propylamine (0.24 g, 4.0 mmol) dissolved in 5 mL of chloroform. The reaction mixture was stirred briefly and allowed to stand for 73 h at room temperature. Then the solvent was removed in vacuo, and the residue was triturated with cold petroleum ether (30–60 °C) and filtered to give 0.23 g of a 50:50 mixture of 1-(isopropylamino)-2-nitro-1-propene (**11**, 41%) and unreacted **7** (41%), as determined by NMR analysis of the olefinic methyl singlets of **11** and **7** at δ 2.00 and 2.32, respectively.

D. Employing 1.1 Molar Equivalents of *n*-Propylamine. A solution of **7** (0.32 g, 2.0 mmol) and *n*-propylamine (0.13 g, 2.2 mmol) in 17 mL of absolute methanol was stirred at room temperature for 48 h. Then the reaction mixture was subjected to TLC plates on silica gel PF 254 and eluted with absolute ether to afford two fractions. Each fraction was washed from the silica gel with absolute methanol, and the methanol was evaporated in vacuo. In this manner a solid and a liquid product were obtained. Recrystallization of the solid material from hexane gave recovered **7** (47 mg, 14%), mp 88–90 °C.

The liquid was 1-(*n*-propylamino)-2-nitro-1-propene (**10**, 110 mg, 38%). The IR and NMR spectra were identical with those of authentic **10**.[1] The high-resolution mass spectrum of **10** exhibited a molecular ion at *m/e* 244.0906 (calcd *m/e* 244.0899).

Reaction of 1-Cyclohexylamino-2-nitro-1-propene (9) with Excess *tert*-Butylamine. Compound **9** (0.50 g, 2.7 mmol) was dissolved in 20 mL of *tert*-butylamine. The solution was refluxed for 1 h and cooled to room temperature, and excess *tert*-butylamine was removed in vacuo to afford 0.47 g of a mixture of unreacted **9** (55%) and 1-(*tert*-butylamino)-2-nitro-1-propene (**1**, 39%), as determined by NMR analysis of the olefinic methyl signals of **9** and **1** at δ 2.04 and 2.08, respectively.

Alkaline Hydrolysis of 1-(*tert*-Butylamino)-2-nitro-1-propene (1). Compound **1** (3.16 g, 0.02 mol) was dissolved in 25 mL of 2 N potassium hydroxide, and one-half of the hydrolysate was distilled into a receiver containing 5 mL of concentrated hydrochloric acid. Evaporating the distillate to dryness in vacuo and recrystallizing the residue from absolute ethanol gave *tert*-butylamine hydrochloride (1.89 g, 87%). The IR spectrum was identical with that of an authentic sample.

Benzamide: mp 138–139 °C (lit.[8] mp 134 °C).

The remainder of the hydrolysate was acidified to pH 1 with hydrochloric acid and extracted with ether. The ether extracts were washed first with a saturated potassium bicarbonate solution, then with water, and dried ($MgSO_4$). Evaporation of the ether in vacuo gave nitroethane (0.74 g, 45%): IR (neat) 1563 and 1370 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 1.57 (t, 3, CH_3), 4.45 (q, 2, CH_2NO_2).

Potassium *N*-Propylidene-*tert*-butylamine-2-nitronate. To a suspension of potassium amide (0.018 mol) in 150 mL of liquid ammonia at −40 °C was added **1** (3.16 g, 0.02 mol) in one portion. The reaction mixture was stirred for 30 min, and the ammonia was replaced with absolute ether (3 h). The suspension was filtered to give a solid which immediately began to darken on exposure to the atmosphere. The solid was dissolved in absolute ethanol and reprecipitated with absolute ether to afford the salt (3.17 g, 91%) as a cream-colored amorphous powder, mp 190–195 °C dec; IR (KBr) 1610 (C=N), 1524 and 1297 cm^{-1} (NO_2^-); NMR (Me_2SO-d_6) δ 1.07 (s, 9, $(CH_3)_3C$), 1.85 (s, 3 CH_3), 8.60 (s, 1, CH=N). Due to its instability the salt could not be purified sufficiently for elemental analysis. NMR analysis indicated that it was approximately 90% pure.

Acidification of Potassium *N*-Propylidene-*tert*-butylamine-2-nitronate. The salt (0.98 g, 5.0 mmol) was dissolved in 50 mL of distilled water at 0 °C, and the solution was acidified with 10% aqueous acetic acid to pH 5–6. The yellow suspension was extracted with three 15-mL portions of chloroform and dried ($MgSO_4$), and the chloroform was removed in vacuo to afford 1-(*tert*-butylamino)-2-nitro-1-propene (**1**, 0.53 g, 67%), mp 111–113 °C. The IR and NMR spectra were identical with those of authentic **1**.

