

Nitration of Aromatic Compounds with Potassium Nitrate in Polyphosphoric Acid

RASHID IQBAL AND MIAN M.ASLAM

*Department of Chemistry, Quaid-i-Azam University,
Islamabad, Pakistan*

(Received 2nd February, 1985)

Summary: A variety of aromatic compounds were subjected to nitration using potassium nitrate in polyphosphoric acid. The method was found useful to obtain single nitro-product in each case. The position of nitration in the aromatic substrate was found to depend on the nature of the substituent already present.

A number of reagents for nitration of aromatic compounds are found in the literature [1-12]. Some of the important reagents employed for this purpose include mixture of concentrated nitric acid and concentrated sulphuric acid [1-7], dinitrogen tetroxide - boron trifluoride [8], nitronium tetrafluoroborate [9], tetranitromethane [10], and cupric nitrate-acetic anhydride [11-12]. However, the mixture of concentrated nitric acid and concentrated sulphuric acid still remains the most common reagent for nitration of aromatic compounds. Sastry et al. [13] have employed a mixture of potassium nitrate and polyphosphoric acid (PPA) for nitration of a few aromatic compounds. Because of the relative convenience of the use of this nitrating mixture as compared to other nitrating agents, we have studied the nitration of a number of aromatic compounds with potassium nitrate in PPA. In this article we wish to report the results of these studies.

In the present studies eleven aromatic compounds were subjected to nitration with potassium nitrate in PPA. The aromatic substrates were anisole, benzaldehyde, benzamide, benzoic acid, benzyl alcohol, ethyl benzoate, 3-nitrobenzoic acid, 2-nitrophenol, 4-nitrophenol, phenol and phenetole.

The equimolar ratio (1:1) of the nitrating mixture of the aromatic substrate, in each case, was maintained so that only one nitro group could be introduced in the substrate. In general, this method of nitration was found to be convenient, neat and rapid. The products of nitration and their % yields alongwith the reaction conditions are shown in Table 1. The yields of the nitro-products may be considered satisfactory in view of the fact that only a single isomer is obtained in each case. Thus, whereas anisole, benzyl alcohol, phenol and phenetole yielded the corresponding 4-nitro compound; benzaldehyde, benzamide, benzoic acid, and ethyl benzoate yielded the respective 3-nitro product. Both the nitrations of 2-nitrophenol and 4-nitrophenol by the present method yielded the same product i.e. 2,4-dinitrophenol. However, it was found that 3-nitrobenzoic acid did not undergo nitration with potassium nitrate in PPA even when the reaction mixture was heated at 200° for an extended time period of twenty hours.

It is interesting to note that the position of the nitro group in the product can be conveniently related to the electronic effects of the substituents already present in the aromatic substrate. It is evident that +R substi-

Table-1: Nitration of Aromatic Compounds with Potassium Nitrate in ppa

Aromatic Substrate	Reagion temp.(C°)	Reaction time(min)	Product	% Yield
Anisole	0 - 5	10	4-Nitroanisole	52
Phenol	0 - 5	10	4-Nitrophenol	46
Phenetole	0 - 5	10	4-Nitrophenetole	53
Benzyl alcohol	0 - 5	10	4-Nitrobenzyl alcohol	46
2-Nitrophenol	15 - 20	180	2,4-Dinitrophenol	50
4-Nitrophenol	15 - 20	180	2,4-Dinitrophenol	46
Benzaldehyde	15 - 20	300	3-Nitrobenzaldehyde	58
Benzamide	70 - 75	180	3-Nitrobenzamide	44
Benzoic acid	70 - 75	30	3-Nitrobenzoic acid	77
Ethyl benzoate	70 - 75	180	Ethyl 3-nitrobenzoate	53
3-Nitrobenzoic acid	200	1200	*	*

* No Reaction.

tutents in the aromatic substrates direct the incoming nitro group to the para position. Similarly, the incoming nitro group is directed to the meta position when the substituent in the aromatic substrate is -R type. These results are in line with the earlier observation of Sastry et al. [13] who obtained, for example, 1,3-dinitrobenzene and methyl 3-nitrobenzoate by nitration of nitrobenzene and methyl benzoate respectively. The results imply that the nitration reaction studied may be used for preparation of specific aromatic nitro-compounds without involving the separation of isomeric nitro-products as is encountered in the case of nitration of aromatic compounds with a mixture of concentrated nitric acid and concentrated sulphuric acid [15a]. Furthermore, it

appears that relatively mild conditions are required for nitration of aromatic compounds with potassium nitrate in PPA. For example, for nitration of benzoic acid to 3-nitrobenzoic acid, using concentrated nitric acid-sulphuric acid mixture, it is required to heat the reaction mixture at 100° for eight hours [6]. On the other hand using the present method, the nitration could be achieved on heating the reaction mixture at 70-75° for half an hour only.

