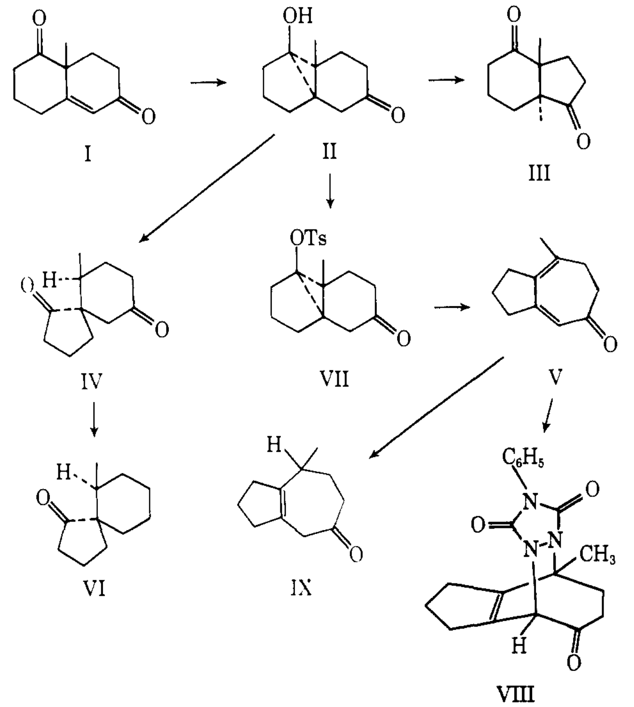

broad 13-proton multiplet from δ 2.2 to 2.7, and a strong parent ion at *m/e* 180 in the mass spectrum.

Confirmation of structure IV and elucidation of its stereochemistry was achieved by reduction of the spirodiketone (*via* an ethylenethioketal derivative) to VI, which proved to be identical (infrared, nmr, and mass spectra) with the 6-methylspiro[4.5]decan-1-one stereoisomer obtained by catalytic reduction of the Diels–Alder adduct from *trans*-2-ethylidenecyclopentanone[4] and 1,3-butadiene. Thus, in the conversion of II to IV, stereospecific protonation with retention of configuration has occurred at C-1 (nomenclature for II).

The conversion of II to 6-methylbicyclo[5.3.0]deca-1,6-dien-3-one (V) requires two steps. Reaction of II with *p*-toluenesulfonyl chloride in pyridine solution gave the unstable tosylate VII, mp 73.5–74.5°, in greater than 75% yield. This intermediate was characterized by infrared absorption at 1712, 1590, 1365, 1188, and 1175 cm$^{-1}$, and nmr absorption at δ 1.15 (3 H, singlet), 1.5–2.4 (12 H, multiplet), 2.43 (3 H, singlet), 7.25, and 7.73 (4 H, AB quartet, $J$ = 8 Hz). Acetolysis of VII produced an unstable liquid, the major component of which was V; the yield of crude dienone exceeded 85%. The ultraviolet absorption spectrum of V ($\lambda_{max}$ 316 ($\epsilon$ 6170) and 242 nm ($\epsilon$ 2970)) is similar to that of eucarvone ($\lambda_{max}$ 303 ($\epsilon$ 6800), with a shoulder at *ca.* 230 nm), and this together with carbonyl absorptions at 1710, 1650 (very strong), and 1510 cm$^{-1}$ in the infrared spectrum, characteristic nmr absorptions for a vinyl hydrogen (δ 5.90) and vinyl methyl (δ 1.95), and a strong parent ion at *m/e* 162 in the mass spectrum establishes the proposed structure V. Reduction of dienone V by a solution of lithium in ammonia gave in over 80% yield a nonconjugated enone believed to be IX[5] on the strength of infrared carbonyl absorption at 1710 cm$^{-1}$, an nmr methyl doublet at δ 1.05 ($J$ = 6 Hz), and a parent ion at *m/e* 164 in the mass spectrum.

