1a,11b-Dihydrobenz[5,6]anthr[1,2-*b*]azirine. A non K-Region Polycyclic Arene Imine

Jochanan Blum* and Shoshanna Ben-Shoshan

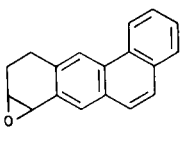
Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel

Received February 24, 1983

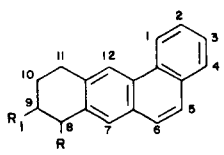
The synthesis of the title compound **9** is described. Benz[*a*]anthracene 8,9-oxide (**6**) was reacted with sodium azide in aqueous acetone and the *trans*-9-azido-8,9-dihydrobenz[*a*]anthr-8-ol (**7**), so formed, was cyclized by tri-*n*-butylphosphine. Attempts to dehydrogenate 10,11-dihydrobenz[*a*]anthracene 8,9-imine (**4**) with DDQ or by allylic bromination followed by base assisted dehydrobromination was unsuccessful. The *N*-tosyl derivative of **4**, prepared from the free imine, *N,O*-bis(trimethylsilyl)acetamide and tosyl chloride underwent rapid aziridine-ring cleavage by the silylating agent to give *trans*-8,9,10,11-tetrahydro-8-(4-methyl)benzensulfonamido-9-[(trimethyl)oxy]benz[*a*]anthracene (**10**).

J. Heterocyclic Chem., **20**, 1461 (1983).

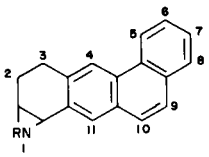
In our study on active metabolites of carcinogenic polycyclic aromatic hydrocarbons we prepared in recent years several K-region arene imines [1-7]. Since these compounds proved to have extremely high mutagenic potencies [8] but nevertheless failed to show significant carcinogenic activity [9], we found it imperative to synthesize and screen the various kinds of polycyclic aromatic aziridines and evaluate their relevance to carcinogenesis.



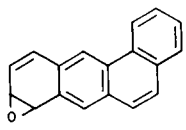
1



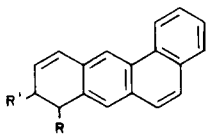
2 R = N_3, R' = OH
3 R = OH, R' = N_3



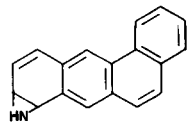
4 R = H
5 R = $SO_2C_7H_7$



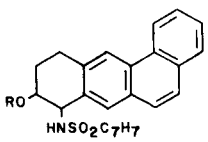
6



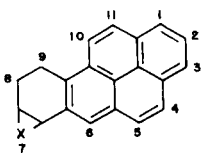
7 R = OH, R' = N_3
8 R = N_3, R' = OH



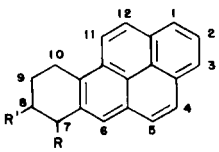
9



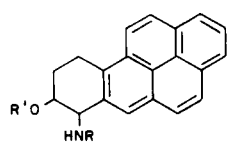
10 R = $Si(CH_3)_3$
11 R = H



12 X = O
13 X = NH



14 R = N_3, R' = OH
15 R = OH, R' = N_3



16 R = $SO_2C_7H_7$, R' = $Si(CH_3)_2$
17 R = H, R' = $Si(CH_3)_3$
18 R = $SO_2C_7H_7$, R' = H

In this paper we describe the preparation of the first polycyclic non-K-region imine, 1a,11b-dihydrobenz[5,6]anthr[1,2-*b*]azirine (benz[*a*]anthracene 8,9-imine) (**9**). In our initial approach we reacted 1a,2,3,11b-tetrahydrobenz[5,6]anthr[1,2-*b*]oxirene (10,11-dihydrobenz[*a*]anthracene 8,9-oxide) (**1**) with sodium azide in aqueous acetone to give *trans*-8-azido-8,9,10,11-tetrahydrobenz[*a*]anthr-9-ol (**2**) as the main product. As expected (see [10]) the other *trans*-azido alcohol, **3**, was formed either in smaller quantities or not at all. (Yields between 0 and 20% were obtained in accordance with the *p*H and reaction temperature employed).

The structures of the isomeric compounds **2** and **3** were established by the 300 MHz pmr spectra. While the H8 and H9 protons of **2** appear as a ddd signal with relatively broad peaks at 4.126 ppm, and as a doublet at 4.605 ppm, respectively, the corresponding signals of **3** are sharp ddd signals at 3.998 ppm and a broad doublet at 4.749 ppm. Deuterium oxide sharpens both the H9 ddd of **2** and the H8 d of **3**. In addition the H7 singlet of **2** at 7.924 ppm is shifted downfield to 8.054 ppm when the positions of the N_3 and OH groups interchange (the H7 resonance of **7** is at 8.018 ppm).

Transformation of the azido alcohols into 1a,2,3,11b-tetrahydrobenz[5,6]anthr[1,2-*b*]azirine (**4**) could be accomplished either by tri-*n*-butylphosphine [3] or by trimethyl phosphite [11].

