reaction is beginning to compete with the intramolecular reaction.

Conclusion. The carboxylate catalysis of the iodine oxidation of *N*-acetylmethionine seems to involve an *inter*molecular reaction to give an intermediate *O*-acyl sulfoxide which is rapidly deacylated by reaction with the *intra*molecular carboxylate. Intramolecular *O*-acyl sulfoxide formation seems to be unfavorable, or does not rapidly lead to products, and is observed only in the buffer-independent reactions.

Acknowledgment. This work was supported by Grant CHE-8000054 from the National Science Foundation.

Registry No. *N*-Acetylmethionine, 65-82-7; I_2, 7553-56-2.

Synthesis of New Functional Acenaphthylene Derivatives. 2. Regioselective Electrophilic Substitution of Silylated Acenaphthenes and Acenaphthylenes

Guy Félix, Michel Laguerre, Jacques Dunoguès,* and Raymond Calas

Laboratoire de Chimie Organique et Laboratoire de Chimie des Composés Organiques du Silicium et de l'Etain Associé au CNRS (No. 35), 33405 Talence, Cédex, France

Received July 29, 1981

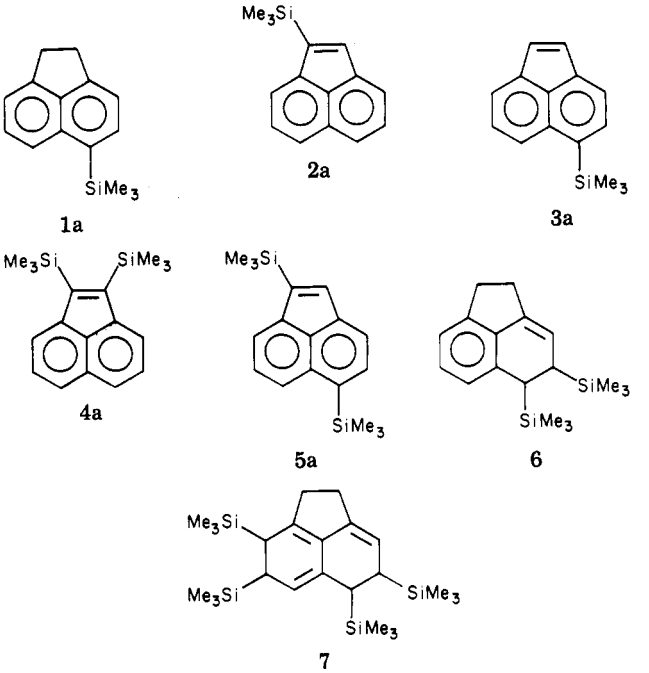
New silylated derivatives have been synthesized in the acenaphthylene series [5-(trimethylsilyl)acenaphthene (**1a**) and -acenaphthylene (**3a**), 4,5-bis(trimethylsilyl)-4,5-dihydroacenaphthene (**6**), and 4,5,7,8-tetrakis(trimethylsilyl)-4,5,7,8-tetrahydroacenaphthene (**7**)] by appropriate silylation reactions, followed by oxidation in the case of **3a**. **1a** and **3a** as well as 1-(trimethylsilyl)- and 1,2- and 1,5-bis(trimethylsilyl)acenaphthylenes (**2a**, **4a**, and **5a**, respectively) have been used as regioselective precursors of 5-functional acenaphthenes and 1-monofunctional and 1,2- and 1,5-bifunctional acenaphthylenes by electrophilic substitution of the trimethylsilyl group(s). Mono- and bisulfonations succeeded in all cases as well as the acylation or iodination of monosilyl derivatives and 1,2-diodination of **4a**. Thus, various novel functional acenaphthenes and acenaphthylenes could be prepared by a convenient route. In contrast, attempts at diodination of **5a** and diacylation of **4a** and **5a** were unsuccessful.

In a previous paper[1] we have described the synthesis of various trimethylsilyl- or bis(trimethylsilyl)acenaphthenes and acenaphthylenes (e.g., **2a**, **4a**, and **5a**; Chart I).

We have now focused our interest on the functionalization of these compounds by regioselective substitution of the trimethylsilyl group(s) because very few of functional acenaphthylene derivatives have been described to date.[2] We thought the silicon route would be applicable to that purpose in view of previous results on the electrophilic substitution of vinyl[3] and arylsilanes,[4] especially in studies in our laboratories.

