Conformational Analysis about the Nitrogen–Nitrogen′ Bond by Nuclear Magnetic Resonance Spectroscopy. N′-Sulfonyl Derivatives of N-Aminocamphorimide

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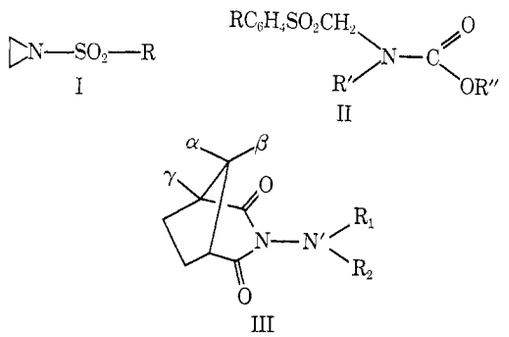
The effect of the sulfonyl groups directly bonded to the exocyclic nitrogen in disubstituted *N*-aminocamphorimides on the conformational process about the N–N′ bond has been investigated by nmr spectroscopy. A number of *N*′-sulfonyl derivatives have been synthesized and their nmr spectra compared with those of the *N*′-acyl analogs. Shielding constants of the β-methyl group of the nonplanar cage structure, *i.e.*, the bicyclic camphorimidyl system, have been used for the conformational study. Temperature-dependent spectral changes have been related to the conformational changes about the N–N′ bond. The free energies of activation, $\Delta G^{\ddagger}$, for rotation about the N–N′ bond in these compounds are of similar order as those for the *N*′,*N*′-diacyl derivatives. Nmr spectra indicate that there is a free rotation about the N′–SO_2 bond in *N*′-mesyl derivatives whereas the tosyl substituents prefer a fixed conformation about the N′–SO_2 bond.

Hindered nitrogen inversion[1,2] and rotation about the N–N bond in cyclic[3] and acyclic[4-6] systems studied by nmr spectroscopy have been reviewed.[7] The large barriers, observed for the nitrogen inversion in *N*-sulfonyl derivatives of dihydroquinolones[1] were attributed to the steric hindrance of the sulfonyl group, whereas the increased rates of N inversion in *N*-sulfonylaziridines[8] (I) were assigned to the delocalization of



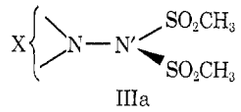
I II III

nitrogen lone-pair electrons on to the sulfonyl group. Hindered rotation about methoxy–carbonyl bond in the compound of the type II was attributed to the presence of the aryl sulfonyl group in the β position to the nitrogen atom.[9]

Recently, we reported[10] the preferred conformations about the N–N′ and N′–CO bonds in a series of *N*′-acyl derivatives of *N*-aminocamphorimide (III) by making use of the shielding constants of the β-methyl group of the nonplanar cage structure. It was of considerable interest to examine the effects of a sulfonyl substituent at the exocyclic nitrogen atom on the conformational processes about the N–N′ and N′–SO_2 bonds. The present communication deals with the syntheses and the nmr studies of some *N*′-sulfonyl-*N*-aminocamphorimides (IIIa–IIIs). The conformations and anisotropic effect of mesyl and tosyl groups were investigated by a comparative study of the shielding constants of the cage β-methyl group. The free energies of activation ($\Delta G^{\ddagger}$) to the rotation about the N–N′ bond were estimated from the variable temperature nmr spectral parameters using Eyring's rate equation[11] (Table I).

The variable temperature nmr spectra of the compounds were studied in nitrobenzene. The general spectral pattern observed in nitrobenzene was similar to that observed in $CDCl_3$. The rate constants (k_t) at $t°$, below the coalescence temperature involved in the Eyring's rate equation, were extracted from the equation $k_t = (\pi/2^{1/2})(\Delta\nu_0^2 - \Delta\nu_t^2)^{1/2}$ where $\Delta\nu_0$ and $\Delta\nu_t$ are the internal chemical shifts (in hertz) of the temperature-dependent signals at 44.5 and $t°$, respectively. This expression for rate constants is actually applicable to the exchanges between two different uncoupled sites of equal populations, and therefore the accuracy of the obtained $\Delta G^{\ddagger}$ values is limited as the rate processes, observed in some cases, involve exchange between sites of unequal populations. However, these values were taken to be sufficiently accurate for comparison purpose.[3,12]

N′,N′-Dimesyl-N-aminocamphorimide (IIIa).—The nmr spectrum of IIIa in $CDCl_3$ shows two sharp singlets for the mesyl groups. The spectrum is temperature dependent and the two signals of the mesyl protons move closer as the temperature is raised ($\Delta\nu$ being 5.7 and 5.05 Hz at 44.5 and 150°, respectively, in nitrobenzene). This behavior provides evidence for some slow conformational change in the molecule in solution.