Since our attempts to dehydrogenate **4** by conventional methods, [e.g. bromination-dehydrobromination [12] or treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone [13]], failed, and since tosylation of the imine with *N,O*-bis-(trimethylsilyl)acetamide and tosyl chloride [14] led to aziridine-ring cleavage (*vide infra*), another approach to **9** was investigated. Bromination of **1** with *N*-bromosuc-

cinimide followed by base-assisted dehydrobromination was found to give in the best trial a 1:3 mixture of the starting material and 1a,11b-dihydrobenz[5,6]anthr[1,2-*b*]-oxirene (**6**) [15-17]. When the mixture of epoxides was reacted with sodium azide in aqueous acetone a mixture of the *three* azido alcohols **2, 3** and **7** was obtained together with some unreacted **1**. Separation of the desired compound **7** was then accomplished by column chromatography on deactivated alumina (see Experimental).

It is noteworthy that while the reaction of **1** with sodium azide gave mainly the azido alcohol having the N_3 group at the benzylic position, **6** afforded exclusively the benzylic alcohol **7**. The different mode of oxirane ring cleavage in **1** and in **6** is rationalized by the existence of an allylic structure in **6** that can stabilize a positive charge on C9 during the attack of N_3^-. Treatment of **7** with tri-*n*-butylphosphine gave the desired imine, **9**.

In our attempts to convert **4** into **9** via the N-tosyl derivative **5**, we found that the latter compound is by far more sensitive to nucleophiles than *N*-tosylphenanthrene 9,10-imine [14]. Thus during the synthesis of **5** from **4**, *N,O*-bis-(trimethylsilyl)acetamide [18] and tosyl chloride by the method described previously [14], the product reacted with $(CH_3)_3SiO^-$ (generated from the silylation agent) to give *trans*-8,9,10,11-tetrahydro-8-(4-methyl)benzensulfonamido-9-[(trimethylsilyl)oxy]benz[*a*]anthracene (**10**). The other possible *trans*-isomer having the silyloxy group on C8 was not formed, probably due to steric effects. In the presence of warm aqueous sodium hydroxide hydrolysis of the trimethylsilyl function took place to give carbinol **11**.

Other *N*-tosyl aziridines having structures similar to **5** seem to be equally sensitive to the trimethylsilyloxy anion. Thus e.g., 6b,7a,8,9-tetrahydrobenzo[10,11]chryseno[1,-2-*b*]azirine (13) (prepared from the corresponding oxirane **12** [19] *via* azido alcohol **14**) was converted by bis(trimethylsilyl)acetamide and tosyl chloride into *trans*-7,8,9,10-tetrahydro-7-(4-methyl)benzensulfonamido-8-[(trimethylsilyl)-oxy]benzo[*a*]pyrene (**16**). Acid hydrolysis yielded the tosyl-free amine **17**, while aqueous sodium hydroxide removed the trimethylsilyl function to form compound **18**.

EXPERIMENTAL

trans-8-Azido-8,9,10,11-tetrahydrobenz[*a*]anthr-9-ol (**2**).

A solution of 20 g of sodium azide in 100 ml of water and 180 ml of acetone was stirred under nitrogen with 0.1 ml of concentrated sulfuric acid. After 15 minutes 1.50 g of powdered **1** [17] [freshly purified by chromatography on silica gel with ether-hexane (3:17) as eluent, mp 159-160° (lit [16] 158-160°)] was added to the mixture. Stirring was continued at room temperature for 36 hours. The acetone was removed under reduced pressure and the precipitate which consisted of the two *trans*-azido alcohols **2** and **3** in ratio 8:1, was taken into 400 ml of dichloromethane. The organic solution was washed with water, dried and chromatographed on silica gel [petroleum ether-ether (9:1) as eluent] to give 1.60 g (90%) of **2** and **3** (4:1), mp 132-135°. Pure **2** was obtained when this mixture was rechromatographed on silica gel with chloroform as eluent, mp 152-154°; ir (nujol) 3350 (OH), 2118 cm^{-1} (N_3); 300 MHz pmr (deuteriochloroform): δ 2.022 (m, 1H, H10), 2.284 (m, 1H, H10'), 3.174 (m, 2H, H11, H11'), 4.126 (ddd, 1H, $J_{8,9} = J_{9,10} = 7.5$ Hz, $J_{9,10'} = 10$ Hz, H9, the peaks sharpen upon addition of deuterium oxide), 4.605 (d, 1H, $J_{8,9} = 7.5$ Hz, H8), 7.582 (td, 1H, $J_{1,3} = 1.2$ Hz, $J_{2,3} = J_{3,4} = 8$ Hz, H3), 7.636 (td, 1H, $J_{1,2} = J_{2,3} = 8$ Hz, $J_{2,4} = 1.6$ Hz, H2), 7.693 (ABq, 2H, $J_{AB} = 10$ Hz, H5, H6), 7.866 (dd, 1H, $J_{2,4} = 1.6$ Hz, $J_{3,4} = 8$ Hz, H4), 7.924 (s, 1H, H7), 8.412 (s, 1H, H12), 8.615 (dd, 1H, $J_{1,2} = 8$ Hz, $J_{1,3} = 1.2$ Hz, H1); ms: (70 eV, 130°) m/e (relative intensity) 289 ($M^{\cdot+}$, 75), 261 [$(M-N_2)^{\cdot+}$, 13], 247 [$(M-N_3)^+$, 100], 246 [$(M-N_3H)^{\cdot+}$, 38], 232 ($C_{18}H_{16}^{\cdot+}$, 65), 229 ($C_{18}H_{13}^+$, 49), 217 ($C_{17}H_{13}^+$, 84).