Reductive silylation of acenaphthene by magnesium in hexamethylphosphortriamide (HMPA)[5] in the presence of trimethylchlorosilane led to 4,5-bis(trimethylsilyl)-4,5-dihydroacenaphthene (**6**,[1] Scheme I). Using lithium with THF as the solvent,[5-7] 4,5,7,8-tetrakis(trimethylsilyl)-4,5,7,8-tetrahydroacenaphthene (**7**), the first product having the 4,5,7,8-tetrahydronaphthalene structure, was

Chart I



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(3) First reports concerning functionalization of vinylsilanes by electrophilic substitution of the silyl group were those of R. Calas, P. Bourgeois, N. Duffaut *C. R. Hebd. Seances Acad. Sci., Ser. C*, **263C**, 243 (1966) (sulfonation) and J.-P. Pillot, J. Dunoguès, and R. Calas, *ibid.*, **278C**, 789 (1974) (acetylation). For a good review see T. H. Chan and I. Fleming, *Synthesis*, 761 (1979).

(4) First reports concerning functionalization of arylsilanes were those of Eaborn et al. For good reviews see: C. Eaborn, *J. Organomet. Chem.*, **100**, 43 (1975); T. H. Chan and I. Fleming, *Synthesis*, 761 (1979); D. Habisch and F. Effenberger, *ibid.*, 841 (1979).

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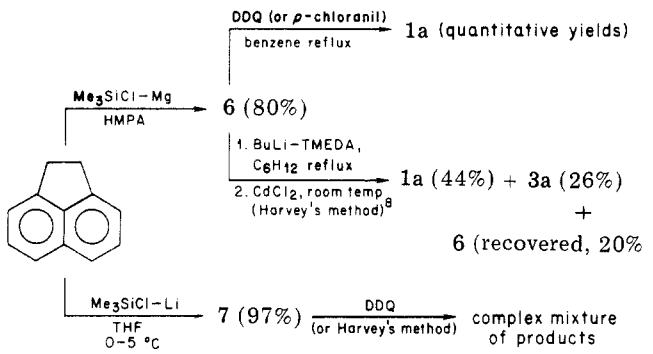
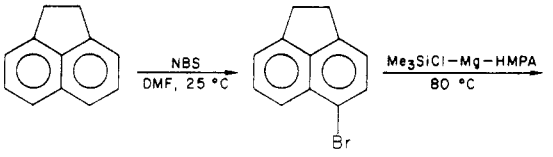
Scheme I



obtained in quantitative yields.

Results

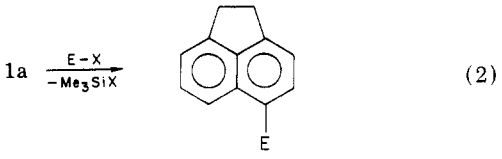
Oxidation of **6** or **7** by Harvey's method[8] gave a complex mixture of products, especially in the case of **7** in which mono- or polydesilylation accompanied the formation of acenaphthylene, acenaphthene, dihydro- or tetrahydroacenaphthene skeletons. In contrast, when oxidation was effected with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), **1a** was produced from **6** in quantitative yield. This product also could be synthesized in a two-step process from acenaphthene in 80% overall yield (eq 1).



$$\mathbf{1a} \xrightarrow[\text{or Harvey's method,}]{\text{DDQ benzene refl}} \mathbf{3a}\ \text{(quantitative yields)} \quad (1)$$

Oxidation of **1a** using DDQ as well as the Harvey's method gave **3a** in quantitative yield, but *p*-chloranil was not a potent enough oxidizing agent to afford complete reaction under our experimental conditions.

Functionalization of **1a** by electrophilic substitution of the trimethylsilyl group occurred in high yield in iodination, sulfonation, and acetylation reactions (eq 2).



(2)

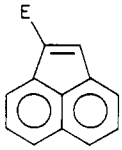
1b, E = I (94%)
c, E = SO_3SiMe_3 (or SO_3Na) (88%)
d, E = COMe (80%)
e, E = $COCH_2Cl$ (65%)

E–X = ICl, Me_3SiOSO_2Cl, $MeCOCl/AlCl_3$, $ClCH_2COCl/AlCl_3$

Sulfonation was carried out by using trimethylsilyl chlorosulfonate (easily prepared by condensation of chlorosulfonic acid with trimethylchlorosilane[9,10]) because of the versatility of this reagent which is particularly effective under very mild conditions.[10-12] In sulfonation as well as in the other electrophilic substitutions the silicon group introduced on the acenaphthene substrate could be recovered.