IIIa

(X represents the bicyclic camphorimidyl cage moiety)

The structure of the exocyclic trivalent nitrogen atom is assumed to be nearly planar since the sulfonyl group

(1) W. N. Speckamp, U. K. Pandit, and H. O. Huisman, *Tetrahedron Lett.*, 3279 (1964); W. N. Speckamp, U. K. Pandit, P. K. Korver, P. J. Van der Haak, and H. O. Huisman, *Tetrahedron*, **22**, 2413 (1966).

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TABLE I

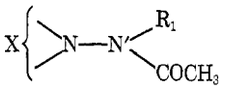
VARIABLE TEMPERATURE SPECTRAL DATA AND THE ESTIMATED FREE ENERGIES OF ACTIVATION ($\Delta G^{\pm}$) TO THE ROTATION ABOUT THE N–N′ BOND IN NITROBENZENE BELOW THE COALESCENCE TEMPERATURE

Compound	Spectral change studied	$\Delta\nu$ at 44.5°	$\Delta\nu$ at t°	$\Delta G^{\pm}$ at t°, kcal/mol
IIIa	Decrease in $\Delta\nu$ of the mesyl signals	5.70	5.05 (150)	23.7
IIIb	Decrease in $\Delta\nu$ of the acetyl signals	7.90	5.80 (100)	20.3
IIIc	Decrease in $\Delta\nu$ of the acetyl signals	9.75	7.25 (120)	21.3
IIId	Decrease in $\Delta\nu$ of the β-methyl signals	78.50	63.75 (120)	19.7
IIIe	Decrease in $\Delta\nu$ of the β-methyl signals	75.50	61.50 (120)	19.8
IIIf	Decrease in $\Delta\nu$ of the β-methyl signals	71.80	60.40 (120)	19.9
IIIh	Decrease in $\Delta\nu$ of the β-methyl signals	74.00	63.50 (120)	19.9
IIIj	Decrease in $\Delta\nu$ of the β-methyl signals	71.00	60.00 (120)	19.9
IIIk	Decrease in $\Delta\nu$ of the β-methyl signals	67.50	56.50 (120)	19.9
IIIl	Decrease in $\Delta\nu$ of the β-methyl signals	40.75	39.50 (100)	19.8
IIIn	Decrease in $\Delta\nu$ of the β-methyl signals	39.50	39.00 (100)	20.2
IIIo	Decrease in $\Delta\nu$ of the β-methyl signals	46.00	39.50 (120)	20.3

is as efficient as a carbonyl group for the delocalization of the nitrogen lone-pair electrons.[13] The possibility of slow rotation about the N′–SO_2 bonds is discarded since the free rotation about this bond is possible even with effective pπ–dπ delocalization.[13,14] The β-methyl signal of IIIa (Figure 1)[15] appearing at δ 1.16 seems to be only slightly deshielded as compared to that of camphorimide[10] (δ 1.05) which also suggests that there is a free rotation about the N′–SO_2 bonds. Hence a slow rotation about the N–N′ bond could be the only possibility for the observed multiplicity in the spectrum.

Noncoplanar structures, similar to those proposed for tetraacylhydrazine[4,16] and certain acyclic diacylhydrazine derivatives, would obviously explain the observed multiplicity for the mesyl groups. One of the two mesyl groups lies above and the other below the common plane of the imide bridge as shown in Figure 1; thus the two groups experience two different magnetic environments due to the cage moiety. $\Delta G^{\pm}$ to the rotation about the N–N′ bond was found to be in excess of 23.7 kcal/mol at 150°. This value is comparable with that of the corresponding *N′,N′*-diacetyl-*N*-aminocamphorimide[10] ($\Delta G^{\pm}$, 22.4 kcal/mol at 150°, below the coalescence temperature).