Anal. Calcd. for $C_{16}H_{15}N_3O$: C, 74.72; H, 5.23; N, 14.52. Found: C, 74.65; H, 5.06; N, 14.50.

1a,2,3,11b-Tetrahydrobenz[5,6]anthra[1,2-*b*]azirine (**4**).

Method A.

A precooled suspension (0°) of 0.212 g of **2** in 500 ml of degassed hexane was treated with 0.317 g of tri-*n*-butylphosphine under exclusion of air and moisture. The mixture was stirred at room temperature for 24 hours. Most of the solvent was evaporated *in vacuo* the solid was filtered and recrystallized twice from benzene or toluene to yield 0.127 g (71%) of colorless crystals, mp 145-146°; 300 MHz pmr (deuteriochloroform): δ 1.957 (m, 1H, H2), 2.323 (m, 1H, H2'), 3.215 (m, 2H, H3, H3'), 3.667 (ddd, 1H, $J_{1a,2} = J_{1a,11b} = 9$ Hz, $J_{1a,2'} = 10.5$ Hz, H1a), 3.855 (d, 1H, $J_{1a,11b} = 9$ Hz, H11b), 7.573 (td, 1H, $J_{5,7} = 1.2$ Hz, $J_{6,7} = J_{7,8} = 7$ Hz, H7), 7.632 (td, 1H, $J_{5,6} = J_{6,7} = 7$ Hz, $J_{6,8} = 1.6$ Hz, H6), 7.683 (ABq, 2H, $J_{AB} = 9$ Hz, H9, H10), 7.864 (dd, 1H, $J_{6,8} = 1.6$ Hz, $J_{7,8} = 7$ Hz, H8), 7.991 (s, 1H, H11), 8.391 (s, 1H, H4), 8.630 (dd, 1H, $J_{5,6} = 7$ Hz, $J_{5,7} = 1.2$ Hz, H5); ms: (70 eV, 120°) m/e (relative intensity) 245 ($M^{\cdot+}$, 100), 244 [$(M-H)^+$, 12], 243 [$(M-2H)^{\cdot+}$, 3], 230 ($C_{18}H_{14}^{\cdot+}$, 4) 229 ($C_{18}H_{13}^+$, 5), 228 ($C_{18}H_{12}^{\cdot+}$, 7), 218 ($C_{17}H_{14}^{\cdot+}$, 98), 217 ($C_{17}H_{13}^+$, 39).

Anal. Calcd. for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.20, H, 6.10; N, 5.35.

Method B.

A solution of 0.30 g of **2** and 0.92 g of trimethyl phosphite in 40 ml of dichloromethane was refluxed under argon for 10 hours. The mixture was cooled, diluted with 300 ml of dichloromethane and stirred for 30 minutes with 300 ml of 5% aqueous sodium hydroxide. The organic layer was separated, washed once with 5% aqueous sodium hydroxide and three times with water. Upon concentration of the dichloromethane solution there separated 0.16 g (21%) of **4** of the same properties as the sample prepard by method A.

trans-9-Azido-8,9-dihydrobenz[*a*]anthr-8-ol (**7**).

In the best trial, a mixture of 385 mg of **1** [20], 14 mg of α,α-azobis-(isobutyronitrile), 315 mg of *N*-bromosuccinimide and 25 ml of dry carbon tetrachloride was refluxed under exclusion of air and moisture for 30 minutes. The succinimide was filtered off and the solvent was removed *in vacuo*. The residue was dissolved *immediately* in 20 ml of freshly dried tetrahydrofuran and 0.8 g of 1,5-diazobicyclo[4.3.0]non-5-ene was added. The mixture was stirred under argon for 48 hours at room temperature. The clear solution was decanted from the oily salt, diluted with water and the resulting oil extracted into dichloromethane. The organic solution was washed several times with water, dried (magnesium sulfate) and concentrated. The residue (329 mg) of pale yellow crystals [16] was shown by pmr analysis to consist of 26% of the starting material **1** and of 74% of 1a,11b-dihydrobenz[5,6]anthra[1,2-*b*]oxirene (**6**); 300 MHz pmr of **1** (deuteriochloroform): δ 1.886 (m, 1H, $J_{1a,2} = J_{2,3'} = 7$ Hz, $J_{2,2'} = 14$ Hz, $J_{2,3} = 15$ Hz, H2), 2.534 (m, 1H, $J_{1a,2'} = 4$ Hz, $J_{2,2'} = 14$ Hz, $J_{2',3} = 7$ Hz, $J_{2',3'} = 3$ Hz, H2'), 2.835 (m, 1H, $J_{2,3'} = 7$ Hz, $J_{2',3'} = 3$ Hz, $J_{3,3'} = 15$ Hz, H3'), 2.040 (m, 1H, $J_{2,3} = J_{3,3'} = 15$ Hz, $J_{2',3} = 7$ Hz, H3), 3.838 (ddd, 1H, $J_{1a,2} = 7$ Hz, $J_{1a,2'} = J_{1a,11b} = 4$ Hz, H1a), 4.075 (d, 1H, $J_{1a,11b} = 4$ Hz, H11b), 7.585 (td, 1H, $J_{5,7} = 1.5$ Hz, $J_{6,7} = J_{7,8} = 7.5$ Hz, H7), 7.642 (td, 1H, $J_{5,6} = J_{6,7} = 7.5$ Hz, $J_{6,8} = 2$ Hz, H6), 7.717 (s, 2H, H9, H10), 7.881 (dd, 1H, $J_{6,8} = 2$ Hz, $J_{7,8} = 7.5$ Hz, H8), 7.919 (s, 1H, H11), 8.383 (s, 1H, H4), 8.645 (dd, 1H, $J_{5,6} = 7.5$ Hz, $J_{5,7} = 1.5$ Hz,

