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Synthesis of Phenanthrene-9,10-imine Tosylate.[1] A Stable Arene Imine

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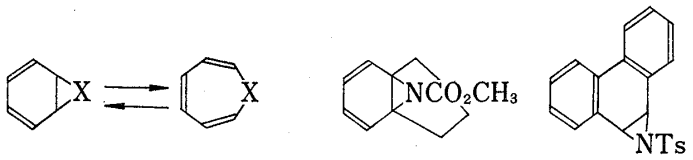
Phenanthrene-9,10-imine tosylate was prepared from phenanthrene-9,10-oxide. The chemical behavior was descrived.

Norcaradiene-cycloheptatriene (**1a**⇄**2a**) and benzene oxide-oxepine (**1b**⇄**2b**) systems have been the subjects of recent organic chemistry.[3] In particular, the epoxides of aromatic systems have been the focus of considerable interest due to the theoretical and biological relevance.[4] The analog of **1a, b** in which nitrogen replaces the carbon or oxygen atom, the benzene imine system (**1c**), is believed to exist as a transient species in the reaction of aromatic compounds and nitrenes.[5] In a special case, where the position 1 and 6 are bridged by a trimethylene carbon, the benzene imine (**3**) can be observed.[6] We wish to report the synthesis of a simple stable arene imine derivative, phenanthrene-9,10-imine tosylate (**4**).

Nucleophilic ring opening of phenanthrene oxide (**5**)[7] by sodium azide in aqueous acetone yielded *trans*-9-azido-10-hydroxy-9,10-dihydrophenanthrene (**6**). The *trans* configuration was confirmed by nuclear magnetic resonance (NMR). Even mild tosylation of **6** gave 9-azidophenanthrene (**7**). Lithium aluminum hydride reduction of **6** in ether gave an amino alcohol (**8**). Reaction of **8** with excess tosyl chloride gave 9-tosylaminophenanthrene (**9**), which is identical with the tosylate of 9-aminophenanthrene.[8] When an equimolar tosyl chloride was used, a monotosylate (**10**) could be obtained. Treatment of the tosylate **10** in tetrahydrofuran with excess sodium hydride, followed by excess tosyl chloride produced a mixture of reaction products. Careful separation by preparative thin-layer chromatography (TLC) and recrystallization gave a white crystalline compound (**4**) as the major product.

The NMR of the imino tosylate (**4**) shows no evidence of the existence of the tautomeric isomer (azepine) and 9-tosylaminophenanthrene (**9**). The imino tosylate is stable at 100°,



1 **2** **3** **4**

a : X=CH_2 **c** : X=NR
b : X=O

Chart 1

1) Studies on Carcinogenic Functional Groups, Part VI. See the previous papers, T. Okamoto, K. Shudo, and S. Nagata, *Chem. Pharm. Bull.* (Tokyo), **23**, 687 (1975); T. Okamoto, K. Shudo, and T. Ohta, *J. Am. Chem. Soc.*, **97**, 7184 (1975).
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3) E. Vogel and H. Gunther, *Angew. Chem.*, **79**, 429 (1967); L.A. Paquette, *ibid.*, *Internat. Ed.*, **10**, 11 (1971).
4) D.M. Jerina and J.W. Daly, *Science*, **185**, 573 (1974), and references cited therein.
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6) L.A. Paquette, D.E. Kuhla, J.H. Barett, and R.J. Haluska, *J. Org. Chem.*, **34**, 2866 (1969).
7) M.S. Newman and S. Blum, *J. Am. Chem. Soc.*, **86**, 5559 (1964).
8) *Beil.* **12**, 1338. Library of Infrared Spectra, Aldrich, 558B.