N′-Sulfonyl-N′-acetyl-N-aminocamphorimides (IIIb and IIIc).—The spectra of IIIb and IIIc in $CDCl_3$ are very similar; both show two singlets for the acetyl protons. Compound IIIb shows two singlets for its

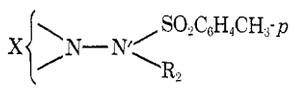


IIIb, $R_1 = SO_2CH_3$
c, $R_1 = SO_2C_6H_4CH_3$-*p*

mesyl methyl protons at δ 3.50 and 3.58, whereas the compound IIIc shows a slightly broad singlet at δ 2.5 (Figure 2)[15] for the tosyl methyl protons. The spectra indicate the possibility of two preferred conformations arising due to restricted rotation about the N–N′ bond as has been observed in *N′,N′*-dimesyl- (IIIa) and *N′,N′*-diacetyl-*N*-aminocamphorimides.[10] A singlet observed for tosyl methyl group suggests that in both the conformations this lies out of the effective zone of the cage moiety, but the tosyl aromatic protons, however, observe the asymmetry in the cage and thus differently shielded in the two conformations. The downfielded doublet of the protons adjacent to sulfonyl group (in AB quartet of aromatic protons) appear as a pair of doublets due to the two conformations.

The tosyl group in IIIc does not have any shielding effect on the β-methyl protons which further supports a fixed conformation about the N′–SO_2 bond where the aryl part of the tosyl group is projected away from the cage moiety. Shielding of a methyl and a *tert*-butyl group has been reported in 2-tosyldiazabicyclo[3.2.0]-heptanone[17] and 2,5-*tert*-butylcyclohexyl tosylate,[18] respectively.

N′-Tosyl-N′-aroyl-N-aminocamphorimides (IIId–IIIg).—A representative spectrum of this series is shown



IIId, $R_2 = COC_6H_5$
e, $R_2 = COC_6H_4CH_3$-*p*
f, $R_2 = COC_6H_4CH_3$-*m*
g, $R_2 = COC_6H_4CH_3$-*o*

in Figure 3[15] for the compound IIIf. The nmr spectra of all *N′*-tosyl-*N′*-aroyl compounds (IIId–IIIg) in $CDCl_3$ are quite characteristic showing four signals for the three methyls of the cage moiety. The ring methylenes are shielded and appear over a wide range (δ 0.5–2.40). The toluoyl methyl protons appear as a pair of singlets and the tosyl methyl protons appear as a slightly broad singlet.

Two different conformations which could arise due to the hindered rotation about the N–N′ bond may be represented as IV and V. The shielding of β-methyl (δ 0.23) in IV is essentially due to the aromatic ring

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(15) See paragraph at end of paper regarding supplementary material.
(16) S. M. Verma and C. Koteswara Rao, *Tetrahedron*, **28**, 5029 (1972).
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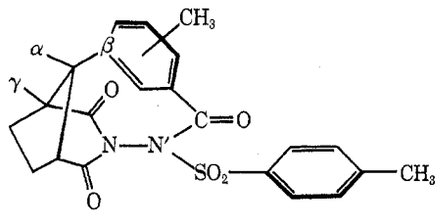
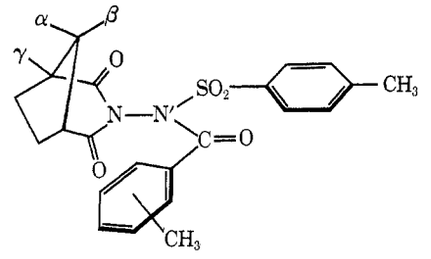


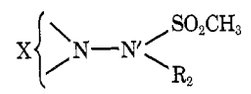
IV



V

of the toluoyl group as no shielding of any of the cage methyls is observed in the spectrum of N'-tosyl-N'-acetyl compound IIIc (Figure 2).[15] Moreover, the tosyl methyl group appears as a singlet (δ 2.5) suggesting that its aromatic part is projected away from the cage. Thus, the abnormal shielding of the β-methyl as well as that of the ring methylenes could only be due to the N'-aroyl group which may be assumed to have a preferred conformation about N′–CO bond as shown in IV and V.