Experimental

The melting points of the nitro-compounds prepared were not corrected and were observed using Gallenkamp melting point apparatus. The infrared

Table-2: Characterization of Nitration Products

Nitration product	M.P.(Obs.) (C°)	M.P.(Lit.) (C°)	Molecular formula	Calcd. %			Analysis %		
				C	H	N	C	H	N
4-Nitrophenol	113	112 ^a	C ₆ H ₅ NO ₃	51.8	3.59	10.7	51.6	3.62	10.8
4-Nitroanisole	52	54 ^b	C ₇ H ₇ NO ₃	54.9	4.57	9.15	54.6	4.50	9.05
4-Nitrophenetole	58	60 ^b	C ₈ H ₉ NO ₃	57.5	5.38	8.38	57.5	5.26	8.30
2,4-Dinitrophenol [*]	113	113 ^c	C ₆ H ₄ N ₂ O ₅	39.1	2.17	15.2	39.6	2.02	15.2
2,4-Dinitrophenol ^{**}	113	113 ^c	C ₆ H ₄ N ₂ O ₅	39.1	2.17	15.2	39.6	2.02	15.2
3-Nitrobenzaldehyde	57	58 ^c	C ₇ H ₅ NO ₃	55.6	3.31	9.27	55.2	3.40	9.35
3-Nitrobenzoic acid	140	141 ^e	C ₇ H ₅ NO ₄	50.3	2.99	8.38	50.0	3.00	8.50
Ethyl 3-nitrobenzoate	45	47 ^f	C ₉ H ₉ NO ₄	55.4	4.62	7.18	55.3	4.50	7.25
4-Nitrobenzyl alcohol	93	93 ^e	C ₇ H ₇ NO ₃	54.9	4.57	9.15	54.6	4.45	9.25
3-Nitrobenzamide	141	142 ^h	C ₇ H ₆ N ₂ O ₃	50.6	3.61	16.9	50.8	3.55	16.7

* Obtained by nitration of 2-nitrophenol; **Obtained by nitration of 4-nitrophenol; (a - g) reference 15a to 15g respectively; (4) reference 16.

spectra were recorded on a Pye-Unicam Infrared Spectrophotometer model SP-1000.

Reagents and Substrates

Anisole, benzamide, ethyl benzoate, potassium nitrate and phenetole were obtained from BDH. Benzoic acid, benzaldehyde, 3-nitrobenzoic acid, 2-nitrophenol, 4-nitrophenol, phenol, phosphorous pentoxide and orthophosphoric acid were supplied by Merck. All the substrates were used without further purification.

The nitrating mixture of potassium nitrate in PPA was prepared by the same method as reported by Sastry

et al. [13]. For this purpose, potassium nitrate (1.01 g, 0.01 mole) was added to PPA prepared by carefully mixing phosphorous pentoxide (12.0 g) and orthophosphoric acid (8.0 ml) and thoroughly stirring the mixture. The mixture was freshly prepared for nitration of each aromatic substrate. Furthermore, the total volume of the mixture was used in each case.

Nitration of Aromatic Substrates

In a typical nitration reaction, to the aromatic substrate (0.01 mole), contained in a round-bottom flask, was added freshly prepared nitrating mixture of potassium nitrate and PPA. The reaction mixture was then stirred

Table-3: Crystalline Derivatives of Some Nitroproducts

Nitro-product	Derivative prepared	M.P. Obs.) C°	M.P.(Lit.) C°	Reference
3-Nitrobenzaldehyde	Phenylhydrozone	120	121	15d
	4-Nitrophenyl hydrozone	247	247	15d
3-Nitrobenzoic acid	Anilide	152	154	15e
	4-Bromophenacyl ester	131	132	15e
4-Nitrobenzyl alcohol	Acetate	77	78	15h
	Benzoate	92	95	15h
4-Nitrophenol	Benzoate	141	142	15c
	4-Toluene-sulphonate	96	97	15c
2,4-Dinitrophenol [*]	Benzoate	130	132	15c
	4-Toluene-sulphonate	119	121	15c
2,4-Dinitrophenol ^{**}	Benzoate	130	132	15c
	4-Toluene-sulphonate	119	121	15c

