troducing an sp^2 center in a three-membered ring.[5a,16] Should the heat of formation of the cyclopropyl cation be as high as indicated from MO calculations (Table I), a large (ca. 25 kcal/mol) destabilizing effect in addition to the simple I-strain effect would be required. Our results indicate clearly that the allyl cation is not readily formed by protonation and concomitant opening of the cyclopropyl ring. Concerted protonation and rearrangement to an allyl cation could, however, explain our results if this process had an energy barrier such that it could only occur at an observable rate when the protonating species has ca. 12 kcal/mol more energy than needed to form an allyl cation. In that case, the transition state might still resemble the cyclopropyl cation in structure and energy, and the apparent PA would at least give a lower limit on $\Delta H_f°(\Delta^+)$. While the structure of the $C_3H_5^+$ ion formed from cyclopropene is not yet certain; the ion formed from allene appears not to be the allyl cation as indicated earlier. In both cases, a significant barrier to a process involving protonation with concomitant rearrangement to the allyl cation must exist.

The PA's of substituted cyclopropenes give derived $\Delta H_f°$ and HA data (Table I) that show reasonable methyl group effects for an interpretation based on cyclopropyl cation formation. The 1-methylcyclopropyl cation[17] has an apparent heat of formation 11 kcal/mol higher than the methallyl cation, and its HA is 11 kcal/mol higher than the unstrained *tert*-butyl cation.[18] Similarly, the 1,2,2-trimethylcyclopropyl cation and the 3,3-dimethylcyclopropyl cation give heats of formation that are respectively 19 and 27 kcal/mol higher than those of corresponding rearranged allyl cations.[18] Thus, in all of the cases studied, either cyclopropyl cations are formed in the initial proton transfer, or the proton transfer must occur with 11–27 kcal/mol barriers to allyl cation formation in the proton transfer step.

Acknowledgment. We acknowledge the National Science Foundation under Grant MPS73-04657, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank M. J. Meshishnek, K. Dougherty, L. Pearlman, and G. S. Helwig for preparation of compounds used in this work.

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The Oxidation of Amines with Sulfonyl Peroxides

Sir:

Oxidative deamination can be achieved by a variety of methods including indirect routes[1,2] as well as direct oxidation of the amine function.[1] Metal containing oxidants such as $Pb(OAc)_4$,[3a] MnO_2,[3b] NiO_2,[3c] and Ag_2CO_3[3d] or peroxidic reagents such as hydroperoxides,[4a] acylperoxides,[4b] and sodium persulfate[4c] can be used to oxidize the amine group. Oxidative deamination with these reagents is characterized by competing oxidation processes that depend on both the amine type (primary and secondary) as well as the oxidizing agent which combine to produce a reaction that is often unpredictable and inefficient. Complex mixtures of oxidized products often result. We wish to report that both primary and secondary amines **1** can be oxidized with *p*-nitrobenzenesulfonyl peroxide (*p*-NBSP) **2** to the corresponding imine **3** (eq 1). The described oxidation is the initial report of the reactions

$$\underset{\mathbf{1}}{R_1CH_2NHR_2} + \underset{\mathbf{2}}{(p\text{-}NO_2C_6H_4SO)_2} \longrightarrow \underset{\mathbf{3}}{R_1CH{=}NR_2} + 2p\text{-}NO_2C_6H_4SO_3H \quad (1)$$

$R_2 = -H, -alkyl$

of sulfonyl peroxides with compounds other than π-electron donors and is a further characterization of the general electrophilic behavior of these peroxdes.[6] The reaction proceeds efficiently with respect to the peroxide and does not exhibit the multiple pathways often present in other amine oxidations. Hydrolysis of the imine **3** completes the oxidative deamination in fair to excellent overall yields with respect to the oxidizing agent (Table I).