Because V proved to be rather unstable, a standard microanalysis was not attempted;[6] instead, the dienone was converted by reaction with 4-phenyl-1,2,4-triazolin-3,5-dione to a crystalline adduct VIII, mp 167.5–169°, in 57% yield. The structure assigned to this adduct, VIII, agrees with its nmr spectrum, which shows clearly defined signals for the bridgehead methyl group (δ 1.93), the bridgehead proton (δ 5.16), and the phenyl group (δ 7.44); the remaining protons give rise to a complex absorption in the δ 2.00–3.12 region. Furthermore, infrared absorptions at 1700 (very strong) and 1760 cm$^{-1}$ confirm the presence of ketone and imide carbonyl functions.

We anticipate that cyclopropanol intermediates related to II will provide advantageous new routes for the synthesis of sesquiterpenes of the vetivane and guaiane classes.

**Acknowledgment.** We thank the National Science Foundation (Grant No. GP-10810) and the National Institutes of Health (Grant No. AM-10849) for their support of this work.

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[4] L. Birkofer, S. M. Kim, and H. D. Engels, *Chem. Ber.*, **95**, 1495 (1962).

[5] C. H. Heathcock and R. Ratcliffe, *Chem. Commun.*, 994 (1968).

[6] With the exception of V and IX, all new compounds described in this communication have elemental compositions confirmed by combustion analysis (Spang Microanalytical Laboratory, Ann Arbor, Mich.) to within 0.3% in carbon, 0.1% in hydrogen, 0.15% in nitrogen, and 0.02% in sulfur.

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## Deaminations with Nitrogen Oxides. A New Synthesis of Alkyl Nitrates

*Sir:*

We reported briefly on the deamination of trimethylsilylamines with dinitrogen tetroxide.[1] Also, we postulated that the trimethylsilyl group may be necessary for the success of the reaction because previous attempts to deaminate amines with nitrogen oxides were unsuccessful;[2] however, deaminations with NOCl are known to be relatively efficient.[2a,3]

Deaminations (replacement of a C–N bond by a C–heteroatom bond) of primary carbinamines may be accomplished *via* thermolysis of *N*-nitrosourethanes, *N*-nitrosoamides, nitroamides, and nitrososulfonamides,[3] solvolysis of diazotate salts,[4] decomposition of triazenes,[5] and displacement of sulfonimides.[6] Nitrous acid deaminations and their nonaqueous counterparts (amyl nitrite nitrosation)[3] have been investigated extensively but the yields of substitution are, in most cases, not competitive with the above-mentioned methods.

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[1] F. Wudl and T. B. K. Lee, *Chem. Commun.*, 490 (1970).

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[3] E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968.

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[5] E. H. White, D. J. Woodcock, and M. A. Schroeder, *Tetrahedron Lett.*, 1713 (1969).

[6] P. J. De Christopher, J. P. Adamek, G. D. Lyon, J. J. Galante, H. E. Haffner, R. J. Boggio, and R. J. Baumgarten, *J. Amer. Chem. Soc.*, **91**, 2384 (1969).

**Table I.** Deaminations of $C_6H_5CH(CH_3)$-$NH_2$

| Amine derivative | Product | Yield, % | Stereo-chemistry,[a] % | Ref |
|---|---|---|---|---|
| $R\overset{NO}{N}COR'$ | ROCOR' | 32–38 | 81r | 3 |
| RN=NNHAr | ROCOR' | 27 | 58r | 5 |
| $RNHSiMe_3$ | $RONO_2$ | 75 | 60–70r | 1 |
| $RNH_2$ | $RONO_2$ | 80 | 60–70r | *b* |

[a] %r + %i = 100%; r = retention, i = inversion. [b] This work.

