# Equilibrium Acidities and Homolytic Bond Dissociation Energies of the H–O Bonds in Oximes and Amidoximes

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*Received September 9, 1991 (Revised Manuscript Received February 7, 1992)*

The equilibrium acidities of 14 aldoximes, 4 amidoximes, and 19 ketoximes have been measured in DMSO solution. Homolytic bond dissociation energies (BDEs) for the O–H bonds in these oximes have been estimated by combining the $pK_{HA}$ values thus obtained with the oxidation potentials of their conjugate bases. The acidities of the corresponding radical cations ($pK_{HA^{+\cdot}}$) were estimated for 32 of these oximes by combining $pK_{HA}$, $E_{ox}(A^-)$, and $E_{OX}(HA)$. Homohydrogen bonding was observed to be as strong for oximes in DMSO as for phenols. The $pK_{HA}$ values for *syn*-benzaldoxime and acetaldoxime were found to be 20.2 and 28.5, respectively. Comparison of these values with those reported in water led to the conclusion that the $pK_{HA}$ values reported in water for the oximes derived from acetaldehyde, acetone, and 3-pentanone and that for acetamidoxime are merely lower limits. The BDEs of the O–H bonds in acetaldoxime and *syn*-benzaldoxime were estimated to be 6 and 14 kcal/mol lower, respectively, than those reported for the O–H bond in alcohols. The O–H bonds in most oximes were found to be in the range of 90 ± 2 kcal/mol; *anti*-benzaldoximes were found to have BDEs about 2 kcal/mol lower than for *syn*-benzaldoximes. The presence of α-dialkylamino groups in acetophenone oximes or β-dialkylamino groups in propiophenone oximes failed to evoke through-space electron transfer on oxidation of their anions, contrary to expectations based on a literature report.

Early acidity measurements by conductivity for benzaldoxime and several ring-substituted benzaldoximes showed that in aqueous solutions *syn*-benzaldoximes were slightly more acidic than their anti isomers. (For *syn*- and *anti*-benzaldoximes the $pK_{HA}$ values reported were 10.68 and 11.33, respectively.[1]) The acidities of the oximes of acetaldehyde, 3-pentanone, and acetone were determined some time later by measuring the hydroxide ion concentrations generated in reactions where the oximes were acting as acids.[2] The $pK_{HA}$ values obtained for $Me_2C{=}NOH$ and $Et_2C{=}NOH$ were 12.42 and 12.60, respectively, and the $pK_{HA}$ value for $CH_3CH{=}NOH$ at ionic strength, $\mu \simeq 0.075$, agreed with a $pK_{HA}$ value of 12.3 obtained earlier by another kinetic method. Kinetic methods were used because of the difficulty encountered in obtaining accurate $pK_{HA}$ values in the 12–13 region by other methods.[2] A few years later Bell and Higginson estimated the $pK_{HA}$ of acetaldoxime to be 12.42 by fitting the rate of the acetaldoxime-catalyzed dehydration of acetaldehyde hydrate to a linear log $k$ vs $pK_{HA}$ Brønsted plot constructed by using rate data for other weak acids for which the $pK_{HA}$ values were known.[3] To the best of our knowledge, no other determinations of $pK_{HA}$ values for aliphatic aldoximes or ketoximes in water have appeared in the literature in the ensuing 42 years. Acetamidoxime, $CH_3C(NH_2){=}NOH$, has been reported to have a $pK_{HA}$ of 12.9 in aqueous solution,[4] but no experimental information was given as to how this value was obtained. Kurtz and D'Silva have recently developed an equation to estimate $pK_{HA}$ values for oximes in water based on these early $pK_{HA}$ values and the NMR chemical shifts of the oximino proton in DMSO solution. They have estimated the $pK_{HA}$ values for over 200 oximes in water in this way.[5a]

In view of the difficulties in making $pK_{HA}$ measurements in the 12–13 aqueous region it seemed desirable to study the effect of structural changes on acidities of oximes and amidoximes in DMSO solution where a wider range of acidities could be examined. It was also of interest to make estimates of the homolytic bond dissociation energies (BDEs) of the O–H bonds in these oximes by measuring the oxidation potentials of their conjugate bases and also to make estimates of the acidities of the corresponding radical cations. The only report of the BDE value for the O–H bonds in oximes of which we are aware is an approximate value of 86 kcal/mol.[6] No information appears to be available as to the acidities of the corresponding radical cations.

## Results and Discussion

**Equilibrium Acidities of Aldoximes, Ketoximes, and Amidoximes.** The equilibrium acidities in DMSO of representative oximes are shown in Table I.

Oximes, like most weak oxygen acids, undergo homohydrogen bonding with their conjugate bases in DMSO solution (eq 1). Homo-H-bonding interferes with $pK_{HA}$

$$R_2C{=}N{-}O^- + R_2C{=}NOH \overset{K_{hb}}{\rightleftharpoons} R_2C{=}N{-}O^-\cdots HON{=}CR_2 \quad (1)$$

$$In^- + H{-}A \rightleftharpoons H{-}In + A^- \quad (2)$$

determinations by the overlapping indicator method because eq 2 is perturbed during the titration. This effect can be minimized, however, by keeping the ratio of $[A^-]/[HA]$ near unity,[7a] and the measurements in Table I were made in this way. We have also made measurements for a few oximes under conditions where the $[A^-]/[HA]$ ratio was varied so as to allow calculations of the $K_{hb}$ constants. The values of log $K_{hb}$ obtained were 2.5 for $Ph_2C{=}NOH$, 3.45 for $CH_3CH_2CH{=}NOH$, 3.24 for cyclohexanone oxime, and 4.26 for $CH_3COCH{=}NOH$. No ion pairing[7b] was observed between oximide ions and $K^+$

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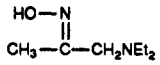
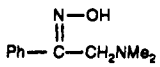
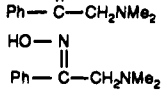
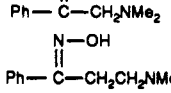
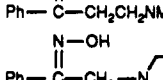
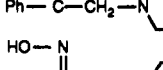
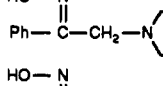
(1) Brady, O. L.; Goldstein, R. F. *J. Chem. Soc.* **1926**, 1918–1924.
(2) King, C. V.; Marion, A. P. *J. Am. Chem. Soc.* **1944**, *66*, 977–980.
(3) Bell, R. P.; Higginson, W. C. E. *Proc. R. Soc. London* **1949**, *197A*, 141–149.
(4) Aubort, J. D.; Hudson, R. F. *J. Chem. Soc., Chem. Commun.* **1970**, 937–938.
(5) (a) Kurtz, A. P.; D'Silva, T. O. J. *J. Pharm. Sci.* **1987**, *76*, 599–610. (b) Green, A. L.; Saville, B. *J. Chem. Soc.* **1956**, 3887–3892. Green, A. L.; Smith, H. J. *Biochem. J.* **1958**, *68*, 28–31.
(6) Mahoney, L. R.; Mendenhall, G. D.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 8610–8614.
(7) (a) Bordwell, F. G.; McCallum, R. J.; Olmstead, W. M. *J. Org. Chem.* **1984**, *49*, 1424–1427. (b) Olmstead, W. N.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3299–3305.