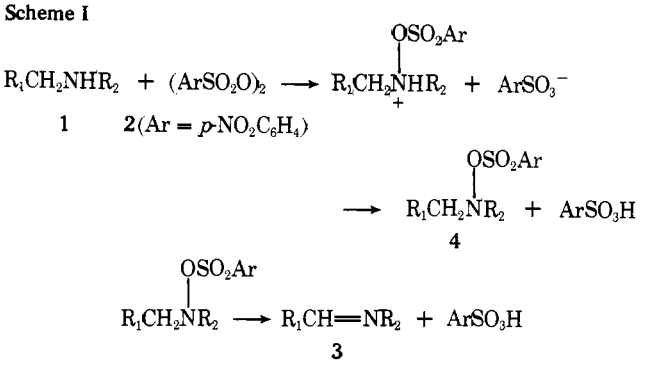
Oxidations were carried out as follows: To a −78 °C solution of *p*-NBSP[6a] (0.6 g, 1.5 mmol) in ethyl acetate (30 ml) under nitrogen was added a solution of the amine (4.5 mmol for secondary amines, 6.0 mmol for primary amines) in ethyl acetate (3 ml). The amine solution was prepared under nitrogen and added by syringe. After vigorous stirring (2 h) at −78 °C, the ethyl acetate was removed on a rotary evaporator and 2 N HCl (40 ml) was added to the pasty residue. The mixture was immersed in a bath preheated to 150 °C and distilled until 15 ml of water had been collected. The distillate was treated with saturated sodium bicarbonate (20 ml) and extracted with

Table I. The Oxidation of Amines with *p*-NBSP in Ethyl Acetate at −78 °C

Amine (equiv)	Product	Yield (%)[a]
$(C_6H_5CH_2)_2NH$ (3)	C_6H_5CHO[b]	96[d]
$C_6H_5CH_2NH_2$ (4)	C_6H_5CHO	84[e]
p-$ClC_6H_4CH_2NH_2$ (4)	p-ClC_6H_4CHO	89
$(c\text{-}C_6H_{11})_2NH$ (3)	Cyclohexanone	53
$c\text{-}C_6H_{11}NH_2$ (4)	Cyclohexanone	57
$(C_4H_9)_2NH$ (3)[c]	C_3H_7CHO	73
$C_4H_9NH_2$ (4)[c]	C_3H_7CHO	39
$(i\text{-}C_3H_7)_2NH$ (3)	CH_3COCH_3	37
$C_6H_5CH(NH_2)CH_3$ (4)	$C_6H_5COCH_3$	66
$C_6H_5CH_2NHCH_3$ (3)	C_6H_5CHO	74

[a] These are isolated yields determined by gas chromatography. [b] One equivalent of benzylamine was also measured. [c] For analytical reasons this reaction was run in CH_2Cl_2 solvent. [d] Yields for other methods of oxidative deamination of dibenzylamine include $Pb(OAc)_4$ (27%),[3a] MnO_2 (62%),[3b] NiO_2 (43%),[3c] $Na_2S_2O_8$ (8-22%).[4c] [e] Yields for other methods of oxidative deamination of benzylamine include $Pb(OAc)_4$ (4%),[3a] MnO_2 (0%),[3b] $Na_2S_2O_8$ (96%).[4c]

Scheme I



ether. The organic extract was dried (Na_2SO_4) and contained only the carbonyl product[5] in the amounts listed in Table I.

Although optimal reaction conditions were not pursued, it was convenient to carry out the oxidations in ethyl acetate solution at −78 °C. The instability of aliphatic imines[7] precluded their isolation in most instances and they were usually hydrolyzed to more tractable carbonyl derivatives. However, *N*-benzylidenebenzylamine (**5**) could be obtained in low yield from the reaction of dibenzylamine with *p*-NBSP, and a compound was separated from the oxidation of *n*-butylamine whose mass spectrum indicated it to be a trimer of butanal imine but which was not studied further. The oxidation of the amine to the imine is thought to proceed quantitatively but the yields of the carbonyl products in Table I seem to reflect the stability of the imine product to the protic reaction conditions. High yields are obtained in those cases where the more stable imines are formed.

The oxidation most likely proceeds as in Scheme I. Initial nucleophilic attack by the amine on the peroxide bond of **2** gives the hydroxylamine *O*-sulfonate adduct **4**.[1,6,8] Elimination of *p*-nitrobenzenesulfonic acid from **4** gives the imine **3**. Since 2 equiv of *p*-nitrobenzenesulfonic acid are produced in the oxidation, at least 3 equiv of amine are required, thus making the peroxide the limiting reagent. If less than 3 equiv of the amine are used, protonation of the unreacted amine by the sulfonic acid renders it nonnucleophilic towards the peroxide, the reaction does not proceed to completion, and yields are significantly lowered (Table II). The yield of carbonyl product from primary amines is increased by using 4 equiv of the amine since transamination gives a more stable N-substituted imine (Table II). Such a transamination product, *N*-benzylidenebenzylamine (**5**), was isolated from the oxidation of 4 equiv of benzylamine (eq 2).