The regioselectivity of the silicon makes this a valuable synthetic method. Thus, in the direct sulfonation of acenaphthene, 3-mono-, 3,5-, 3,6-, and 3,5-di-, and 3,5,8-trisulfonic acid derivatives of acenaphthene were formed in addition to acenaphthene-5-sulfonic acid.[13] Similarly, usual acetylation of acenaphthene also provides 3-acetylacenaphthene besides **1d**.[14] By use of magnesium perchlorate[15] to decrease the formation of the 3-acyl derivative, **1d** only was obtained, in 40% yields. Consequently, the silicon route is useful for the synthesis of **1c,d**. **1b**[16] and **1d**[13] had been prepared previously, but with much more difficulty.

Similarly, electrophilic substitution of **2a** led to **2b–e**, whereas **3a** cannot be used as precursor for the synthesis of 5-functional acenaphthylenes because of the very high reactivity of the $C_1{=}C_2$ double bond toward electrophiles and its instability in the presence of a Lewis acid (polymerization).



2b, E = I (50-60%), **2b'**, E = Cl (10-30%)
c, E = SO_3SiMe_3 (or SO_3Na) (85%)
d, E = COMe (35%)
e, E = COEt (86%)

The silicon route to these functional acenaphthylenes involves the formation of Me_3SiCl (instead of HCl in common Friedel–Crafts substitution). This offers an advantage regarding the low stability of the acenaphthylenic double bond in acidic medium.

However, the results of acylation reactions depended on the reagent used. Thus, acetyl chloride (in the presence of $AlCl_3$ at −80 °C or $AgBF_4$ at 0 °C) or fluoride (in the presence of BF_3 at −10 °C) led to **4d** (~10%) in addition to **2d** (30–35%). With propionyl fluoride the reaction became completely regioselective (86% yield). In this case an addition–elimination process is sterically favored, but we think that the experimental procedure (nature and boiling point of the acyl halide and the catalyst) was responsible for the observed differences. With acetyl chloride/$AlCl_3$ it is necessary to carry out the reaction at −30 °C in order to limit polymerization of the acenaphthylene derivative induced by $AlCl_3$, a Lewis acid stronger than BF_3.

From **4a**, 1,2-diiodo compound **4b'** and 1,2-bis(trimethylsilyl)sulfonate **4c'** were regiospecifically obtained in useful yield, whereas **4d** did not undergo a second acetylation (eq 3).

Attempts to isolate **4b** failed, under our reaction conditions, probably because of the facility of trimethylsilyl iodide elimination in this compound. **4c** could be obtained

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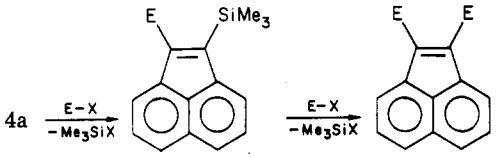


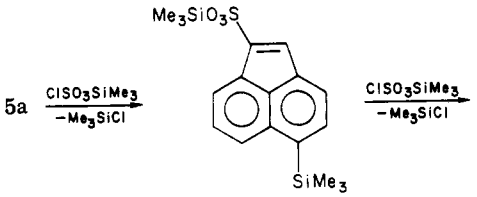
(3)

4b, E = I
(could not be isolated);
4b', E = I (73%)
c, E = SO_3SiMe_3
(or SO_3Na) (86%);
4c', E = SO_3SiMe_3
(or SO_3Na) (86%)
d, E = COMe (88%)

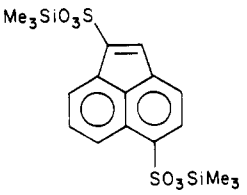
by using equimolar amounts of **4a** and trimethylsilyl chlorosulfonate. The corresponding sodium salt was obtained upon hydrolysis at pH 7. Under basic or acidic conditions desilylation occurred, and we obtained **2c** quantitatively.