0022-3263/92/1957-3019$03.00/0 

**Table I. Equilibrium Acidities of Aldoximes, Ketoximes, and Amidoximes in DMSO**

| oxime | HIn[a] | $pK_{HIn}$ | $pK_{HA}$ | $pK_{HA}^{(avg)}$ |
|---|---|---|---|---|
| $C_6H_5CH{=}NOH$ | | | | |
| syn | 2NPANH | 20.66 | 20.21 ± 0.01 | |
| | | | 20.20 ± 0.01 | 20.2 ± 0.01 |
| anti | 2NPANH | 20.66 | 20.28 ± 0.04 | |
| | | | 20.29 ± 0.05 | 20.3 ± 0.05 |
| $p$-$MeC_6H_4CH{=}NOH$ | | | | |
| syn | 2NPANH | 20.66 | 20.56 ± 0.01 | |
| | | | 20.54 ± 0.01 | 20.55 ± 0.01 |
| anti | 2NPANH | 20.66 | 20.65 ± 0.01 | |
| | | | 20.63 ± 0.01 | 20.64 ± 0.01 |
| $p$-$MeOC_6H_4CH{=}NOH$ | | | | |
| syn | 2NPANH | 20.66 | 20.80 ± 0.01 | 20.80 ± 0.01 |
| anti | 2NPANH | 20.66 | 20.73 ± 0.02 | |
| | | | 20.71 ± 0.05 | 20.72 ± 0.05 |
| $m$-$NO_2C_6H_4{=}NOH$ | | | | |
| syn | $Ph_2CHCN$[b] | 17.5 | 17.73 ± 0.02 | |
| | | | 17.73 ± 0.01 | 17.73 ± 0.02 |
| anti | $Ph_2CHCN$[b] | 17.5 | 17.59 ± 0.01 | |
| | | | 17.61 ± 0.01 | 17.60 ± 0.01 |
| $p$-$NO_2C_6H_4CH{=}NOH$ | | | | |
| syn | $Ph_2CHCN$[b] | 17.5 | 17.02 ● 0.03 | |
| | | | 17.00 ± 0.01 | 17.01 ± 0.03 |
| $PhCH{=}CHCH{=}NOH$ | 2NPANH | 20.66 | 20.49 ± 0.01 | |
| | | | 20.48 ± 0.01 | 20.48 ± 0.01 |
| $PhCOCH{=}NOH$ | PhSFH | 15.4 | 14.90 ± 0.03 | |
| | | | 14.83 ± 0.05 | 14.9 ± 0.05 |
| $CH_3COCH{=}NOH$ | PhSFH | 15.4 | 15.19 ± 0.14 | |
| | | | 15.10 ± 0.10 | 15.1 ± 0.14 |
| $Ph_2C{=}NOH$ | | | | 20.1 ± 0.01[c] |
| $Fl{=}NOH$ | | | | 16.2 ± 0.01[c] |
| 2,7-diBrFl=NOH | | | | 14.0[c] |
| 2-$PhSO_2Fl{=}NOH$ | | | | 14.2 ± 0.01[c] |
| $PhC(CH_3){=}NOH$ | | | | |
| syn | 2NPANH | 20.66 | 21.18 ± 0.03 | |
| | | | 21.16 ± 0.01 | 21.17 ± 0.02 |
| anti | 2NPANH | 20.66 | 21.65 ± 0.03 | |
| | | | 21.77 ± 0.02 | |
| | FH | 22.6 | 21.91 ± 0.01 | 21.7 |
| | | | 21.94 ± 0.04 | 21.8 ± 0.15 |
| $(PhCH_2)_2C{=}NOH$ | FH | 22.6 | 22.58 ± 0.04 | |
| | | | 22.52 ± 0.05 | 22.55 ± 0.05 |
| $(PhCH_2)_2C{=}NOMe$ | PXH | 27.9 | 27.80 ± 0.01 | |
| | | | 27.81 ± 0.02 | |
| | PMPXH | 28.43 | 27.76 ± 0.02 | |
| | | | 27.78 ± 0.02 | 27.79 ± 0.03 |
| cyclohexanone oxime | 9-$t$-BuFH | 24.3 | 24.26 ± 0.05 | |
| | | | 24.28 ± 0.06 | 24.27 ± 0.06 |
| cyclododecanone oxime | TP2H | 25.6 | 25.04 ± 0.01 | |
| | | | 24.98 ± 0.05 | 25.0 ± 0.04 |
| | HB1 | 26.1 | 24.69 ± 0.03 | |
| $Et_2C{=}NOH$ | TP2H | 25.6 | 25.14 ± 0.04 | |
| | | | 25.24 ± 0.08 | |
| | | | 25.35 ± 0.04 | 25.2 ± 0.15 |
| $Me_2C{=}NOH$ | TP2H | 25.6 | 26.02 ± 0.05 | |
| | | | 25.97 ± 0.07 | |
| | HB1 | 26.1 | 26.25 ± 0.04 | |
| | | | 25.91 ± 0.07 | 26.0 ± 0.15 |
| $CH_3CH{=}NOH$ | PMPXH | 28.43 | 28.52 ± 0.01 | |
| (syn–anti mixture) | | | 28.54 ± 0.02 | |
| | PXH | 27.90 | 28.42 ± 0.04 | |
| | | | 28.42 ± 0.03 | 28.48 ± 0.06 |
| $CH_3CH_2CH{=}NOH$ | | | | |
| (syn–anti mixture) | PMPXH | 28.43 | 28.79 ± 0.03 | |
| | | | 28.77 ± 0.02 | |
| | | | 28.80 ± 0.07 | 28.80 ± 0.03 |
| $CH_3C(NH_2){=}NOH$ | MCLPXH | 26.6 | 25.81 ± 0.01 | |
| | | | 25.82 ± 0.01 | |
| | TP2H | 25.6 | 25.82 ± 0.02 | |
| | | | 25.84 ± 0.02 | |
| | HB1 | 26.1 | 25.80 ± 0.02 | 25.82 ± 0.02 |
| $PhC(NH_2){=}NOH$ | TBUFH | 24.35 | 22.93 ± 0.02 | |
| | | | 23.05 ± 0.02 | |
| | | | 22.97 ± 0.04 | |
| | FH | 22.6 | 23.08 ± 0.05 | |
| | | | 23.03 ± 0.04 | 23.0 ± 0.06 |
| $PhC(NH_2){=}NOMe$ | MCLPXH | 26.6 | 25.92 ± 0.01 | |
| | TP2H | 25.6 | 25.98 ± 0.02 | |
| | | | 26.02 ± 0.02 | 26.0 ± 0.05 |

Table I (Continued)

| oxime | HIn[a] | $pK_{HIn}$ | $pK_{HA}$ | $pK_{HA}^{(avg)}$ |
|---|---|---|---|---|
| $HC(NH_2)$=NOH | TP2H | 25.6 | 25.58 ± 0.03<br>25.63 ± 0.02 | 25.61 ± 0.04 |
|  | TBUFH | 24.35 | 23.80 ± 0.04<br>23.843 ± 0.01 | 23.82 ± 0.04 |
|  | 2NPANH | 20.66 | 20.53 ± 0.01<br>20.51 ± 0.02 | 20.52 ± 0.01 |
|  | 2NPANH | 20.66 | 21.03 ± 0.02<br>20.97 ± 0.01 | 21.00 ± 0.04 |
|  | 2NPANH | 20.66 | 20.94 ± 0.01<br>20.99 ± 0.03 | 20.96 ± 0.04 |
|  | 2NPANH | 20.66 | 20.15 ± 0.05<br>20.14 ± 0.04 | 20.15 ± 0.01 |
|  | 2NPANH | 20.66 | 20.80 ± 0.02<br>20.79 ± 0.01 | 20.80 ± 0.01 |
|  | CNAH | 18.9 | 18.90 ± 0.02<br>18.88 ± 0.02 | 18.89 ± 0.02 |

[a] Indicators: 2NPANH, 2-naphthylacetonitrile; CNAH, 4-chloro-2-nitroaniline; PhSFl, 9-(phenylthio)fluorene; FH, fluorene; PXH, 9-phenylxanthene, PMPXH, 9-(*p*-methoxyphenyl)xanthene; 9-*t*-BuFH, 9-*tert*-butylfluorene; TP2H, 1,3,3-triphenylpropene; HBl, iminostilbene; MCLPXH, 9-(*m*-chlorophenyl)xanthene. [b] $CH_3SOCH_2K$ quenched with $(PhCH_2)_2SO_2$ to prevent electron transfer. [c] Measured by C. A. Wilson.

