Synthesis and Reactions of Sydnone Oximes

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Oximino sydnones **1a,b** have been prepared and subjected to reaction with a variety of electrophilic reagents. The aldoxime reacted with all of the latter (except acetic anhydride) to give 3-(2-cyanophenyl)sydnone **1h**. With acetic anhydride, both sydnone oximes formed the corresponding *O*-acetates **1i,m**. Similarly, *O*-sulfonates **1l,k,j**, respectively, were obtained by reaction of the ketoxime with benzene-, methane- and *para*-toluenesulfonyl chloride. Thermolysis (on silica) of the *O*-sulfonates and the *O*-acetates has been examined.

As part of another study we required the fused sydnoquinazolines **3a,b**. Oximino sydnones **1a,b** appeared likely precursors and it is with the preparation and reactions of such species that this paper deals.

Tien and coworkers [1] recently reported unsuccessful attempts to effect Beckmann rearrangement upon the sydnone oxime **2**. Despite this failure, it was of interest to study similar reactions for **1a,b** because of the additional opportunity for cyclization to the sydnone ring either before or after rearrangement (to give *e.g.* **3**, **4** or **5**).
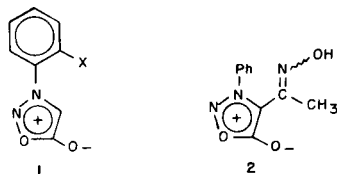
a, X = CH=NOH	e, X = COOMe	i, X = CH=NOAc	m, X = C(Me)=NOAc		
b, X = C(Me)=NOH	f, X = CHO	j, X = C(Me)=NOTs	n, X = C(R)=NOCOCF₃		
c, X = COOH	g, X = COMe	k, X = C(Me)=NOMs	o, X = NHCOMe		
d, X = CH₂OH	h, X = CN	l, X = C(Me)=NOSO₂Ph	p, X = CONHMe		

Recent reports concerning the efficacy of borane-methyl sulfide complex (BMS) as a mild, highly efficient reductant for carboxylic acids [2] suggested a pathway to the aldoxime **1a** involving reduction of 3-(2-carboxyphenyl)sydnone **1c** [3] to the corresponding alcohol, oxidation to the aldehyde with pyridinium dichromate [4] and subsequent reaction with hydroxylamine hydrochloride. Similarly, it was anticipated that the ketoxime **1b** could be prepared from *o*-aminoacetophenone in four steps [5].

Treatment of **1c** with BMS (2*M* in tetrahydrofuran) at room temperature under nitrogen (conditions under which most aromatic carboxylic acids are substantially reduced [2a]) gave an 85% recovery of starting material. A trace amount of the sydnone alcohol **1d** was isolated from the remaining complex mixture. Heating similar mixtures at 50° for periods up to two hours increased the complexity of the reaction but not the yield of the alcohol. Likewise, the use of trimethylborate (which reportedly [2a] enhances the room temperature BMS reduction of carboxylic acids) with BMS and **1c** gave, after several hours, predominantly starting material and a complex mixture containing a trace amount of the alcohol.

The reluctance of **1c** to react with an electrophilic reductant is undoubtedly due to the electron withdrawing effect of the sydnone ring (the N-3 position bears a fractional positive charge [6]) which lowers the nucleophilicity of the carboxyl group sufficiently to allow competitive sydnone ring reduction. These data suggested the use of a nucleophilic hydride reductant with, *e.g.* **1e** [7]. The sensitivity of the sydnone ring to nucleophiles [6] militated against the use of lithium aluminum hydride and the milder sodium borohydride in *t*-butyl alcohol [8] was instead employed.