N'-Mesyl-N'-aroyl-N-aminocamphorimides (IIIh–IIIk).—The nmr spectrum of compound IIIj in $CDCl_3$

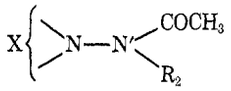


IIIh, R_2 = COC_6H_5
i, R_2 = $COC_6H_4CH_3$-p
j, R_2 = $COC_6H_4CH_3$-m
k, R_2 = $COC_6H_4CH_3$-o

(Figure 4)[15] shows two signals for the mesyl methyl protons, two signals for the m-toluoyl methyl protons, and the ring methylene protons shielded over a wide range. Two signals of the β-methyl are also observed (δ 0.08 and 1.19), the downfielded signal of which accidentally overlaps on that of the γ-methyl. (This accidental overlap was, however, removed by the "solvent shift" while studying the high temperature spectra in nitrobenzene.) Slight splittings are also observed in the α- and γ-methyl signals (Figure 4).[15] All the compounds of this series (IIIh–IIIk) show a similar nmr pattern.

Two preferred conformations about the N–N′ bond similar to IV and V would explain the observed multiplicities. The abnormal shielding observed for the β-methyl group as well as that of the ring methylenes in N'-mesyl-N'-aroyl compounds (IIIh–IIIk) could only be due to the N'-aroyl group, oriented towards the cage moiety about the N′–CO bond. The nmr spectral pattern of these compounds (IIIh–IIIk) is very similar to that of the N'-tosyl-N'-aroyl compounds (IIId–IIIg) supporting the conformations IV and V, where shielding of the β-methyl and the ring methylenes has been shown to be due to the N'-aroyl group and not due to the N'-tosyl group.

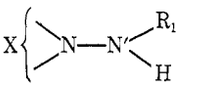
N'-Acetyl-N'-aroyl-N-aminocamphorimides (IIIl–IIIo).—The spectra of IIIl–IIIo, which constitute a



IIIl, R_2 = COC_6H_5
m, R_2 = $COC_6H_4CH_3$-p
n, R_2 = $COC_6H_4CH_3$-m
o, R_2 = $COC_6H_4CH_3$-o

class of tetraacylhydrazine compounds, are very similar to those of their N'-sulfonyl analogs (IIId–IIIk). The nmr spectrum of the compound IIIn in $CDCl_3$ (Figure 5)[15] shows two signals for the acetyl methyl protons, two signals for the β-methyl protons and a slightly broad singlet for the m-toluoyl methyl protons (δ 2.41). The ring methylene protons are shielded and appear in the range of δ 0.6–2.30. A similar resonance pattern is observed for other N'-acetyl-N'-aroyl derivatives (IIIl–IIIo, Table I), where N'-aroyl group has strong shielding effect on β-methyl and the ring methylene protons.

N'-Monosubstituted N-Aminocamphorimides (IIIp–IIIs).—N'-Monoacyl derivatives[10] have been shown



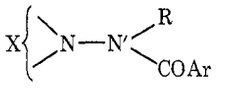
IIIp, R_1 = $COC_6H_4CH_3$-p
q, R_1 = $COC_6H_4CH_3$-o
r, R_1 = SO_2CH_3
s, R_1 = $SO_2C_6H_4CH_3$-p

to have a restricted rotation about N′–CO bond, and consequently the β-methyl signal of the cage is distributed accidentally among the α- and γ-methyl resonances giving rise to only two peaks of 4.5-H intensity for the three methyl groups. Two similar derivatives, IIIp and IIIq, also show this characteristic behavior.

N'-Monosulfonyl derivatives IIIr and IIIs show normal spectra (three singlets for the three methyls) and indicate a free rotation about N′–SO_2 and N–N′ bonds.

Discussion

The nature of the spectra of the three analogous series (A, B, and C) described earlier are typical and reveal

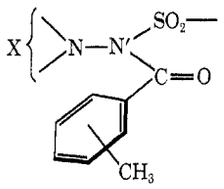


series A, R = tosyl (IIId–IIIg)
B, R = mesyl (IIIh–IIIk)
C, R = acetyl (IIIl–IIIo)

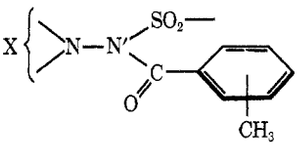
some interesting results regarding the orientation of the substituents at the exocyclic nitrogen atom.