Acknowledgment. The support of this work by a grant from the Eli Lilly and Company is greatly appreciated.

Registry No.—(*Z*)-**1**, 64331-63-1; (*E*)-**1**, 64331-62-0; **2**, 64957-53-5; (*Z*)-**3**, 64331-65-3; (*E*)-**3**, 64331-64-2; **4**, 64957-54-6; **5**, 5447-96-1; **6**, 64957-55-7; (*E*)-**7**, 64957-56-8; (*E*)-**8**, 64957-57-9; (*Z*)-**9**, 64331-56-2; 2-bromo-2-nitropropanal, 64957-58-0; 1-bromo-1-nitroethane, 563-97-3; pyrrolidine, 123-75-1; nitroethane, 79-24-3; potassium *N*-propylidene-*tert*-butylamine-2-nitronate, 65000-07-9; potassium amide, 17242-52-3.

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Notes

Fluoronitroanilines. Reaction Control via Hydrogen Bonding

Michael E. Sitzmann

Naval Surface Weapons Center, White Oak, Silver Spring, Maryland 20910

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Recent work[1,2] has shown that although pentafluoronitrobenzene reacts with most nucleophiles to give predominantly displacement of a *p*-fluorine atom, it reacts with ammonia and methylamine to give mainly *o*-fluorine displacement. The higher percentage of ortho replacement for amine nucleophiles was attributed to hydrogen bonding between the attacking amine and the nitro group. However, evidence for the hydrogen-bonding hypothesis was not unequivocal since the ortho/para ratio for the reaction of ammonia and methylamine with pentafluoronitrobenzene (69:31 and 65:35, respectively) was not far from statistical and the preferential ortho (relative to para) directing effect of the fluorine atoms in nucleophilic substitution was a complicating factor.[3]

We have found that treatment of 2,4,6-trifluoronitrobenzene (**1**) with ammonia in tetrahydrofuran gives essentially all ortho-displacement product. Thin-layer chromatographic analysis[4] shows only trace amounts of two unidentified products in addition to the ortho-displacement product, 3,5-difluoro-2-nitroaniline (**2**), which was isolated in 88% yield (a small amount of unreacted **1** is also present). Similarly, treatment of 1,3-dinitro-2,4,6-trifluorobenzene (**3**) with ammonium hydroxide in tetrahydrofuran at −10 °C gives only one monoamine, 3,5-difluoro-2,6-dinitroaniline (**4**). A small amount of diamine, 2,6-dinitro-5-fluoro-1,3-phenylenediamine (**5**), is formed from further reaction of **4** with ammonia but no other products were detected by thin-layer chromatographic analysis.[5]

It is significant that substitution occurs exclusively at the more hindered ortho positions in compounds **1** and **3**. These results strongly support the hypothesis of Allen et al.[2] that the reaction of ammonia with fluoronitrobenzenes is controlled by the degree of hydrogen bonding in the reaction intermediates.[6] For compound **1**, stabilization of the reaction intermediate by hydrogen bonding can occur at the position ortho to nitro but not at the position para. For compound **3**, the in-

termediate formed by attack at the 2-fluorine can be stabilized by hydrogen bonding to two nitro groups[7] whereas attack at the 4-fluorine gives an intermediate stabilized by hydrogen bonding to only one nitro group.

Fluoronitroanilines have found recent use as reagents for analysis of amino acids and peptides.[8] Previously, most fluoronitroanilines had been prepared by nitration of fluoroacetanilides followed by removal of the acetyl group. The fact that hydrogen bonding gives sufficient reaction control to produce essentially only one product from ammonia and trifluoronitrobenzenes suggests that this is a convenient route for the preparation of other fluoronitroanilines.

Attempts to prepare 3,5-difluoro-2,4,6-trinitroaniline (**7**) by nitration of **2** or **4** were unsuccessful.[9] Under mild conditions the nitration product from **4** was the nitramine derivative, *N*-2,6-trinitro-3,5-difluoroaniline (**8**). Compound **8** was also isolated from the nitration of **2**. Presumably **2** first forms the nitramine derivative, *N*-2-dinitro-3,5-difluoroaniline, which rearranges to **4**, but the analogous rearrangement of **8** to **7** does not take place. Evidently $NNO_2 \rightarrow o\text{-}NO_2$ rearrangement in this series is strongly preferred to $NNO_2 \rightarrow p\text{-}NO_2$.[10]

Experimental Section[11]

Fluoronitrobenzenes and Their Derivatives Should be Handled with Care as 2,4-Dinitro-1-fluorobenzene Has Mutagenic and Carcinogenic Properties (M. Levitt and C. Bon, Chemical and Engineering News, Vol. 55, No. 29, July 18, 1977, p 30).

