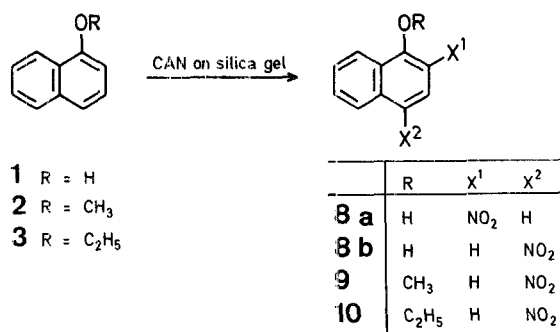


able percentage of dinitro derivatives^{13,15} or the corresponding quinones^{6,7}. Thus, the method described herein can be used for the selective preparation of mononitro derivatives; in most cases, it affords the products in an almost pure state upon elution with a suitable solvent, thus making cumbersome extraction methods unnecessary. Acetoxyated products which were observed in the G. L. C.-monitored functionalization of anisole^{11,12} with cerium ammonium nitrate are not formed in our procedure. Besides, the yields of substitution products with substituents in positions otherwise unfavourable for direct electrophilic attack, are better in reactions with silica gel-supported cerium(IV) ammonium nitrate than in the analogous oxidative nitration in solution. Thus, 2-hydroxynaphthalene is converted into a mixture of 4,5-dinitro-, 4,8-dinitro-, and 5,8-dinitro-2-hydroxynaphthalenes when treated with cerium(IV) ammonium nitrate in acetic acid whereas 1-nitro- and 4-nitro-2-hydroxynaphthalene are obtained when cerium(IV)-ammonium nitrate on silica gel is used. The present method thus provides a convenient synthesis of 2-hydroxy-1-nitronaphthalene the preparation of which from 2-hydroxynaphthalene has earlier been performed by nitration with the difficultly accessible diacetylorthonitric acid¹⁷ in the cold. 1-Hydroxynaphthalene is nit-



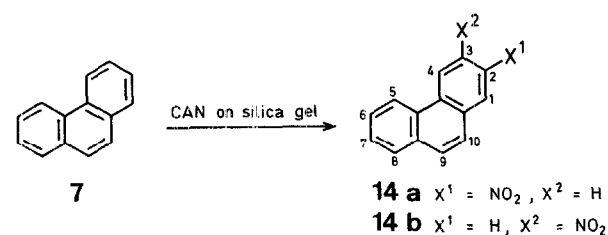
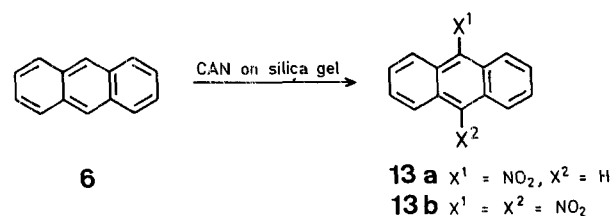
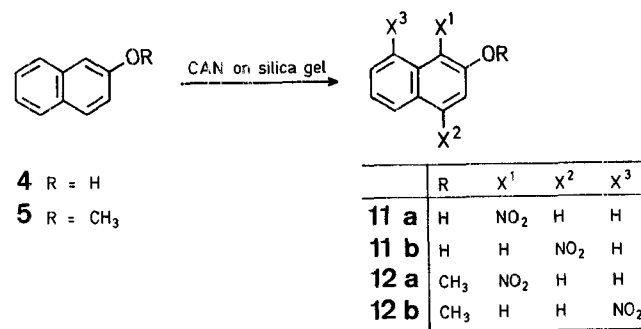
Oxidative Nitration by Silica Gel-Supported Cerium(IV) Ammonium Nitrate

H. Mohindra CHAWLA*, Ram S. MITTAL

Department of Chemistry, Indian Institute of Technology, New Delhi-110016, India

Organic reactions on solid inorganic supports have attracted much attention in recent years¹ since it has been found that reagents adsorbed on silica gel can catalyse substitution reactions^{2,3,4} or can even alter their mode of action completely^{2,5,6,7} and give different products. Cerium(IV) ammonium nitrate and cerium(IV) ammonium sulphate have been employed for oxidative derivatisation of aromatic ethers and hydrocarbons⁸⁻¹⁵. However, the strong oxidizing power of tetravalent cerium salts sometimes is of limited synthetic value because it often leads to undesired and over-oxidized products. On investigating the problem of over-reaction in oxidations with cerium(IV) salts as a part of our biomimetic studies, we have developed a new procedure which uses silica gel-supported cerium(IV) ammonium nitrate for controlled oxidative nitration of some naphthalene derivatives.