H5): pmr of **6** (deuteriochloroform): δ 4.176 (ddd, 1H, $J_{1a,11b}$ = 4 Hz, $J_{1a,2}$ = 6 Hz, $J_{1a,3}$ = 1 Hz, H1a), 4.643 (d, 1H, $J_{1a,11b}$ = 4 Hz, H11b), 6.504 (dd, 1H, $J_{1a,2}$ = 6 Hz, $J_{2,3}$ = 9 Hz, H2), 7.031 (dd, 1H, $J_{1a,2}$ = 6 Hz, $J_{2,3}$ = 9 Hz, H2), 7.031 (dd, 1H, $J_{1a,3}$ = 1 Hz, $J_{2,3}$ = 9 Hz, H3), 7.330-7.697 (m, 2H, H6, H7), 7.741 (s, 2H, H9, H10), 7.887 (dd, 1H, $J_{6,8}$ = 6 Hz, H8), 8.093 (s, 1H, H11), 8.542 (s, 1H, H4), 8.645 (dd, 1H, $J_{5,6}$ = 7.5 Hz, $J_{5,7}$ = 1.5 Hz, H5).

The mixture of **1** and **6** in 300 ml of acetone was added to a solution of 10 g of sodium azide in 175 ml of water and 300 ml of acetone that has been adjusted to *p*H-8 with dilute (10%) sulfuric acid. The mixture was stirred at room temperature under argon for 24 hours. The acetone was removed under reduced pressure and the residue washed several times with water to yield 222 mg of pale yellow crystals that were separated by chromatography on alumina (activity III). A mixture of 20% ether and 80% hexane eluted mainly epoxide **1**. By raising the percentage of ether to 40%, there was eluted first 93 mg of **7** (yield 32% from **6**) followed by 48 mg of **2** and traces of **3**. Compound **7**, colorless crystals, mp 150-152° dec (from benzene-hexane); ir (nujol) 3200 (OH), 2105 cm^{-1} (N_3); 300 MHz pmr (deuteriochloroform): δ 4.356 (ddd, 1H, $J_{8,9}$ = 8.6 Hz, $J_{9,10}$ = 3 Hz, $J_{9,11}$ = 2 Hz, H9), 5.027 (d, 1H, $J_{8,9}$ = 8.6 Hz, H8, sharpens upon addition of deuterium oxide), 6.063 (dd, 1H, $J_{9,10}$ = 3 Hz, $J_{10,11}$ = 9.8 Hz, H10), 6.918 (dd, 1H, $J_{9,11}$ = 2 Hz, $J_{10,11}$ = 9.8 Hz, H11), 7.626 (td, $J_{1,3}$ = 1.1 Hz, $J_{2,3}$ = $J_{3,4}$ = 7.5 Hz, H3), 7.642 (td, 1H, $J_{1,2}$ = $J_{2,3}$ = 7.5 Hz, $J_{2,4}$ = 1.6 Hz, H2), 7.893 (dd, 1H, $J_{3,4}$ = 7.5 Hz, $J_{2,4}$ = 1.6 Hz, H4), 8.018 (s, 1H, H7), 8.402 (s, 1H, H12), 8.638 (dd, 1H, $J_{1,2}$ = 7.5 Hz, $J_{1,3}$ = 1.1 Hz, H1); ms: (70 eV, 180°) m/e (relative intensity) 244 [(M-N)$^+$, 22], 245 [(M-N_3)$^+$, 19], 244 ($C_{18}H_{12}O^{\cdot}$, 100), 228 ($C_{18}H_{12}^{\cdot}$, 31), 215 ($C_{17}H_{11}^+$, 75).

Anal. Calcd. for $C_{18}H_{13}N_3O$: C, 75.25; H, 4.56; N, 14.62. Found: C, 75.19; H, 4.77; N, 14.38.

1a,11b-Dihydrobenz[5,6]anthra[1,2-*b*]azirine (**9**).

