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A CONVENIENT METHOD OF *META*-DIRECTING NITRATION OF 3-SUBSTITUTED PHENOL BY LANTHANIDE (III) NITRATES

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Abstract: Thirteen compounds of 3-substituted phenols were nitrated by lanthanide(III) nitrates in a solution of ethyl acetate. Whether the substituents were ortho-, para-directing groups or meta-directing groups, only one kind nitrated product, 3-substituted-5-nitropenol, and its intermediate were obtained respectively.

The nitration of aromatic hydrocarbons can be achieved with many nitrating reagents and is a very useful way in organic synthesis^{1,2}. Lanthanide (III) nitrates have received considerable attention in this respect and the nitration of phenols has been achieved by employing them as catalysts or nitrating reagents^{3,4}. The results showed using lanthanide (III) salts as catalysts or nitrating reagents for the nitration of phenol are very useful methods. Comparing with the usual way, they can be handled easily and give a high yield. Herein, we report the intermediates of all nitrating reactions and the final nitrated products,3-substituted-5-nitrophenol.

Experimental

General methods: The IR spectra were recorded on a 170SX FTIR spectrophotometer as KBr pellet in the range of 4000-400cm⁻¹. Elemental analyses were

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Intermediate				⁻ ¹ H NMR (ppm)			
	<u>VC-H</u>	VAr-H	V _{NO2}	VC-0			
	3100	1609	1524	1293	$\delta_{\rm Ha} = 7.92({\rm s}, 2{\rm H})$		
	850,814	1596	1346	1223	$\delta_{\text{Hb}} = 8.70(\text{s}, 1\text{H})$		
	3041	1608	1523	1234	δ_{Ha} =2.45(s,3H), δ_{Hb} =7.20(s,1H)		
(_{02N} O ^C _{GH3}) ₃ La	828,725	1582	1349		δ_{Hc} =7.81(s,1H), δ_{Hd} =7.90(s,1H)		
	3072	1600	1524	1230	δ_{Ha} =7.48(s,1H), δ_{Hb} =7.89(s,1H)		
$\left(\begin{array}{c} 0_{2} \mathbf{N} \begin{array}{c} 0_{1} \end{array} \right)_{\mathbf{b}} \left(\begin{array}{c} 0_{1} \end{array} \right)_{\mathbf{b}} \mathbf{L} \mathbf{a}$	814,723	1576	1344	1189	o _{He} =7.96(s,1H)		
l l	3035	1596	1526	1226	δ_{Ha} =5.61(s,2H), δ_{Hb} =7.05(s,1H)		
$\left(\begin{array}{c} 0_2 \mathbf{N} & \mathbf{O} \\ \mathbf{H}_2 \end{array} \right)_3 \mathbf{C} \mathbf{e}$	811,730	1511	1343	1199	δ_{Hc} =7.16(s,1H), δ_{Hd} =7.54(s,1H)		
$(0_2 N \bigcirc a \bigcirc b \bigcirc b \bigcirc 3^{P}_2$	3106	1610	1520	1400	$\delta_{\text{Ha}} = 7.38(m, 1\text{H})$		
	808,722		1345	1288	δ _{Hb} =8.05(m,2H)		
ę	3059	1609	1522	1232	$\delta_{\text{Ha}} = 2.24(s, 3H), \delta_{\text{Hb}} = 7.71(s, 1H)$		
	846,710		1346	1204	$\delta_{\text{He}} = 7.93(s, 1H), \delta_{\text{Hd}} = 8.24(s, 1H)$		
					$\delta_{He} = 10.31(s, 1H)$		
(and at at) Ho	3049	1604	1531	1239	δ_{Ha} =1.28(s,3H), δ_{Hb} =2.39(s,2H)		
	833,715		1344	1185	δ_{Hc} =7.21(s,1H), δ_{Hd} =7.80(s,1H)		
10211 6 012013 73					$\delta_{He} = 7.86(s, 1H)$		
	3104	1601	1533	1247	δ_{Ha} =7.31(s,1H), δ_{Hb} =7.86(s,2H)		
(₀₂ N ^D Q ^a Br) ₃ La	820,725	1572	1352	1196	$\delta_{\rm He} = 7.91(s, 1H)$		
. 2 .	3034	1598	1522	1219	$\delta_{\text{Ha}} = 7.78(s, 1H), \delta_{\text{Hb}} = 8.00(s, 2H)$		
(_{0.1} , , , , , , , , , , , , , , , , , , ,	857,826		1341	1175	$\delta_{Hc} = 8.77(s, 1H)$		
	703						
, Ch	3062	1607	1529	1218	$\delta_{Ha} = 4.08(s, 3H), \delta_{Hb} = 6.93(s, 1H)$		
$(0_2 N O O O H_3)_3 S m$	843,809	1592	1342	1173	δ_{Hc} =7.65(s,1H), δ_{Hd} =7.73(s,1H)		
. 2 .	3040	1603	1524	1236	$\delta_{H_8} = 7.68(s, 1H), \delta_{H_P} = 8.01(s, 1H)$		
(₀₂ рф ² сно) ₃ но	862,824	1578	1342	1198	δ_{He} =8.62(s,1H), δ_{Hd} =10.31(s,1H)		
p	3044	1599	1538	1222	δ_{Ha} =3.91(s,3H), δ_{Hb} =7.59(s,1H)		
(_{02N} O ^b _{COC} A ₃) ₃ Dy	890,848		1357	1183	δ_{He} =8.06(s,1H), δ_{Hd} =8.61(s,1H)		
p	3031	1601	1335	1218	$\delta_{Ha} = 1.25(s, 3H), \delta_{Hh} = 4.01(s, 2H)$		
	899,852	1579	1354	1178	$\delta_{\text{He}} = 7.61(s, 1H), \delta_{\text{He}} = 8.07(s, 1H)$		
w2m ¥ .00015013/3_ 1					δ _{He} =8.55(s,1H)		

