazol, while this fragment was absent in the mass spectrum of **5b**.

1-[(4-(*Hydroxyimino*)-1,2,3,4-*tetrahydro*-1-*phenanthryl*]-1-*azonia*-8-*azabicyclo*[5.4.0]*undec*-7-*ene*-*bromide* (**8**). The crystalline product which separated from the mixture, contained mostly DBU'HBr, as expected. This was dissolved in abs EtOH and on standing a crystalline product separated which was recrystallized from abs EtOH, (95 mg, 3·6%), m.p. 257–259°; λ_{max} (EtOH): 241 (ε 45,000), and 305·5 nm (8000); IR (cm^{-1}): 3120–3180 and 935 (=N–OH, broad for OH), 1600 (C=N); NMR (d_6 MeOH): 5 aromatic H between 7·3–8 and H-5 9·10 ppm (1) (part of ABCX-system); H-1 (Table 1), 10 H between 1·88–2·40, 10 H between 3·0–4·0 ppm (Found: C, 62·05; H, 6·44; N, 9·17; $C_{23}H_{28}BrN_3O$ requires: C, 62·44; H, 6·33; N, 9·5%).

Dehydrobromination in presence of different compounds. Dehydrobromination of **1** (1·5 g) with DBU (2·5 mole equiv) in benzene under N_2 was also carried out in presence of Ac_2O (1·5 mole equiv), α-naphthol (2·0 mole equiv), α-naphthylamine (1·5 mole equiv), 4-hydroxy-diphenylamine (1·25 mole equiv) and hydrazobenzene.

In presence of acetic anhydride. On TLC (benzene-EtOAc 85:15) of this mixture, it was found that the spot (R_f 0·29) corresponding to **6** was quite thick and that the spot (R_f 0·11) corresponding to **7a** and **7b** was thin in comparison to TLC of the mixture without Ac_2O. The mixture processed as usual was chromatographed on silica gel (150 g) and eluted with benzene–EtOAc (90:10). Fraction (500–600 ml) gave **6** (432 mg). Fraction (620–900 ml) gave a viscous oily product which on TLC gave two spots with R_f 0·49 and 0·38 (**5a**), with $CHCl_3$–MeOH (200:1) as solvent. This solvent system was also used for PTLC.

The compound corresponding to R_f 0·49 was crystallized from a benzene-light petroleum mixture (18 mg) and identified as *N,N,O-triacetyl-4-amino-3-phenanthrol*, m.p. 170–171° (lit. 170–171°)[13]. Its identification was confirmed by synthesis from 4-acetamino-3-phenanthrol.[1]

In presence of α-naphthol. TLC of the mixture in the benzene-EtOAc (85:15) solvent system indicated that spot R_f 0·47 was very dense when compared to TLC of the mixture without α-naphthol. Another difference was that during TLC with benzene as solvent a new reddish-violet spot R_f 0·28 appeared. The mixture was processed as usual and chromatographed on silica gel (150 g) and eluted first with benzene (500 ml) and then with benzene-EtOAc 90:10.

N-(4-Phenanthryl)-1,4-naphthaquinone-4-imine (**10**). Fractions 410–490 ml gave a reddish-violet residue which was crystallized from MeOH (21 mg), m.p. 135–137° (R_f 0·28, solvent benzene); λ_{max} (EtOH): 213·5 (ε 42,000), 250 (45,000), 274·5 (34,000) and 496 nm (3000); IR (cm^{-1}): 1650 (>C=O); MS: M^+ 333, M^+–CO–H (304). Acid hydrolysis was carried out as described for **2a**. The products isolated were identified as naphthaquinone-1,4 and 4-amino-phenanthrene.

4-Acetoxyimino-1-(1-naphthoxy)-1,2,3,4-tetrahydro phenanthrene (**12**). (Spot corresponding to R_f 0·47). The residue from fractions 520–570 ml gave a slightly pinkish crystalline product on crystallization from benzene (610 mg), m.p. 158–160°; λ_{max} (dioxane) 234 (ε 85,000), 296 (18,000), 306 (16,000) and 320·5 nm (9000); IR (cm^{-1}): 1760, 1200 and 930 (=NOCO·CH_3); NMR: 13 aromatic H, therefrom H-5 9·21 (1) (part of ABCX-system) and 12 H between 7·0–8·2 ppm, H-1 (Table 1), H-2 2·2–2·6 (2), H-3 3·1–3·4 ppm (2); MS: M^+ 395, M^+–$C_{10}H_7O$ (252) (Found: C, 80·45; H, 5·71; N, 3·91; $C_{26}H_{21}NO_3$ requires: C, 78·98; H, 5·12; N, 3·54%).