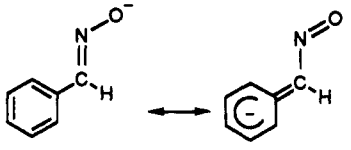
or even with $Li^+$ under the conditions of the $pK_{HA}$ measurements.

Examination of Table I shows that *syn*- and *anti*-benzaldoximes have nearly the same acidities, contrary to the finding in aqueous solution where the anti isomers are less acidic. The lower acidity of the anti isomer in aqueous solution is probably due to steric inhibition of solvation of the strongly hydrogen-bonded oxide ion by the phenyl group, a factor that is absent in DMSO. The essential identity of the acidities of the *syn* and *anti* isomers in DMSO made us wonder whether isomerization was occurring during our $pK_{HA}$ determinations, but NMR experiments ruled out this possibility (see the Experimental Section).

The substituent effects on the acidities of the benzaldoximes are for the most part small because the substituents are relatively far from the acidic site.

In aqueous solution the $pK_{HA}$ values for the oximes derived from aliphatic ketones have been reported to be only about 1 $pK_{HA}$ unit higher than that of benzaldoxime, but in DMSO solution we find differences of 4–6 $pK_{HA}$ units. Also, our $pK_{HA}$ value in DMSO for acetaldoxime is 8.5 units higher than for benzaldoxime, whereas that reported in aqueous solution is only about 1 unit higher. The $pK_{HA}$ value in DMSO for *syn*-benzaldoxime is 9.4 units higher than that in water, which agrees reasonably well with the 8 unit higher $pK_{HA}$ value for phenol in DMSO than in water. (The higher acidities in water are due to strong stabilization of the oxide anions by hydrogen bonding. DMSO is a good H-bond acceptor, but does not act as an H-bond donor.) The differences between the $pK_{HA}$ values in DMSO and the *apparent* $pK_{HA}$ values in $H_2O$ for benzaldehyde, 3-pentanone, acetone, and acetaldehyde oximes become progressively larger as the $pK_{HA}$ values in DMSO increase. They are higher in DMSO than $H_2O$ by 12.9, 17.3, 18.6, and 22 kcal, respectively. In view of the difficulties in measuring $pK_{HA}$ values above 12 in water,[2] we interpret the increasing differences to mean that the $pK_{HA}$ values reported in water above 12 are merely lower limits and that the true values are much higher. If we take the difference of about 13 kcal (9.4 $pK_{HA}$ units) between $pK_{HA}$ of *syn*-benzaldoxime in $H_2O$ and DMSO as a bench mark, the $pK_{HA}$ values in water estimated for the oximes of 3-pentanone, acetone, and acetaldehyde from the $pK_{HA}$ values in DMSO would be about 15.5, 16.5, and 19, respectively. Since the equation used by Kurtz and D'Silva was anchored, in part, on oxime $pK_{HA}$s presumed to be in the 12–13 region,[5a] their estimates of acidities need to be revised.

The 8.5 $pK_{HA}$ unit difference between the acidity of acetaldoxime and benzaldoxime in DMSO points to appreciable delocalization of the negative charge in the benzaldoximide ion into the benzene ring (**1a** ↔ **1b**). Similar stabilization of the anions derived from the oximes of acetophenone, cinnamaldehyde, benzophenone, etc. accounts for the higher acidities of most of the other oximes in Table I bearing a phenyl ring.



**1a** **1b**

The $pK_{HA}$ values of the aldoximes wherein the phenyl group in benzaldoxime has been replaced by PhCO or $CH_3CO$ are about 5 $pK_{HA}$ units lower because of the more effective delocalization of the negative charge in the anion by the carbonyl group than by the phenyl group. The $pK_{HA}$s for $CH_3COCH$=NOH and PhCOCH=NOH have each been reported to be 8.3 in aqueous solution.[5b] This is 2.4 units lower than the $pK_{HA}$ of *syn*-PhCH=NOH. A test for ion pairing with $K^+$ in DMSO for $PhCOCH=NO^-$ ion was negative, so the smaller difference in $H_2O$ must be due to a solvent effect.

The two phenyl groups in the $Ph_2C=NO^-$ ion are no better than the one in the benzaldoximide ion at delocalizing the charge in the anion, but the fluorene ring is as effective as a carbonyl group in this respect because of the stabilization provided by the 14 $\pi$ electron fluorenide moiety.

The *O*-methyl derivative of the oxime of dibenzyl ketone (**2**) is less acidic than the parent oxime by over 5 $pK_{HA}$ units because a change from an O–H to a C–H acid has

Table II. Homolytic Bond Dissociation Energies and Radical Cation Acidities of Oximes

| no. | oxime | $pK_{HA}$[a] | $E_{ox}(A^-)$[b] | $E_{ox}(HA)$[b] | BDE[c] | $pK_{HA^{+\bullet}}$[d] |
|---|---|---|---|---|---|---|
| 1 | $CH_3CH$=NOH | 28.5 | −0.613 (107) | 1.104 (235) | 98.2 | −0.4 |
| 2 | $CH_3CH_2CH$=NOH | 28.8 | −0.635 (84) | 1.083 (160) | 98.1 | −0.12 |
| 3 | $Me_2C$=NOH | 26.0 | −0.569 (108) | 1.984 (112) | 95.8 | −17 |
| 4 | $Et_2C$=NOH | 25.2 | −0.673 (83) | 1.856 (191) | 92.3 | −17 |
| 5 | $(PhCH_2)_2C$=NOH | 22.5 | −0.653 (60) | | 89.1 | |
| 6 | c-$C_5H_{10}C$=NOH | 24.2 | −0.700 | | 90.3 | |
| 7 | c-$C_{11}H_{22}C$=NOH | 25.0 | −0.749 | 1.753 | 90.3 | −17 |
| 8a | *syn*-PhCH=NOH | 20.2 | −0.342 (54) | 1.663 | 90.2 | −13 |
| 8b | *anti*-PhCH=NOH | 20.3 | −0.422 (54) | 1.620 | 86.9 | −15 |
| 9a | *syn*-*p*-$MeC_6H_4CH$=NOH | 20.55 | −0.395 (107) | 1.448 | 89.0 | −11 |
| 9b | *anti*-*p*-$MeC_6H_4CH$=NOH | 20.64 | −0.529 (107) | 1.432 | 86.5 | −12 |
| 10a | *syn*-*p*-$MeOC_6H_4CH$=NOH | 20.8 | −0.527 (67) | 0.667 (155) | 89.9 | 0.7 |
| 10b | *anti*-*p*-$MeOC_6H_4CH$=NOH | 20.7 | −0.616 (60) | 0.616 (107) | 87.5 | 0.1 |
| 11a | *syn*-*m*-$NO_2C_6H_4CH$=NOH | 17.7 | −0.390 (71) | 1.937 (143) | 88.6 | −21 |
| 11b | *anti*-*m*-$NO_2C_6H_4CH$=NOH | 17.6 | −0.456 (71) | 1.893 (143) | 86.9 | −22 |
| 12 | *syn*-*p*-$NO_2C_6H_4CH$=NOH | 17.0 | −0.371 (66) | 1.956 (172) | 88.0 | −22 |
| 13 | *syn*-PhCH=CHCH=NOH | 20.48 | −0.555 (66) | | 88.6 | |
| 14a | *syn*-$CH_3C(Ph)$=NOH | 21.17 | −0.485 (72) | 1.558 | 91.1 | −13 |
| 14b | *anti*-$CH_3C(Ph)$=NOH | 21.8 | −0.521 (72) | 1.526 | 91.2 | −13 |
| 15 | *anti*-*p*-$MeC_6H_4SCH_2C(Ph)$=NOH | 18.89 | −0.425 (72) | 1.008 | 89.4 | −5.2 |
| 16 | $Ph_2C$=NOH | 20.1 | −0.525 | | 89.0 | |
| 17 | Fl=NOH | 16.2 | −0.347 | | 87.5 | |
| 18 | 2,7-diBrFl=NOH | 14.0 | −0.125 (48) | 1.583 | 89.6 | −13 |
| 19 | 2-$PhSO_2$Fl=NOH | 14.2 | −0.192 | 1.807 | 89.0 | −17 |
| 20 | $CH_3COCH$=NOH | 15.1 | −0.192 (60) | 1.526 | 89.6 | −14 |
| 21 | PhCOCH=NOH | 14.9 | −0.210 (60) | 1.510 | 88.9 | −14 |

