Anhydrous $LiClO_4$ was obtained from Alfa Products. It was dried in a drying pistol at 100 °C (0.38mmHg) in the presence of P_2O_5 for at least 12 h.

Norbornene was obtained from Aldrich Chemical Co. and used without further purification. No impurities were detected by GLC analysis on a 3% OV-101 column with CHRM GHP as the support (80/100 mesh) at 80 °C with N_2 as a carrier gas and an FID detector.

2,4-Dinitrobenzenesulfenyl chloride (2,4-DNBSCl) was obtained from Aldrich Chemical Co. and recrystallized from CCl_4; mp 95.6–96.6 °C (lit.[24] mp 95–96 °C)

Kinetics. Separate solutions of 2,4-DNBSCl in acetic acid and a mixture of norbornene and $LiClO_4$ in acetic acid were equilibrated in an oil bath at 25.00 ± 0.05 °C. After the solutions were mixed, aliquots were withdrawn periodically, and the remaining 2,4-DNBSCl was analyzed by the method of Kharasch and Wald.[25]

Acknowledgment. Continued financial support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. 2,4-DNBSCl, 528-76-7; $LiClO_4$, 7791-03-9; norbornene, 498-66-8.

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Directing Effects of Phosphorus-Containing Groups in Aromatic Substitution. Orientation in Nitration of Some *N*-Arylphosphoramidates and Phosphorthioamidates in Protic and Aprotic Media

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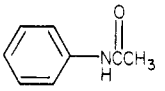
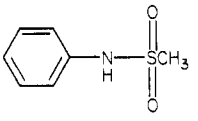
The nitration of acetanilide **1** in strong acid is known.[1,2] to give predominantly para product with some ortho substitution and negligible meta product (Table I).



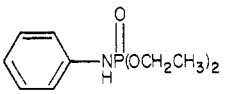
1

Under identical conditions,[1] the corresponding sulfur compound **2** gives a 70:30 para/ortho nitration product distribution (Table I).



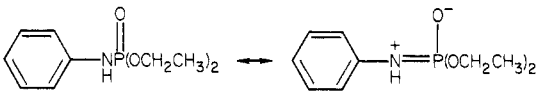
2

Published results for the related phosphorus derivative **3** are substantially different, with a considerable amount



3

of meta product being formed (Table I).[3] The meta product for **3** was rationalized in terms of two possible phenomena: (a) nitration via the N-protonated form or (b) a substantial amount of N–P $p\pi$–$d\pi$ bonding leading to important contributions from the resonance form **3b**.



3a **3b**

Recently we have carried out ^{15}N and ^{13}C NMR studies of **3** and related phosphoramidates[4,5] which show that there is negligible contribution from resonance forms such as **3b**, since N lone-pair delocalization into the aromatic ring is found to be the dominant process.

One is led therefore to the conclusion that systems such as **3** nitrate to a significant extent via the N-protonated form in acidic media. In aprotic media, one might expect to see, however, a return to mainly ortho–para product distribution.

To check this point, we have carried out the nitration of **3** in an aprotic medium, namely, via the pyridine–nitronium tetrafluoroborate complex.[6]

Also we have repeated the protic media nitration of **3** and related compounds in order to verify the reported[3] high degree of ortho products. No yields of isolated and separated products were quoted[3] in previous work, and isomer ratios were given to a ±10% accuracy by using a TLC–spectrophotometric procedure.[7]

In the present work, we have isolated and characterized the nitration products (in the form of their nitroaniline derivatives) and compared them to commercially available standards in order to obtain more reliable data regarding the nitration product distribution.

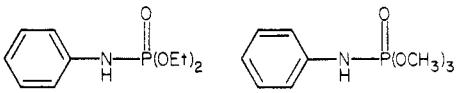
Table I. Isomers from Nitration in Protic Media

compd	conditions	distribution, % ortho	meta	para
1[1,2]	HNO_3–98% H_2SO_4, 25 °C	5	<2	95
2[1]	HNO_3–98% H_2SO_4, 25 °C	30	<1	70
3[3]	HNO_3–97% H_2SO_4, 0 °C	42	38	20
3[a]	HNO_3–97% H_2SO_4, 0 °C	3	70	27
4	HNO_3–97% H_2SO_4, 0 °C	<2	72	28
5	HNO_3–97% H_2SO_4, 0 °C	3	79	18
6	HNO_3–97% H_2SO_4, 0 °C	7	<2	93

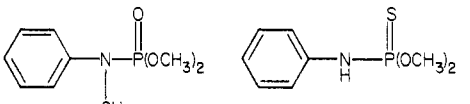
[a] Present work.

Results and Discussion

Protic Nitrations. Nitrations in protic media were carried out for compounds **3–6**, and results are summarized in Table I along with those reported previously.



3 **4**



5 **6**

Each value in the present work represents an average of at least four determinations with standard deviations

(1) Hartshorn, S. R.; Moodie, R. B.; Schofield, K. *J. Chem. B* **1971**, 2454.
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(5) Buchanan, G. W.; Morin, F. G. *Org. Magn. Reson.* **1980**, *14*, 517.
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(7) Modro, T. A.; Pioch, J. *Rocz. Chem.* **1974**, *48*, 161.

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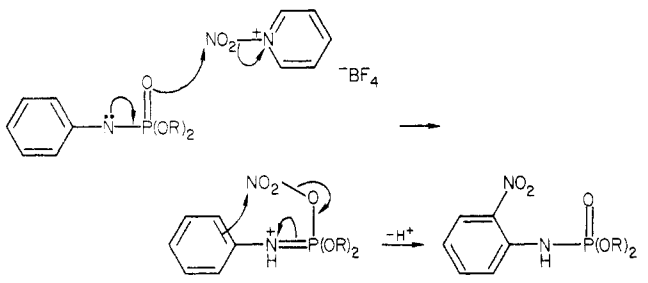
Scheme I



in isomer percentages of ±3%. Our lower limit of detectability as determined from trial runs is 2%.