To a stirred suspension of 100 mg of **7** in 250 ml of *n*-hexane was added under nitrogen 0.35 ml of tri-*n*-butylphosphine. The mixture was heated at 42° for 30 minutes, then cooled, and excess of starting material filtered off. The solvent was removed and the resulting pale yellow oil was crystallized from a mixture of dichloromethane and hexane. Recrystallization from the same mixture of solvents afforded 30 mg (35%) of **9**, mp 134-136°; 300 MHz pmr (deuteriochloroform): δ 3.692 (broad ddd, 1H, $J_{1a,2}$ = 2 Hz, $J_{1a,3}$ = 1 Hz, $J_{1a,11b}$ = 10 Hz, H1a), 4.746 (broad d, 1H, $J_{1a,11b}$ = 10 Hz, H11b), 5.993 (dd, 1H, $J_{1a,2}$ = 2 Hz, $J_{2,3}$ = 9 Hz, H2), 6.718 (dd, 1H, $J_{1a,3}$ = 1 Hz, $J_{2,3}$ = 9 Hz, H3), 7.587 (dd, 1H, $J_{6,5}$ = $J_{6,7}$ = 7.8 Hz, H6), 7.644 (dd, 1H, $J_{6,7}$ = $J_{7,8}$ = 7.8 Hz, H7), 7.734 (ABq, 2H, J_{AB} = 9.4 Hz, H9, H10), 7.846 (d, 1H, $J_{7,8}$ = 7.8 Hz, H8), 8.035 (s, 1H, H11), 8.347 (s, 1H, H4), 8.636 (d, 1H, $J_{5,6}$ = 7.8 Hz, H5); ms: (70 eV, 130°), m/e (relative intensity), 244 (MH$^+$, 98), 243 (M$^{\cdot}$, 100), 228 ($C_{18}H_{12}^{\cdot}$, 18), 216 ($C_{17}H_{12}^{\cdot}$, 42), 215 ($C_{17}H_{11}^+$, 67).

Anal. Calcd. for $C_{18}H_{13}N$: C, 88.86; H, 5.39; N, 5.76. Found: C, 89.08; H, 5.18; N, 6.00.

trans-8,9,10,11-Tetrahydro-8-(4-methyl)benzensulfonamidobenz[*a*]anthr-9-ol (**11**).

To a solution of 212 mg of **4** in 100 ml of dry tetrahydrofuran was added under exclusion of air and moisture 0.2 ml of *N,O*-bis(trimethylsilyl)-acetamide. The mixture was stirred for 2 minutes at 40° and then for 30 minutes at 25°. *p*-Toluenesulfonyl chloride (185 mg) was added and the temperature was raised to 40°. After 90 minutes the reaction mixture was cooled below room temperature, washed successively with 5% ammonia solution, 5% aqueous sodium bicarbonate and water. Upon addition of cold ether the resulting pale yellow oil afforded 262 mg (62%) of crystalline *trans*-8,9,10,11-tetrahydro-8-(4-methyl)benzenesulfonamido-9-[(trimethylsilyl)oxy]benz[*a*]anthracene (**10**), mp 170.5° (from ether); 300 MHz pmr (deuteriochloroform): δ 0.115 (s, 9H, $SiCH_3$), 1.903 (m, 1H, H10'), 2.117 (m, 1H, H10), 2.553 (s, 3H, $C_6H_4CH_3$), 2.93l (m, 1H, H11'), 3.234 (m, 1H, H11), 4.272 (m, 1H, H9), 4.350 (dd, 1H, $J_{8,9}$ = 6 Hz, $J_{8,NH}$ = 6.7 Hz, H8, decouples upon addition of deuterium oxide), 4.505 (d, 1H, $J_{8,NH}$ = 6.7 Hz, NH, disappears upon addition of deuterium oxide), 6.906 (s, 1H, H7), 7.349-7.904 (m, 9H, ArH), 8.356 (s, 1H, H12), 8.607 (d, 1H, $J_{1,2}$ = 8.2 Hz, H1); ms: (70 eV, 200°), m/e (relative intensity) 489 (M$^{\cdot}$, 10), 488 [(M-H)$^+$, 17], 320 [(M-$C_7H_7SO_2N$)$^{\cdot}$, 9], 319 [(M-$C_7H_7SO_2$-NH)$^+$, 30], 318 [(M-$C_7H_7SO_2NH_2$)$^{\cdot}$, 100], 245 ($C_{18}H_{14}N^+$, 10), 244 ($C_{18}H_{13}N^{\cdot}$, 17), 230 ($C_{18}H_{14}^{\cdot}$, 10), 229 ($C_{18}H_{13}^+$, 16), 228 ($C_{18}H_{12}^{\cdot}$, 34), 218 ($C_{17}H_{14}^{\cdot}$, 45), 217 ($C_{17}H_{13}^+$, 37), 91 ($C_7H_7^+$, 43), 73 ($SiC_3H_9^+$, 80).

When the reaction was repeated but the *warm* mixture was washed with 5% ammonia solution and with 5% warm aqueous sodium hydroxide, the resulting crystals proved to be silicon-free **11**; colorless crystals; mp 192-194° [from ether-hexane (20:1)], ir (nujol): 3495 (OH), 2160 cm^{-1} (NH); 300 MHz pmr (deuteriochloroform): δ 1.914 (m, 1H, H10'), 2.282 (m, 1H, H10), 2.489 (s, 3H, CH_3), 2.951 (broad s, 1H, OH, disappears with addition of deuterium oxide), 3.123 (m, 2H, H11, H11'), 3.992 (m, 1H, H9), 4.476 (dd, 1H, $J_{8,9}$ = 6.4 Hz, $J_{8,NH}$ = 8.2 Hz, H8, decouples with addition of deuterium oxide), 4.901 (d, 1H, $J_{8,NH}$ = 8.2 Hz, NH, disappears upon addition of deuterium oxide), 7.806 (s, 1H, H7), 7.309-7.963 (m, 9H, Ar), 8.322 (s, 1H, H12), 8.563 (d, 1H, J = 7.8 Hz, H1); ms: (70 eV, 200°) m/e (relative intensity) 418 (MH$^+$, 5), 417 (M$^{\cdot}$, 8), 416 (M-H$^+$, 26), 262 ($C_{18}H_{16}NO^+$, 16), 247 ($C_{18}H_{17}N^{\cdot}$, 20), 246 ($C_{18}H_{16}N^+$, 100), 245 ($C_{18}H_{15}$-N$^{\cdot}$, 15), 232 ($C_{17}H_{14}N^+$, 55), 230 ($C_{18}H_{14}^{\cdot}$, 14), 229 ($C_{18}H_{13}^+$, 11), 228 ($C_{18}H_{12}^{\cdot}$, 14), 218 ($C_{17}H_{14}^{\cdot}$, 72), 217 ($C_{17}H_{13}^+$), 216 ($C_{17}H_{12}^{\cdot}$, 22), 91 ($C_7H_7^+$, 29).