(i) The toluoyl methyl protons show a singlet in N'-acetyl-N'-aroyl compounds (series C), whereas they are observed as pair of singlets when the acetyl group is replaced by a sulfonyl group (series A and B). This remarkable effect of the sulfonyl group can be

explained by assuming, along with slow rotation about the N–N′ bond, a preferred conformation, VI, about



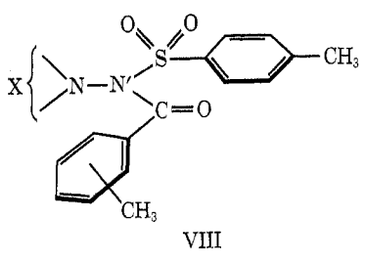
VI



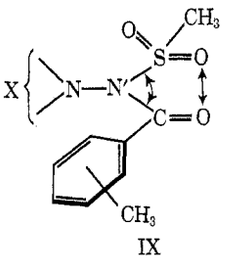
VII

the N′–CO bond. The toluoyl methyl protons, being oriented nearer to the cage moiety, about the N′–CO bond in VI, effectively experience the changes in the magnetic environments due to the conformational changes about the N–N′ bond and therefore appear as two signals corresponding to the two conformations. The other conformation VII about the N′–CO bond is not stable probably because of the large steric hindrance between the *N*′-sulfonyl group and the aryl part of the *N*′-aroyl groups. In case of the corresponding acetyl compounds (series C), the toluoyl group can take either of the two conformations about the N′–CO bond with more or less equal probability because of less hindrance of the acetyl group; thus the toluoyl methyl protons, being less sensitive towards the cage moiety magnetic environments, appear as a singlet only. It is also supported by the observation of the shielding effect of the *N*′-aroyl group on the β-methyl to be more in the *N*′-sulfonyl-*N*′-aroyl compounds (series A and B) than in the *N*′-acetyl-*N*′-aroyl compounds (series C).

(ii) It is further seen that, in *N*′-mesyl-*N*′-aroyl compounds (series B), the upfield β-methyl signal is more shielded and at the same time the downfielded β-methyl signal is less deshielded (overlapping on the γ-methyl signal) as compared to the corresponding signals in the *N*′-tosyl-*N*′-aroyl compounds (series A). As discussed earlier, the tosyl group assumes a fixed conformation about the N′–SO_2 bond as shown in VIII



VIII



IX

and thus has a strong deshielding effect on β-methyl. Further, a free rotation about the N′–SO_2 bond has been established (in compounds IIIa and IIIb). The reduced deshielding of the β-methyl signal in series B is in accordance with the free rotation about N′–SO_2 bond.

The strong shielding of the β-methyl group in *N*′-mesyl-*N*′-aroyl compounds (series B) suggests that the *N*′-aroyl group sits very close over the β-methyl group; *i.e.*, the S–N′–C bond angle in the compounds of series B is larger than that in the compounds of series A. The increased S–N′–C bond angle in series B (IX) may be the result of large stereoelectronic interactions between the sulfonyl and carbonyl oxygens, which are absent in *N*′-tosyl-*N*′-aroyl compounds (A) due to the fixed conformations of the substituents.

Conclusion

From the foregoing account, it is evident that the *N*′,*N*′-disulfonyl and the *N*′-sulfonyl-*N*′-acyl derivatives prefer a noneclipsed conformations about the N–N′ bond. High torsional barriers due to the stereoelectronic repulsive interactions between the carbonyl and sulfonyl groups at the two nitrogens are of the same order of those in the *N*,*N*′-diacyl compounds (Table I). It is interesting to note that, in the *N*′-sulfonyl-*N*′-acyl derivatives (with hindered rotation about the N–N bond), the mesyl derivatives show a free rotation about the N′–SO_2 bond and the tosyl derivatives have a fixed conformation about the N′–SO_2 bond. The orientation of the tosyl group is such that its aromatic ring does not have any shielding effect on the cage moiety protons.

