^{15}N NMR Investigations on the Tautomeric Structures of the Covalent σ-Adducts Formed between 5-Nitropyrimidines and Liquid Ammonia[1]

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In a previous paper we have reported on the covalent addition of ammonia to 5-nitropyrimidine (**1a**) and some of its derivatives.[2] In this study it has been shown that **1a** in the temperature range between −60 °C and −33 °C gives two different σ-adducts, i.e., the C-2 adduct **2a** and the C-4 adduct **3a**; by allowing the solution to stand for 1 h at −40 °C or for 5 min at room temperature only **3a** is present.

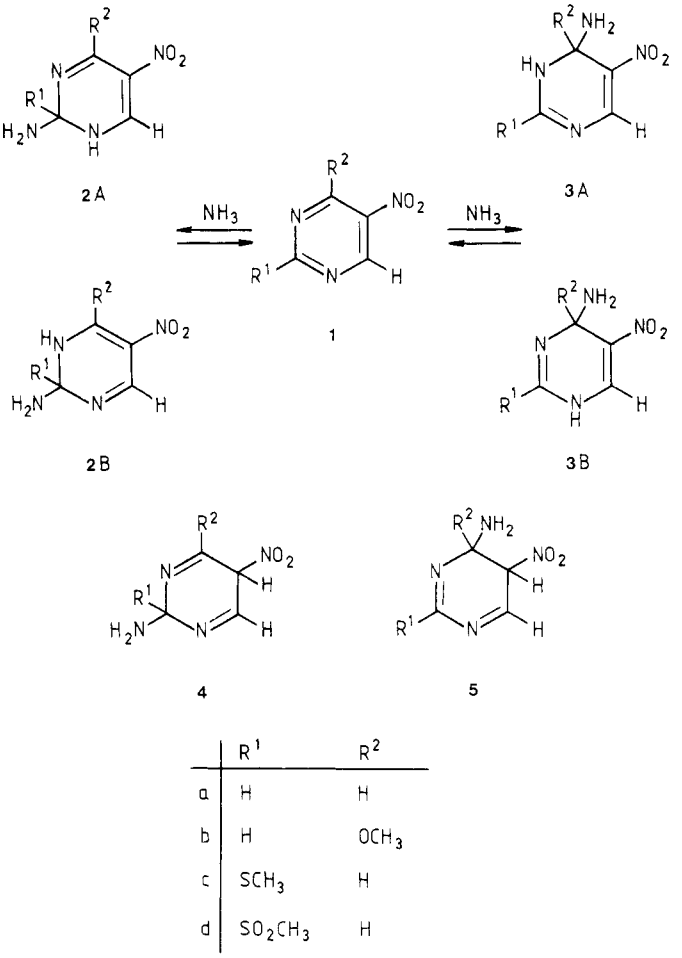
Each of both σ-adducts can be represented in two tautomeric structures, i.e., the cyclic enamines **2**(A) and **2**(B) or **3**(A) and **3**(B), respectively. Based on ^{1}H and ^{13}C NMR spectroscopic measurements, cyclic imino structures for the C-2 and C-4 adducts, as represented in **4** and **5**, respectively, can be excluded.[1] This is in agreement with calculations of the energy of unsubstituted dihydropyrimidines predicting that the cyclic imino structures are much less stable than the enamine ones.[3] Both tautomers **2A** and **2B** feature a 1,2-dihydropyrimidine structure, while the C-4 adduct **3A** had a 3,4- and **3B** a 1,4-dihydro structure. These structures are potentially homoaromatic as they contain a pπ-delocalized entity, obeying the 4π + 2 Hückel rule.[4]

^{1}H and ^{13}C NMR spectroscopic measurements do not allow, however, the assignment of the position of the proton attached to nitrogen, i.e., on N-1 or N-3 or on both ring nitrogens in an equilibrium state.

In order to obtain more detailed information on the tautomeric structure of these neutral aminodihydropyrimidines, we initiated a ^{15}N NMR investigation on the amino σ-adducts, obtained from **1a** and its 4-methoxy (**1b**), 2-methylthio (**1c**), and 2-methylsulfonyl (**1d**) derivatives.