Anal. Calcd. for $C_{25}H_{23}NO_3S$: C, 71.92; H, 5.55; N, 3.35. Found: C, 71.94; H, 5.79; N, 3.35.

6b,7a,8,9-Tetrahydrobenzo[10,11]chryseno[1,2-*b*]oxirene (**12**).

Since the current syntheses of **12** [19] [21] proved to be low yielding, the following procedure was applied. A solution of 5 g of sodium bicarbonate in 120 ml of water was added to a solution of 3.0 g of *m*-chloroperbenzoic acid and 2.4 g of 9,10-dihydrobenzo[*a*]pyrene in 250 ml of dichloromethane. The mixture was stirred under nitrogen for 3.5 hours at room temperature. The organic layer was separated, washed with water, dried and concentrated. The residue was recrystallized from petroleum ether to yield 2.4 g (94%) of **12** which was identical in every respect with an authentic sample prepared according to Waterfall and Sims [19].

trans-7,8,9,10-Tetrahydro-7-azidobenzo[*a*]pyren-8-ol (**14**).

To a solution of 32 g of sodium azide in 300 ml of water and 500 ml of acetone was added 0.1 ml of concentrated sulfuric acid. After 15 minutes 1.0 g of **12** was added and the mixture stirred under nitrogen for 20 hours at room temperature. Evaporation of the acetone afforded 0.8 g of light tan crystals of mp 171-175°. Recrystallization from chloroform and from a benzene-hexane mixture gave 0.33 g (28%) of pure **14**, mp 181-183°; ir (nujol): 3400 (OH), 2105 cm^{-1} (N_3); 300 MHz pmr (deuteriochloroform): δ 2.206 (m, 1H, H9'), 2.228 (broad s, 1H, OH, disappears with addition of deuterium oxide), 2.449 (m, 1H, H9), 3.500 (m, 1H, H10'), 3.688 (m, 1H, H10), 4.25l (m, 1H, H8, signals sharpen upon addition of deuterium oxide), 4.864 (d, 1H, $J_{7,8}$ = 7 Hz, H7), 7.975-8.239 (m, 8H, ArH); no signals of the isomeric azido alcohol **15** could be detected [22]; ms: (70 eV, 120°), m/e (relative intensity), 313 (M$^{\cdot}$, 37), 285 [(M-N_2)$^{\cdot}$, 11], 271 [(M-N_3)$^+$, 20], 270 ($C_{20}H_{14}O^{\cdot}$, 17), 267 [(M-N_2-H_2O)$^{\cdot}$, 25], 255 ($C_{20}H_{15}^+$, 24), 254 ($C_{20}H_{14}^{\cdot}$, 40), 253 ($C_{20}H_{13}^+$, 42), 252 ($C_{20}H_{12}^{\cdot}$, 38), 242 ($C_{19}H_{14}^{\cdot}$, 53), 241 ($C_{19}H_{13}^+$, 100), 240 ($C_{19}H_{12}^{\cdot}$, 74), 239 ($C_{19}H_{11}^+$, 69).

Anal. Calcd. for $C_{20}H_{15}N_3O$: C, 76.66; H, 4.83; N, 13.41. Found: C, 76.60; H, 4.99; N, 13.22.

6b,7a,8,9-Tetrahydrobenzo[10,11]chryseno[1,2-*b*]azirine (**13**).

A solution of 108 mg of the previous azido alcohol and 0.18 ml of tri-*n*-butylphosphine in 250 ml degassed hexane was stirred for 20 hours at 25°. The solvent was decanted and the sticky colorless residue was washed with hexane and recrystallized from a mixture of benzene and hexane; yield 71 mg (76%); mp 107°; 300 MHz pmr (deuteriochloroform): δ 2.163 (m, 1H, H9'), 2.535 (m, 1H, H9), 3.499 (m, 1H, H8), 3.748 (m, 1H, H10), 4.111 (d, 1H, $J_{7,8}$ = 8.2 Hz, H7), 7.969-8.326 (m, 8H, ArH); ms: (70 eV, 150°) m/e (relative intensity) 269 (M$^{\cdot}$, 100), 268 [(M-H)$^+$, 34), 267 [(M-2H)$^{\cdot}$, 8], 254 ($C_{20}H_{14}^{\cdot}$, 17), 253 ($C_{20}H_{13}^+$, 41), 252 ($C_{20}H_{12}^{\cdot}$, 21), 243 ($C_{19}H_{15}^+$, 60), 242 ($C_{19}H_{14}^{\cdot}$, 51), 241 ($C_{19}H_{13}^+$, 47), 240 ($C_{19}H_{12}^{\cdot}$, 26), 239 ($C_{19}H_{11}^+$, 36), 228 ($C_{18}H_{12}^{\cdot}$, 10), 227 ($C_{18}H_{11}^+$, 12), 226 ($C_{18}H_{10}^{\cdot}$, 19).