The formation of **4c'** constitutes the first example of direct, 1,2-disulfonation by electrophilic substitution at a vinylic position. Previous attempts in the sulfonation of *trans*-1,2-bis(trimethylsilyl)ethylene had provided a quantitative monosulfonation derivative but no disulfonic acid derivatives.[17]

Mono- and disulfonation of **5a** were regioselective, the vinylic position being the more reactive (eq 4). On the



5c (87%)



(4)

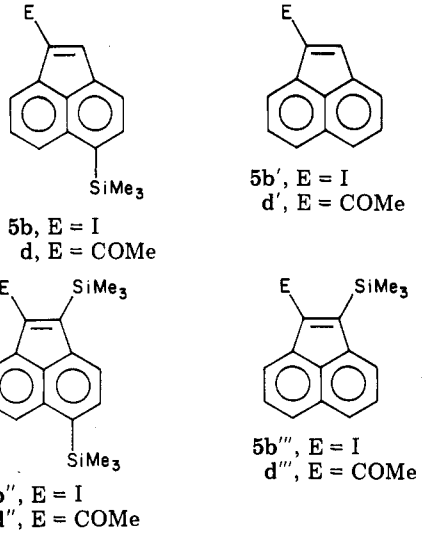
5c' (83%)

other hand, in acetylation as well as iodination, only the vinylic silylated position underwent functionalization under our reaction conditions. Although polyiodination was previously successful in the benzene series,[18,19] the fragility of the acenaphthylene skeleton did not permit us to operate under more drastic conditions.

Thus, acetylation or iodination of **5a** with 2 equiv of ICl or MeCOCl/$AlCl_3$ gave **5b,b',b'',b'''** or **5d,d',d'',d'''**, respectively.

In the acetylation reaction, **5d'** (10%) and **5d'''** (30%) could be isolated as pure compounds whereas a mixture of **5d** (~10%) and **5d''** (~10%) was identified by ^1H NMR spectroscopy. These derivatives resulted from acetylation by substitution of hydrogen eventually accompanied by protodesilylation.

The desilylation reaction can be interpreted in terms of an acidic cleavage of the Si–C_{Ar} bond by HCl formed at the same time as **5d''** and **5d'''** (eq 5 and 6).

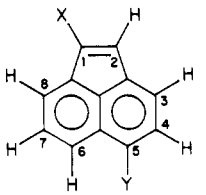


$$\mathbf{5a} \xrightarrow{MeCOCl/AlCl_3} \mathbf{5d''} + HCl \rightarrow \mathbf{5d'''} + Me_3SiCl \quad (5)$$

$$\mathbf{5d} \xrightarrow{HCl} \mathbf{5d'} + Me_3SiCl \quad (6)$$

In contrast, because of its low stability in the reaction medium, **5b** was not isolated but was identified unambiguously, while the ^1H NMr spectrum of the mixture was in accordance with the possible formation of **5b'–b'''**. Moreover, formation of chlorinated compounds, especially in position 1, was demonstrated both by ^1H NMR and mass spectra.

The **5a** functionalization products were identifed by comparison of their ^1H NMR spectra with those of products identified with certainty, **1b–e** and **2b–d**. When functionalized in position 1, the chemical shift of H_8 undergoes a deshielding by comparison with the other aromatic protons (0.13 ppm for X = SO_3SiMe_3, 0.40 ppm for X = COMe, and ~0.05 ppm for X = I or Cl). Consequently, H_8 appears as the part A of an ABX spectrum for all these derivatives; $J_{8,7} \approx 7$ Hz, and $J_{8,6} \approx 0,7$ Hz.



Identification of the 5-substituted derivatives was based on the effect of the substituent Y on H_6 and H_4 in the ^1H NMR spectrum. In all cases (even when Y = $SiMe_3$), H_6 is largely deshielded by comparison with Y = H; H_6 is ~0.13 (Y = $SiMe_3$), ~0.42 (Y = SO_3Na), ~0.47 (Y = I), 0.63 (Y = COMe), and ~1.42 ppm (Y = $COCH_2Cl$) from the signal for the group of the other aromatic protons. Consequently, we can observe H_6 as the A part of an ABX spectrum; $J_{6,7} \approx 7$ Hz, and $J_{6,8} \approx 0.7$ Hz. Moreover, when Y = $SiMe_3$, the coupling constant $J_{6,8} \approx 1.8$ Hz confers to the proton H_6 a characteristic aspect.