It was observed that treatment without solvent of polynuclear arenes and hydroxynaphthalenes with cerium(IV) ammonium nitrate adsorbed on silica gel affords mononitro derivatives whereas the reaction of the same substrates with cerium(IV) ammonium nitrate in solution affords a consider-



CAN = Ce(NH₄)₂(NO₃)₆

Table 1. Nitration of Naphthalene Derivatives (1-5), Anthracene (6), and Phenanthrene (7) with Silica Gel-Supported Cerium(IV) Ammonium Nitrate

Ed-uct	Eluent ^a	Prod-ucts	Yield ^b [%]	m.p. ^c [°C]	m.p. [°C] from Lit. ^{17,18} or Molecular Formula	M.S. <i>m/e</i> (relative intensity, %)	Products obtained using Ce(NH ₄) ₂ (NO ₃) ₄ in AcOH ^{13, 15, 16}	Yield [%]
1	PE PE/benzene (7/3)	8a	42	127°	128°		1-hydroxy-4,6-dinitronaphthalene	28
		8b	38	162-163°	164°		1-hydroxy-2,4-dinitronaphthalene	32
2	PE/benzene (9/1)	9	65	79°	81°	203 (100), 173 (39), 157 (30.2), 145 (22.8), 130 (22.3), 128 (8.5), 127 (38.5)	1-methoxy-4-nitronaphthalene	57
							1-methoxy-4,5-dinitronaphthalene	35
3	PE/benzene (1/1)	10	68	116°	117°	217 (100), 189 (36.0), 159 (43.3), 143 (42), 131 (30.4), 115 (70), 114 (9.0)	1-ethoxy-4-nitronaphthalene	65
							4,4'-diethoxy-3,3'-dinitro-1,1'-binaphthalene	25
4	PE/benzene (8/2)	11a	49	103°	103°	190 (9.4), 189 (100), 172 (25.5), 161 (27), 159 (30.2), 156 (12), 144 (11.8), 143 (22), 133 (8.9)	2-hydroxy-1-nitronaphthalene	25
							2-hydroxy-5,8-dinitronaphthalene	22
	PE/benzene (6/4)	11b	36	119°	120°		2-hydroxy-4,5-dinitronaphthalene	15
							2-hydroxy-4,8-dinitronaphthalene	12
5	PE/benzene (9/1)	12a	45	128°	128°	204 (20.3), 203 (100), 189 (90), 173 (18.2), 158 (15.4), 157 (51), 156 (11.8), 146 (24), 145 (41.8), 144 (10.2), 142 (30.3), 130 (14.2)	2-methoxy-8-nitronaphthalene	30
							2-methoxy-6-nitronaphthalene	46
	PE/benzene (7/3)	12b	38	67°	69°	204 (1.2), 203 (100), 173 (15), 171 (21), 157 (20.2), 146 (21.8), 142 (28)	2-methoxy-1-nitronaphthalene	30
							2-methoxy-1,8-dinitronaphthalene	15
6	PE/benzene (9/1) PE/benzene (7/3)	13a	55	145-146°	146°		9,10-dinitroanthracene	35
		13b	27	289-291°	293°		9,10-anthraquinone	65
7	PE/benzene (8/2) PE/benzene (1/1)	14a	45	103°	99°	C ₁₄ H ₉ NO ₂ ^d (223.2)	2-nitrophenanthrene	30
					171°		3-nitrophenanthrene-9,10-quinone	68

^a PE = petroleum ether.^b Yield of pure isolated product. T.L.C. for purity control was performed on silica gel plates using iodine and U.V. light for visualisation. The yields have not been optimised.^c Melting points were measured in open capillaries and are uncorrected.^d calc. C 75.33 H 4.03 N 6.23
found 75.23 4.5 6.0

rated to give the 2,4- and 4,6-dinitro derivatives when cerium(IV) ammonium nitrate in acetic acid is used but only a mononitro derivative by our method. Further examples demonstrating the superiority of our method as compared to the nitration with cerium(IV) ammonium nitrate in solution can be seen from the Table. It is worthy of note that under certain conditions (tetrahydrofuran or acetic acid as solvent) the reaction of naphthalene derivatives with cerium(IV) ammonium nitrate affords naphthoquinones.