**Table II.** Scope of $N_2O_4$ Deaminations in THF

| Amine | Product | Yield, % |
|---|---|---|
| $CH_3(CH_2)_5NH_2$ | $CH_3(CH_2)_5ONO_2$ | 20[a] |
| $CH_3(CH_2)_3CH(C_2H_5)CH_2NH_2$ | $CH_3(CH_2)_3CH(C_2H_5)CH_2ONO_2$[c] | 65 |
| $C_6H_5CH(CH_3)NH_2$ | $C_6H_5CH(CH_3)ONO_2$ | 80 |
| $(CH_3)_2CHCH_2NH_2$ | $(CH_3)_2CHCH_2O(CH_2)_4ONO_2$[c] | 20[b] |

[a] The other volatile products are hexenes and 26% of $CH_3(CH_2)_5CH_2O(CH_2)_4ONO_2$. [b] Some isobutyl nitrate was also formed; its yield was not determined because it is volatile and was lost upon work-up (codistillation with THF). (Reaction conditions were the same as described previously.[1] Upon evaporation of the THF, the residue was extracted with petroleum ether. The petroleum ether insoluble fraction consisted of "nonvolatiles" (alkylammonium nitrite, alkylammonium nitrate, and alkylnitramine). The petroleum ether soluble fraction contained the "volatiles" (mostly alkyl nitrate) with some alkene, alcohol, carbonyl, and products resulting from carbonium ion trapped by THF; *e.g.*, the product of isobutylamine deamination. The relative amounts of these minor side products and their importance will be discussed in the full paper. The numbers in the table were determined by vpc.[1]) [c] Elemental analysis of all new compounds was satisfactory.

In this communication we report on the direct deamination (one step) of primary carbinamines with dinitrogen tetroxide to yield alkyl nitrates; *i.e.*, a new synthesis of nitrate esters (reaction 1).

$$R\text{-}NH_2 + N_2O_4 \xrightarrow[-78\text{-}(-60°)]{THF} R\text{-}ONO_2 + N_2 + H_2O \qquad (1)$$

A comparison of this deaminative process, for R = $C_6H_5CH(CH_3)$-, with the processes mentioned above is shown in Table I. Table II comprises a short survey of the scope of this procedure. The yields reported in Table II do not represent the best possible yields. In most cases reaction conditions have not been optimized.

Deaminations with dinitrogen tetroxide are sensitive to the reaction medium. Table III represents a set of experiments in different solvents.

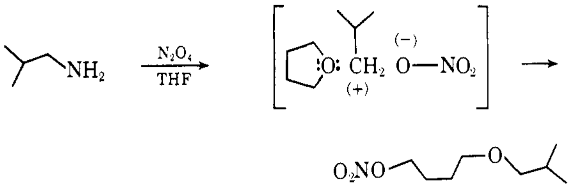
**Table III.** Solvent Effect on Deamination of $C_6H_5CH(CH_3)NH_2$ and Nitrate Production

| Solvent | Temp, °C | Yield, % |
|---|---|---|
| THF | −60 | 80–90 |
| $Et_2O$ | −60 | 70 |
| $CH_2Cl_2$ | −65 | 15[a] |
| $CH_3CN$ | −30 | 40 |
| $H_2O$ | 0 | 3[b] |
| $CH_3CO_2H$ | 25 | Trace[c] |
| $HCON(CH_3)_2$ (DMF) | −30 | 44[d] |

[a] The major products are nitramine, alkylammonium nitrate, and alkylammonium nitrite (*cf.* ref 2c). [b] 7% alcohol, 4% ketone, and 86% alkylammonium salts (recovered as pure amine). [c] 50% acetate. [d] 15% formate ester, 9% alcohol.

Reactions with dinitrogen tetroxide are strongly dependent on the reaction medium.[7] Furthermore, dinitrogen tetroxide forms strong complexes with solvents which can serve as Lewis bases (*e.g.*, THF, dioxane). The physical properties of these complexes have been investigated.[8] The results recorded in Table III indicate that the yields of nitrate are good in ether solvents, worse in acetonitrile, and worst in $CH_2Cl_2$, provided the comparison is limited to aprotic solvents. Clearly, nitrate ester production is independent of the dielectric constant of the solvent but apparently dependent on its Lewis basicity.