[a] See Table I. [b] Irreversible oxidation potentials measured in DMSO by cyclic voltammetry using platinum working and auxiliary electrodes and a Ag/AgI reference electrode with 0.1 M $Et_2N^+BF_4^-$ electrolyte and $Fc/Fc^+$ as a standard. Wave widths are given in parentheses. Potentials more positive than 0.7 V were measured in MeCN solution. [c] Calculated using eq 3. The oxidation potentials are reported relative to the ferrocene/ferrocenium couple, rather than to the standard hydrogen electrode, as was done in our earlier papers on BDEs and $pK_{HA^{+\bullet}}$ values. This results in a shift of 0.750 V to more negative potentials and a change in the value of $C$ in eq 3 from 56 to 73.3 kcal/mol; the reasons for making this change are given in ref 9b. Reference 9b contains examples of 31 compounds where BDEs have been established by this method to ±2 kcal/mol, or better. [d] Calculated using eq 4, with $E_{ox}(A^-)$ and $E_{ox}(HA)$ referenced to Ag/AgI, i.e., with 0.750 V added to each potential.

been made. The acidity of this C–H acid depends on charge delocalization into the phenyl ring and allylic-type resonance (**2b**). Delocalization of the charge as in **2b** is

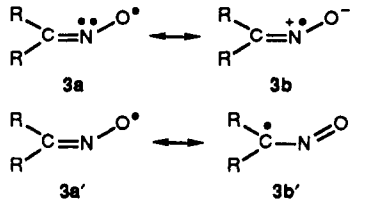
**2a** **2b**

evidently far less effective at stabilizing the anion than delocalization of the charge in the anion of the corresponding ketone where the charge can reside on oxygen, since the latter is more acidic than **2** by 12.5 kcal.[8a]

Acetamidoxime, $CH_3C(NH_2)$=NOH, has a $pK_{HA}$ value in DMSO of 25.8, which is close to that of acetamide (25.5),[8b] and the $pK_{HA}$ of benzamidoxime (23.0) is close to that of benzamide (23.35). Nevertheless, the amidoximes are O–H acids, not N–H acids, as is brought out by the appreciably higher $pK_{HA}$ of benzamidoxime *O*-methyl derivative (26.0). The latter has a $pK_{HA}$ in DMSO close to that of benzamidine, $PhC(NH_2)$=NH (26.7).[9a] If we assume that the acidity of acetamidoxime will be about 9.5 $pK_{HA}$ units lower in water than in DMSO (see above) its aqueous $pK_{HA}$ value will be about 16, instead of the value of 12.9 reported earlier.[4]

**Electronegativity Effects in Hetero-Allylic-Type Radicals on RSEs** (kcal/mol will be abbreviated as kcal). In an earlier paper we presented evidence to support the postulate[11a] that radical stabilization energies (RSEs) for hetero-allylic-type radicals decrease dramatically as the electronegativities of the terminal atoms increase from carbon in C=C—C$^\bullet$ (RSE = 18 kcal[10a]) to nitrogen in N=C(Ph)—N$^\bullet$ (5 kcal) to oxygen in O=C(Ph)—O$^\bullet$ (0 kcal).[11b] The nature of the substituent in N=C(R)—N$^\bullet$ when changed from R = Ph to R = Me had little or no effect on the RSE, which is not surprising since the central atom in an allylic system is a position of low electron density. On the other hand, when R in the allylic-type radical, O=C(Ph)ĊHR, is on the terminal carbon, a change from H to Me caused a 5 kcal increase in RSE, and a change from H to Ph caused the RSE to increase by 10 kcal.[8a]

**Aldoximes and Ketoximes.** The radicals derived by homolytic cleavage of the H–O bond in oximes differ from the allylic-type radicals examined earlier in having nitrogen as the central atom. The BDEs of the H–O bonds in both acetaldoxime and propionaldoxime (entries 1 and 2 in Table II) are each 98 kcal. The ΔBDEs, relative to that of the H–O bond in alcohols (104 kcal[10b]) give the RSEs as 6 kcal. This extra stabilization of the radical could possibly come from delocalization involving the lone pair on nitrogen, as in **3a** ↔ **3b**, or alternatively the oxygen



**3a** **3b**



**3a′** **3b′**

(8) (a) Bordwell, F. G.; Harrelson, J. A., Jr. *Can. J. Chem.* **1990**, *68*, 1714–1718. (b) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463.

(9) (a) Bordwell, F. G.; Ji, G.-Z. *J. Am. Chem. Soc.* **1991**, *113*, 8398–8401. (b) Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang, X. *J. Am. Chem. Soc.* **1991**, *113*, 9790–9795. (c) Bordwell, F. G.; Lynch, T.-Y. *J. Am. Chem. Soc.* **1989**, *111*, 7558–7562.

(10) (a) Rossi, M.; Golden, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1230–1235. (b) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.

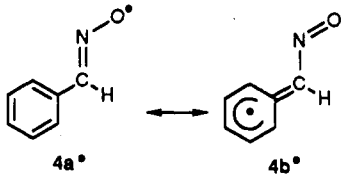
(11) (a) Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1984**, *106*, 2513–2519. (b) Bordwell, F. G.; Ji, G.-Z.; Zhang, X. *J. Org. Chem.* **1991**, *56*, 5254–5256. (c) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979–1985.