Accordingly, **1e** was treated with excess sodium borohydride in refluxing *t*-butyl alcohol for two hours. "Workup" gave the sydnone alcohol **1d** as a colourless, crystalline solid (70%, mp 73-75°) characterized by ir, nmr and mass spectrometry, as well as a satisfactory elemental analysis. Conversion to the aldehyde **1f** was effected in 65%
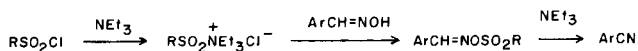
Table I

Reagent	Product from **1a**	Time hours	Yield %	Product from **1b**	Time hours	Yield %
a. Tosyl chloride/Triethylamine	**1h**	12	56	**1j**	12	62
b. Mesyl chloride/Triethylamine	**1h**	4	83	**1k**	1	81
c. Benzenesulfonyl chloride/Triethylamine	**1h**	12	77	**1l**	12	49
d. Triflyl chloride/Triethylamine	**1h**	12	73	[9]	—	—
e. Thionyl chloride/Triethylamine	**1h**	2	77	[9]	—	—
f. Phosphorus pentachloride/Triethylamine	**1h**	12	70	[9]	—	—
g. Tetraphosphorus decasulfide	**1h**	48	45	[9]	—	—
h. Acetic anhydride	**1i**	24	66	**1m**	24	62

yield (after column chromatography) by reaction with pyridinium dichromate for 26 hours at room temperature in dichloromethane. The aldoxime **1a** was prepared in moderate yield (65%) by reaction of the aldehyde with hydroxylamine hydrochloride in pyridine. The corresponding ketoxime **1b** was obtained from *o*-aminoacetophenone in standard fashion [5].
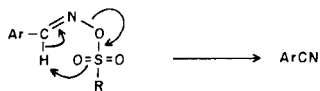
Subsequently, treatment of both oximes with a variety of electrophilic reagents was examined (see Table I).

The identity of the cyanosydnone **1h** was confirmed by its synthesis from anthranilonitrile in 12% overall yield using standard methods [6]. Its formation from reaction of **1a** with benzene-, methane-, toluene- and trifluoromethanesulfonyl chloride is presumably *via* base catalyzed elimination from an intermediate sulfonate (see Scheme 1) although an intramolecular process (see Scheme 2) cannot be ruled out. Similar mechanisms can be postulated for reaction with thionyl chloride or phosphorus pentachloride. With tetraphosphorus decasulfide it is possible that an intramolecular process, similar to that in Scheme 2, occurs. Similar results have been obtained for other aldoximes [10], although not usually under such mild conditions. The strong electron-withdrawing effect of the sydnone ring undoubtedly aids elimination.

Scheme 1

$$RSO_2Cl \xrightarrow{NEt_3} RSO_2\overset{+}{N}Et_3Cl^- \xrightarrow{ArCH=NOH} ArCH=NOSO_2R \xrightarrow{NEt_3} ArCN$$

Scheme 2

Reaction of benzene-, methane- or *para* toluenesulfonyl chloride with the ketoxime **1b** gave the corresponding *O*-sulfonates (see Table 1). Complex, inseparable mixtures were obtained with trifluoromethanesulfonyl chloride, thionyl chloride, tetraphosphorus decasulfide, phosphorus pentachloride and sulfuric acid. Presumably, with these reagents, rearrangement followed by sydnone ring opening occurs.

Analogous to Tien's results with **2**, both oximes reacted with acetic anhydride to form the corresponding *O*-acetates as stable, crystalline solids. With trifluoroacetic anhydride, "work-up" of the reaction mixtures by pouring into water gave oils which quickly crystallized. Recovery of the starting oximes was thus effected. It is reasonable to assume that the corresponding *O*-trifluoroacetates **1n** were initially formed and subsequently hydrolyzed by addition to water. This susceptibility to even weak nucleophiles suggested little advantage to their further study.