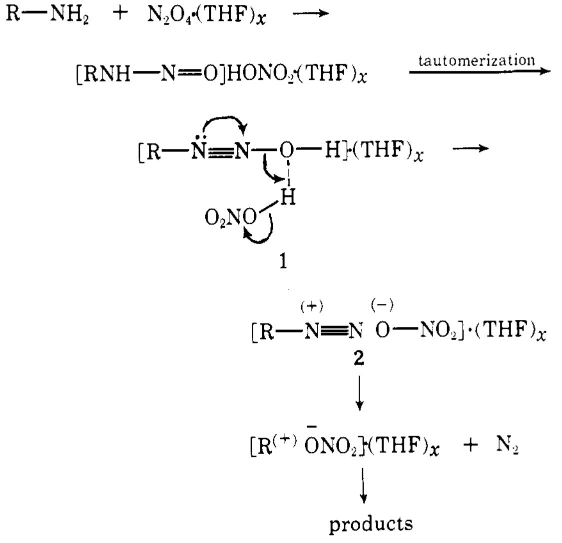
That this deaminative process involves an ionic process may be inferred from the stereochemical results (high degree of retention, *cf.* Table I) and from product distribution, *i.e.*, solvent coordination by an unstable carbonium ion (*cf.* Table II, last entry, and ref 3, p 447).



(2)

The above data support the simplified scheme (Scheme I) for the deaminative formation of nitrate esters with dinitrogen tetroxide in THF.

**Scheme I**



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(8) B. Rubin, H. H. Sisler, and H. Schechter, *J. Amer. Chem. Soc.*, 74, 877 (1952).

The decomposition of the diazotic acid **1** is entirely in accord with the proposed decomposition of diazotate salts with hydroxylic species.[4] Decomposition of **2** affords less olefinic products than decomposition of diazonium carboxylates[3] or diazonium hydroxides[4] because the nitrate counterion is less basic than the carboxylate or hydroxide counterions.

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## Biosynthetic Studies with Carbon-13. Asperlin

*Sir:*

We report on the biosynthesis of the antibiotic lactone asperlin[1] isolated from growing cultures of *Aspergillus nidulans* (NRRL 3134) supplemented with sodium 2-$^{13}C$-acetate (61%).

In the cmr spectrum (Figure 1) of the labeled antibiotic obtained at 25.15 MHz in dioxane as the lock signal with simultaneous proton noise decoupling (pnd), the carbons appear as singlets. Signals from $C_2$, $C_4$, $C_6$, $C_8$, and $C_{10}$ of increased intensity from these isotope-enriched sites are evident as are the resonances from the carbons at natural abundance at $C_1$, $C_3$, $C_5$, $C_7$, and $C_9$. The labeling pattern indicated verifies the tetracetyl origin of the eight-carbon epoxy γ-lactone in the antibiotic.

Application of off-resonance continuous-wave (cw) decoupling aided in unequivocal assignment of the carbon signals in asperlin. The magnitude of the residual splitting ($J_r$) is given by expression 1 derived by Ernst,[2]

$$J_r \approx \frac{\Delta f J}{\gamma^{H_2}/2\pi} \qquad (1)$$

where $\Delta f$ is the separation of the proton signal from the applied decoupling frequency (solvent signal) in hertz, $J$ is the $^{13}C$–H coupling constant, and $\gamma^{H_2}/2\pi$ is the decoupling field strength.

The proton spectrum of asperlin shows $H_8$ (δ 1.31) further separated from the dioxane proton (δ 3.70) than the acetyl-methyl $H_{10}$ protons (δ 2.10). In the cw spectrum of asperlin in dioxane (Figure 2), these methyl carbons $C_8$ and $C_{10}$ appear as quartets, and the assignments are based on $J_r = 13.5$ Hz as observed for $C_8$ relative to $J_r = 10.0$ Hz for $C_{10}$.