**Table III. Homolytic Bond Dissociation Energies of the H–O Bonds in α- and β-Dialkylamine Ketoximes**

| no. | oxime | $pK_{HA}$[a] | $E_{ox}(A^-)$[b] | $E_{ox}(HA)$[b] | BDE[c] | $pK_{HA^{+\bullet}}$[d] |
|---|---|---|---|---|---|---|
| 1 | $Et_2NCH_2C(CH_3)$=NOH | 23.82 | −0.632 (95) | 0.577 (104) | 91.4 | 3.5 |
| 2 | *anti*-$Me_2NCH_2C(CH_3)$=NOH | 23.5 | −0.587 (71) | 0.603 (125) | 92.0 | 3.5 |
| 3 | *syn*-$Me_2NCH_2C(Ph)$=NOH | 20.52 | −0.562 (60) | 0.547 (205) | 88.5 | 1.9 |
| 4 | *anti*-$Me_2NCH_2C(Ph)$=NOH | 21.00 | −0.626 (83) | 0.577 (105) | 87.6 | 0.8 |
| 5 | *syn*-(c-$OC_4H_8N$)$CH_2C(Ph)$=NOH | 20.15 | −0.533 (80) | 0.720 (120) | 88.6 | −0.9 |
| 6 | *anti*-(c-$OC_4H_8N$)$CH_2C(Ph)$=NOH | 20.80 | −0.551 (112) | 0.734 (115) | 89.1 | −0.8 |
| 7 | *syn*-$Me_2NCH_2CH_2C(Ph)$=NOH | 20.96 | −0.578 (48) | 0.497 (85) | 88.7 | 2.9 |

[a] See Table I. [b] Irreversible oxidation potentials measured in DMSO by cyclic voltammetry using platinum working and auxiliary electrodes and a Ag/AgI reference electrode with 0.1 M $Et_4N^+BF_4^-$ electrolyte and $Fc/Fc^+$ as a standard. Wave widths are given in parentheses. [c] Calculated using eq 3. The oxidation potentials are reported relative to the ferrocene/ferrocenium couple, rather than to the standard hydrogen electrode, as was done in our earlier papers on BDEs and $pK_{HA^{+\bullet}}$ values.[9b] This results in a shift of 0.750 V to more negative potentials, and a change in the value of $C$ in eq 3 from 56 to 73.3 kcal/mol; the reasons for making this change are given in ref 9b. Reference 9b contains examples of 31 compounds where BDEs have been established by this method to ±2 kcal/mol or better. [d] Calculated using eq 4.

atom bearing the odd electron could align itself parallel to the π system, and the donor properties of the Me (or Et) group could be used for stabilization **3a′** ↔ **3b′**). (In any event the resonance energy in the parent C=N—O• radical, where nitrogen is the central atom, appears to be small.) The increased RSEs observed for aliphatic ketoximes (entries 3–7), relative to acetaldoxime, are evidence that the latter is the better representation. This view is strongly supported by the 9–11 kcal increase in RSE for benzaldoxime (entries 8a and 8b) compared to acetaldoxime, which is best accounted for by the increased possibility for delocalization of the odd electron into the Ph ring.



**4a•** **4b•**

The relatively high acidity of benzaldoxime (Table I) points to a structure for the benzaldoximide anion in which there is overlap between the oxide anion and the benzene ring, as shown in **1b**. Loss of an electron will naturally lead to a radical wherein there is overlap of the odd electron with the benzene ring (**4a•** ↔ **4b•**). The (less stable) *anti*-benzaldoxime isomers have H–O BDEs that are about 2 kcal lower than those of the syn isomers in the four anti–syn pairs (entries 8–11 in Table II).

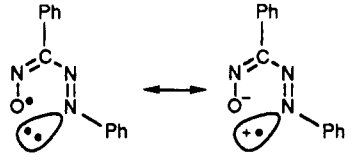
Examination of eq 3 reveals that, since the $pK_{HA}$ values in DMSO are nearly the same for syn and anti isomers, the lower BDEs for the anti isomers must arise from more negative $E_{ox}(A^-)$ values. The greater ease of oxidation of the anti isomer is probably associated with a higher ground-state energy and smaller degree of solvation in a more congested oxide ion, but, if so, it is surprising that the anti isomers do not have higher $pK_{HA}$ values, as is true in water.

$$BDE = 1.37pK_{HA} + 23.06E_{ox}(A^-) + C \qquad (3)$$

Remote substituents in benzaldoximes have small effects on anion stabilities, as judged by $pK_{HA}$ values, and usually have small effects on radicals stabilities,[11c] so the failure of the para substituents to have much effect on the BDEs of benzaldoximes is not surprising.

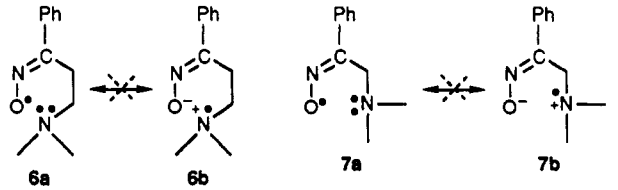
Replacement of the =CH hydrogen in PhCH=NOH by Me to give PhC(Me)=NOH (entries 14a and 14b) causes a small *increase* in BDE attributable to steric inhibition of resonance. Similar effects in other oximes where Ph is part of the function (entries 8–12 and 14–20) cause the BDEs to fall in the range 89 ± 2 kcal. Aldoximes in which PhCH=CH, PhCO, or $CH_3CO$ have replaced the Me group of acetaldoxime (entries 13, 20, and 21) also fall in this range.

**α- and β-Dialkylamino Ketoximes.** The BDEs of the H–O bonds in oximes derived from a number of α- and β-(dialkylamino)alkyl ketones have been included in this study (Table III) in order to test for through-space stabilization of the imidoxyl radicals by electron transfer from the dialkylamino groups. A report of detecting a through-space interaction of this type for **5a** ↔ **5b** by ESR made such a phenomenon appear likely.[12a]



**5a** **5b**

One would expect at least analogous through-space electron transfer in **6a** ↔ **6b** and/or **7a** ↔ **7b** because dialkylamino groups are much better donors than the PhN=N moiety. If intramolecular electron transfer occurs one would expect to find a lowering of the BDE of the H–O bond in the corresponding oxime. Examination of Table III shows, however, that the BDEs of the H–O bonds in the syn isomers, where the H–O bond is on the same side as the dialkylamino group, are within experimental error (±2 kcal) of those of the anti isomers.



**6a** **6b** **7a** **7b**

**Amidoximes and Related Compounds.** In an earlier section we have seen that the RSE of the allylic-type radical, C=N—O•, is small, but that attachment of groups such as Me, Ph, PhCH=CH, or RCO at carbon produces a sizable increase in RSE, presumably because of the ability of these groups to delocalize the odd electron. Amidoximes are of interest in this respect because they allow the effect on BDE of attaching an amino group to carbon to be tested. Formamidoxime has been shown by X-ray crystallography to be a planar molecule with a C–$NH_2$ distance of 1.33 Å, i.e., close to that of the C=N bond (1.30 Å).[12b] The similarity in these bond distances indicates extensive delocalization of the nitrogen lone pair

(12) Neugebauer, F. A. *Tetrahedron Lett.* **1970**, 2345–2348. (b) Gieren, A.; Dederer, B.; Ugi, L.; Stuber, S. *Tetrahedron Lett.* **1977**, 1507–1511.