However, the isolation of stable ketoxime-*O*-sulfonates allowed us to further investigate potential cyclization routes, *e.g.* thermolysis of **1k**. In this regard it proved convenient to perform the thermolysis directly on a tlc plate. This method offered the advantages of low cost, rapidity and small scale. Thus, the sample was spotted onto a pre-dried [11] tlc plate, the whole placed in an oven and a range of temperatures utilized (with different tlc plates) until reaction was observed. By this method it was found that complete reaction (3 products by tlc) occurred in fifteen minutes at 100°. Scale up (preparative tlc and adsorption on silica) gave the fused sydnone **3b** (7%), characterized by a satisfactory elemental analysis, its spectral data and its widely different melting point from that of its known isomer **4b** [12], and 3-(2-acetamidophenyl)sydnone **1o**, identical (ir, mp, tlc) to an authentic sample [13,14]. Similar results were obtained with the benzenesulfonate and tosylate analogues. We intend to study further the effects of oxime orientation (*E* or *Z*) and *O*-substitution upon the course of the thermal reaction.

It is interesting that the products obtained from the thermolysis did not include the cyclized products from rearrangement, *viz.* **4b** (prepared fro comparison by the method of Coburn and O'Donnell [12]) and **5**, or the Beckmann rearrangement product derived from methyl (rather than aryl) migration, *viz.* **1p**. The latter was prepared by treatment of 3-(2-carbomethoxyphenyl)sydnone [7] with methylamine.
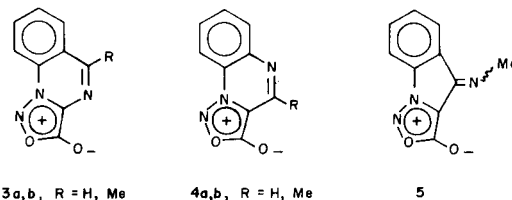
3a,b, R = H, Me   4a,b, R = H, Me   5

These data are perhaps not unexpected since the greater migratory aptitude, in the Beckmann rearrangement, of an aryl group compared to a methyl, is well known [15]. Thus, migration of the aryl group, followed by reaction of the incipient carbenium ion with adventitious water, would lead to the acetamido compound **1o**. The absence of **4b** may indicate that as rearrangement occurs, the sydnone ring, being a part of the migrating species, is not in a position to trap the reactive intermediate and this allows time for adventitious water (from the silica) to react. Our attempts to increase the yield by careful drying of the tlc plates were not fruitful and this may reflect the relative amounts of the oxime (*E*) and (*Z*) isomers [analytical hplc indicated a 5:2 ratio, presumably *(E):(Z)*]. It is tempting to speculate that, since the relative amounts of **1o** and **3b** are akin to this 5:2 ratio, the former is derived from the *(E)* isomer and the latter from the *(Z)*. The preference for an *anti*

migration stereochemistry is well established and this lends support to the derivation of **1o** from the *(E)* isomer. In the *(Z)*, the *anti* group is the poorly migratory methyl and, hence, sydnone ring neighbouring group participation becomes viable; resulting in formation of **3b**. However, in view of the very low product yields, it is as likely that both products derive only from the *(E)* isomer, the *(Z)* fragmenting to ring opened materials. Further research is required to clarify the situation.

Not surprisingly, the *O*-acetates **1i,m** were considerably more thermally stable than the *O*-sulfonates, indeed, **1i** did not react at 200°. At 170° **1m** was slowly transformed into the parent oxime **1b** in good yield. Apparently, the relatively poor leaving group ability of the acetate ion allows simple hydrolysis of the ester. The mechanism probably involves direct attack of water on the ester carbonyl, but, in the absence of labelling studies, this point remains moot.

EXPERIMENTAL [16]

2-(3-Sydnonyl)phenylmethanol 1d.

To a refluxing mixture of methyl 2-(3-sydnonyl)benzoate **1e** (11.00 g, 0.05 mole) and sodium borohydride (4.75 g, 0.125 mole) in *t*-butyl alcohol (200 ml) was added methanol (40 ml) dropwise over one hour. Water (200 ml) was added and the methanol/tertiary butanol was removed *in vacuo*. The mixture was extracted with dichloromethane (5 × 60 ml), the combined organics dried (drierite) and evaporated *in vacuo* to yield a brown oil which solidified on trituration with ether. Filtration, washing with ether and recrystallization from dichloromethane/petroleum ether gave **1d** (6.30 g, 70%), mp 73-75°; ir: 3385 (O-H str), 3060 (sydnone C-H str), 1735 (sydnone C=O str) cm⁻¹; nmr (deuteriochloroform/deuteriodimethylsulfoxide 4:1): δ 4.55 (s, 2H), 5.06 (s, 1H), 6.86 (s, 1H), 7.57 (m, 4H).