Table 1. The IR and ¹H NMR spectra of intermediates

International	Yield	Time	T(℃) [∎]		Elemental	analyses(%)	
intermediate	(%)	(min)		С	Н	N	Ln ³⁺
(C ₆ H ₃ N ₂ O ₅) ₃ Sm	70.2	47	80~96	30.63(30.90) ^b	1.57(1.30)	12.29(12.01)	21.25(21.49)
(C7H6NO3)3La	76.9	45	85~108	42.62(42.36)	3.31(3.03)	6.78(7.06)	23.58(23.35)
$(C_6H_3CINO_3)_3La$	73.1	45	85~105	33.17(32.91)	1.11(1.37)	6.14(6.39)	21.44(21.16)
(C ₆ H ₅ N ₂ O ₃) ₃ Ce	84.2	40	$80\!\sim\!108$	36.31(36.06)	2.78(2.50)	14.28(14.02)	23.66(23.38)
$(C_6H_3NO_4)_3Y_2$	82.8	50	80~110	33.62(33.91)	1.67(1.41)	6.33(6.59)	27.69(27.94)
$(C_8H_7N_2O_4)_3Ce$	77.5	45	82~108	39.44(39.72)	2.65(2.90)	11.85(11.58)	19.60(19.32)
(C8H8NO3)3Ho	72.8	50	80~108	43.71(43.45)	3.90(3.62)	6.62(6.34)	24.59(24.88)
(C6H3NO3)3La	72.5	50	80~110	27.59(27.36)	1.42(1.14)	5.59(5.32)	17.31(17.59)
(C7H3NO5)3Sm2	67.9	55	80~92	29.48(29.76)	1.68(1.42)	4.67(4.96)	35.78(35.52)
(C7H6NO4)3Sm	84.9	40	80~108	38.25(38.51)	2.48(2.75)	6.14(6.42)	23.23(22.98)
(C7H4NO3)3Ho	67.1	65	80~105	38.24(38.01)	1.53(1.81)	6.07(6.34)	24.60(24.88)
(C ₈ H ₆ NO ₄)₃Dy	58 .7	75	85~105	41.24(41.00)	2.84(2.56)	5.74(5.98)	23.39(23.13)
(C₂H ₈ NO₄)₂Dy	60.4	80	85~105	43.24(43.52)	3.49(3.22)	5.38(5.64)	21.54(21.83)

Table 2. The condition of reaction and elemental analyses of intermediate

a: intermediate appeared temperature ~ highest temperature b: calculated value

determined using a Carlo-Erba 1106 elemental analyzer. The mass spectra were obtained using a ZBA-HS type mass spectrometer. The ¹H NMR spectra were recorded on a AC-80A instrument using DMSO-d₆ as a solvent. Melting point were determined using a RY-1 type apparatus, but the temperature was not calibrated.