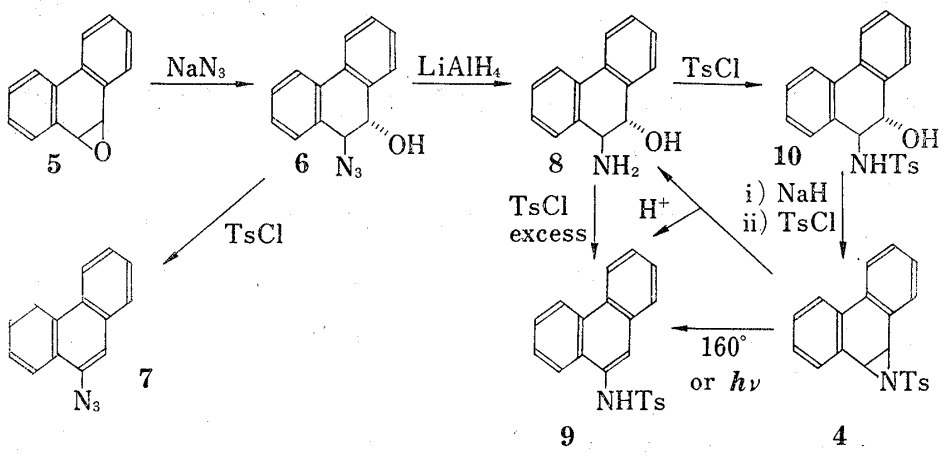

Chart 2

but was converted to 9-tosylaminophenanthrene at 160°. Treatment of **4** in aqueous acetone with 2% trifluoroacetic acid, led to a mixture of **9** and **10**. These chemical reactions correspond to the reactivity of phenanthrene oxide.[7] Photolysis of **4** gave **9** as the only isolable product.[9] We are trying to identify the minor components.

Experimental

***trans*-9-Azide-10-hydroxy-9,10-dihydrophenanthrene (6)**——A solution of 2 g of phenanthrene oxide (**5**)[7] and sodium azide (3 g) in acetone (40 ml) and H_2O (30 ml) was refluxed for 8.5 hr. Evaporation of acetone under a reduced pressure gave crystalline precipitates, 2.3 g. Recrystallization from aqueous acetone gave colorless needles, mp 142—143°. IR ν_{max}^{KBr}: 2130 cm^{-1} (N_3). NMR ($CDCl_3$, δ); 4.52 and 4.68 (J=8 cps). *Anal.* Calcd. for $C_{14}H_{11}ON_3$ C, 70.87; H, 4.67; N, 17.71. Found: C, 71.09; H, 4.70; N, 18.00.

9-Azidophenanthrene (7)——To a solution of 254 mg of **6** was added TsCl (300 mg) and the mixture was left at room temperature for 7 hr. Water was added and the mixture was extracted with $CHCl_3$. $CHCl_3$ was washed with dil HCl, and H_2O, dried over Na_2SO_4 and evaporated under a reduced pressure. Though a small amount of the starting material (**6**) was observed on TLC, recrystallization from methanol gave pure straw colored needles, mp 112—113°, 188 mg. IR ν_{max}^{KBr}: 2110 cm^{-1} (N_3). *Anal.* Calcd. for $C_{14}H_9N_3$, C, 76.69; H, 4.14; N, 19.17. Found: C, 76.70; H, 4.11; N, 19.31.

***trans*-9-Amino-10-hydroxy-9,10-dihydrophenanthrene (8)**——To an ethereal solution of **6** (450 mg) was added 300 mg of $LiAlH_4$, and the mixture was stirred for 2 hr at room temperature. Excess hydride was decomposed by wet ether and precipitates were removed by filtration. The ether was evaporated to give 95 mg of almost pure white needles. The precipitates was extracted with hot ethyl acetate to give 150 mg of crude product. Recrystallization from CH_2Cl_2–hexane gave needles, mp 125—126°. *Anal.* Calcd. for $C_{14}H_{13}ON$, C, 79.59; H, 6.20, N, 6.63. Found: C, 79.42; H, 6.18; N, 6.68.

9-Tosylaminophenanthrene (9)——To a solution of 30 mg of **8** in 1 ml of pyridine was added 100 mg of TsCl. The mixture was allowed to stand at 10° for 15 hrs. Water was added and the mixture was worked up as the preparation of **7**. The crude product, which was almost pure, judged from TLC, was recrystallized from ethanol to afford 18 mg of prisms. Sometimes needles were obtained. They were different crystals, but interconvertible by recrystallization with seeding of the crystals, mp 198—199° (both needles and prisms show the same melting point). *Anal.* Calcd. for $C_{21}H_{17}O_2NS$, C, 72.61; H, 4.93; N, 4.03. Found: C, 72.29; H, 4.96; N, 4.08.