Al these considerations, which are in accordance with some partial results given in the literature,[15,20] permitted us to attribute unambiguously the position of electrophilic substitution, especially when the compounds were obtained in a pure state.

In the case of Y = SO_3SiMe_3 (or SO_3Na), COMe, and $COCH_2Cl$, H_4 also is deshielded and is not within the multiplet due to the other aromatic protons (but is less

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deshielded than H_6), as the A part of a pure AB spectrum; $J_{3,4} \simeq 7$ Hz.

Experimental Section

^1H NMR spectra were recorded on Perkin-Elmer R-12 and R-24 B (60 MHz) instruments. Unless otherwise specified, CCl_4 with Me_4Si as the standard was used for all NMR spectra, and results are given as δ values. Generally, NMR spectra were complicated, and only the characteristic signals of $SiMe_3$ (9 H) and COMe (3 H) in addition to the data given in the Results were used in the identification of the products. Consequently, a complete description of the spectra will not be given, but all the spectra are available on request.

Preparative high-pressure LC was carried out on a Jobin-Yvon Model Chromatospac Prep 10 instrument (reverse-phase Lichropep RP8). Melting points are not corrected.

In some cases products were purified by passing them through a silica gel column.

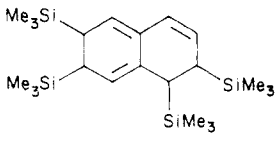
New compounds **1a–e**, **3a**, **4b′,c,c′,d**, and **5b′,b‴,c,c′** gave satisfactory elemental analyses which were submitted for review, and their formulas were confirmed by high-resolution mass spectroscopy (VG Micromass 70/70; presence of the molecular peak). Other products which could not be purified were identified by means of physicochemical data.

Synthesis of 5-(Trimethylsilyl)acenaphthene (1a). This compound was prepared by bromination (at position 5) of acenaphthene by *N*-bromosuccinimide in DMF followed by silylation using the Me_3SiCl–Mg–HMPA reagent at 80 °C, according to the process previously described for the synthesis of 1,2-bis(trimethylsilyl)acenaphthene.[1] 5-Bromoacenaphthene (7 g, 0.030 mol) in HMPA (50 mL) added dropwise to Mg (0.75 g, 0.031 mol + excess), Me_3SiCl (6 g, 0.055 mol), and HMPA (100 mL). We obtained **1a**: mp 107 °C; 5.2 g (80% yield); ^1H NMR (CCl_4, Me_4Si) 0.43 (s, 9 H, $SiMe_3$), 3.30 (s, 4) H, benzylic protons), 7.0–7.8 (m, 5 H), aromatic protons).

Synthesis of 5-(Trimethylsilyl)acenaphthylene (3a). Oxidation reactions using DDQ or Harvey's method[8] were previously described by us.[1] We prepared **3a** (yellow liquid) from **1a** (97% yield) or **6** (>90%) using these methods. **3a**: ^1H NMR 0.50 (s, 9 H, $SiMe_3$), 7.40 (s, 2 H, CH=CH), 7.90–8.30 (m, 4 H, H_3, H_4, H_7, H_8), 2 d centered at 8.40 and 8.54 (part A of an ABX spectrum, 1 H, H_6, $J_{6,7} = 8$ Hz, $J_{6,8} = 0.7$ Hz).

Synthesis of 4,5-Bis(trimethylsilyl)-4,5-dihydroacenaphthene (6). This compound was synthesized from acenaphthene and the Me_3SiCl–Mg–HMPA reagent according to the conditions previously reported for the synthesis of 1,2-bis(trimethylsilyl)acenaphthene.[1] For **6**: mp 70–71 °C (EtOH); 90% yield; ^1H NMR −0.13 and −0.05 (2 s, 2 × 9 H, $2SiMe_3$), 1.85 (m, 1 H, C=C—CH—Si), 2.15 (d, 1 H, ArCHSi, $J = 6$ Hz), 2.70 (m, 4 H, $(CH_2)_2$, 5.25 (d, 1 H, C=CH), 6.40–7.0 (m, 3 H, aromatic H).