Anal. Calcd. for $C_9H_8N_2O_3$: C, 56.25; H, 4.17; N, 14.58. Found: C, 55.91; H, 4.09; N, 14.29.

2-(3-Sydnonyl)benzaldehyde 1f.

To the alcohol **1d** (5.65 g, 29.43 mmoles) in dichloromethane (400 ml) was added pyridinium dichromate (16.92 g, 44.97 mmoles) with stirring. After 26 hours the mixture was filtered and the filtrate was reduced to approximately 10 ml. Column chromatograhy (silica gel) using gradation elution (dichloromethane to dichloromethane/acetone 3:1) afforded **1f** (3.64 g, 65%), mp 93-94°; ir: 3070 (sydnone C-H str), 1750 (sydnone C=O str), 1700 (aldehyde C=O str) cm⁻¹; nmr (deuteriochloroform/deuteriodimethylsulfoxide 4:1): δ 7.07 (s, 1H), 7.90 (m, 4H), 9.97 (s, 1H).

Anal. Calcd. for $C_9H_6N_2O_3$: C, 56.84; H, 3.16; N, 14.74. Found: C, 57.12; H, 3.07; N, 14.49.

2-(3-Sydnonyl)benzaldehyde Oxime 1a.

A mixture of 2-(3-sydnonyl)benzaldehyde **1f** (1.00 g, 5.26 mmoles), hydroxylamine hydrochloride (1.00 g, 20.20 mmoles), pyridine (5 ml) and absolute ethanol (20 ml) was heated at 65° for 40 minutes. After cooling for a further 30 minutes, water (60 ml) was added and, on standing, crystallization occurred. Filtration, a water wash and drying gave **1a** (0.7 g, 65%) as colourless needles, mp 140-141°; ir: 3320 (O-H str), 3155 (sydnone C-H str), 1755 (sydnone C=O str) cm⁻¹; nmr (deuteriochloroform/deuteriodimethylsulfoxide 3:1): δ 6.98 (s, 1H), 7.55 (brd s, 3H), 7.93 (brd s, 2H), 11.67 (s, exchanged with deuterium oxide).

Anal. Calcd. for $C_9H_7N_3O_3$: C, 48.78; H, 3.41; N, 20.49. Found: C, 49.09; H, 3.27; N, 20.66.

3-(2-Acetylphenyl)sydnone 1g.

The title compound was prepared in 12% overall yield from *o*-amino-

acetophenone using the method employed by Puranik [5] for 3-(4-acetylphenyl)sydnone. No attempt was made to purify the intermediate glycine or *N*-nitrosoglycine products.

Crystallization of crude **1g** from dichloromethane/petroleum ether gave colourless crystals, mp 113-115°; ir: 3120 (sydnone C-H str), 1740 (sydnone C=O str), 1670 (acetyl C=O str) cm⁻¹; nmr (deuteriochloroform): δ 2.44 (s, 3H), 6.68 (s, 1H), 7.83 (m, 4H).

Anal. Calcd. for $C_{10}H_8N_2O_3$: C, 58.82; H, 3.92; N, 13.73. Found: C, 58.69; H, 3.84; N, 13.49.

3-(2-Acetylphenyl)sydnone Oxime 1b.

