Nitration of Some Substituted Aromatic Compounds with Potassium Nitrate in Polyphosphoric Acid

[1]RASHID IQBAL, [1]NASIM HASAN RAMA, [1]MUHAMMAD ZIA UL HAQ
AND [2]FARAG ALI MADHWA
[1]*Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan*
[2]*Department of Chemistry, University of Garyonis, Benghazi, Libya*

(Received 28th October, 1996, revised 12th Feburary, 1997)

Summary: Some 4-substituted benzaldehydes, 4-substituted benzoic acids and substituted nitrobenzenes were subjected to nitration using potassium nitrate in polyphosphoric acid. The method was found useful to obtain single nitro-product in each case.

Introduction

A number of nitrating systems have been employed for aromatic nitration. Among these, mixture of concentrated nitric acid and concentrated sulfuric acid [1-7], dinitrogen tetraoxide borontrifluride [8], nitrogen tetrafluoroborate [9], tetranitro-methane [10], and cupric nitrate-acetic anhydride [11-12] are important. Yet not all of them are in common use. Dilute nitric acid is useful for nitrating reactive substances e.g. phenol but the oxidizing property of more con. nitric acid have often been disadvantageous [13]. Similarly the mixture of nitric acid and sufluric acid, so commonly used for aromatic nitration, has the advantage of increasing the solubilities of aromatic substrates but seriously suffers from the disadvantage of being able to sulfonate some aromatic compounds. Nitric acid in organic solvents have proved to be much milder nitrating agent. Nitronium salts are advantageous only in special cases and often the selection of solvent is difficult for them [14]. Acetyl nitrate and benzoyl nitrate have been reported as dangerous and difficult to handle [15]. Tetranitromethane, when mixed with some aromatic hydrocarbons, is known to be very sensitive to shocks and may detonate with considerable violence [16]. Furthermore, in most of the aromatic nitration reactions with various agents mixture of nitro products are formed. Sastry et al [17] have employed a mixture of potassium nitrate and polyphosphoric acid (PPA) for nitration of a few aromatic compounds. In contrast to sulfuric acid and nitric acid, polyphosphoric acid is not an oxidizing agent and it has not tendency to enter into aromatic substitution [18], and also it has good solvent power and also contains anhydride group which removes generated water from the reaction mixture with the preservation of effective activity. Mixture of potassium nitrate in PPA has been successfully employed for nitrating some mono-substituted benzenes and substituted nitrobenzene [19].

Results and Discussion

In the present work a variety of aromatic substrates e.g. 4-substituted benzaldehydes, 4-substituted benzoic acids and substituted nitrobenzenes were subjected to nitration with the mixture of potassium nitrate and polyphosphoric acid. Since in each nitration attempt, introduction of only one nitro group was desired, equimolar ratio 1:1 of the substrate and the nitrating mixture was maintained. As reported earlier [19], this method of nitration was found to be convenient, neat and rapid. The nitration products, their % age yields along with the reaction conditions are shown in Table-1. The major aim of this work was to establish the general applicability of potassium nitrate in PPA as a reagent for nitration of aromatic compounds. For this purpose a number of aromatic substrates, varying widely in their reactivity towards nitration, were subjected to nitration, at different reaction conditions, with this reagent to achieve the objective of the general applicability of the nitrating mixture. The nitration of 4-substituted benzaldehydes yielded 3-nitro products (I-V) in each case. At elevated temperatures 70-75°, compounds I and II were obtained in 61.7-73.7% yields. However, due to decomposition and

