Synthesis of 1,2- and 1,7-Disubstituted Pyrenes

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Owing to the very weak interaction of the nitro group with the aromatic system in 2-nitropyrene, acetoxylation and nitration afford considerable amounts of 1,2- next to 1,7-disubstituted products.

Nitropyrenes are important environmental contaminants. In an earlier paper[1] we have described the preparation of the three nitropyrenes and reported on their spectroscopic, thermal, and photochemical properties. 1-Nitropyrene was found to be very sensitive to light: upon irradiation it is efficiently converted into a mixture of 1-hydroxypyrene (88%) and 1-hydroxy-2-nitropyrene† (7%). 1-Hydroxy-2-nitropyrene, a potent mutagen,[2] may therefore occur in polluted

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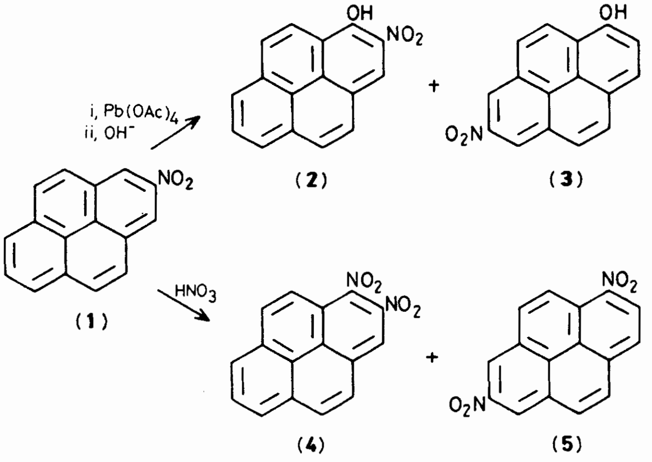
† In ref. 2, the minor photoproduct was described as 1-nitro-2-hydroxypyrene; its spectral data indicate, however, that it is identical with 1-hydroxy-2-nitropyrene.

air. In order to detect 1-hydroxy-2-nitropyrene quantitatively and to study its biological properties the pure compound must be available in sufficient quantities. The photochemical preparation is not practicable for large amounts, nor is 1-hydroxy-2-nitropyrene available *via* direct nitration of 1-hydroxypyrene.[1]

We now report that the readily available 2-nitropyrene (**1**) can be converted with lead tetra-acetate in refluxing acetic acid–dichloromethane (5 : 1) into 1-acetoxy-2-nitropyrene and 1-acetoxy-7-nitropyrene (1 : 1.7) in 38% yield. After hydrolysis of the acetoxy-compounds, the resulting 1-hydroxy-2-nitropyrene (**2**)‡ and 1-hydroxy-7-nitropyrene (**3**)‡ were easily separated by chromatography on silica; compound (**2**), owing to its internal hydrogen bond, has a much higher R_f value than (**3**).

The relatively easy electrophilic substitution at a position *ortho* to a nitro group is remarkable because usually the deactivating nitro group directs the substitution towards another ring in the polycyclic hydrocarbon. In order to examine further the reactivity of 2-nitropyrene towards electrophilic substitution, we treated (**1**) with concentrated nitric acid in dichloromethane. Two novel compounds could be isolated: 1,2-dinitropyrene (**4**) (38%) and 1,7-dinitropyrene (**5**)‡ (57%). The fact that the nitro group at position 2 hardly deactivates position 1 towards electrophilic substitution is nicely in agreement with the weak interaction of the nitro group and the aromatic system of (**1**), revealed by its spectroscopic properties.[1] It is to be expected that 1,2- and 1,7-dinitropyrene occur in the environment as a result of nitration of the ubiquitous 2-nitropyrene[3] with NO_x or nitric acid.



The peculiar reactivity of 2-nitropyrene may provide a clue to understanding the chemical and biological properties of nitro aromatic systems and it will allow the preparation of other hitherto unknown pyrene derivatives.

Received, 25th March 1987; Com. 381

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‡ *N.m.r. and mass spectral data:* (**2**), ^{1}H n.m.r. (300 MHz, $CDCl_3$, $SiMe_4$, J in Hz) δ: 7.83 (d, 1H, H-5, J 9.1), 7.87 (d, 1H, H-4, J 9.1), 8.04 (t, 1H, H-7, J 7.8), 8.09 (dd, 1H, H-6, J 7.8, 1.7), 8.12 (d, 1H, H-9, J 9.1), 8.55 (d, 1H, H-10, J 9.1), 8.15 (dd, 1H, H-8, J 7.8, 1.7), 8.72 (s, 1H, H-3), 11.59 (s, 1H, OH); m/z ($C_{16}H_9NO_3$): calc. 263.0582; found: 263.0591. (**3**), ^{1}H n.m.r. (300 MHz, CD_3COCD_3, $SiMe_4$, J in Hz) δ: 2.9 (br s, OH), 7.78 (d, 1H, H-2, J 8.3), 8.10 (d, 1H, H-4/5, J 9.0), 8.19 (d, 1H, H-5/4, J 9.0), 8.24 (d, 1H, H-9, J 9.2), 8.25 (d, 1H, H-3, J 8.3), 8.57 (d, 1H, H-10, J 9.2), 8.91 (s, 2H, H-6,8); m/z ($C_{16}H_9NO_3$): found: 263.0593. (**4**), ^{1}H n.m.r. (300 MHz, $CDCl_3$, $SiMe_4$, J in Hz) δ: 8.06 (d, 1H, H-10, J 9.2), 8.22 (d, 1H, H-4, J 9.0), 8.26 (t, 1H, H-7, J 8.0), 8.37 (d, 1H, H-5, J 9.0), 8.38 (d, 1H, H-9, J 9.2), 8.41 (d, 1H, H-8/6, J 8.0), 8.44 (d, 1H, H-6/8, J 8.0), 8.87 (s, 1H, H-3); m/z ($C_{16}H_8N_2O_4$): calc. 292.0484; found 292.0481. (**5**), ^{1}H n.m.r. (300 MHz, $CDCl_3$, $SiMe_4$, J in Hz) δ: 8.28 (d, 1H, H-4/5, J 9.0), 8.34 (d, 1H, H-3, J 8.5), 8.38 (d, 1H, H-5/4, J 9.0), 8.45 (d, 1H, H-9, J 9.5), 8.79 (d, 1H, H-2, J 8.5), 9.02 (d, 1H, H-10, J 9.5), 9.14 (s, 2H, H-6,8); m/z ($C_{16}H_8N_2O_4$): found 292.0494.