3,5-Difluoro-2-nitroaniline (2). A solution of 5.3 g of 2,4,6-trifluoronitrobenzene[12] in 50 mL of tetrahydrofuran was stirred at ambient temperature as ammonia gas was bubbled in over a period of 7 h. The mixture was filtered to remove precipitated ammonium fluoride and the solvent was removed under reduced pressure to give a red-orange solid which was crystallized from benzene–hexane to yield 4.6 g (88%) of yellow-orange crystals, mp 104–108 °C. Recrystallization from benzene gave mp 107–108 °C (lit.[13] mp 107–108 °C): NMR (acetone) δ 6.87 (broad s, NH_2) 6.64–6.24 (two multiplets with slight overlap, 13 peaks); mass spectrum *m/e* 174 (M^+).

***N*-Acetyl-3,5-difluoro-2-nitroaniline.** A solution of 1.40 g of 3,5-difluoro-2-nitroaniline in 14 mL of acetyl chloride (dissolve by warming) was allowed to stand overnight at ambient temperature before the acetyl chloride was removed to give 1.73 g (100%) of a yellow-orange crystalline residue, mp 98–100 °C. Crystallization from hexane gave mp 100–101 °C (lit.[14] mp 137–138 °C): NMR (acetone) δ 9.46 (broad s, 1 H, NH), 7.92–7.76 (m, 6 peaks, 1 H), 7.19–6.97 (m, 7 peaks, 1 H), 2.15 (s, 3 H, CH_3); IR (KBr) 3285 (NH), 1680 (C=O) cm^{-1}.

Anal. Calcd for $C_8H_6N_2F_2O_3$: C, 44.45, H, 2.80; N, 12.96; F, 17.58. Found: C, 44.64; H, 2.88; N, 12.80; F, 17.83.

3,5-Difluoro-2,6-dinitroaniline (4) and 2,6-Dinitro-5-fluoro-1,3-phenylenediamine (5). A solution of 1.1 g (0.005 mol) of 1,3-dinitro-2,4,6-trifluorobenzene[15] in 10 mL of tetrahydrofuran was well stirred at −10 °C during the dropwise addition of 0.65 mL (0.01 mol) of ammonium hydroxide (29% NH_3) over a 1-min period. Stirring at −10 °C was continued for an additional 3 min before the reaction mixture was poured into ice water to precipitate a yellow solid (0.92g) which was immediately removed, washed with cold water, and dried in vacuo. TLC of the yellow solid showed mainly **4** with a small amount of **5**. The yellow solid was stirred with 15 mL of methylene chloride at ambient temperature for 10 min before the insoluble material (diamino compound, 66 mg) was removed. Concentration of the methylene chloride solution and addition of hexane gave 0.61 g (55%) of yellow crystals of 3,5-difluoro-2,6-dinitroaniline, mp 113–117 °C. The analytical sample (mp 117.5–118.5 °C) was obtained by column chromatography on silica gel: NMR (acetone) δ 7.61 (broad s, 2 H, NH_2), 6.81 (t, 1 H, aromatic H); IR (KBr) 3535, 3410 (NH_2) cm^{-1}; mass spectrum *m/e* 219 (M^+). Anal. Calcd for $C_6H_3N_3O_4F_2$: C, 32.89; H, 1.38; N, 19.18; F, 17.34. Found: C, 33.05; H, 1.48; N, 19.33; F, 17.57.

The diamino compound (2,6-dinitro-5-fluoro-1,3-phenylenediamine) after crystallization from acetone has mp 284–85 °C dec: NMR (Me_2SO) δ 9.21 (s, 2 H, NH_2), 8.64 (s, 2 H, NH_2), 6.07 (d, 1 H, aromatic H); mass spectrum *m/e* 216 (M^+). Anal. Calcd for $C_6H_5N_4O_4F$: C, 33.33; H, 2.33; N, 25.92; F, 8.79. Found: C, 33.20; H, 2.36; N, 25.76; F, 9.01.