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

S.No.	Aromatic substrate	Reaction temp. (°C)	Reaction time(h)	Isolated product	% Yield
1.	4-Bromobenzaldehyde	18-20	6.0	4-Bromo-3-Nitrobenzaldehyde (I)	12.7
		70-75	3.0	4-Bromo-3-Nitrobenzaldehyde(I)	72.5
2.	4-Chlorobenzaldehyde	18-20	6.0	No reaction	-
		70-75	3.0	4-Chloro-3-Nitrobenzaldehyde(II)	61.7
3.	4-Hydroxybenzaldehyde	18-20	6.0	4-Hydroxy-3-nitrobenzaldehyde(III)	31.2
		35-40	1.0	4-Hydroxy-3-nitrobenzaldehyde(III)	58.7
4.	4-Methoxybenzaldehyde	18-20	6.0	4-Methoxy-3-nitrobenzaldehyde(IV)	29.4
		35-40	1.0	4-Methoxy-3-nitrobenzaldehyde(IV)	62.5
5.	4-Methylbenzaldehyde	18-20	6.0	4-Methyl-3-nitrobenzaldehyde(V)	30.2
		70-75	1.0	4-Methyl-3-nitrobenzaldehyde(V)	73.7
6.	4-Aminobenzoic Acid	18-20	6.0	4-Amino-3-nitrobenzoic acid(VI)	18.3
		35-40	1.0	4-Amino-3-nitrobenzoic acid(VI)	54.2
7.	4-Bromobenzoic Acid	18-20	6.0	No reaction	-
		115-120	4.0	4-Bromo-3-nitrobenzoic acid (VII)	70.6
8.	4-Chlorobenzoic Acid	18-20	6.0	No reaction	-
		115-120	4.0	4-Chloro-3-nitrobenzoic acid(VIII)	72.3
9.	4-Fluorobenzoic Acid	18-20	6.0	No reaction	-
		145-150	4.0	4-Fluoro-3-nitrobenzoic acid (IX)	48.5
10.	4-Hydroxybenzoic Acid	18-20	6.0	4-Hydroxy-3-nitrobenzoic acid(X)	21.5
		35-40	2.0	4-Hydroxy-3-nitrobenzoic acid(X)	56.3
11.	4-Methoxybenzoic acid	18-20	6.0	4-Methoxy-3-nitrobenzoic acid (XI)	18.5
		70-75	1.0	4-Methoxy-3-nitrobenzoic acid(XI)	85.6
12.	4-Methylbenzoic acid	18-20	6.0	4-Methyl-3-nitrobenzoic acid(XII)	18.7
		70-75	1.0	4-Methyl-3-nitrobenzoic acid (XII)	82.4
13.	2-Nitroanisole	70-75	3.0	2,4-Dinitroanisole(XIII)	68.8
14.	4-Nitroanisole	70-75	3.0	2,4-Dinitroanisole(XIII)	61.3

formation of side product at elevated temperatures, compounds III-V could be obtained in 58.7-73.7% yields at lower temperatures (35-40°). The nitration of 4-substituted benzoic acids also yield 3-nitro products(VI-XII) with respect to carboxylic acid group in each case. At room temperature (18-20°), 4-bromobenzoic acid, 4-chlorobenzoic acid and 4-fluorobenzoic acid did not undergo aromatic nitration. All other substituted benzoic acids yielded about 20% of the 3-nitro-products. Like 4-substituted benzaldehyde, the decomposition of reaction mixture was observed above 35-40° in the case of 4-hydroxybenzoic acid and 4-aminobenzoic acid. However 4-methoxybenzoic acid, could be heated at 70-75° without any decomposition. Compound XI and XII were obtained in excellent yield (82.5-85.6%) by this method, whereas compound IX was obtained in 48.5% yield when mixture was heated upto 145-150°. 2-Nitroanisole and 4-nitroanisole on nitration yield 2,4-dinitroanisole in 68.8 and 61.3% yield respectively. While 3-nitrobenzoic acid, 4-nitrobenzaldehyde and 4-nitrobenzoic acid did not give any dinitro-product even when heated at 200° for ten hours.

The results of present investigation reveals that the mixture of potassium nitrate and polyphosphoric acid is of moderate strength to bring about nitration of aromatic substrates. Thus, it was found possible to nitrate a wide range of aromatic compounds, differing to a great extent in their reactivity towards aromatic nitration, simply by varying the reaction conditions. However this method failed when applied to nitration of aromatic substrates substituted with two deactivating substituents e.g. 3-nitrobenzoic acid, 4-nitrobenzoic acid and 4-nitrobenzaldehyde. In each of these cases, no dinitro-product was obtained even when the reaction mixture was heated at 200° for ten hours.