General procedure: A typical procedure is as follows: A mixture of resorcinol (30mmol) and yttrium nitrate (20mmol) in ethyl acetate (25ml) were refluxing for 20 min then distilled off the solvent until the brown-red gas of NO₂ appeared and the temperature of the mixture approach to 110°C during 30 min. After cooling, the residue was washed with ethyl acetate 5 times, gave the intermediate $Y_2(C_6H_3NO_4)_3$ in 82.8% yield. The intermediate was characterized by the IR., ¹H NMR (Table 1.), and elemental analysis (Table 2.).

The intermediate was dissolved in 6N HCl, then the organic phase was separated and the water phase was extracted with diethyl ether (3×10 ml). The combination solution of organic phase and ether phase was dried with anhydrous sodium sulfate and concentrated. The crude product was purified by recrystallization from alcohol. The only product, 5-nitroresorcinol was obtained in 77.4% final yield as a pale yellow solid. Other 3-substituted-5-nitrophenols listed in Table 3. were also characterized by the M.S., m.p. and elemental analyses.

Entry	n	Yield	m.p.(°C)		Elemental analysis(%)			
	ĸ	(%)		M.S.	С	Н	И	
1	NO2	64.7	122-123(123) ^a	185, 184, 93 ^b	39.42(39.13) ^c	2.46(2.17)	15.48(15.22)	
2	CH3	70.2	113-113.5	153, 152, 92	54.62(54.90)	4.80(4.58)	9.43(9.15)	
3	C1	67.7	147-148(147)	173, 172, 110	41.77 (41.50)	2.54(2.31)	7.79(8.07)	
4	NH2	78.3	165-166(165)	155, 154, 91	46.48(46.75)	3.62(3.90)	18.46(18.18)	
5	OH	77.4	158-159(158)	155, 92	46.17(46.45)	3.50(3.23)	9.31(9.03)	
6	NHCOCH3	71.6	208-210	197, 196, 92	49.26(49.98)	4.33(4.08)	14.02(14.29)	
7	C ₂ H ₅	66.3	118-120	167, 166, 104	57.76(57.49)	5.14(5.39)	8.12(8.38)	
8	Br	65.2	155-157	218, 217, 154	33.32(33.04)	1.56(1.84)	6.71(6.42)	
9	COOH	60.7	239-243	184, 183, 93	45.62(45.90)	2.48(2.73)	7.38(7.65)	
10	OCH3	75.2	109-110	169, 168, 106	49.98(49 .70)	4.40(4.14)	8.55(8.28)	
11	CHO	55.1	186-188	167, 104	50.56(50.30)	2.71(2.99)	8.13(8.38)	
12	COCH3	50.4	122-124	182, 181, 92	53.32(53.04)	3.58(3.87)	7.44(7.73)	
13	COC ₂ H ₅	52.2	130-132	195, 103	55.66(55.38)	4.35(4.62)	7.46(7.18)	

 Table 3. Nitration of 3-substituted phenol to 3-substituted-5-nitrophenol

a: literature value b: M+1 or M peak, M or M-1 peak, 100% peak c: calculated value

The meta-nitrated products were given by the different kinds of lanthanide(III) nitrate in the yield above 50.4 %. Ethyl acetate was an important solvent for this reaction because it could dissolve lanthanide(III) nitrate and 3-substituted phenol at same time. According to our research results, the intermediates were all the lanthanide complexes in which the oxygen of phenol is coordinated to the lanthanide ion(III). It's notable, comparing with the well known nitrating reaction¹, that this nitrating system give only one kind nitrated product whether other substituent is electron-withdrawing group or electron-donating group. It could be also seen that the phenol containing a electron-donating group offered a higher yield than that of containing a electron-withdrawing group. Our results may provide a convenient and useful method for the synthesis of 3-substituted-5-nitrophenol. Further investigation of mechanism of this kind reaction is being continued in our laboratory.

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