Anal. Calcd. for $C_{20}H_{15}N$: C, 89.19; H, 5.61; N, 5.20. Found: C, 89.13; H, 5.61; N, 5.16.

trans-7,8,9,10-Tetrahydro-7-(4-methyl)benzensulfonylamido-8-[(trimethylsilyl)oxy]benzo[*a*]pyrene (**16**).

As for **10** a solution of 456 mg of **13** in 200 ml of dry tetrahydrofuran was treated under exclusion of air with 0.5 ml of *N,O*-bis(trimethylsilyl)-acetamide. After 2 minutes at 40° and 90 minutes at 25° 674 mg of *p*-toluenesulfonyl chloride was added. The reaction mixture was heated for 5 minutes at 40° and then allowed to cool to room temperature (40 minutes). The mixture was diluted with an equal volume of ether, washed successively with 5% ammonia solution, 5% aqueous sodium bicarbonate and water. The organic solution was dried (magnesium sulfate) and the solvent removed *in vacuo*. The resulting tan oil crystallized upon addition of chloroform to yield 416 mg (48%) of colorless **16**, mp 151° (from chloroform-heptane); ir (nujol) 3270 cm^{-1} (NH); 300 MHz pmr (deuteriochloroform): δ 0.051 (s, 9H, $SiCH_3$), 1.711 (m, 1H, H9'), 1.901 (m, 1H, H9), 2.511 (s, 3H, $C_6H_4CH_3$), 3.370 (m, 2H, H10, H10'), 4.383 (m, 1H, H8), 4.480 (dd, 1H, $J_{7,8}$ = 3.1 Hz, $J_{7,NH}$ = 6.3 Hz, H_7, decouples upon addition of deuterium oxide), 4.624 (d, 1H, $J_{7,NH}$ = 6.3 Hz, NH, disappears upon addition of deuterium oxide), 7.135 (s, 1H, H6), 7.354-8.163 (m, 10H, ArH), 8.237 (d, 1H, J = 9 Hz, H11); ms: (70 eV, 200°) m/e (relative intensity) 513 ($M^{\cdot}$, 16), 512 [(M-H)$^+$, 42], 344 [(M-$C_7H_7SO_2N$)$^{\cdot}$, 9], 343 [(M-$C_7H_7SO_2NH$)$^+$, 31], 342 [(M-$C_7H_7SO_2NH_2$)$^{\cdot}$, 100], 269 ($C_{20}H_{15}N^{\cdot}$, 12), 268 ($C_{20}H_{14}N^+$, 36), 253 ($C_{20}H_{13}^+$, 22), 252 ($C_{20}H_{12}^{\cdot}$, 45), 242 ($C_{19}H_{14}^{\cdot}$, 65), 241 ($C_{19}H_{13}^+$, 60), 240 ($C_{19}H_{12}^{\cdot}$, 23), 239 ($C_{18}H_{11}^+$, 23), 73 ($SiC_3H_9^+$, 42).

Anal. Calcd. for $C_{30}H_{31}NO_3SSi$: C, 70.13; H, 6.08; N, 2.73. Found: C, 69.60; H, 6.40; N, 2.91.

When the above reaction mixture was washed initially with water instead of ammonia and sodium bicarbonate, the acidic medium caused instantanious cleavage of the *N*-tosyl group leading after neutralization and recrystallization from chloroform-hexane to colorless crystals of 7,8,9,10-tetrahydro-7-amino-8-[(trimethylsilyl)oxy]benzo[*a*]pyrene (**17**) admixed with traces of **16**, mp 221°; ir (nujol) 3390, 3270, 1600 cm^{-1} (NH_2); 300 MHz pmr (deuteriochloroform): δ 0.036 (s, 9H, $SiCH_3$), 1.821 (m, 1H, H9'), 2.304 (m, 1H, H9), 3.364 (dist t, 2H, J = 6.6 Hz, H10, H10'), 4.425 (m, 1H, H8), 4.487 (m, 1H, H7, turns into d upon addition of deuterium oxide, $J_{7,8}$ = 4.7 Hz), 7.349-8.499 (m, 8H, ArH), 9.070 (broad s, 2H, NH_2, disappears upon addition of deuterium oxide); ms: (70 eV, 200°) m/e (relative intensity) 359 ($M^{\cdot}$, 5), 343 [(M-NH_2)$^+$, 24], 342 [(M-NH_3)$^{\cdot}$, 100], 270 ($C_{20}H_{16}N^+$, 9), 269 ($C_{20}H_{15}N^{\cdot}$, 15), 268 ($C_{20}H_{14}N^+$, 8), 253 ($C_{20}H_{13}^+$, 16), 252 ($C_{20}H_{12}^{\cdot}$, 27), 243 ($C_{19}H_{15}^+$, 34), 242 ($C_{19}H_{14}^{\cdot}$, 29), 241 ($C_{19}H_{13}^+$, 25), 240 ($C_{19}H_{12}^{\cdot}$, 12), 239 ($C_{19}H_{11}^+$, 16), 73 ($SiC_3H_9^+$, 22).