A solution of 3-(2-acetylphenyl)sydnone **1g** (1.81 g, 8.87 mmoles) and hydroxylamine hydrochloride (1.87 g, 26.90 mmoles) in pyridine (9.5 ml) and ethanol (36.5 ml) was refluxed (steam bath) for 2 hours. After cooling to room temperature, the volume was reduced to 10 ml, water (40 ml) was added and the mixture was extracted with dichloromethane (3 × 25 ml). Separation, drying (drierite) and evaporation *in vacuo* gave a brown oil which crystallized on standing. Repeated recrystallization from methanol/ether gave colourless plates (0.7 g, 36%), mp 124-126° [17]; ir: 3297 (O-H str), 3121 (sydnone C-H str), 1726 (sydnone C=O str); nmr (deuteriochloroform/deuteriodimethylsulfoxide 5:1) δ 2.10 (s, 3H), 6.72, 6.79 (s, 1H, relative ratio of 8:3), 7.66 (s, 4H), 10.30, 10.53 (s, relative ratio of 3:8) [18].

Anal. Calcd. for $C_{10}H_9N_3O_3$: C, 54.79; H, 4.11; N, 19.18. Found: C, 54.66; H, 4.09; N, 19.03.

2-(3-Sydnonyl)benzaldehyde Oxime-*O*-acetate 1i.

A mixture of the oxime **1a** (0.10 g, 0.49 mmole) and acetic anhydride (1 ml, 10.61 mmoles) was briefly warmed to effect dissolution. After 24 hours at room temperature, the solution was poured into water (10 ml) and on standing crystallization occurred. Filtration gave a tan solid which recrystallized from ethanol as light tan plates (0.079 g, 66%), mp 124-126°; ir: 3120 (sydnone C-H str), 1770 (sydnone C=O str), 1735 (ester C=O str), 1230 (C-O str) cm⁻¹; nmr (deuteriochloroform): δ 2.22 (s, 3H), 6.70 (s, 1H), 7.64 (s, 1H), 7.77 (s, 2H), 8.25 (s, 1H), 8.33 (s, 1H).

Anal. Calcd. for $C_{11}H_9N_3O_4$: C, 53.44; H, 3.64; N, 17.00. Found: C, 53.21; H, 3.66; N, 16.75.

3-(2-Acetylphenyl)sydnone Oxime-*O*-acetate 1m.

The oxime **1b** (0.10 g, 0.46 mmole) was treated as above to give the *O*-acetate **1m** as light tan plates (0.074 g, 62%), mp 146-147°; ir: 3153 (sydnone C-H str), 1750 (sydnone C=O str), 1730 (acetate C=O str), 1200 (C-O str) cm⁻¹; nmr (deuteriochloroform): δ 2.19 (s, 3H), 2.23 (s, 3H), 6.68 (s, 1H), 7.71 (s, 4H).

Anal. Calcd. for $C_{12}H_{11}N_3O_4$: C, 55.17; H, 4.21; N, 16.09. Found: C, 54.89; H, 4.06; N, 15.81.

General Procedure for the Reactions of 1a and 1b with Electrophilic Reagents:

To a stirred solution of the oxime **1a** or **b** (0.2 g) in dichloromethane (5 ml)/triethylamine (0.5 ml) was added the electrophilic reagent (0.2 g) [see Table 1] either dropwise or in portions. After the appropriate period of time (see Table 1) the mixture was poued into water (20 ml). The separated organic layer was then washed successively with hydrochloric acid (10%, 2 × 10 ml), aqueous sodium bicarbonate (10%, 2 × 10 ml) and brine (10 ml). The dried (drierite) extract was evaporated *in vacuo* to yield the appropriate product (see Table 1) [19].

3-(2-Cyanophenyl)sydnone 1h.

The title compound was prepared in 12% overall yield (from anthranilonitrile) by trifluoroacetic anhydride cyclization [6] of the corresponding *N*-nitrosoglycine (prepared in conventional fashion [6] from *N*-(2-cyanophenyl)glycine [20]).