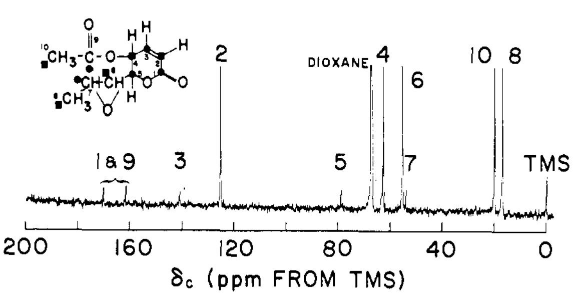

Figure 1. The proton noise-decoupled cmr spectrum (25.15 MHz) of asperlin from sodium 2-$^{13}C$-acetate. The spectrum was obtained on 153 mg in 1.0 ml of dioxane in an 8-mm spinning tube. A V-3530 RF/AF sweep unit with a Spectro System 100 was used to accumulate 107 scans of 5030 Hz (200 ppm) at 200 sec/scan. Dioxane was used as the homonuclear lock signal. Chemical shifts were measured relative to the $^{13}C$ signal of dioxane and converted to parts per million from dissolved TMS ($\delta_c$) using $\delta_c$(dioxane) = 67.4 ppm.

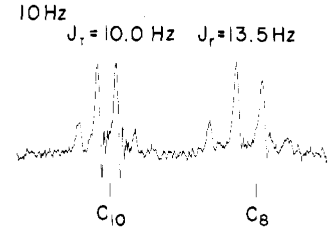

Figure 2. Continuous-wave decoupled cmr spectrum of asperlin from sodium 2-$^{13}C$-acetate, 153 mg/1.0 ml of dioxane; 57 scans of 252 Hz at 26 sec/scan were accumulated.

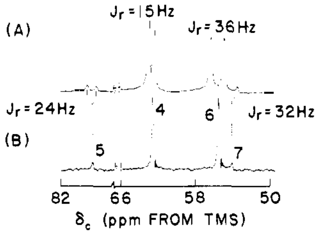

Figure 3. Portions of the cmr spectra of asperlin from sodium 2-$^{13}C$-acetate in benzene, 153 mg/1.0 ml; lock signal, benzene: (A) cw decoupled, 2052 scans of 1006 Hz, 26 sec/scan; (B) pnd, 56 scans of 1006 Hz, 26 sec/scan.

$C_4$, $C_5$, $C_6$, and $C_7$ are in similar chemical environments and the shift assignments as indicated in Figure 1 were made from the cw decoupled spectrum in Figure 3. The $H_6$, $H_7$, $H_5$, and $H_4$ shifts are very near the dioxane proton shift, and $J_r$ for the corresponding carbons will be very small. However, in benzene (δ 7.37) the proton shift separations are much larger ($H_4$, δ 5.22; $H_5$, δ 3.90; $H_6$, δ 3.05; $H_7$, δ 2.93) and the relative magnitudes of $J_r$ increase in that order. These large shift differences facilitate the assignment as shown in Figure 3 with $J_r(C_6) = 36$ Hz $> J_r(C_7) = 32$ Hz and $J_r(C_5) = 24$ Hz $> J_r(C_4) = 15$ Hz. All of the observed $J_r$ values are in good agreement with values calculated from (1).[3] This multiple-solvent technique in cw decoupling allows unequivocal specification of the 2-$^{13}C$-acetate origin of $C_4$ and $C_6$ as well as $C_8$ and $C_{10}$, despite their similar cmr chemical shifts and identical splitting patterns when cw decoupled.

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(1) A. D. Argoudelis and J. F. Zieserl, *Tetrahedron Lett.*, 1969 (1966).

(2) R. R. Ernst, *J. Chem. Phys.*, **45**, 3845 (1966).

(3) Using the observed $J_{^{13}C-H}$ coupling constants from Table I and $\gamma^{H_2}/2\pi$ set at 2100 Hz in these experiments, (1) yielded calculated $J_r$ values for $C_8$ of 14.3, $C_{10}$ of 9.9, $C_4$ of 15.5, $C_5$ of 24, and $C_6$ of 31.9 Hz, respectively. $J_{^{13}C-H}$ at C-5 of 145 Hz was estimated by the method of E. R. Malinowski, *J. Amer. Chem. Soc.*, **83**, 4479 (1961).