***N*-Acetyl-3,5-difluoro-2,6-dinitroaniline.** A solution of 625 mg of 3,5-difluoro-2,6-dinitroaniline in 3.5 mL of acetyl chloride was allowed to stand at ambient temperature overnight (crystals precipitate). Ether (10 mL) was added and the crystals (647 mg, 87%, mp 198–199 °C) were removed and washed with ether. Recrystallization from 1,2-dichloroethane gave pale yellow needles, mp 198–199 °C: NMR (acetone) δ 9.72 (broad s, 1 H, NH), 7.71 (t, 1 H, aromatic H), 2.12 (s, 3 H, CH_3); IR (KBr) 3285 (NH), 1685 (C=O) cm^{-1}. Anal. Calcd for $C_8H_5N_3F_2O_5$: C, 36.79; H, 1.93; N, 16.09; F, 14.55. Found: C, 36.86; H, 1.98; N, 15.94; F, 14.73.

***N*-2,6-Trinitro-3,5-difluoroaniline (8) (Caution! 8 is an Explosive and Can be Detonated with a Hammer Blow).** Nitric acid (90%) (3.6 mL) was added to 20 mL of 30% fuming sulfuric acid with cooling. To the nitric–sulfuric acid mixture stirred in an ice bath was added 1.2 g of 3,5-difluoro-2,6-dinitroaniline in small portions. The solution was stirred for 1 h at room temperature and then was poured onto ice and extracted with 3 × 50 mL of ether. The extracts were combined and dried over magnesium sulfate. The ether was removed under reduced pressure to give 1.3 g of a yellow solid which was crystallized from methylene chloride to yield 1.1 g (76%) of yellow crystals, mp between 80 and 85 °C dec depending on the rate of heating: NMR (acetone) δ 10.56 (broad s, 1 H, NH), 8.14 (t, 1 H, aromatic H); IR (KBr) 3385 (NH) 3120 (aromatic H) cm^{-1}.

Anal. Calcd for $C_6H_2N_4F_2O_6$: C, 27.28; H, 0.76; N, 21.21; F, 14.39. Found: C, 27.28; H, 0.76; N, 21.09; F, 14.53.

Registry No.—**1**, 315-14-0; **2**, 361-72-8; **3**, 392-51-8; **4**, 64884-81-7; **5**, 64884-82-8; **8**, 64884-83-9; *N*-acetyl-3,5-difluoro-2-nitroaniline, 361-71-7; acetyl chloride, 75-36-5; *N*-acetyl-3,5-difluoro-2,6-dinitroaniline, 64884-84-0; nitric acid, 7697-37-2; 1,3,5-trifluorobenzene, 372-38-3.

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(2) J. G. Allen, J. Burdon, and J. C. Tatlow, *J. Chem. Soc.*, 1045 (1965).
(3) Pentafluorobenzene, with its electronically neutral hydrogen substituent, is substituted by nucleophiles almost entirely in the position para to hydrogen. Pentafluoroanisole, even though it contains the strongly deactivating methoxyl group, still gives the isomer para to methoxy as the major substitution product. From these results the authors[1] concluded that the activating influence of the five fluorine atoms to nucleophilic substitution must be considerable.
(4) The analyses were performed on silica gel F-254 TLC plates (Brinkmann). Benzene was the developer and the spots were visualized with UV light.
(5) The structures for **2**, **4**, and **5** were assigned on the basis of their NMR spectra. The spectra of **2** and its acetyl derivative each show two types of ring protons. The isomer of **2**, 3,5-difluoro-4-nitroaniline, would contain equivalent fluorine atoms and ring protons. The spectra of **4** and its acetyl derivative show the expected triplet for a ring proton ortho to two equivalent fluorine atoms. Such a spectrum is not possible for 3,5-difluoro-2,4-dinitroaniline, the isomer of **4**. Compound **5** contains nonequivalent amino groups which is consistent with the structure assigned.
(6) C. F. Bernasconi and R. H. deRossi, *J. Org. Chem.*, **41**, 44 (1976). These authors have also suggested that such intermediates are formed in the reaction of fluoronitro-aromatic compounds with amines. Similar intermediates can be envisioned for the reaction of **1** and **3** with ammonia.
(7) The interatomic potential curves [J. R. Holden and C. Dickinson, *J. Phys. Chem.*, **81**, 1505 (1977)] indicate there would be attraction between ammonia hydrogen atoms and the oxygens from both nitro groups as the ammonia approached to form the reaction intermediate. An amino group between two nitro groups can simultaneously hydrogen bond to both. J. R. Holden, *Acta Crystallogr.*, **22**, 545 (1967); H. H. Cady and A. C. Larson, *ibid.*, **18**, 485 (1965).
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(9) Procedures for the preparation of pentanitroaniline, 2,3,4,6-tetranitroaniline, and 2,4,6-trinitroaniline from 3,5-dinitroaniline, 3-nitroaniline, and 2-nitroaniline, respectively, have been reported. B. Flürscheim and E. Holmes, *J. Chem. Soc.*, 3041 (1928); B. Flürscheim, *J. Soc. Chem. Ind., London*, **40**, 97 (1921); O. Witt and E. Witte, *Ber.*, **41**, 3090 (1908). These procedures with **2** or **4** did not give **7**.
(10) This result is not unambiguous. Some **7** could be formed during the nitration and then lost due to conversion to its nitramine derivative. However, **8** in 30% fuming sulfuric acid did not rearrange to **7** even after prolonged reaction time. Conversion of **7** to its nitramine derivative under these conditions could only occur if **4** were also formed. No **4** was observed.
(11) NMR spectra were determined on a Varian HA-100 spectrometer and the chemical shifts are relative to tetramethylsilane. The melting points are corrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.
(12) PCR, Inc., Gainesville, Fla.
(13) G. C. Finger, F. H. Reed, and J. L. Finnerty, *J. Am. Chem. Soc.*, **73**, 154 (1951).
(14) Reference 13. The reason for the discrepency in the melting points is not known. In ref 13 the crystallization solvent was *m*-fluorobenzo trifluoride and an elemental analysis was not given.