**Table IV. Homolytic Bond Dissociation Energies for the Acidic Bonds in Amidoximes and Related Molecules**

| no. | oxime | $pK_{HA}$[a] | $E_{ox}(A^-)$[b] | $E_{ox}(HA)$[b] | BDE[c] | $pK_{HA^{+\cdot}}$[d] |
|---|---|---|---|---|---|---|
| | $HC(NH_2)$=NOH | 25.6 | −0.850 (95) | 0.757 (200) | 88.8 | 1.6 |
| | $CH_3C(NH_2)$=NOH | 25.8 | −0.951 (84) | 0.460 (120) | 86.7 | 4.2 |
| | $PhC(NH_2)$=NOH | 23.0 | −0.776 (96) | 0.595 (90) | 86.9 | 2.0 |
| | $PhC(NH_2)$=NOMe | 26.0 | −0.607 (48) | 0.685 | 94.9 | −4.3 |
| | $PhC(NH_2)$=NH | 26.7 | −0.348 | 1.272 | 102 | −0.6 |
| | $PhC(NHNMe_2)$=NPh | 22.9 | −0.867 (60) | 0.753 | 84.7 | 8.3 |
| | $(PhCH_2)_2C$=NOMe | 27.8 | −1.235 (62) | | 82.9 | |
| | $(PhCH_2)_2C$=O | 18.7 | −0.720 | | 82.3 | |

[a] See Table I. [b] Irreversible oxidation potentials measured in DMSO by cyclic voltammetry using platinum working and auxiliary electrodes and a Ag/AgI reference electrode with 0.1 M $Et_4N^+BF_4^-$ electrolyte and $Fc/Fc^+$ as a standard. Wave widths are given in parentheses. [c] Calculated using eq 3. The oxidation potentials are reported relative to the ferrocene/ferrocenium couple, rather than to the standard hydrogen electrode, as was done in our earlier papers on BDEs and $pK_{HA^{+\cdot}}$ values.[9b] This results in a shift of 0.750 V to more negative potentials and a change in the value of $C$ in eq 3 from 56 to 73.3 kcal/mol; the reasons for making this change are given in ref 9b. Reference 9b contains examples of 31 compounds where BDEs have been established by this method to ±2 kcal/mol, or better. [d] Calculated using eq 4.

**Table V. Melting Points and $^1H$ NMR Spectra of Oximes**

| oxime | mp, °C | lit. mp, °C | ref | $^1H$ NMR $CDCl_3$ (δ) |
|---|---|---|---|---|
| *anti*-*p*-methylbenzaldoxime | 121–122 | 122–124 | 14 | |
| *syn*-acetophenone oxime | 57–58 | 59 | 15 | 7.73–7.41 (m, 5 H), 2.32 (s, 3 H) |
| *anti*-acetophenone oxime | 79–81 | 81–82 | 16 | |
| *syn*-*m*-nitrobenzaldoxime | 120–121 | 121–123 | 17 | 8.5 (m, 1 H), 8.33–8.38 (m, 2 H), 8.00–7.55 (m, 3 H) |
| *anti*-*m*-nitrobenzaldoxime | 90–91 | | | 8.4 (m, 1 H), 8.25–8.17 (m, 2 H), 7.93–7.47 (m, 3H) |
| *syn*-*p*-methoxybenzaldoxime | 64–65 | 65 | 17 | 8.07 (s, 1 H), 7.53–6.78 (q, 4 H), 3.80 (s, 3 H) |
| *anti*-*p*-methoxybenzaldoxime | 73–74 | | | 8.07 (s, 1 H), 7.57–6.82 (q, 1 H), 3.80 (s, 3 H) |
| *anti*-α-(dimethylamino)acetone | 97–97.5 | 98–98.5 | 18 | 8.27 (b, 1 H), 2.95 (s, 2 H), 2.23 (s, 6 H), 1.93 (s, 3 H) |
| *anti*-α-(diethylamino)acetone | 44–45 | 40 | 19 | 2.97 (s, 2 H), 2.42 (q, 4 H), 1.86 (s, 3 H), 0.95 (t, 6 H) |
| *anti*-α-(dimethylamino)acetophenone | 87–89 | 80–83 | 19 | 7.7–7.37 (m, 5 H), 3.40 (s, 2 H), 2.30 (s, 6 H) |
| *syn*-α-(dimethylamino)acetophenone | 118–120 | 117–119 | 20 | 7.72–7.60 (m, 2 H), 7.42–7.33 (m, 3 H), 3.75 (s, 2 H), 2.42 (s, 6 H) |
| *syn*-β-(dimethylamino)propiophenone | 106–108 | 108 | 21 | 7.67–7.57 (m, 2 H), 7.38–7.33 (m, 3 H), 3.03–2.90 (m, 2 H), 2.6–2.5 (m, 2 H), 2.33 (s, 6 H) |
| *syn*-α-morpholinoacetophenone | 140–141 | 146–149 | 3 | 7.67–7.3 (m, 5 H), 3.77 (m, 6 H), 2.67–2.53 (m, 4 H) |
| *anti*-α-morpholinoacetophenone | 115–117 | 116–120 | 20 | 7.67–7.43 (m, 5 H), 3.70 (m, 4 H), 3.35 (s, 2 H), 2.52 (m, 4 H) |
| *anti*-α-(*p*-tolylthio)acetophenone | 80–82 | 84–85 | 3 | 7.7–7.0 (m, 9 H), 4.18 (s, 2 H), 2.33 (s, 3 H) |
| propionaldoxime | bp 130–134 | 131.5 | 23 | 9.70 (s, 1 H), 7.20 (dt, 1 H), 2.33 (m, 2 H), 1.10 (t, 3 H) |
| *syn*-*p*-nitrobenzaldoxime | 128–130 | 129 | 17 | 8.32 (s, 1 H), 8.23 (m, 2 H), 7.78 (s, 2 H), 7.68 (s, 1 H) |
| dibenzyl ketone oxime | 118–120 | 122 | 24 | 8.13 (br, 1 H), 7.27 (m, 10 H), 3.67 (s, 4 H), 3.43 (s, 4 H) |
| *O*-methyldibenzyl ketone oxime | bp 130–134 (0.4 mm) | 100–110 (3 mm) | 25 | 7.23 (m, 10 H), 3.93 (s, 3 H), 3.55 (s, 4 H), 3.38 (s, 4 H) |
| 1,1-dimethyl-2-(*N*-phenylbenzimidoyl)-hydrazine | 69–71 | 71–72.5 | 26 | |

within the π system. We can expect similar delocalization to occur in the radical. Examination of the first entries in Table IV shows that the BDE of the H–O bond in formamidoxime is 88.8 kcal, which leads to a RSE of 15 kcal when compared to that of the H–O bond in an alcohol (104 kcal[10b]). (For comparison, the RSE of the $H_2N$–Ċ–C(Ph)=O radical is ~22 kcal.[9c]) The presence of a Me or Ph group at the central carbon atom in entries 2 and 3 causes a further increase of about 2 kcal in RSE.

The BDE of the H–N bond of benzamidoxime *O*-methyl ether (entry 4) is 95 kcal, which leads to an RSE for the corresponding radical of 12 kcal (assuming a BDE = 107 kcal for the H–N bond in $NH_3$). The RSE of the radical derived by removing a hydrogen atom from the $NH_2$ group of $PhC(NH_2)$=NH is only 5 kcal,[9a] which indicates that the stabilizing effect of the MeO group on the N=C—N· radical is worth about 7 kcal. A similar analysis of entry 6 shows that the $Me_2N$ and Ph groups at the termini of the N=C—N· radical increases the RSE to 20 kcal. The RSE of the PhĊ—C=N—OMe radical formed from entry 7 by breaking the benzylic H–C bond is 22 kcal (relative) to the H–C bond of 105 kcal in $CH_3$–H). This combined effect of the Ph and OMe groups at the termini is about equal to the effect of Ph alone on the RSE of the Ph—Ċ—C=O radical derived from entry 8.