* Obtained from nitration of 2-nitrophenol; ** Obtained from nitration of 4-nitrophenol.

at the required temperature for a certain period of time. These reaction conditions were different for different compounds. The optimum conditions required for nitration of each aromatic substrate were determined by repeating the reaction several times at different conditions and are reported in Table 1. After the reaction time was over, the reaction mixture was poured into about 400 ml of ice-cold water and allowed to stand for about two hours. Except for the nitration of 3-

nitrobenzoic acid which failed, in each case a yellow solid precipitated which was filtered off and recrystallized from 50% aqueous ethanol. This product of nitration was then characterized. The product of nitration and % yield of each is also listed in Table 1.

Characterization of the Nitro-products

The purity of the nitration products was established by TLC. In two different solvent systems i.e. acetone-pet-

roleum ether (1:5) and methanol-water (1:4), on silica plate, each nitro-product yielded a single spot.

The characterization of these products was based on the comparison of the observed melting points with the values reported in the literature in addition to the microanalytical data. This is illustrated in Table 2. The IR spectrum of each nitro-product in nujol displayed an asymmetric NO_2 stretching band [14] in the region of $1535\text{--}1550\text{ cm}^{-1}$. Further evidence for the identity of some of the nitro-products was obtained by preparing their derivatives and comparing the values of their observed and reported melting points. The agreement of these is shown in Table 3.

References

1. R.J. Gillespie and D.J. Millen, *Quart. Rev.*, **2**, 277 (1948)
2. K. Schofield, *Quart. Rev.*, **4**, 382 (1950)
3. H.M. Fitch, *Org. Synth.*, Coll. Vol. III (Ed. E.C. Horning), John Wiley and Sons, New York (1967) p. 658.
4. A.G. Anderson, Jr., R. Scotoni, E.J. Cowles and G. Fritz, *J. Org. Chem.*, **22**, 1193 (1957)
5. R.N. Icke, C.E. Redemann, B.B. Wisegarver and G.A. Alles, *Org. Synth.*, Coll. Vol. III (Ed. E.C. Horning), John Wiley and Sons, New York (1967), p. 644.
6. R.Q. Brewster, B. Williams and R. Phillips, *Org. Synth. Coll. Vol. III* (Ed. E.C. Horning), John Wiley and Sons, New York (1967), p. 337.
7. H.P. Schultz, *Org. Synth.*, Coll. Vol. IV (Ed. N. Rabjohn), John Wiley and Sons, New York (1967), p. 364.
8. G.B. Bachman, H. Fever, B.R. Bluestein and C.M. Vogt, *J. Am. Chem. Soc.*, **77**, 6188 (1955), G.B. Bachman and C.M. Vogt, *J. Am. Chem. Soc.*, **80**, 2987 (1958)
9. S.J. Kuhn and G.A. Olah, *J. Am. Chem. Soc.*, **83**, 4564 (1961)
10. J.F. Riordan, W.E.C. Wacker and B.L. Vallee, *J. Am. Chem. Soc.* **88**, 4140 (1966)
11. A.G. Anderson Jr., J.A. Nelson and J.T. Tazuma, *J. Am. Chem. Soc.*, **75**, 4980 (1953)
12. K.I.H. Williams, S.E. Cremer, F. W. Kent, E.J. Sehn and D.S. Tarbell, *J. Am. Chem. Soc.*, **82**, 3982 (1960)
13. S. Sastry and N.A. Kudav, *Indian J. Chem.*, **18B**, 198 (1979)
14. J.C.D. Brand and G. Eglinton, *Applications of Spectroscopy to Organic Chemistry*, Oldbourne Press, London (1965), p. 111.
15. A.I. Vogel, *A Text Book of Practical Organic Chemistry*, Longmans, London (1967), a) p. 677, b) p. 674, c) p. 685, d) p. 723, e) p. 778 f) p. 788, g) p. 818.
16. J.R.A. Pollock and R. Stevens (Editors) *Dictionary of Organic Compounds*, 4th Edition, Eyre and Spottiswoode, London (1965), p. 2431.