(15) The dinitrotrifluorobenzene was prepared as follows: 120 mL of 90% nitric acid was added to 180 mL of 30% fuming sulfuric acid with cooling; 52.8 g of 1,3,5-trifluorobenzene[12] was added dropwise with stirring at 10–15 °C and the mixture was warmed to 45–50 °C for 45 min; the cooled reaction mixture was poured onto ice and the precipitated product was immediately removed, washed with cold water, and dried in vacuo to give 79.5 g (90%), mp 47–52 °C; crystallization from dry carbon tetrachloride gave mp 51–53 °C (lit. mp 52–53 °C: G. C. Finger and C. W. Kruse, *J. Am. Chem. Soc.*, **78**, 6036 (1956)).

Azetidinone Antibiotics. 19. A Simple Method for the Removal of *p*-Nitrobenzyl Acid Protective Group[1]

Steven R. Lammert, Alvin I. Ellis,[2] Robert R. Chauvette, and Stjepan Kukolja*

The Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana 46206

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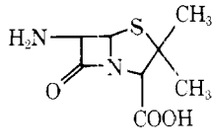
The chemistry of azetidinone antibiotics has undergone considerable progress during the last two decades.[3] This outstanding development has been largely possible due to the appropriate blocking of the amino and carboxyl groups in the nucleii **1** and **2**. In particular, the protection of the carboxyl



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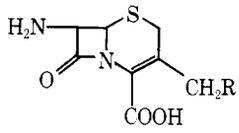

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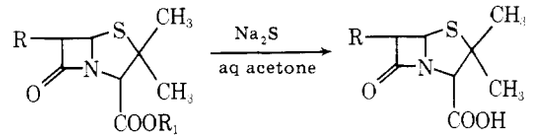
group from undesirable side reactions has been very beneficial. A wide variety of carboxyl protective groups, together with different methods for their selective removal, has been utilized. These include the *tert*-butyl, trichloroethyl, *p*-methoxybenzyl, phenacyl, 2-haloethyl, alkoxymethyl, benzyl, benzhydryl, *p*-nitrobenzyl, and others. Among these the *p*-nitrobenzyl (pNB) group has been frequently used in the chemical modifications of bicyclic azetidinones.[4] The pNB esters of penicillins and cephalosporins are easily prepared by treating the corresponding acid with *p*-nitrobenzyl bromide in the presence of base at temperatures between 0 and 20 °C. The significant advantage of the pNB protective group is relative stability to most acidic and basic reaction conditions. The additional advantage is that it can be selectively removed by catalytic or chemical reduction. Chemical reductions have been widely used in a number of circumstances. Catalytic hydrogenolysis has also been used although these sulfur-containing molecules occasionally caused a "poisoning" effect on hydrogenation catalysts.

