

Letter

Nitration of Polycyclic Aromatic Hydrocarbons with Dinitrogen Tetroxide. A Simple and Selective Synthesis of Mononitro Derivatives

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SwedenPolycyclic aromatic hydrocarbons (PAH:s) are generally nitrated with HNO₃ in acetic acid oracetic anhydride.¹ Yields are normally good, but work-up procedures are often tedious and polynitration is sometimes encountered.^{1,2} A few reports on the reaction between PAH:s and nitrogen oxides have appeared,^{3,4} most recently 9-nitrophenanthrene being detected in the complex reaction mixture from the UV-irradiation of a solution of N₂O₄ and phenanthrene in CCl₄.^{3c} The exposure of some PAH:s to gaseous NO₂/N₂O₄ led to the formation of nitro PAH:s, some of which have been discussed in relation to the carcinogenic effects of automobile exhaust and tobacco smoke.^{4,5} In this letter we present our initial studies on the reaction between some PAH:s and N₂O₄ in Cl₂Cl₂ solution. The reaction is very clean and rapid and provides, under mild

Table 1. Nitration of polycyclic aromatic hydrocarbons with dinitrogen tetroxide.

PAH	Catalytic amount of CH ₃ SO ₃ H added	Reaction time/h	Yield ^a /%	Isomer distribution ^c /%
Perylene	No	0.2	95 ^b	3-nitro 99.2 1- 0.8
Pyrene	No	0.5	97 ^b	1- 100
Anthracene	No	1	>90 ^{c,d}	9- 100 6- 97
Chrysene	No	24	>90 ^c	other mononitro 3
Naphtalene	No	48	59 ^c	1- 96 2- 4
Fluorene	No	24	>90 ^c	2- 90
	Yes	2	92 ^b	3- 1 4- 9
Fluoranthene	No	24	75 ^c	3- 63
	Yes	0.4	90 ^c	8- 27 other mononitro 10
Binaphtyl	No	24	>90 ^c	4- 100
	Yes	1	89 ^b	
Triphenylene	No	120	50 ^c	1- 22
	Yes	2	92 ^b	2- 78

^a Yield based on PAH; identity and purity confirmed by MS^e and GLC.^f ^b Isolated yield. ^c Determined by GLC. ^d 5-7% of 9,10-anthraquinone was also formed. ^e Finnegan 4021 spectrometer operating at 70 eV. ^f HP 5380A gas chromatograph equipped with an HP 18850A integrator. 0.5 m×1.8 mm glass-lined column; 5% OV 1701 on Chromosorb W.

Table 2. Isomer distribution in the nitration of some PAH:s with HNO₃ in acetic anhydride and with N₂O₄ in CH₂Cl₂.

PAH Isomers	Fluorene			Triphenylene		Chrysene		Fluoranthene		
	2-	3-	4-	1-	2-	6-	other mono- nitro	3-	8-	other mono- nitro
Conditions for nitration										
HNO ₃ /Ac ₂ O ^a	69	2	29	54 ^c	46	90	10	44	27	29
HNO ₃ /Ac ₂ O ^b	71	1	28	55	45	89	11	45	26	29
N ₂ O ₄ /CH ₂ Cl ₂	90	1	9	22	78	97	3	63	27	10

^a Fluorene: 0°C; ^{7a} triphenylene: 60°C; ^{7b} chrysene: 0°C; ^{7c} fluoranthene: 25°C. ^{7d} ^b 0°C, this work. ^c A value of 50:50±5% has also been reported. ^{7e}

conditions, almost quantitative yields of mononitrated PAH:s after a simple work-up procedure that minimizes handling of these hazardous compounds.

We have earlier reported⁶ that the reaction between N₂O₄ and naphthalene in CH₃CN or CH₂Cl₂ yields mononitronaphthalenes with a 1/2 ratio of 25 and that the reaction is acid catalyzed. During the continuation of these studies with more reactive substrates we found that perylene was very rapidly nitrated by N₂O₄ in nearly quantitative yield in the absence of any acid catalyst. We therefore decided to extend our studies to some other PAH:s (Table 1), and found that pyrene and anthracene were also rapidly nitrated without added acid while the other compounds in the study required longer reaction times and/or acid catalysis. The reaction shows high positional selectivity (Table 2), and in the case of triphenylene nitration takes place predominantly at the less hindered but less reactive 2-position (as does sulfonation, acylation and bromination), while nitration with HNO₃ in acetic anhydride gives a small excess of 1-nitrotriphenylene.^{7b,c} Mechanistic studies on the reaction are in progress.

Experimental. Materials. The PAH:s used were of highest commercial quality available and used without further purification. Dichloromethane (Merck zur Rückstandsanalyse) was dried and stored over 3 Å molecular sieves. Solutions of N₂O₄ were made up as described previously.^{6a}

Nitrations with N₂O₄. The PAH (2.5 mmol) in 125 ml CH₂Cl₂ and 2.7 mmol of N₂O₄ in 25 ml CH₂Cl₂ were mixed and allowed to stand at room temperature for the appropriate time. In some cases 0.5 mmol CH₃SO₃H was added. Most of the solvent was evaporated and 1 g of silica gel 60 (Merck, 230–400 mesh) was added. After completed evaporation the yellowish powder was

placed on top of a column packed with silica gel and eluted with CCl₄ (containing up to 10% CH₂Cl₂). Order of elution: Triphenylene, 1-, 2-; fluorene, 3-, 4-, 2-; perylene, 1-, 3-; fluoranthene, 1-, 7-, 3-, 8-; naphthalene, 1-, 2-;

Nitrations with HNO₃/Ac₂O. To the PAH (5 mmol) in 5 ml Ac₂O at 0°C was added 0.33 ml of concentrated HNO₃ in 1.67 ml Ac₂O over 30 min. After another 30 min of stirring the reaction mixture was poured onto ice/CH₂Cl₂ and the organic layer washed with water and analyzed by GLC.

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