Synthesis of 4,5,7,8-Tetrakis(trimethylsilyl)-4,5,7,8-tetrahydroacenaphthene (7). The reaction, carried out according to a previously reported procedure[7] with acenaphthene (6.2 g, ~0.04 mol), Li (1.7 g, ~0.24 mol), Me_3SiCl (27.1 g, ~0.25 mol), and THF (100 mL), afforded **7**: mp 161 °C; 17.6 g (97%). The structure of **7** was established by microanalysis, mass spectroscopy (molecular peak m/z 454), and comparison of its physicochemical data with those of the tetrasilylated derivatives of naphthalene 8.[21]



8

1-(Trimethylsilyl)- and 1,2- and 1,5-Bis(trimethylsilyl)-acenaphthylenes (2a, 4a, and 5a). Synthesis and physicochemical properties of these compounds have been reported previously.[1]

Monoiodination Reactions. ICl (5.5 mmol) in CCl_4 (20 mL) was added, dropwise at 0 °C, to a solution of the silylated derivative (5.3 mmol) in CCl_4 (30 mL). Stirring was continued for 3 h at 0 °C and then for 1 h at room temperature. The reaction mixture was washed with an aqueous solution of sodium thiosulfate and then with water and was dried over Na_2SO_4, and the CCl_4 was evaporated. The crude product was passed through a silica column (Merck Si 60, 70–230-mesh ASTM, activity 2–3, pH 7) with pentane as the eluent. We obtained **1b** (94%), **2b** (50–60%), **2b′** (30–10%), and **4b**, (mp 136–137 °C; 73%). **5b,b′,b″** formed in a similar iodination of **5a** were not isolated.

5-Iodoacenaphthene (1b): ^1H NMR 3.15 (s, 4 H, benzylic protons), 6.73 and 6.87 (part A of an AB spectrum, 1 H, H_4, $J_{3,4} = 8$ Hz), 6.90–8.05 (m, 4 H, H_3, H_6, H_7, H_8), AB part between 6.90 and 8.05 (4 H). An ABC spectrum is visible signals at δ 7.38 and 7.52 (H_7) and 7.63 and 7.77 (H_6); $J_{6,7} = 8$ Hz, $J_{6,8} \simeq 0.5$ Hz.

1-Iodoacenaphthylene (2b) and 1-Chloroacenaphthylene (2b′). These halo derivatives have not differentiated seven protons between 7.23 and 8.0 ppm for **2b** and seven between 7.1 and 7.53 ppm for **2b′**.

Diodination. These reactions involved a similar procedure but use 2 equiv of ICl.

1,2-Diiodoacenaphthylene (4b′). Compound **4b′** has a melting point of 136–137 °C. In the NMR spectrum all the proton signals are found between 7.40 and 7.90 ppm.

Sulfonation Reactions. These were carried out according to previously described procedures.[19]

Except for **2c** all the ^1H NMR spectra of the sodium sulfonates were measured with $(D_3C)_2SO$ as the solvent and Me_2CO (singlet at 2.17 ppm) as the internal reference. All the sodium sulfonates gave satisfactory C and H microanalytical results.

Sodium 5-acenaphthenesulfonate (1c): ^1H NMR 3.38 (s, 4 H, benzylic protons), 1 m between 7.12 and 7.62 (3 H, H_3, H_7, H_8), part B of an AB spectrum slightly enlarged signals at 7.93 and 8.05 (1 H, H_4, $J_{4,3} \simeq 7$ Hz), 8.24 and 8.36 (two enlarged signals, part B of an ABC spectrum, 1 H, H_6, $J_{6,7} \simeq 7$ Hz, $J_{6,8} \simeq 0.7$ Hz).

Sodium 1-acenaphthylenesulfonate (2c): ^1H NMR (HMPA as the solvent with the singlets of HMPA at δ 2.53 and 2.68 as the internal references) 7.18 (s, 1 H), 7.35–8.40 (m, 5 H). For other protons in which part B of an AB spectrum (in reality ABC, but J_{BC} is very small) is visible, the signals are at δ 8.25 and 8.37 (H_8, $J_{7,8} = 7$ Hz).

Sodium 2-(trimethylsilyl)-1-acenaphthylenesulfonate (4c): ^1H NMR 0.48 (s, 9 H, $SiMe_3$), 7.42–8.12 (m, 6 H, aromatic protons).