Table II. Effect of Excess Amine on Oxidation Yield

Expt	Amine	Equiv of amine	Yield (%)[a]
1	$c\text{-}C_6H_{11}NH_2$	2	32
2	$c\text{-}C_6H_{11}NH_2$	3	55
3	$c\text{-}C_6H_{11}NH_2$	4	57
4	$C_6H_5CH_2NH_2$	3	65
5	$C_6H_5CH_2NH_2$	4	84

[a] See footnote *a*, Table I.

Table III. The Oxidation of Amines with *p*-NBSP with Added KOH

Amine (equiv)	*p*-NPSP equiv	KOH equiv[a]	Product	Yield (%)[b]
$(C_6H_5CH_2)_2NH$ (1)	1	6	C_6H_5CHO	75
$C_6H_5CH_2NH_2$ (1)	1.1	4	C_6H_5CHO	52
$C_6H_5CH_2NHCH_3$ (1)	1	5	C_6H_5CHO	60

[a] A suspension of powdered KOH in ethyl acetate was used. [b] Isolated yield with respect to the amine.

The use of 1 equiv of amine and a heterogeneous base (powdered KOH) to remove the sulfonic cid formed gave good yields of carbonyl product with respect to the amine (Table III). One equivalent of the amine was added to a −78 °C mixture of **2** (1 equiv) and powdered KOH (4–6 equiv) and stirred vigorously. Workup was the same as previously described; however, the reaction time is lengthened considerably (6 h) due to the slow proton transfer between the ammonium salt and the base. This results in some decomposition of the imine product before hydrolysis. We are investigating soluble bases which may shorten the reaction time.

An important aspect of this oxidation is the in situ production of the *N*-sulfonoxy derivative **4** from nucleophilic attack of the amine on the peroxide oxygens. Analogous *N*-acyloxy derivatives have been isolated from reaction of amines with acyl peroxides;[9] however, subsequent decomposition of these adducts proceeds by competing free radical pathways.[8,10] *N*-Sulfonoxy derivatives **4** may be much less prone to homolytic decompositions due to the much better leaving ability of the sulfonoxy group over the carboxyl group. The present results are compatible with such an expectation and the two-electron oxidation of amines may be achieved chemically by this procedure. We are investigating the further synthetic and mechanistic implications of this reaction.

Acknowledgment. This work was supported in part by the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and The Arts and Sciences Research Center of New Mexico State University. The help of Ruben Cadena in several experiments is gratefully acknowledged.

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The Structure of Xylomollin, a Secoiridoid Hemiacetal Acetal

Sir:

During the course of studies on *Xylocarpus molluscensis* (Meliaceae),[1] a tree widely used in folk medicine in East Africa, we had occasions to study its unripe and bitter fruits. The fruits (each weighing ca. 200 g) are used as aphrodisiacs[2] while young, but with ripening the bitterness is rapidly lost and the fruits become edible. We have isolated the bitter principle "xylomollin", which besides being an antifeedant against the African army worm *Spodoptera exempta*, strongly inhibits the respiratory reactions of mitochondria from rat liver.[3] Spectral data lead to the unusual monoterpenoid secoiridoid structure **1** having a nonglycosidic hemiacetal function at C-1 and an acetal function at C-3.

Xylomollin was readily obtained by extraction of the fruit flesh with aqueous methanol, removal of methanol, extraction of residual aqueous concentrate with ether and concentration; yield 0.1% of wet weight.

The physical constants of xylomollin **1** are as follows; mp 138–139 °C (ethanol), high resolution MS 275.1529 (M + H) (calculated for $C_{12}H_{19}O_7$ M + H, 275.1533);[4] chemical ionization MS[5] 275 (M + 1), 243 (275 − CH_3OH); ir (dilute $CHCl_3$) 3600, 1733, 1720 cm^{-1}. The nature of all carbon atoms was clarified by ^{13}C NMR (JEOL PS-100) with the techniques of PND, PRFT,[6] and off-resonance decoupling. The undecoupled ^{13}C NMR (Figure 1) was very revealing in that the doublet of quartets at 56.1 ppm (J = 6 and 0.5 Hz) showed for the first time that one of the two methoxyl peaks in the ^1H NMR (**1a**) was due to a methoxyl group attached to a methine carbon (C-3) with a J value of 0.5 Hz. All the protons attached to the skeleton, which contains no quaternary carbon and hence consists of one continuous proton system, was clarified by 100-MHz and 220-MHz (Varian) ^1H NMR as shown in **1a**; pyridine-d_5 was used as solvent owing to poor solubility of xylomollin in $CDCl_3$. An unusual feature was that all coupling constants were large, the smallest being the 3 Hz value for $J_{1,9}$. In addition, in spite of numerous attempts, no W type couplings or NOE's could be detected. Combination of these data leads uniquely to the structure shown in **1a** (or **1**). The structure is corroborated by the shifts seen in the ^1H NMR (pyridine-d_5) of the benzoate, mp 188 °C. Namely, as expected, the two protons in 1,3-diaxial relations to the 1-benzoate group were shifted from 5.45 to 5.00 ppm (3-H) and from 3.00 to 2.75 ppm (5-H), respectively.