Experimental Section

Nmr spectra were recorded on a Varian A-60D nmr spectrometer, equipped with a variable temperature controller (Model No. V-6040) at 44.5° in $CDCl_3$ using TMS as internal reference standard. The nmr data of the compounds are recorded in Table II.[15] The variable temperature spectral parameters are given in Table I. Ir spectra were recorded in Nujol medium on a Perkin-Elmer 257 spectrophotometer. The melting points of the compounds are fairly sharp and melt within the range of ±1° and are recorded in Table III,[15] along with the analytical data and characteristic ir peaks.

Preparation of Compounds. ***N*′-Mesyl Compounds (IIIa, IIIb, IIIh–IIIk, and IIIr).**—*N*′,*N*′-Dimesyl-*N*-aminocamphorimide (IIIa) was prepared by heating 1 mol of *N*-aminocamphorimide[10] with 2 mol of methanesulfonyl chloride in presence of pyridine at ~120° for 2 hr. It was recrystallized from ethanol.

N′-Monomesyl compound (IIIr) was prepared by heating on water bath the *N*-aminocamphorimide with equimolar quantities of methanesulfonyl chloride and pyridine. The product obtained had a gummy consistency, and the ir and nmr spectra were found to be quite satisfactory (Tables II and III).[15] The *N*′-mesyl-*N*′-acetyl derivative IIIb was obtained by acetylation of compound IIIr with excess of acetic anhydride. All the aroyl derivatives (IIIh–IIIk) were obtained by refluxing compound IIIr in dry benzene with corresponding aroyl chloride in presence of pyridine and were recrystallized from ethanol.

***N*′-Tosyl Compounds (IIIc–IIIg and IIIs).**—The *N*′-monotosyl compound (IIIs) was prepared by heating the *N*-aminocamphorimide with equimolar quantities of *p*-toluenesulfonyl chloride and pyridine at about 120° for 2 hr. It was recrystallized from ethanol. *N*′-Tosyl-*N*′-acetyl compound IIIc was prepared by acetylation of compound IIIs with excess of acetic anhydride in presence of pyridine at water bath. All the aroyl derivatives (IIId–IIIg) were obtained by refluxing compound IIIs in dry benzene with equimolar quantities of the corresponding aroyl chloride and pyridine. These compounds were recrystallized from ethanol.

***N*′-Acyl Compounds (IIIl–IIIq).**—*N*′-Monoaroyl compounds IIIp and IIIq were prepared by refluxing the *N*-aminocamphorimide in dry benzene with equimolar quantities of the corresponding aroyl chloride and pyridine. IIIp, IIIq, and *N*′-monoaroyl-*N*-aminocamphorimides[10] on acetylation with excess of acetic anhydride in presence of pyridine yielded the compounds IIIl–IIIo. These compounds were recrystallized from ethanol.

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Registry No.—IIIa, 41262-98-0; IIIb, 41262-99-1; IIIc, 41263-00-7; IIId, 41263-01-8; IIIe, 41263-02-9; IIIf, 41263-03-0; IIIg, 41263-04-1; IIIh, 41263-05-2; IIIi, 41263-06-3; IIIj, 41312-33-8; IIIk, 41263-07-4; IIIl, 41263-08-5; IIIm,

41263-09-6; IIIn, 41263-10-9; IIIo, 41263-11-0; IIIp, 41263-12-1; IIIq, 41263-13-2; IIIr, 41263-14-3; IIIs, 41263-15-4; *N*-aminocamphorimide, 37710-30-8; methanesulfonyl chloride, 124-63-0; acetic anhydride, 108-24-7; *p*-toluenesulfonyl chloride, 98-59-9; benzoyl chloride, 98-88-4; *p*-toluoyl chloride, 933-88-0; *m*-toluoyl chloride, 1711-06-4; *o*-toluoyl chloride, 933-88-0.

Supplementary Material Available.—Tables of nmr, analytical, and ir data and figures showing the nmr of IIIa, IIIc, IIIf, IIIj, and IIIn will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-73-3745.