**Radical Cation Acidities.** Estimates of radical cation acidities are also given in Table II. The acidities of radical cations are usually dictated primarily by the size of the $E_{OX}(HA)$ term in eq 4. Molecules with $E_{OX}(HA)$ values above 1.7 V vs Ag/AgI cannot be measured in DMSO because of solvent oxidation, but the $E_{OX}(HA)$ values can be measured in MeCN. This allows $pK_{HA^{+\cdot}}$ values to be estimated since the potentials in the two solvents below 1.7 V usually do not differ greatly, but such values are subject to an additional uncertainty.

$$pK_{HA^{\bullet+}} = pK_{HA} + [E_{ox}(A^-) - E_{OX}(HA)]23.06/1.37 \quad (4)$$

Examination of Table II shows that the radical cations derived from benzaldoxime and the oximes of acetophenone, aliphatic ketones, fluorenones and the like have $pK_{HA^{+\cdot}}$ values in the −11 to −17 region. The presence of a *p*-MeO group in benzaldoxime decreases the acidity of the radical cation dramatically, and a *m*- or *p*-$NO_2$ group has the opposite effect. Acetaldoxime and propionaldoxime have higher $pK_{HA}$ values and appreciably lower $E_{OX}(HA)$ values than other oximes. This combination leads to higher radical cation acidities.

The presence of an amino function in the oxime provides a site for stabilizing the radical cation and decreases its acidity markedly. Similar effects of structural changes on radical cation acidities have been reported in earlier papers from this laboratory.

## Conclusions

The $pK_a$ values for aliphatic aldoximes and ketoximes obtained in aqueous solutions by kinetic methods are

shown to be merely lower limits. Measurements in DMSO predict that the values in water should be higher by about 3–6.5 p$K_a$ units. The inherent resonance energy of the parent iminoxyl radical, $H_2C{=}N{-}O^{\bullet}$, is judged to be small, but when one (or both) of the hydrogen atoms is (are) replaced by Me, Ph, PhCO, or $NH_2$, the radical stabilization energy (RSE) is increased by 5–15 kcal. Similarly, the RSE of the N=C—N$^{\bullet}$ radical, which is inherently ca. 5 kcal, is increased to ca. 12 kcal by attachment of a MeO group at one of the termini and to ca. 20 kcal when $Me_2N$ and Ph groups are present at the termini.

## Experimental Section

The oximes were obtained from Aldrich Chemical Co. and purified by crystallization or were prepared by the general method of Vogel[13] or by literature methods.

*anti*-Benzaldoxime was prepared from *syn*-benzaldoxime (Aldrich) by acidifying the salt of hydrogen chloride according to the method of Vogel.[13] Initial attempts were unsuccessful, but repetition of the procedure using *recovered syn*-benzaldoxime proved successful; mp 127 °C (lit.[13] mp 128–130 °C). Melting points for representative oximes are compared with literature mps in Table V. NMR resonances are listed for oximes where this information is lacking in the literature.

**Tests of the Stability of *anti*- and *syn*-Benzaldoximes in Basic DMSO Solution.** A 50–100-mg sample of *anti*-oxime dissolved in 0.16 mL of DMSO-$d_6$ gave a sharp signal at $\delta$ 10.58 for the OH proton in a $^1$H NMR spectrum. Addition of 3 drops of ~200 mM $CH_3SOCH_2K$, an excess, caused this peak to disappear completely, but addition of 50 mg of 9-PhS-fluorene (p$K_{HA}$ = 15.4) caused the peak to reappear. Repetition of this experiment with the syn isomer showed that its proton at $\delta$ 11.6 exhibited the same behavior. These experiments show that no rearrangement of the syn or anti isomers occurs during the p$K_{HA}$ measurements.

**Acknowledgment** is made to Craig A. Wilson for p$K_{HA}$ measurements for cyclohexanone, benzophenone, and fluorenone oximes. This work was sponsored by the National Science Foundation. We thank the Gaylord Chemical Corp., P. O. Box 1209, Slidell, LA 70459-1209 for a generous gift of DMSO.

