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Preparation of 1,2-Diaminopyrene via a 1,2,5-Thiadiazole Route[1)]

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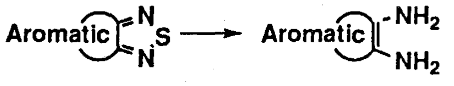
1,2-Diaminopyrene hydrochloride was prepared by the reduction of pyreno[1,2-c]-1,2,5-thiadiazole with tin powder in concentrated hydrochloric acid in 38 % yield.

Introduction

In our search for a light-emitting material suitable for an electroluminescent display[2-6)], our attention was directed to pyrene derivatives, as pyrene is strongly fluorescent. 1,2-Diaminopyrene is a useful starting compound for heterocycle-annelated pyrenes, which are expected to exhibit deeper-colored fluorescence than pyrene itself.

Recently, the authors have developed a preparative method for aromatic vicinal diamines by reduction of 1,2,5-thiadiazolo aromatics.[7-11)]

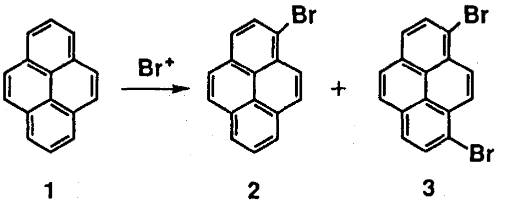


The present paper describes the preparation of 1,2-diaminopyrene by applying the preparative method mentioned above.

Results and Discussion

Pyrene (1) is reactive towards electrophilic reagents at the 1-, 3-, 6- and 8-positions and 1-substituted pyrenes are readily available by direct electrophilic substitution. However, 1-bromopyrene (2)[13)] was obtained with dibrominated pyrene 3 as a by-product in the reactions as will be described below (Scheme 1 and Table 1).

When a bromination reaction of pyrene (1) with bromine was carried out in tetrachloromethane under reflux for 6 h, a mixture of unreacted pyrene, 1-bromopyrene (2)[12)] and dibromopyrene 3 was produced in a ratio of 3:70:27. Alumina-supported copper (II) bromide ($CuBr_2/Al_2O_3$) was less satisfactory in the reaction in tetrachloromethane. A mixture containing starting pyrene 1, monobromopyrene 2 and dibromo-



Scheme 1

Table 1. Bromination of pyrene (1)

Reagent /solvent	Temp. (Time)	Rel.Yield 2/(1+3) (%)
Br_2	0-2 ℃(20 min)	70/(3+27)
$/CCl_4$	then rt (6 h)	
$CuBr_2$-Al_2O_3	rt (2 h)	64/36
$/CCl_4$	80 ℃ (2 h)	64/36
$BTMABr_3$	rt (2 h)	81/19
$/CH_2Cl_2$	0-5 ℃ (5 h)	85/(6+9)

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Dedicated to Professor Hitoshi Takeshita on the occasion of his retirement.

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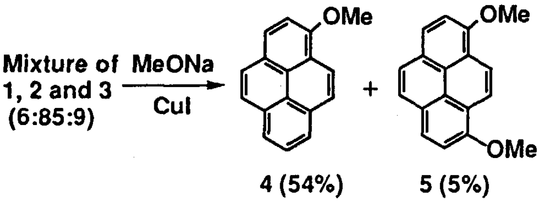
pyrene 3 was formed and the relative yield of the desired 1-bromopyrene (2) was 64%.

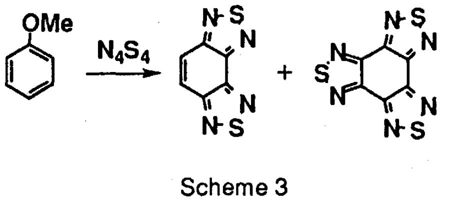
Recently, benzyltrimethylammonium tribromide ($BTMABr_3$) has been recognized as a convenient, easy-to-handle brominating reagent.[14-16] The reagent brominated pyrene (1) in dichloromethane at 0-5 ℃. When an equivalent amount of the reagent was used, the relative yield of 1-bromopyrene (2) in the reaction product rose to 85%. As it was difficult to isolate pure 2 from the reaction mixture in a ten-gram scale, the substitution reaction of the bromo atom with a methoxyl group was carried out using the bromination reaction mixture obtained above. The desired 1-methoxypyrene (4)[17] was obtained in 54% yield when the bromination reaction products prepared above were treated with a 10-fold excess of sodium methoxide in dry N,N-dimethylformamide under reflux in the presence of CuI (Scheme 2). In the reaction, pyrene (1) was recovered in 2% yield and dimethoxypyrene 5 was isolated in 5% yield. The ^1H NMR spectrum disclosed the 1,8-disubstituted structure of 5; protons at the 4- and 5-positions of the pyrene ring were observed as a singlet at $\delta = 7.70$ ppm, while the singlet at a low magnetic field ($\delta = 8.34$ ppm) was assigned to protons at the 9- and 10-positions next to the methoxyl groups.