The first striking feature of the data in Table I is the large difference in isomer ratios obtained for the present work on **3** as opposed to the earlier published results.[3] We do not observe the large proportion of ortho isomer, and indeed the system shows a substantial preference for the meta product, consistent with reaction via the N-protonated form. It appears that in the earlier work,[3] the substrates were nitrated at least partially as free bases, thus giving an anomalously high amount of ortho product.[8]

There is little effect on the product ratios when the $(OR)_2$ group on phosphorus is changed from $(OEt)_2$ to $(OCH_3)_2$ as shown by results for **3** and **4**.

The minor increase in the amount of meta nitration product for **5** relative to **4** may reflect the increased stability of the N-protonated species in **5** which would be expected on the basis of the electron-donating inductive effect of the CH_3 group.

Interestingly, the thioamidate **6** shows essentially *no meta* nitration, indicating that introduction of the sulfur atom converts the substituent into an ortho–para director, and no appreciable reaction occurs via the N-protonated conjugate acid. If protonation on sulfur does occur, the directing effects of this substituent suggest that the N lone pair is not significantly involved in conjugative interactions with it.

Aprotic Nitrations. Nitration of **3** via the pyridine–nitronium tetrafluoroborate complex[6] gives dramatically different isomer distributions, namely, 66% ortho, 7% meta, and 27% para product. These findings are rather similar to those reported[3] for **3** when nitration is performed in acetic anhydride, and the reaction via the conjugate acid of **3** is not possible.

In conclusion, it appears that phosphoramidate nitrations in protic media lead to a predominance of meta product, indicating that the reaction occurs via the N-protonated form. There is no need to postulate a special "ortho" mechanism as was done previously,[3] since the ortho products are in fact formed to a minimal extent.

In aprotic media, however, there is a tendency for ortho product predominance over the para product in excess of the statistical value of 2. It is known[6] that the *N*-nitropyridinium ions themselves participate in the rate-determining transition state of transfer nitrations, rather than "free" nitronium ions. To rationalize the preferred ortho pathway, one could suggest a mechanism such as that outlined in Scheme I. An analogous pathway could be suggested for the nitration of **3** in acetic anhydride, with N_2O_5 believed to be the electrophile.[1,9]

Experimental Section

Materials **3–6** were prepared via published methods.[3,5] The nitration reactions and subsequent hydrolyses to the nitroaniline derivatives were carried out in a manner similar to that reported previously by Modro and Pioch.[3] Our quantitative separations were obtained on silica gel 60 F_{254} 20 × 20 cm preparative TLC plates obtained from Merck, Darmstadt, Germany. The solvent system was a 50:50 volume mixture of diethyl ether and low-boiling (30–60 °C) petroleum ether.

Yields of separated products are greater than 80% in all cases. Authentic samples of all the nitroanilines were obtained from Aldrich Chemical Corp., Milwaukee WI.

^1H NMR spectra of the products (nitroanilines) were compared to those of authentic samples on Varian T-60, XL-100, and XL-200 NMR spectrometers with $CDCl_3$ as the solvent and Me_4Si as an internal reference.

It was also shown that when no nitric acid was added, starting materials **3–6** could be recovered quantitatively from the sulfuric acid solutions under the conditions of the nitration reaction. This proves that there is no nitroaniline in the reaction product which arises from nitration of an initially hydrolyzed starting material.

Nitrations using the pyridine–nitronium tetrafluoroborate complex were carried out according to the published method,[6] modified as described below.

To a flask under an N_2 atmosphere at 0 °C were added 10 mL of dry acetonitrile, 2.4 g (18.2 mmol) of nitronium tetrafluoroborate and 1.5 g (18.1 mmol) of pyridine, in that order. The resulting stirred solution was allowed to warm to 20 °C over a 0.5-h period. This solution was then transferred via pipet into another flask (under N_2) containing 9.0 mmol of **3** in 15 mL of dry acetonitrile.

After this solution was stirred at 20 °C for 1 h, 25 mL of 6 N HCl was added, and the solution was refluxed for 2 h to hydrolyze the phosphoramidate to the nitroaniline derivative. The solution was then neutralized by addition of NaOH and was then extracted with ether. Quantitative separations were done via preparative TLC (vide supra) and products analyzed with the aid of ^1H NMR on a Varian XL-200 system.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for summer research fellowships (to S.H.P.) and operating grant funds (to G.W.B.).

Registry No. **3**, 1445-38-1; **4**, 58046-12-1; **5**, 7006-95-3; **6**, 83436-57-1; *m*-nitroaniline, 99-09-2; *p*-nitroaniline, 100-01-6; *o*-nitroaniline, 88-74-4.

(8) Modro, T. A., private communication, March 1982.
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Organic Sonochemistry. Sonic Acceleration of the Reformatsky Reaction

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The Reformatsky reaction is the most generally applicable procedure for converting aldehydes and ketones to β-hydroxy esters, and, consequently, it has been the subject of extensive synthetic and mechanistic study.[1] Significant improvements in the yields of this reaction have been obtained by using freshly prepared zinc powder,[2] a heated column of zinc dust,[3] and a trimethyl borate–tetrahydrofuran solvent system.[4] Recently we[5] and others[6] have

(1) Rathke, M. W. *Org. React. (NY)* **1975**, *22*, 423–458.
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(3) White, J. D.; Ruppert, J. F. *J. Org. Chem.* **1974**, *39*, 269–270.
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