**Registry No.** *syn*-$C_6H_5CH{=}NOH$, 622-32-2; *anti*-$C_6H_5CH{=}NOH$, 622-31-1; *syn*-*p*-$MeC_6H_4CH{=}NOH$, 3717-16-6; *anti*-*p*-$MeC_6H_4CH{=}NOH$, 3717-15-5; *syn*-*p*-$MeOC_6H_4CH{=}NOH$, 3717-22-4; *anti*-*p*-$MeOC_6H_4CH{=}NOH$, 3717-21-3; *syn*-*m*-$NO_2C_6H_4CH{=}NOH$, 3717-20-2; *anti*-*m*-$NO_2C_6H_4CH{=}NOH$, 3717-19-9; *syn*-*p*-$NO_2C_6H_4CH{=}NOH$, 3717-20-2; $PhCH{=}CHCH{=}NOH$, 13372-81-1; $PhCOCH{=}NOH$, 532-54-7; $CH_3COCH{=}NOH$, 306-44-5; $Ph_2C{=}NOH$, 574-66-3; Fl=NOH, 2157-52-0; 2,7-diBrFl=NOH, 139895-34-4; 2-$PhSO_2Fl$=NOH, 139895-35-5; *syn*-$PhC(CH_3){=}NOH$, 50314-86-8; *anti*-$PhC(CH_3){=}NOH$, 10341-75-0; $(PhCH_2)_2C{=}NOH$, 1788-31-4; $(PhCH_2)_2C{=}NOMe$, 2913-02-2; $Et_2C{=}NOH$, 1188-11-0; $Me_2C{=}NOH$, 127-06-0; *syn*-$CH_3CH{=}NOH$, 5775-72-4; *anti*-$CH_3CH{=}NOH$, 5780-37-0; *syn*-$CH_3CH_2CH{=}NOH$, 22067-09-0; *anti*-$CH_3CH_2CH{=}NOH$, 22042-15-5; $CH_3C(NH_2){=}NOH$, 22059-22-9; $PhC(NH_2){=}NOH$, 613-92-3; $PhC(NH_2){=}NOMe$, 4424-16-2; $HC(NH_2){=}NOH$, 624-82-8; *anti*-$Et_2NCH_2C(CH_3){=}NOH$, 139895-36-6; *syn*-$Me_2NCH_2C(Ph){=}NOH$, 65986-58-5; *anti*-$Me_2NCH_2C(Ph){=}NOH$, 16451-83-5; *anti*-$Me_2N(CH_2)_2C(Ph){=}NOH$, 46313-77-3; *syn*-(*c*-$OC_4H_8N)CH_2C(Ph){=}NOH$, 15437-08-8; *anti*-(*c*-$OC_4H_8N)CH_2C(Ph){=}NOH$, 15437-09-9; *anti*-$MeC_6H_4$-*p*-$SCH_2C(Ph){=}NOH$, 50314-84-6; $Et_2NCH_2C(CH_3){=}NOH$, 673-20-1; *anti*-$Me_2NCH_2C(CH_3){=}NOH$, 120724-26-7; cyclohexanone oxime, 100-64-1; cyclododecanone oxime, 2972-01-2; $CH_3CH{=}NO^-$, 140390-74-5; $CH_3CH_2CH{=}NO^-$, 140390-75-6; $Me_2C{=}NO^-$, 42331-32-8; $Et_2C{=}NO^-$, 42331-31-7; $(PhCH_2)_2C{=}NO^-$, 140390-76-7; c-$C_5H_{10}C{=}NO^-$, 140390-77-8; c-$C_{11}H_{22}C{=}NO^-$, 140390-78-9; *syn*-$PhCH{=}NO^-$, 52707-73-0; *anti*-$PhCH{=}NO^-$, 52739-47-6; *syn*-*p*-$MeC_6H_4CH{=}NO^-$, 52707-76-3; *anti*-*p*-$MeC_6H_4CH{=}NO^-$, 52707-62-7; *syn*-*p*-$MeOC_6H_4CH{=}NO^-$, 52707-85-4; *anti*-*p*-$MeOC_6H_4CH{=}NO^-$, 52707-70-7; *syn*-*m*-$NO_2C_6H_4CH{=}NO^-$, 52707-82-1; *anti*-*m*-$NO_2C_6H_4CH{=}NO^-$, 52739-49-8; *syn*-*p*-$NO_2C_6H_4CH{=}NO^-$, 52707-83-2; *syn*-$PhCH{=}CHCH{=}NO^-$, 140390-79-0; *syn*-$CH_3C(Ph){=}NO^-$, 140390-80-3; *anti*-$CH_3C(Ph){=}NO^-$, 101023-32-9; *anti*-*p*-$MeC_6H_4SCH_2C(Ph){=}NO^-$, 140390-81-4; $Ph_2C{=}NO^-$, 58074-11-6; Fl=NO$^-$, 140390-82-5; 2,7-diBrFl=NO$^-$, 140390-83-6; 2-$PhSO_2Fl{=}NO^-$, 140390-84-7; $CH_3COCH{=}NO^-$, 75938-09-9; $PhCOCH{=}NO^-$, 138888-62-7; $Et_2NCH_2C(CH_3){=}NO^-$, 140390-88-1; *anti*-$Me_2NCH_2C(CH_3){=}NO^-$, 140390-89-2; *syn*-$Me_2NCH_2C(CH_3){=}NO^-$, 140390-90-5; *anti*-$Me_2NCH_2C(Ph){=}NO^-$, 140390-91-6; *syn*-(*c*-$OC_4H_8N)CH_2C(Ph){=}NO^-$, 140390-92-7; *anti*-(*c*-$OC_4H_8N)CH_2C(Ph){=}NO^-$, 57031-42-2; *syn*-$Me_2N(CH_2)_2C(Ph){=}NO^-$, 140390-93-8; $HC(NH_2){=}NO^-$, 140390-95-0; $CH_3C(NH_2){=}NO^-$, 42331-30-6; $PhC(NH_2){=}NO^-$, 140390-96-1; $PhC(=NH)NH^-$, 136342-62-6; $PhC(N^-NMe_2){=}NPh$, 136342-67-1; $(PhCH^-)C(CH_2Ph){=}NOMe$, 140390-98-3; $PhC(=NCMe)NH^-$, 140390-97-2; $(PhCH_2)COCH^-Ph$, 140390-99-4; $CH_3CH{=}NOH^{\bullet+}$, 140461-23-0; $CH_3CH_2CH{=}NOH^{\bullet+}$, 140629-61-4; $Me_2C{=}NOH^{\bullet+}$, 140409-83-2; $Et_2C{=}NOH^{\bullet+}$, 140390-85-8; c-$C_{11}H_{22}C{=}NOH^{\bullet+}$, 140390-86-9; *syn*-$PhCH{=}NOH^{\bullet+}$, 140461-24-1; *anti*-$PhCH{=}NOH^{\bullet+}$, 140461-25-2; *syn*-*p*-$MeC_6H_4CH{=}NOH^{\bullet+}$, 140461-26-3; *anti*-*p*-$MeC_6H_4CH{=}NOH^{\bullet+}$, 140461-27-4; *syn*-*p*-$MeOC_6H_4CH{=}NOH^{\bullet+}$, 140461-28-5; *anti*-*p*-$MeOC_6H_4CH{=}NOH^{\bullet+}$, 140461-29-6; *syn*-*m*-$NO_2C_6H_4CH{=}NOH^{\bullet+}$, 140461-30-9; *anti*-*m*-$NO_2C_6H_4CH{=}NOH^{\bullet+}$, 140461-31-0; *syn*-*p*-$NO_2C_6H_4CH{=}NOH^{\bullet+}$, 140461-32-1; *syn*-$CH_3C(Ph){=}NOH^{\bullet+}$, 140461-33-2; *anti*-$CH_3C(Ph){=}NOH^{\bullet+}$, 140629-62-5; *anti*-*p*-$MeC_6H_4SCH_2C(Ph){=}NOH^{\bullet+}$, 140461-34-3; 2,7-diBrFl=$NOH^{\bullet+}$, 140390-87-0; 2-$PhSO_2Fl{=}NOH^{\bullet+}$, 140409-94-5; $CH_3COCH{=}NOH^{\bullet+}$, 140461-35-4; $PhCOCH{=}NOH^{\bullet+}$, 140461-36-5; $Et_2NCH_2C(CH_3){=}NOH^{\bullet+}$, 140390-94-9; *anti*-$Me_2NCH_2C(CH_3){=}NOH^{\bullet+}$, 140629-63-6; *syn*-$Me_2NCH_2C(Ph){=}NOH^{\bullet+}$, 140461-37-6; *anti*-$Me_2NCH_2C(Ph){=}NOH^{\bullet+}$, 140461-38-7; *syn*-(*c*-$OC_4H_8N)CH_2C(Ph){=}NOH^{\bullet+}$, 140461-39-8; *anti*-(*c*-$OC_4H_8N)CH_2C(Ph){=}NOH^{\bullet+}$, 140461-40-1; *syn*-$Me_2N(CH_2)_2C(Ph){=}NOH^{\bullet+}$, 140461-41-2; $HC(NH_2){=}NOH^{\bullet+}$, 140391-00-0; $CH_3C(NH_2){=}NOH^{\bullet+}$, 140461-42-3; $PhC(NH_2){=}NOH^{\bullet+}$, 140461-43-4; $PhC(NH_2){=}NOMe^{\bullet+}$, 140391-01-1; $PhC(NH_2){=}NH^{\bullet+}$, 140391-02-2; $PhC(NHNMe_2){=}NPh^{\bullet+}$, 140391-03-3.

(13) *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Furniss, B., Hannaford, A. J., Smith, P. W. G., Jatchell, A. R., Eds.; Wiley: New York, 1989; p 1048.
(14) Crawford, R. J.; Woo, C. *Can. J. Chem.* **1965**, *43*, 3178–3187.
(15) Campbell, K. N.; Campbell, B. K.; Chaput, E. P. *J. Org. Chem.* **1943**, *8*, 101–102.
(16) Smith, J. H.; Kaiser, E. T. *J. Org. Chem.* **1974**, *39*, 728–730.
(17) Dalton, D. R.; Foley, H. G. *J. Org. Chem.* **1973**, *38*, 4200–4203.
(18) Stoermer, R.; Dzimski, O. *Chem. Ber.* **1895**, *28*, 2220–2227.
(19) Luening, B. *Acta Chem. Scand.* **1959**, *19*, 1623–1633.
(20) Chow, Y. L.; Colón, C. L. *J. Org. Chem.* **1968**, *33*, 2598–2601.
(21) Scott, F. L.; MacConaill, R. J.; Riordan, J. C. *J. Chem. Soc. C* **1967**, 44–47.
(22) Smith, J. H.; Heidema, J. H.; Kaiser, E. T.; Wetherington, J. B.; Moncrief, J. W. *J. Am. Chem. Soc.* **1972**, *94*, 9274–9276.
(23) *CRC Handbook of Chemistry and Physics*, 56th ed.; Weast, R. C., Ed.; CRS Press: Boca Raton, FL, 1975; p C-439.
(24) Neber, P. W.; Uber, A. *Ann.* **1928**, *467*, 52–72.
(25) Feuer, H.; Vincent, B. F., Jr.; Barlett, R. S. *J. Org. Chem.* **1965**, *30*, 2877–2880.
(26) Smith, R. F.; Johnson, D. S.; Hyde, C. L.; Rosenthal, T. C. *J. Org. Chem.* **1971**, *36*, 1155–1158.