Scheme 2

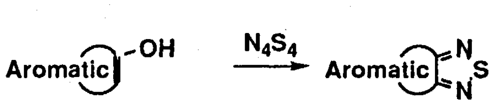
From the above results, it is highly probable that in the bromination of 1 with $BTMABr_3$, the second bromo atom is introduced on the carbon atom of the 8-position of monobromopyrene 2.

It was earlier reported that, though yields are very poor, benzo[1,2-c][3,4-c']bis- and benzo[1,2-c][3,4-c'][5,6-c"]tris-1,2,5-thiadiazole were formed in the reaction of methoxybenzene with tetrasulfur tetranitride (N_4S_4)[18] (Scheme 3). The reactions of methoxypyrene 4 and 5 with tetrasulfur tetranitride were disappointing and gave no 1,2,5-thiadiazolo product.

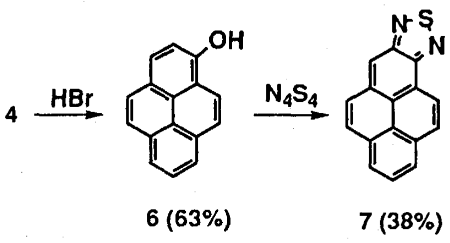


Scheme 3

The reaction of tetrasulfur tetranitride with hydroxyl-substituted aromatic compounds has been well documented as a 1,2,5-thiadiazole-ring formation method.[19-23]

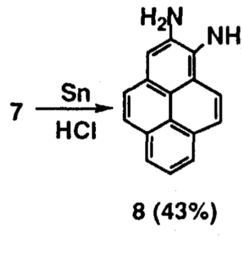


Thus, the methyl ether linkage of 4 was cleaved according to the method reported; the treatment of 4 with 47% hydrobromic acid in acetic acid under reflux gave the desired 1-hydroxypyrene (6)[24] in 63% yield. The reaction of 6 with tetrasulfur tetranitride in toluene under reflux gave the expected pyreno[1,2-c]-1,2,5-thiadiazole (7) in 38% yield. Use of twice the amount of tetrasulfur tetranitride did not increase the yield of 7 (Scheme 4).



Scheme 4

The titled 1,2-diaminopyrene (8) was obtained in 43% yield as a form of hydrochloride 8•HCl when 7 was reduced with tin powder in a mixture of dioxane and concentrated hydrochloric acid (Scheme 5).



Scheme 5

In conclusion, 1,2-diaminopyrene (8) is accessible from pyrene (1) via a sequence of bromination, cleavage reaction of the methyl ether linkage, reaction with tetrasulfur tetranitride and reduction of the 1,2,5-thiadiazole ring.

Experimental Section

General. All melting points were determined on a Mitamurariken Melt Thermo and are uncorrected. The

IR spectra were measured as KBr pellet on a Nippon Bunko IR-700. The ^{1}H NMR spectra were recorded at 270 MHz with a JEOL GSX-270 using TMS as an internal standard. The mass spectra were obtained on a JEOL JMS-01-SG-2 mass spectrometer at 75 eV using a direct inlet system. Column chromatography was carried out on silica gel (Wako gel, C-300).

Bromination of 1 with benzyltrimethylammonium tribromide.

BTMABr$_3$ (10.45 g, 26.8 mmol) was added gradually to a solution of **1** (4.94 g, 24.4 mmol) in dichloromethane (200 ml) at room temperature for 10 min and the reaction mixture was stirred at room temperature for 5 h. The reaction mixture was washed with saturated sodium hydrogen carbonate and water, dried over magnesium sulfate and evaporated in vacuo, leaving a solid residue (5.13 g, mp 89-92 ℃) which was analyzed by gas chromatography to contain 1-bromopyrene (**2**) in 84%.

1-Methoxypyrene (4) and 1,8-dimethoxypyrene (5).