In presence of α-naphthylamine. TLC of the mixture indicated a new spot of R_f 0·50 (yellow reddish) and a very faint reddish-violet streak 0·22 to 0·28 (benzene as solvent). The mixture was processed as usual and chromatographed on silica gel (150 g) with benzene as eluent.

Naphthalene-(1-azo-4)-phenanthrene (**11**) (R_f 0·50). The fraction corresponding to the first 100 ml, gave a reddish residue. This was further purified by PTLC, and on crystallization from MeOH gave reddish crystals (15 mg), m.p. 99–102°; λ_{max} (EtOH) 218·5 (ε 70,000), 238 (49,000), 267 (29,000), 297 (14,000), 315 (9000) and 378 nm (8000); IR (cm^{-1}): 820, 800, 790, 765, 735 and 710 (indicating adjacent 2H, 3H and 4H respectively); MS: M^+ 332, M^+–$C_{10}H_7$ (205), M^+–$C_{14}H_9$ (155).

R_f 0·22–0·28: *Compound* 10. Fractions 400–470 ml gave a reddish-violet residue, which was further purified by PTLC (6 mg) and identified as **10**.

In presence of 4-hydroxy-diphenylamine. TLC of the mixture in the solvent system benzene-EtOAc 95:5 showed the presence of three new spots, R_f 0·30, 0·26 and 0·22 (yellow). The mixture was processed as usual and chromatographed (silica gel 120 g) with benzene as solvent. Fractions 320–570 ml gave a brownish residue which on TLC indicated spots with R_f 0·30 and 0·26 (benzene–EtOAc 95:5). Both these compounds were separated by PTLC using this solvent system.

4-Anilinophenyl-acetate (**13**), (R_f 0·30), on crystallization from benzene-light petroleum gave colourless crystals (20 mg), m.p. 60–62°; λ_{max} (dioxane): 286 nm (ε 22,000); IR (cm^{-1}): 3390 (N–H), 1735 and 1225 (ester); NMR: 9 aromatic H between 6·9–7·35 ppm: CH_3CO– 2·28 ppm (3), s; MS: M^+ 227, M^+-ketene (185) (Found: C, 73·96; H, 5·35; N, 5·79; $C_{14}H_{13}NO_2$ requires: C, 74·01; H, 5·73; N, 6·19%).

4-(Acetoxyimino)-1-(4-anilino-phenoxy)-1,2,3,4-tetrahydrophenanthrene (**15**), (R_f 0·26), on crystallization from benzene-light petroleum gave colourless needles (125 mg), m.p. 128–130°; λ_{max} (dioxane) 226 (ε 44,000), 240 (34,000) and 288·5 nm (26,000); IR (cm^{-1}) 3360 (N–H), 1750, 1200 and 935 (=NO·CO·CH_3); NMR: 15 aromatic H, therefrom H-5 9·20 (1) (part of ABCX-system) and the other 14 between 6·9–7·94 ppm; H-1 (Table 1), H-2 2·15–2·4 (2), H-3 2·9–3·4 (2), CH_3–CO 2·33 (3), s, and N–H 5·54 ppm (1), s; MS: M^+ 436 (Found: C, 76·91; H, 5·21; N, 5·87; $C_{28}H_{24}N_2O_3$ requires: C, 77·06; H, 5·50; N, 6·42%).

4-(Phenylimino)-cyclohexa-2,5-dien-1-one (**14**) (R_f 0·22): Fractions 620–700 ml gave a reddish residue which was purified by PTLC, and on crystallization from light petroleum gave red crystals (42 mg), m.p. 100–101° (lit. 101°)[12]; MS: M^+ 183, M^+–CO–H (154).

In presence of hydrazobenzene. A mixture composed of **1** (400 mg), DBU (500 mg) and hydrazobenzene (200 mg) in benzene (50 ml) under N_2 was kept at room temp for 24 hr. TLC (benzene as solvent) indicated the presence of a new intensely yellow spot, R_f 0·56 (**16**), but spots corresponding to **2a**, **2b**, **4a** and **4b** were absent. The reaction mixture after the usual initial processing was chromatographed on silica gel (100 g), with benzene as solvent.

Azobenzene (**16**). The fraction corresponding to the first 100 ml gave a reddish-yellow residue and on crystallization from light petroleum reddish crystals (218 mg), m.p. 67–68° (lit. 68°)[13]; MS: M^+ 182.

For the quantitative estimation of azobenzene (**16**), **1** (200 mg), hydrazobenzene (100 mg) and DBU (300 mg) were dissolved in benzene (final volume 25 ml) and kept under N_2 for 24 hr. A control reaction was also set up in exactly the same manner except for the omission of **1**. As the mixture and azobenzene both had similar UV spectra in the range 420–560 nm with λ_{max} 447 nm, this wavelength was used for the quantitative estimation of azobenzene. After 24 hr, azobenzene formation in the control amounted to 12·2% while in the experimental reaction it was 68%.

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