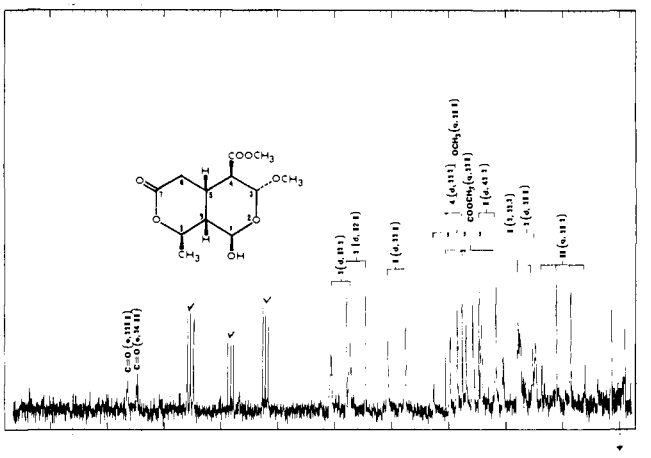


Figure 1. Undecoupled ^{13}C NMR of xyllomolin in pyridine-d_5, JEOL PS-100. The numerals outside the parentheses denote carbon atoms, and those inside the ppm and J values (Hz). The solvent peaks are indicated by check marks.

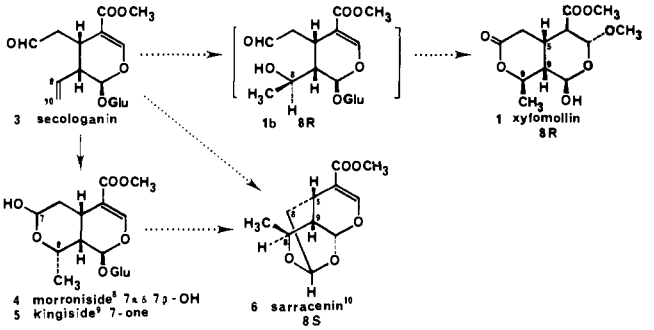
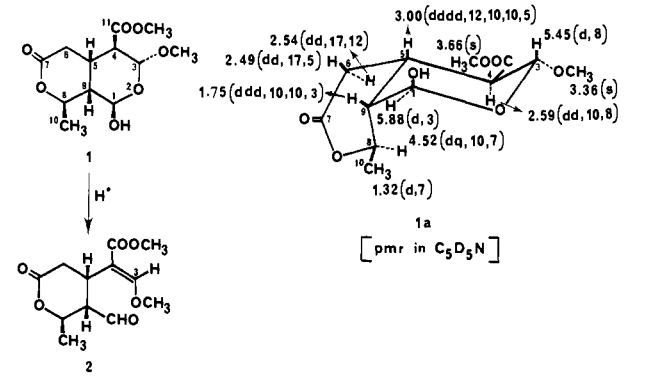


Figure 2. Biogenetic relationships. The transformation **3** → **4** has been proven experimentally.



Repeated chromatography of the ethereal mother liquid of the extract (vide supra) afforded numerous compounds, the major product being the enol ether aldehydes **2**, oil, mixture of cis and trans 3-ene isomers. The uv(MeOH) 238.5 nm (ε 12 000) and other spectral data, e.g., 3-H at 7.58 and 7.52 ppm, were in full agreement with structure **2**. The cis and trans mixture was also readily obtainable by leaving xylomollin in 1 N HCl/50% eq. MeOH at room temperature for 1 h (100% conversion).

As shown in Figure 2, xylomollin can be derived from secologanin **3** via the hydrated intermediate **1b** having an 8*R* configuration; the absolute configuration **1** is based on biogenetic considerations that all iridoids known to date have 5β,9β-H configurations. Hydration of the secologanin[7] 8,10-ene from the opposite side of the 8-ene leads to morroniside **4**[8] and kingiside[9] with 8S configuration; another related