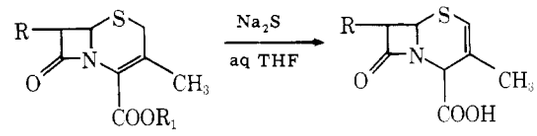
In connection with our work on the removal of the phthaloyl group,[5] a simple, rapid, and high-yield method for the removal of the *p*-nitrobenzyl group from highly sensitive azetidinone antibiotics has been found and our results are reported here.

We have observed that the pNB group can be removed easily by alkaline hydrolysis with sodium sulfide ($Na_2S·9H_2O$). The hydrolysis is performed in an aqueous THF, DMF, or acetone solution at ice-bath temperature within 25–35 min. The progress of hydrolysis can be followed by thin-layer chromatography. The expected acid is usually isolated by acidification of an aqueous portion and if desired recrystallized from the appropriate solvent.

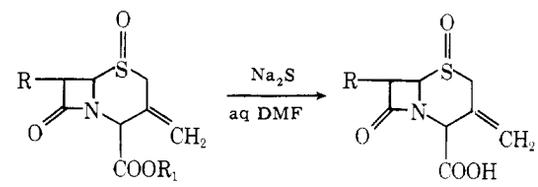
When this method was applied to *p*-nitrobenzyl esters of penicillin G and V (**3g** and **3v**), the corresponding penicillanic acids **4g** and **4v** were obtained in about 80% yield. A similar hydrolysis of deacetoxycephalosporin esters **5h, 5g,** and **5v** afforded 2-cephem acids **6h, 6g,** and **6v** in 75–83% yield. Apparently, in the case of pNB esters of 3-cephem derivatives, the ester group was hydrolyzed, and at the same time, the double bond was isomerized from the Δ^3 to the Δ^2 position. Accordingly, this is a very practical method for preparation of 2-cephem acids **6**.



3g or **3v** **4g** or **4v**



5h, 5g, or **5v** **6h, 6g,** or **6v**



7v **8v**

g, R = $PhCH_2CONH-$; **v**, R = $PhOCH_2CONH-$; **h**, R = NH_2, R_1 = *p*-nitrobenzyl (pNB)

However, an analogous hydrolysis of the pNB ester of 3-methylene cepham **7v** with $Na_2S·9H_2O$ in aqueous DMF resulted only in the removal of the ester group without isomerization of the exocyclic double bond. The acid **8v** was isolated in 45% yield.

The results described in this paper demonstrate that the hydrolysis of pNB esters of various azetidinone derivatives with $Na_2S·9H_2O$ is feasible, even with highly sensitive azetidinone antibiotics. Removal of the pNB group may be used as an alternative to chemical reduction and hydrogenolysis, although the simplicity, expediency, and high yields could be considered as being advantageous. Therefore, we believe that the hydrolysis with $Na_2S·9H_2O$ will find widespread application in the removal of the pNB group.

Experimental Section

Representative Hydrolyses of pNB Esters of Azetidinone Antibiotics. A. 6-Phenylacetamidopenicillanic Acid. A solution of 469 mg (1 mmol) of *p*-nitrobenzyl 6-phenylacetamidopenicillanate in 12 mL of THF and 6 mL of water was cooled in an ice bath, and a solution of 240 mg (1 mmol) of $Na_2S·9H_2O$ in 5 mL of water was added. The mixture was stirred at 0–5 °C for 25 min, 1 mL of 1 N HCl added, and THF was evaporated in vacuo. In order to remove the nonacidic material, 15 mL of ethyl acetate was added to the aqueous solution, pH adjusted to 8.5, and the organic layer was discarded. The pH of the aqueous solution was adjusted to 2.5 with 1 N HCl, and the desired acid was extracted with 20 mL of ethyl acetate. The extract was washed with brine and dried ($MgSO_4$). After evaporation of the solvent 270 mg (81%) of the corresponding acid was obtained. NMR, IR, and TLC of this material were in agreement with those of an authentic sample.

B. 7-Phenoxyacetamido-3-methyl-2-cephem-4-carboxylic Acid. A mixture of 4.83 g (10 mmol) of *p*-nitrobenzyl 7-phenoxyacetamido-3-methyl-3-cephem-4-carboxylate, 100 mL of THF, 10 mL of water, and 2.4 g (10 mmol) of $Na_2S·9H_2O$ was stirred in an ice bath for 30 min.

HCl (10 mL, 1 N) was added and THF was evaporated on a rotavapor and the solution was extracted with 30 mL of ethyl acetate. The extract was discarded. The pH of the aqueous layer was adjusted to 3.2 with hydrochloric acid, and soon the oily product commenced to

0022-3263/78/1943-1243$01.00/0