The ^{15}N-nucleus is difficult to detect[5] due to its low natural abundance (0.36%) and its low and negative gyromagnetic constant and long relaxation times. Therefore we applied a special sequence, DEPT,[6] making use of the nitrogen–hydrogen coupling in the N=C—H moiety of the dihydropyrimidine ring, since the ring nitrogens have an unfavorable small and negative nuclear Overhauser effect (NOE) (Scheme I).

Scheme I



	R^1	R^2
a	H	H
b	H	OCH_3
c	SCH_3	H
d	SO_2CH_3	H

Results and Discussion

A. ^{15}N NMR Spectroscopy of the 5-Nitropyrimidines 1a–d. ^{15}N chemical shifts and nitrogen–hydrogen coupling constants (J_{N-H}) obtained for the pyrimidines **1a–d** are summarized in Table I. The resonance signals for the ring nitrogens have been obtained from spectra recorded with the DEPT pulse sequence making use of the $^{2}J_{N-H}$ coupling, which is approximately 12 Hz.[7] The resonance of the nitrogen of the nitro group has mostly been obtained from proton-coupled spectra because the nitro group has just as the nitrogens a small and negative NOE effect. As a consequence the sensitivity decreases and it is nearly impossible to detect the nitrogen with the proton decoupler turned on. When measuring the ^{15}N NMR data for **1a** in chloroform and in dimethyl sulfoxide we only observe a small solvent effect on the resonances of both ring nitrogens as well as the nitrogen of the nitro group. In the proton-coupled ^{15}N NMR spectrum of **1b** in chloroform one of the ring nitrogens is present as a doublet of doublets and therefore must be assigned to a nitrogen in a H—C=N—CH= moiety, i.e., N-1 (coupling with H-2 and H-6). The other nitrogen features a doublet structure and therefore it is assigned to N-3 (only coupling with H-2).

As shown in Table I the chemical shifts of the pyrimidine nitrogens for the compounds **1b–d** are shielded when compared with **1a**. This shielding effect and its magnitude are in accordance with the substituent increments reported for pyrimidines.[8]

B. ^{15}N NMR Spectroscopy of the σ-Adducts Formed between 1a and Liquid Ammonia. As already mentioned above, **1a** when dissolved in liquid ammonia at room temperature is completely converted into the C-4 adduct **3a**. The proton-coupled ^{15}N NMR spectrum of **3a** in liquid

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Table I. ^{15}N Chemical Shifts (ppm) and $^{2}J_{N-H}$ and $^{4}J_{N-H}$ Coupling Constants (hertz) of 5-Nitropyrimidine (1a) and Its Derivatives 1b–d

compd	solvent	δN-1		δN-3		δNO_2
1a	$CHCl_3$	296.4	J_{N1-H2} = 15.1 J_{N1-H6} = 11.1 J_{N1-H4} = 1.5	296.4	J_{N3-H2} = 15.1 J_{N3-H4} = 11.1 J_{N3-H6} = 1.5	360.9
1a	Me_2SO	295.6	J_{N1-H2} = 15.1 J_{N1-H6} = 11.1 J_{N1-H4} = 1.5	295.6	J_{N3-H2} = 15.1 J_{N3-H4} = 11.1 J_{N3-H6} = 1.5	363.5
1b	$CHCl_3$	274.1	J_{N1-H2} = 13.5 J_{N1-H6} = 10.5	258.7	J_{N3-H2} = 17.8	361.4
1c	$CHCl_3$	282.4	J_{N1-H6} = 12.2 J_{N1-H4} = 1.2	282.4	J_{N3-H4} = 12.2 J_{N3-H6} = 1.2	361.0
1d	Me_2SO	285.8	J_{N1-H6} = 11.8	285.8	J_{N3-H4} = 11.8	362.1