O-(1-Alkyl- or -arylthioalkyl)hydroxylamines. A New Class of Oxime Reagents, Their Preparation and Synthetic Utility

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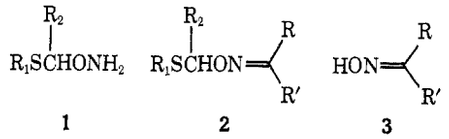
O-(1-Methyl-, -benzyl-, and phenylthioalkyl)hydroxylamines **1a–e** were synthesized by solvolysis of the corresponding *N*-(1-methyl-, benzyl-, and -phenylthioalkoxy)phthalimides **5a–e**. The (1-methyl-, -benzyl-, and -phenylthioalkoxy) oximes, **7a–e**, of the cyclopentanone were prepared, and their stability in acidic, basic, reductive, and oxidative media was determined. The mercury(II)-promoted hydrolysis of **7a–e** to the corresponding hydroxy ketoxime **10** is described.

In connection with the synthesis and chemical transformations of the E prostaglandins, the masking and unmasking of the reactive β-ketol moiety in the cyclopentane ring has been a challenging problem for the organic chemist. Oxime reagents have already been used to stabilize the β-ketol functionality;[1-3] however, the regeneration of prostaglandins from them, in good yield, has so far only been achieved in the case of the *O*-unsubstituted ketoxime derivative.[3] However, the sensitivity of the labile hydroxy ketoximes to acidic and oxidative media[4] substantially limits their role as synthetic intermediates.

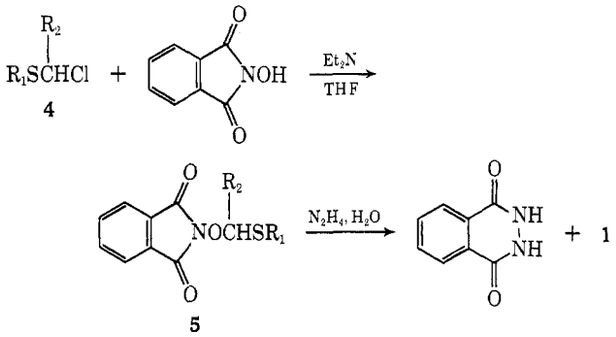
In this paper we wish to report on the development of a new class of oxime reagents, namely the *O*-(1-alkyl- and -phenylthioalkyl)hydroxylamines **1**, to demonstrate the synthetic versatility of such ketoxime derivatives **2**[5] and describe the hydrolysis of **2**, under mild conditions, to the corresponding free oxime derivatives **3**.



1 **2** **3**

The synthesis of the hydroxylamine derivatives **1a–e** was accomplished as outlined in Scheme I. The chloroalkylthio ethers, **4a–e**, were prepared by the method of Bohme, *et al.*[6] The crude reaction products of **4c** and **4e** were unstable to fractional distillation[7] and were used without further purification. Reaction of *N*-hydroxyphthalimide and triethylamine with **4a–e** in refluxing tetrahydrofuran gave the crystalline

SCHEME I



5

a, $R_1 = CH_3$; $R_2 = H$
b, $R_1 = C_6H_5CH_2$; $R_2 = H$
c, $R_1 = C_6H_5CH_2$; $R_2 = CH_3$
d, $R_1 = C_6H_5$; $R_2 = H$
e, $R_1 = C_6H_5$; $R_2 = CH_3$

phthalimide derivatives **5a–e**[8] in good yield. Solvolysis of **5a–e** with hydrazine hydrate in refluxing ethanol produced the hydroxylamine derivatives **1a–e** as stable distillable liquids. Although the free bases could be stored indefinitely at 0°, their addition salts (*e.g.*, hydrochlorides) slowly decomposed on standing at room temperature.

The hydroxylamine derivatives **1a–e** were treated with the model cyclopentanone **6**[9] in pyridine, in the presence of equivalent amounts of pyridine hydrochloride at room temperature, to give the oximes **7a–e** quantitatively (Scheme II). A variety of conditions were employed in the mercury(II)-promoted hydrolysis of the oximes **7a–e**. By far the best results were obtained when **7a–e** were treated in glacial acetic acid with excess of mercuric chloride and sodium acetate as buffer. Under these conditions acidolysis of **7a–e** resulted in the formation of the stable *O*-acetoxyme-

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