When the above reaction mixture of **13**, bis(trimethylsilyl)acetamide and tosyl chloride in tetrahydrofuran was heated with 5% sodium hydroxide at 35° followed by washing with water the resulting brown oil crystallized upon addition of chloroform and heptane to yield 36% of cream colored **18**, mp 174°; ir (nujol) 3480 (OH), 3280 cm^{-1} (NH); 300 MHz pmr (deuteriochloroform): δ 1.604 (m, 1H, H9'), 1.760 (br s, 1H, OH, disappears upon addition of deuterium oxide), 1.977 (m, 1H, H9), 3.322 (m, 1H, H10'), 3.483 (m, 1H, H10), 4.061 (m, 1H, H8), 4.660 (dd, 1H, $J_{7,8}$ = 7.5 Hz, $J_{7,NH}$ = 8.2 Hz, H7), 5.228 (d, 1H, $J_{7,NH}$ = 8.2 Hz, NH, disappears with addition of deuterium oxide), 7.266-8.104 (m, 12H, ArH); ms: (70 eV, 270°) m/e (relative intensity 442 (MH^+, 9), 441 ($M^{\cdot}$, 28), 271 ($C_{20}H_{17}N^{\cdot}$, 28), 270 ($C_{20}H_{16}N^+$, 100), 269 ($C_{20}H_{15}N^{\cdot}$, 28), 256 ($C_{19}H_{14}N^+$, 10), 254 ($C_{20}H_{14}^{\cdot}$, 17), 253 ($C_{20}H_{13}^+$, 26), 252 ($C_{20}H_{12}^{\cdot}$, 30), 242 ($C_{19}H_{14}^{\cdot}$, 53), 241 ($C_{19}H_{13}^+$, 61), 240 ($C_{19}H_{12}^{\cdot}$, 25), 239 ($C_{19}H_{11}^+$, 39), 170 ($C_7H_7SO_2NH^+$, 22), 169 ($C_7H_7SO_2N^{\cdot}$, 15), 155 ($C_7H_7SO_2^+$, 29), 91 ($C_7H_7^+$, 99).

Acknowledgement.

We are grateful to the Israel Cancer Association for financial support of this study.

REFERENCES AND NOTES

[1] J. Blum, Y. Ittah and I. Shahak, *Tetrahedron Letters*, 4601 (1975).

[2] Y. Ittah, I. Shahak and J. Blum, *J. Org. Chem.*, **43**, 397 (1978).

[3] Y. Ittah, Y. Sasson, I. Shahak, S. Tsaroom and J. Blum, *ibid.*, **43**, 4271 (1978).

[4] J. Blum, I. Yona, S. Tsaroom and Y. Sasson, *ibid.*, **44**, 4178 (1979).

[5] M. Weitzberg, Z. Aizenshtat, P. Jerushalmy and J. Blum, *ibid.*, 4252 (1980).

[6] I. Yona and J. Blum, *Org. Prep. Proced. Int.*, **13**, 109 (1981).

[7] I.Yona and J. Blum, *J. Heterocyclic Chem.*, **18**, 1473 (1981).

[8] Ames test for mutagenic potencies were carried out by F. Oesch, Institute of Pharmacology, University of Mainz, Mainz, West Germany.

[9] Tests for carcinogenic activities on the back skin of NMRI mice were carried out by E. Hecker, The German Center for Cancer Research, Institute of Biochemistry, Heidelberg, West Germany.

[10] P. P. Fu, R. G. Harvey and F. A. Beland, *Tetrahedron*, **34**, 857 (1978).

[11] M. Weitzberg, D. Avnir, Z. Aizenshtat and J. Blum, *J. Heterocyclic Chem.*, **20**, 1019 (1983).

[12] H. Yagi and D. M. Jerina, *J. Am. Chem. Soc.*, **97**, 3185 (1975).

[13] P. P. Fu and R. G. Harvey, *Chem. Rev.*, **78**, 317 (1978).

[14] M. Weitzberg, Z. Aizenshtat and J. Blum, *J. Heterocyclic Chem.*, **18**, 1513 (1981).

[15] The synthesis of "pure" **5** has been reported [16] [17], but neither elemental analysis nor convincing spectral data for this compound are given in the literature.

[16] P. Sims, *Biochem. J.*, **125**, 159 (1971).

[17] P. P. Fu, D. Cortez, K. B. Sukumaran and R. G. Harvey, *J. Org. Chem.*, **44**, 4265 (1979).

[18] J. F. Klebe, H. Finkbeiner and D. M. White, *J. Am. Chem. Soc.*, **85**, 3390 (1966).

[19] J. F. Waterfall and P. Sims, *Biochem. J.*, **128**, 265 (1972).

[20] When the reaction was carried out on a larger scale than 0.5 g of **1** the yield of **6** dropped and the ratio of **1:6** increased.

[21] H. Yagi and D. M. Jerina, *J. Am. Chem. Soc.*, **97**, 3185 (1975).

[22] W. C. Herndon, *Tetrahedron Letters*, **22**, 983 (1981).