Recrystallization of **1h** from dichloromethane/petroleum ether gave pale tan needles, mp 121-122°; ir: 3060 (sydnone C-H str), 2245 (CN str), 1785, 1735 (sydnone C=O str) cm⁻¹; nmr (deuteriochloroform/deuteriodimethylsulfoxide 1:1): δ 7.38 (s, 1H), 7.97 (brd s, 4H).

Anal. Calcd. for $C_9H_5N_3O_2$: C, 57.75; H, 2.67; N, 22.46. Found: C, 57.65; H, 2.58; N, 22.24.

3-(2-Acetylphenyl)sydnone Oxime-*O*-methanesulfonate **1k**.

Using the general procedure, **1k** was obtained as a tan solid which was recrystallized from methanol/acetonitrile to yield pale tan plates (0.22 g, 81%), mp 134-137°; ir: 3140 (sydnone C-H str), 1735 (sydnone C=O str), 1352, 1183 (SO$_2$ str) cm^{-1}; nmr (deuteriochloroform/deuteriodimethylsulfoxide 1:1): δ 2.48 (s, 3H), 3.22 (s, 3H), 7.33 (s, 1H), 7.88 (s, 4H).

Anal. Calcd. for C$_{11}$H$_{11}$N$_3$O$_5$S: C, 44.44; H, 3.70; N, 14.14. Found: C, 44.36; H, 3.85; N, 13.99.

3-(2-Acetylphenyl)sydnone Oxime-*O*-benzenesulfonate **1l**.

Using the general procedure, **1l** was obtained as a tan solid which was recrystallized twice from dichloromethane/petroleum ether to yield pale tan plates (0.16 g, 49%), mp 125-128°; ir: 3110 (sydnone C-H str), 1753 (sydnone C=O str), 1378, 1191 (SO$_2$ str); nmr (deuteriochloroform/deuteriodimethylsulfoxide 3:1): δ 2.32 (s, 3H), 6.82 (s, 1H), 7.75 (m, 9H).

Anal. Calcd. for C$_{16}$H$_{13}$N$_3$O$_5$S: C, 53.48; H, 3.62; N, 11.70. Found: C, 53.17; H, 3.48; N, 11.48.

3-(2-Acetylphenyl)sydnone Oxime-*O*-(*p*-toluenesulfonate) **1j**.

Using the general procedure, **1j** was obtained as a tan powder which was recrystallized twice from dichloromethane/petroleum ether to afford colourless plates (0.21 g, 62%), mp 133-134° dec; ir: 3156 (sydnone C-H str), 2905 (aliphatic C-H str), 1750 (sydnone C=O str), 1370, 1195, 1185 (SO$_2$ str) cm^{-1}; nmr (deuteriochloroform): δ 2.25 (s, 3H), 2.45 (s, 3H), 6.33 (s, 1H), 7.55 (m, 8H).

Anal. Calcd. for C$_{17}$H$_{15}$N$_3$O$_5$S: C, 54.69; H, 4.02; N, 11.26. Found: C, 55.04; H, 3.94; N, 11.26.

Thermolysis of Ketoxime-*O*-sulfonates **1j-l**: Small Scale.

A small sample of each of the *O*-sulfonates was dissolved in dichloromethane and the resulting solutions were spotted onto a tlc plate (Eastman-Kodak Chromagram plastic backed silica gel). Several plates were prepared in this manner. The plate was then heated in an oven at a temperature ranging from 55-120° for 5-50 minutes. The plate was allowed to cool to ambient temperature whereupon the starting materials were respotted and the plate was eluted with dichloromethane. Thus, it was shown that complete conversion of the *O*-sulfonates occurred at 100° for 10 minutes; apparently providing the same products.

Larger Scale.