Although the mechanism of the reaction is still unclear we would like to mention that no reaction was observed when cerium(IV) ammonium nitrate was replaced by a mixture of ammonium nitrate and cerium(IV) ammonium sulphate and the procedure repeated in the manner as described. Efforts to unravel the mechanism of the reaction are underway.

9-Nitroanthracene (13a); Typical Procedure:

Anthracene (1 g, 5 mmol) and cerium(IV) ammonium nitrate (3 g, 5.5 mmol) are separately dissolved in acetonitrile (4 ml) and these

Table 2. Spectral Data of Compounds 8-14

Compound	I.R. (KBr) ^a ν [cm ⁻¹]	¹ H-N.M.R. (CDCl ₃ /TMS _{int}) ^b δ [ppm]
8a	3050-3100, 1610, 1600, 1520, 1500, 1440, 1410, 1380, 1320	12.3 (s, 1H); 7.6 (m, 6H)
8b	3150, 3000, 1600, 1540, 1530, 1500, 1450, 1430, 1365, 1325	12.4 (s, 1H); 7.5 (m, 6H)
9	1620, 1600, 1570, 1520, 1460, 1425, 1380, 1325, 1275, 1250, 1160, 1100, 960, 740	4.1 (s, 3H); 7.8 (m, 6H)
10	1620, 1600, 1570, 1510, 1450, 1430, 1380, 1320, 1200, 1170, 1090, 915, 825, 745, 650	1.4 (t, 3H, $J = 7$ Hz); 4.2 (q, $J = 7$ Hz); 7.7 (m, 6H)
11a	3350-3400, 1620, 1600, 1530, 1500, 1470, 1430, 1370, 1340, 880, 830	12.5 (s, 1H); 7.5 (m, 6H)
11b	3400, 1610, 1530, 1450, 1400, 1350, 1320, 840	12.6 (s, 1H); 7.8 (m, 6H)
12a	1620, 1600, 1570, 1460, 1390, 1350, 1250, 1215, 1150, 1020, 960, 810, 750	3.95 (s, 3H); 7.6 (m, 6H)
12b	1620, 1600, 1560, 1520, 1460, 1385, 1360, 1310, 1240, 1135, 1030, 830, 730, 700	3.9 (s, 3H); 7.7 (m, 6H)
13a	1610, 1600, 1540, 1525, 1460, 1330, 1320	7.5 (m, 9H)
13b	1620, 1600, 1550, 1535, 1465, 1380, 1320, 1250, 1215, 1100, 900, 750, 720	7.2 (m, 8H)
14a	1620, 1600, 1560, 1520, 1500, 1450, 1395, 1340, 1320, 1280, 1250, 1220, 1185, 1170, 1150, 1110, 985, 910, 880, 815, 770, 730	7.8 (m, 9H)
14b	1600, 1560, 1540, 1500, 1460, 1380, 1345, 1325, 1290	7.9 (m, 9H)

^a Recorded on a Perkin-Elmer 577 spectrophotometer.

^b Recorded on a Varian 60 MHz spectrometer.

solutions are mixed to a slurry each with silica gel (2 g and 5 g, respectively). The slurries are dried in a hot-air oven at 60-65°C for 1 h. The dried masses are mixed well and this mixture is added to a prepacked column of silica gel (30 g). The column is eluted with petroleum ether/benzene (9/1). Concentration of the eluate affords 9-nitroanthracene in a T.L.C. pure state as yellow needles; yield: 0.72 g (55%); m.p. 146°C (Ref.¹³, m.p. 146°C).

This work is dedicated to Prof. Alfred Hussner on his 54th birthday.

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* Address for correspondence.

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