***trans*-9-Hydroxy-10-tosylamino-9,10-dihydrophenanthrene (10)**——One hundred miligrams of amino alcohol (**8**) was dissolved in 5 ml of tetrahydrofuran (THF) and 0.1 ml of pyridine. TsCl (100 mg) was added to the solution and the mixture was left for 24 hr at room temperature. Work up as above, and recrystallization from CH_2Cl_2–ethanol gave prisms, mp 196—197° (80 mg). The analytical sample was dried at 100°. NMR ($CDCl_3$, δ); 4.45 and 4.63 (J=7.5 cps.) (after deuteration of hydroxyl). *Anal.* Calcd. for $C_{21}H_{19}O_3NS$, C, 69.03, H, 5.24; N, 3.83. Found: C, 68.63; H, 5.27; N, 3.68.

9,10-Dihydro-9,10-tosyliminophenanthrene (4)——To a solution of tosylate **10**, (590 mg, 1.63 mmoles) in anhydrous THF (30 ml) was added sodium hydride (118 mg, 4.8 mmoles). After the completion of evolution of hydrogen gas, solid TsCl (934 mg, 4.8 mmoles) was added to the solution. The mixture was stirred

9) *Cf.* The photolysis of phenanthrene oxide, N.E. Brightwell and G.W. Griffin, *Chem. Commun.*, **1973**, 37; K. Shudo and T. Okamoto, *Chem. Pharm. Bull.* (Tokyo), **21**, 2809 (1973).

at 15° for 24 hrs. Though TLC of the reaction mixture showed the presence of unreacted starting material (about 1/3), a small amount of H_2O was added to decompose the excess TsCl (3 hr). After addition of H_2O, the mixture was extracted with CH_2Cl_2, CH_2Cl_2 was washed with aq. K_2CO_3, aq. NaCl and aq. K_2CO_3, and evaporated. The mixture was purified by preparative TLC (Kiesel gel G, PF_{254}, Merck) multiply developed by hexane–CH_2Cl_2 (9: 1) for 5 times. The major band was extracted with CH_2Cl_2–CH_3OH (2: 1) to give 300 mg of crude crystalline product. Recrystallization from CH_2Cl_2–EtOH gave needles, which showed double melting points, mp 95—105° and 170—171°. Analytical sample was recrystallised from AcOEt, prisms, mp 168—171°. IR ν_{max}^{KBr} cm^{-1}: 1595, 1493, 1457, 1392, 1321, 1152, 1090, 1019, 887, 832, 785, 744, 715, 668, (prisms, anhydrous). NMR ($CDCl_3$, δ): 2.37 (CH_3), 4.44 (2H, 9 and 10). UV_{max} (95% EtOH, log ε): 232 (sh. 4.49), 267 (4.16), 275 (sh. 4.19), 276 (4.21), 290 (4.03). *Anal.* Calcd. for, $C_{21}H_{17}O_2NS$: C, 72.61; H, 4.93; N, 4.03. Found: C, 72.44; H, 4.94; N, 3.85. From a more polar band, the crude starting compound, 110 mg, was recovered.

Thermal Isomerization of 4——The imine (5 mg) was heated in a sealed tube at 165° for 1 hr. Quantitative isomerization was observed on TLC, and the product was recrystallised from EtOH and identified with **9** by mixed mp measurements and infrared (IR) spectral comparison.

Acid Hydrolysis of 4——The imine (**4**, 20 mg) was dissolved in 70% acetone (3 ml), and 60 μl (2%) of CF_3CO_2H was added. The mixture was allowed to stand for 30 min. The mixture was evaporated at 40°. The residue was dissolved in CH_2Cl_2, and applied to a silica gel column (10 ml, Waco gel C-200). The fastest moving part (6 mg) was recrystallized from EtOH to give pure **9**. The main part (14 mg) was also recrystallized from EtOH to give **10**. These products were fully identified with authentic samples obtained above.

Photolysis of 4——The imine in acetonitrile (7 mg in 4 ml) was irradiated with ultraviolet light (275 nm). The major product isolated by TLC was 9-tosyliminophenanthrene (2.5 mg, **9**), which was identified with a sample obtained above.