Sodium 1,2-acenaphthylenedisulfonate (4c′): ^1H NMR 7.83–7.98 (m, 4 H, H_4, H_5, H_6, H_7); part B of an AB spectrum (in reality ABC in which J_{BC} is very small) has signals at 8.17 and 8.29 (H_3 and H_8, $J_{3,4} = J_{8,7} \simeq 7$ Hz).

Sodium (5-trimethylsilyl)-1-acenaphthylenesulfonate (5c): ^1H NMR 0.62 (s, 9 H, $SiMe_3$), 7.25 (s, 1 H, C=CH), 7.55–8.30 (m, 5 H, aromatic H).

Sodium 1,5-Acenaphthylenedisulfonate (5c′). The ^1H NMR characteristics of the compound are given in the Results, especially the H_8 signals at δ 7.32 and 7.44 ($J_{8,7} \simeq 7$ Hz) and the H_6 signals at δ 8.79 and 8.91 ($J_{6,7} \simeq 7$ Hz).

Acetylation Reactions. For a general procedure, see ref 22. All the acetyl derivatives gave satisfactory C and H microanalytical data, and we observed in the IR the presence of $\nu_{C=O}$ around 1650–1660 cm^{-1} (except for **1c**, $\nu_{C=O} = 1675$ cm^{-1}).

5-Acetylacenaphthene (1d): mp 69 °C (lit.[14a] mp 68–70 °C); ^1H NMR 2.66 (s, 3 H, COMe), 3.30 (s, 4 H, benzylic protons), 7.0–8.0 (m, 3 H, H_3, H_7, H_8); as expected H_4 exhibits two signals at 8.15 and 8.27 (multiplet among signals, $J_{4,3} \simeq 7$ Hz), 8.66 and 8.80 (H_6, $J_{6,7} \simeq 8$ Hz).

5-(Chloroacetyl)acenaphthene (1c): mp 104 °C;[23] ^1H NMR $(D_3C)_2CO$, Me_4Si) 3.50 (s, 4 H, benzylic protons), 5.17 (s, 2 H, $COCH_2Cl$), 7.8–8.2 (m, 3 H, H_3, H_7, H_8); as expected H_4 gives two signals at 8.44 and 8.56 ($J_{4,3} \simeq 7$ Hz).

1-Acetylacenaphthylene (2d): ^1H NMR 2.43 (s, 3 H, COMe), 7.15–7.85 (m, 6 H); 2 m (H_2, H_3, H_4, H_5, H_6, H_7) in which there is the singlet corresponding to H_2 at 7.40; as expected, H_8 exhibits two doublets at 8.14 and 8.26 ($J_{8,7} = 7$ Hz, $J_{8,6} \simeq 0.7$ Hz).

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1-(Trimethylsilyl)-2-acetylacenaphthylene (4d): mp 119–120 °C; ^{1}H NMR 0.43 (s, 9 H, $SiMe_3$), 2.60 (s, 3 H, COMe), 7.10–7.85 (m, 5 H, H_4, H_5, H_6, H_7, H_8); as expected H_3 exhibits 2 d at 7.90 and 8.02 ($J_{3,4} \simeq 7$ Hz, $J_{3,5} \simeq 0.7$ Hz).

Acknowledgment. We thank Professor Dietmar Seyferth (Massachussetts Institute of Technology), who agreed to check our article for correct English and Rhône-Poulenc Industries for providing us with the Me_3SiCl necessary for the synthesis of the silyl derivatives.

Registry No. **1a**, 60989-58-4; **1b**, 6861-64-9; **1c**, 31202-24-1; **1d**, 10047-18-4; **1e**, 80262-61-9; **2a**, 71582-67-7; **2b**, 80262-62-0; **2b′**, 65726-91-2; **2c**, 80262-63-1; **2d**, 80262-64-2; **2e**, 80262-65-3; **3a**, 80262-66-4; **4a**, 71582-66-6; **4b**, 80262-67-5; **4b′**, 80262-68-6; **4c**, 80262-69-7; **4c′**, 80262-70-0; **4d**, 80262-71-1; **5a**, 71582-69-9; **5b**, 80262-72-2; **5b″**, 80262-73-3; **5c**, 80262-74-4; **5c′**, 80262-75-5; **5d**, 80262-76-6; **5d″**, 80262-77-7; **6**, 80287-49-6; **7**, 80262-78-8; 5-bromoacenaphthene, 2051-98-1; acenaphthene, 83-32-9.