The ketoxime-*O*-mesylate **1k** [21] (0.60 g, 3.37 mmoles) was dissolved in dichloromethane (15 ml) and silica gel (15 g, Type H, Sigma Chemical Company) was added. The whole was carefully evaporated to dryness *in vacuo*. Heating, as above, at 100° for 15 minutes followed by extraction with warm acetonitrile (3 × 30 ml) gave a yellow solution which was passed through a silica gel column (acetonitrile as eluant). The first eluted yellow band was collected and, on standing, it deposited 5-methylsydno-[3,4-*a*]quinazoline **3b** as golden needles (0.03 g, 7%), mp 242-243° dec; ir: 3050 (aromatic C-H str), 2906 (aliphatic C-H str), 1725 (sydnone C=O str); nmr (deuteriochloroform/deuteriodimethylsulfoxide 1:1): δ 2.89 (s, 3H), 8.07 (m, 3H), 8.32 (dd, J$_{AB}$ = 9 Hz, J$_{AC}$ = 2 Hz, 1H), 8.41 (dd, J$_{DC}$ = 9 Hz, J$_{DB}$ = 2 Hz).

Anal. Calcd. for C$_{10}$H$_7$N$_3$O$_2$: C, 59.70; H, 3.48; N, 20.90. Found: C, 59.85; H, 3.44; N, 20.89.

Later column fractions gave 3-(2-acetamidophenyl)sydnone **1o** (0.05 g, 11%) identical (mp, tlc, ir) to an authentic sample [13].

Thermolysis of Aldoxime and Ketoxime-*O*-acetates **1i,m**.

The thermolysis on the small scale was conducted in the same manner as described for the *O*-sulfonates, except that temperatures up to 200° were utilized. The aldoxime-*O*-acetate **1i** was stable up to 200° and was not further pursued. In contrast, the ketoxime-*O*-acetate **1m** was transformed cleanly to a product of lower R$_f$ in 30 minutes at 170°. Scale up of the latter (0.2 g, 0.77 mmole), in the manner previously described, gave the sydnone ketoxime **1b** (0.11 g, 66%) identical (mp, tlc, ir) to an authentic sample.

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[9] Complex, inseparable mixtures were obtained.

[10] *Inter alia*: T. J. Bentley, J. F. McGhie and D. H. R. Barton, *Tetrahedron Letters*, 2497 (1965); J. G. Krause and S. Shaikh, *Synthesis*, 502 (1975); J. B. Hendrickson, K. W. Bair and P. M. Keehn, *Tetrahedron Letters*, 603 (1976) and *loc. cit.*

[11] The plates were left in an oven at 100° for 5 hours.

[12] R. A. Coburn and J. P. O'Donnell, *J. Org. Chem.*, **37**, 1707 (1972).

[13] S. J. Hodson and K. Turnbull, *J. Heterocyclic Chem.*, **22**, 1223 (1985).

[14] Analytical tlc showed another product running just above the acetamido species **1o**, however, we were not able to isolate this material on scale up. The possibility that this is a facet of the different types of silica gel used on analytical and preparative tlc plates and for column chromatography, has not been ruled out. Concentration effects may also be involved.

[15] J. March in "Advanced Organic Chemistry", Third Edition, J. Wiley and Sons, New York, 1985, p 988.

[16] All melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared spectra (potassium bromide) were measured on a Perkin Elmer 1330 and nuclear magnetic resonance spectra on a Varian EM 360 with tetramethylsilane as the internal standard, chemical shifts reported in ppm (δ). Combustion analyses were performed on a Perkin Elmer 240B instrument.

[17] It should be noted that when this compound was prepared on another occasion the product had a widely different melting point (149-151°) but identical ir and tlc characteristics. This probably reflects their different isomeric content.

[18] The combined integration for the peaks above 10 δ was substantially less than one; a circumstance which we have previously encountered for other compounds containing labile protons [13]. We have no reason to question the assignment of the product as the oxime **1b**.

[19] The only slight deviations from this general procedure were for the reactions with thionyl chloride (run at 10°) and tetraphosphorus decasulfide (no triethylamine used).

[20] N. P. Peet and S. Sunder, *J. Heterocyclic Chem.*, **14**, 561 (1977).

[21] Chosen because it was apparently more stable and more easily purified than **1j** or **1l**.