The purity of the nitro products was established by the TLC in two different solvent systems i.e. acetone:pet ether (40-60°) (1:3) and methanol:water (1:4), on silica gel. Each nitro-product showed a single spot.

The nitro-products were characterized on the basis of their observed and reported melting points. Infra red spectra (KBr-disc) of each of these isolated compounds exhibited an asymmetric stretching band in the region 1535-1550 cm^{-1}. Further evidence for their identity was based on the preparation of their derivatives and comparing

Table-2: Characterization of the isolated Nitro-products

S.No.	Isolated product	Melting point obs.(lit.)°C	Derivative prepared	Melting point obs.(lit) °C
1.	4-Chloro-3-nitrobenzaldehyde	63-64(64-65)[21b]	Phenylhydrazone	147-148(148)[21b]
2.	4-Bromo-3-nitrobenzaldehyde	104-106(105-106)[21a]	Phenylhydrazone	181-182(182-183)[21a]
3.	4-Methoxy-3-nitrobenzaldehyde	86-87(86-87)[21d]	Phenylhydrazone	128-129 (130)[21d]
4.	4-Hydroxy-3-nitrobenzaldehyde	139-140(139-140)[21e]	Phenylhydrazone	173-175(175-176)[21e]
5.	4-Methyl-3-nitrobenzaldehyde	48-50 (48-49)[21f]	Phenylhydrazone	104-105(105)[21f]
6.	4-Methoxy-3-nitrobenzoic acid	194-195 (195-196)[21d]	Methyl ester	108-109(109-110)[21d]
7.	4-Methyl-3-nitrobenzoic acid	188-190(190-196)[21g]	Methyl ester	51(51)[21g]
8.	4-Chloro-3-nitrobenzoic acid	180-181(181-182)[21c]	Methyl ester	82-83(83)[21c]
9.	4-Fluoro-3-nitrobenzoic acid	119-121(121-122)[21h]	Ethyl ester	43-44(45)[21h]
10.	4-Hydroxy-3-nitrobenzoic acid	186-187(186-187)[21i]	Ethyl ester	74-75(75-76)[21i]
11.	4-Bromo-3-nitrobenzoic acid	203-204 (203-204)[22]	Methyl ester	103-104 (104)[22]
12.	4-Amino-3-nitrobenzoic acid	283-284(284)[23]	2-Nitroaniline	70-71(71)[21j]
13.	2,4-Dinitroanisol	94-95(95)[21l]	2,4-Dinitrophenol	111-112(113)[21k]

their observed melting points with those reported in the literature (Table-2).

Experimental

The melting points are uncorrected and were observed on Gallenkamp melting point apparatus. IR spectra were recorded on a Hitachi Model 270-50 IR spectrophotometer.

Reagents and substrates

4-Methylbenzaldehyde, 4-chlorobenzaldehyde, 4-methoxybenzyldehyde, 4-methylbenzoic acid, phosphorus pentoxide and orthophosphoric acid were obtained from E. Merck, 4-hydroxybenzaldihyde, and 4-chlorobenzoic acid were supplied by B.D.H. 4-Fluorobenzoic acid and 4-aminobenzoic acid were purchased from Sigam. All these substrates were used without further purification. 4-Nitrobenzaldehyde and 4-bromobenzaldehyde were prepared using standard method [20a] starting from 4-nitrotoluene and 4-bromotoluene respectively. Similarly 4-nitrobenzoic acid and 4-bromobenzoic acid were prepared from 4-nitro-toluene and 4-bromotoluene respectively.

The nitration mixture of potassium nitrate in PPA was prepared by the reported method [17]. Potassium nitrate (1.01 g, 0.01 moles) was added to PPA prepared by carefully mixing phosphorous pentoxide (12.0g) and orthophosphoric acid (8.0 ml) and thoroughly stirring the mixture. The mixture was freshly prepared for nitration of each aromatic substrate. Total volume of the freshly prepared 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 nitration mixture of potassium nitrate and PPA. The reaction mixture was then stirred at the required temperature for a certain period of time. The reaction conditions were expected to be different for different compounds. The optimum conditions required for nitration of each aromatic substrate were determined by repeating the reaction several times at difrerent reaction conditions. These are given 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. In each case a yellow solid precipitated which was filtered off and recrystallized from 50% aq.ethanol. The product of nitration was then characterized. The product of nitration and %age yield of different reaction are also listed in Table-1.