A mixture of crude 1-bromopyrene (**2**) (15.0 g) prepared by the procedure mentioned above, sodium methoxide (28.8 g, 534 mmol), CuI (11.2 g) in dry N,N-dimethylformamide (250 ml) was heated under reflux for 24 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature and filtered. The filtrate was poured into water, neutralized with dilute hydrochloric acid and extracted with dichloromethane. The extract was washed with water, dried over magnesium sulfate, and evaporated in vacuo to leave a residue, which was chromatographed. From the first fraction, **1** (0.79 g) was recovered. 1-Methoxypyrene (**4**) (8.58 g) was obtained from the second fraction and recrystallized from hexane, giving 6.7 g of a pure sample of **4**; mp 89-91 ℃ (mp lit.[17] 88-90℃). The last fraction gave dimethoxypyrene **5** (0.99 g), which was recrystallized from hexane/benzene (2/1), giving pale yellow needles (0.72 g) of mp 188-193 ℃; IR 3025, 2950, 2925, 2840, 1595, 1510, 1495, 1425, 1260, 1250, 1224, 1167, 1142, 1122, 1025, 835 cm^{-1}; ^{1}H NMR δ = 4.10 (6H, s), 7.50 (2H, d, J = 10 Hz), 7.70 (2H, s), 7.96 (2H, d, J = 10 Hz), 8.34 (2H, s); MS m/z 262 (M$^+$). Found: C, 82.55; H, 5.47. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.76.

1-Hydroxypyrene (6).

A mixture of **5** (10 g, 43 mmol), hydrobromic acid (47%, 30 ml) and acetic acid (100 ml) was heated under reflux for 9 h. After the reaction mixture was cooled to room temperature, insoluble materials were filtered and dissolved in ether. The ether solution was dried over magnesium sulfate and evaporated in vacuo to leave a residue, which was washed well with benzene to give **6**. The washing was chromatographed eluting with chloroform. After unchanged **5** (0.40 g, 4%) was eluted, 1-hydroxypyrene (**6**) was obtained. Recrystallization from chloroform gave **6** (5.9 g) of mp 180-184 ℃ (lit.[24] 179℃); Found: C, 87.77; H, 4.95. Calcd for $C_{16}H_{10}O$: C, 88.05; H, 4.61.

Pyreno[1,2-c]-1,2,5-thiadiazole (7).

A mixture of **6** (0.5 g, 2.29 mmol) and tetrasulfur tetranitride (0.47 g, 2.52 mmol) in toluene (20 ml) was heated under reflux for 24 h. After the reaction mixture was cooled to room temperature, insoluble materials were filtered. The filtrate was evaporated in vacuo to leave a residue, which was chromatographed. Sulfur was eluted with hexane, then pyreno[1,2-c]-1,2,5-thiadiazole (**7**) was obtained from the fraction eluted with hexane/benzene (2/1). Recrystallization from ethanol/toluene (9/1) gave **7** (0.22 g, 38%) as brown plates, mp 180-183 ℃; IR 3050, 1590, 1490, 1475, 1440, 1395, 1370, 1335, 1280, 1235, 1175, 1145, 910, 860, 850, 840, 825, 760 cm^{-1}; ^{1}H NMR δ = 7.95 (2H, d, J = 8 Hz), 8.0-8.3 (3h, m), 8.38 (1H, s), 9.12 (2H, d, J = 8 Hz); MS m/z 260 (M$^+$). Found: C, 73.34; H, 3.53; N, 10.56. Calcd for $C_{16}H_8N_2S$: C, 73.82; H, 3.10; N, 10.76.

1,2-Diaminopyrene hydrochloride (8 HCl).

A mixture of **7** (0.20 g, 0.77 mmol), powdered tin (0.90 g, 7.7 mmol), concentrated hydrochloric acid (5 ml) and dioxane (10 ml) was heated under reflux for 6 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature and filtered, giving 1,2-diaminopyrene hydrochloride (**8** HCl). Purification by reprecipitation from ethanol solution by an addition of hexane gave **8** HCl (0.09 g, 43%); IR 3425, 3360, 3255, 2850, 1660, 1620, 1570, 1500, 1490, 1440, 1410, 1380, 1320, 1300, 1260, 880, 840, 820, 750, 720 cm-1. Found: C, 71.05; H, 4.51; N, 10.41. Calcd for $C_{16}H_{12}N_2Cl$: C, 71.51; H, 4.99; N, 10.32.

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