Reactions of the K-Region Epoxides of Polycyclic Aromatic Hydrocarbons with Phosphodiesters. A Potential Detoxification Reaction

P. Di Raddo and T. H. Chan*

Department of Chemistry, McGill University, Montreal, Quebec, Canada, H3A 2K6

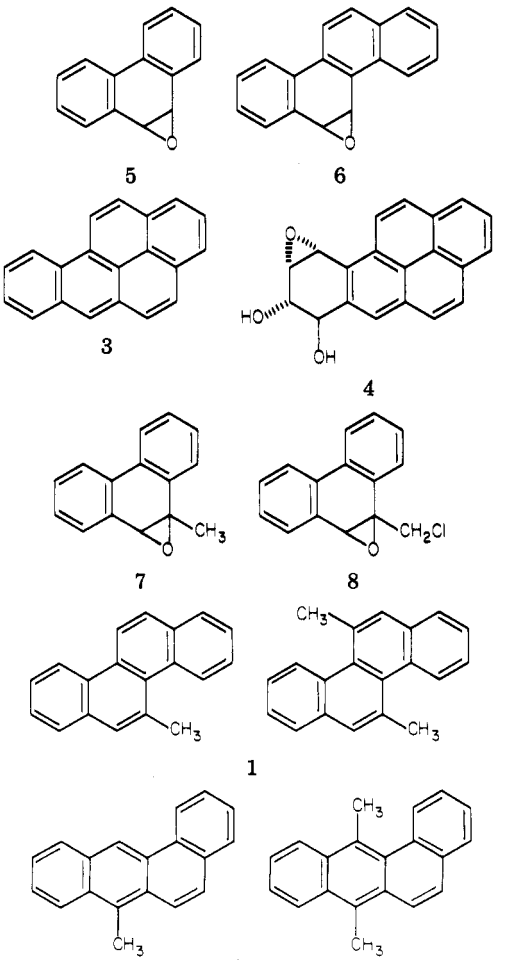
Received June 23, 1981

Phenanthrene 9,10-oxide reacts with diethyl hydrogen phosphate to give 9-phenanthrol. The reaction was first order in both epoxide and phosphate concentrations, with a pseudo-first-order rate constant $k_\psi = 6.2 \times 10^{-1}$ mol^{-1} L s^{-1}. Similarly, chrysene 5,6-oxide on reaction with phosphate opened regiospecifically to give 6-chrysenol. Several anilinium phosphate salts were prepared and reacted with phenanthrene 9,10-oxide. The extent of reaction was markedly influenced by the pK_a of the anilinium salt. The biological implications of this study in understanding the relative noncarcinogenicity of K-region arene oxides are discussed.

Polycyclic aromatic hydrocarbons (PAH) are considered as the most prevalent environmental carcinogens.[1] They are universal products of the combustion of organic matter. Burning of wood or refuse and, indeed, cigarette smoking can all contribute to the concentration of PAH in the environment. PAH are also present in fossil fuels such as petroleum or coal. There is no question that many of these PAH are carcinogenic. As early as 1930, dibenz[*a*,*h*]anthracene was found to induce tumors in mouse skin.[2] In 1933, the carcinogen benzo[*a*]pyrene (BP) was isolated from coal tar extract.[3] Since that time many PAH have been identified as carcinogens according to in vivo testings.

Because PAH as such do not bind covalently to DNA, RNA, proteins, and other biomolecules, it is generally accepted that they must be metabolically activated in vivo to a chemically reactive form which then combines covalently with the macromolecular target. Several theories have been put forward to established correlations between the structure of PAH, metabolism, covalent binding, and carcinogenicity. Among these, the "K-region" theory of Pullman and Pullman has received wide attention.[4] This theory suggests that it is the "K region" of a PAH which is transformed during metabolic activation and is responsible for the carcinogenic activity for the hydrocarbon. With this theory, it is possible to provide a reasonable ranking of carcinogenic activity of a number of PAH. It is also in apparent agreement with some structure–activity relationships observed for substituted chrysenes (**1**) and benz[*a*]anthracenes (**2**) where substitution by fluoro or methyl groups on the K region has a dramatic effect on the biological activity of the hydrocarbon[5,6] (see Chart I).

Chart I



Recently, the "bay region" theory of carcinogenesis by PAH has been proposed mainly through the effort of

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