References

1. R.J. Gillespie and D.J. Millen, *Quart. Rev.*, **2** 211 (1948).
2. K. Schofield, *Quart. Rev.*, **4**, 382 (1950).
3. H.M. Fitch, *Org. Synth., Coll.* Vol. **III** (ed. E.C. Horning), John Wiley Sons, New York p. 659 (1967).
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. Wiseqarver and G.A. Alles, *Org. Synth., Coll.*, Vol. **III** (ed. E.C. Horning), John Wiley Sons, New York, p. 644 (1967).

6. R.Q. Brewster, B. Williams and R. Phillips, *Org. Synth., Coll.* Vol. **III** (ed. E.C. Horning), John Wiley Sons, New York, p. 337 (1967).
7. H.P. Schultz, *Org. Synth., Coll.* Vol. **IV** (ed. N. Rabjohn), John Wiley Sons, New York p. 364 (1967).
8. G.B. Bachman, H. Fever, B.R. Bluestein and C.M. Vogt, *J. Amer. Chem. Soc.*, **77**, 6188 (1955).
9. S.J. Khun and G.A. Olah, *J. Amer. Chem. Soc.*, **83**, 4564 (1961).
10. J.F. Riordan, W.E.C. Wacker and B.L. Vallee, *J. Amer. Chem. Soc.*, **88**, 4140 (1966).
11. A.G. Anderson Jr., J.A. Nelson and J.T. Tazuma , *J. Amer. Chem. Soc.*, **75**, 4980 (1953).
12. K.I.H. Williams, S.E. Cremer, F.W. Kent, E.J. Sehn and D.S. Tarbell, *J. Amer. Chem. Soc.*, **82**, 3982 (1960).
13. M. Lemaire, A. Guy, J. Roussel and J. Guette, *Tetrahedron*, **43,** 835 (1987).
14. J.G. Hoggett, R.B. Moddie, J.R. Penton and K. Schofield "Nitration and Aromatic Reactivity", Cambridge Univ. Press, Cambridge p. 61 (1971).
15. W. Koniq, *Angew. Chem.*, **67**, 157 (1955).
16. I.T. Miller and H.D. Spinqall, "Sidquick's Organic Chemistry of Nitrogen", Clarendon Press, Oxford, 3rd ed. p. 379 (1966).
17. S. Sastry and N.A.Kudav, *Indian J. Chem.*, **188**, 198 (1979).
18. L.M. Fieser and M. Fieser, "Reagents for Organic Synthesis", John Wiley Sons, New York, p. 894 (1967).
19. R. Iqbal and M.M. Aslam, *J. Chem. Soc. Pak.*, **8**, 443 (1986).
20. A.I. Vogel, "A Text Book of Practical Organic Chemistry", Longman, London, 3rd ed. p. 695 (1972).
21. J.R.A. Pollock and R. Stevens (Editors), "Dictionary of Organic Compounds", Eyre and Spottiswoode, London, 4th Ed (1965), a) Vol. **2**, p. 660, b) Vol. **1**, p. 468, c) Vol. **2**, p. 662, d) Vol. **4**, p. 2108, e) Vol. **3**, p. 1754, f) Vol. **4**, p. 2516, g) Vol. **4**, p. 2515, h) Vol. **3**, p. 1449 I) Vol. **3**, p. 1757, j) Vol.4, p. 2476,k) Vol. 3, **p.** 1251, l) Vol. 3, **p.** 1238.
22. Z. Rapport (Editor), "Handbook of Tables of Organic Compounds", The Chemical Rubber Co., Ohio p. 206 (1967).
23. R.C. Weast (Editor), "Hand book of Chemistry and Physics:, 54th ed., CRC Press, Ohio C-179 (1973-74)