Table II. ^{15}N Chemical Shifts (ppm) and Coupling Constants $^{2}J_{N-H}$ (hertz) of the σ-Adducts Formed between the 5-Nitropyrimidines 1a–d and Liquid Ammonia[a]

substrate	σ-adduct	δN-3	δN-1	δNO_2	δNH_2
1a	**2a**(A)/**2a**(B)	282 (J_{N3-H4} = 11.1)	282 (J_{N1-H6} = 11.1)	349	54
	3a(B)[b]	288 (J_{N3-H2} = 12.0)	124 (c)	333	45
1b	**2b**(A)/**2b**(B)	217 (c)	284 (J_{N1-H6} = 7.4)	349	54
1c	**3c**(A)/**3c**(B)	239 (J_{N3-H4} = 3.7)	233 (J_{N1-H6} = 12.0)	362	53
1d	**3d**(A)/**3d**(B)	250 (c)	202 (J_{N1-H6} = 11.1)	369	56

[a] The temperature during measurement was −50 °C. [b] These δ values were obtained after a solution of **1a** in liquid ammonia was allowed to come to room temperature and then cooled to −50 °C. [c] No coupling was observed.

ammonia (measured at −50 °C) exhibits a singlet at 124 ppm, a doublet at 288 ppm, a singlet at 333 ppm, and a singlet at 45 ppm. The singlets at 333 ppm and 45 ppm have been assigned to the nitrogen of the nitro group and the amino group, respectively. The doublet at 288 ppm shows the occurrence of nitrogen in a N=C—H fragment and has been ascribed to N-3, being coupled with H-2, present in the 1,4-dihydropyrimidine **3a**(B). The singlet at 124 ppm is ascribed to the N(1)-H group in **3a**(B).[9] Tautomer **3a**(A) can only be present in a very minor concentration, since a doublet of doublets of N-1 above 200 ppm was not observed. This has not been found. The conclusion seems justified in that **3a** only exists in the 1,4-dihydro tautomer **3a**(B).

The ^{15}N NMR spectrum of C-2 adduct **2a** (observed besides **3a**, when **1a** is dissolved in liquid ammonia at −50 °C) shows one doublet at 282 ppm. This observation indicates that **2a** exists as a mixture of **2a**(A) and **2a**(B), being in fast equilibrium. ^{1}H and ^{13}C NMR spectroscopy showing[2] that H-4 and H-6 and C-4 and C-6, respectively, have identical chemical shifts confirm this result. The proton transfer between the two heteroatoms is usually rapid (on NMR timescale).[10,11] In cyclic amidines proton transfer is intermolecular[10] as proved by the concentration dependency of the tautomerism. Also the possibility that this tautomeric equilibration occurs via a suprafacial [1,5] sigmatropic hydrogen shift cannot be excluded.[12]

C. ^{15}N NMR Spectroscopy of σ-Adducts Formed between 1b–d and Liquid Ammonia. In order to investigate the influence of substituents on the tautomeric equilibria **2**(A) ⇄ **2**(B) and **3**(A) ⇄ **3**(B), we have measured the ^{15}N NMR spectra of a few substituted aminodihydro-5-nitropyrimidines (Table II). It has already been reported[2] that **1b** when dissolved in liquid ammonia at −50 °C is converted into C-2 adduct **2b**. The ^{15}N NMR spectrum of **2b** shows the ^{15}N-resonances for the ring nitrogens at 284 ppm and 217 ppm. In the proton-coupled spectrum only the signal at 284 ppm appears as a doublet ($^{2}J_{N-H}$ = 7.4 Hz); this absorption has been ascribed to N-1, being coupled with H-6. The high field resonance at 217 ppm shows no coupling. This chemical shift is at too low field for a ring NH group and therefore the conclusion seems justified that the C-2 adduct **2b** is present as a tautomeric mixture of the 1,2-dihydropyrimidines **2b**(A) and **2b**(B).

When position 2 of the 5-nitropyrimidine ring is occupied by a methylthio or methylsulfonylgroup the addition of ammonia does not occur at C-2 but at C-4, i.e., formation of **3c** and **3d**, respectively. Measuring the proton-coupled ^{15}N NMR spectrum of **3c** we observed of two doublets, one at 233 ppm and the other at 239 ppm. It is evident that **3c** exists as a mixture of the 4-amino-3,4-dihydropyrimidine (**3c**(A)) and the 4-amino-1,4-dihydropyrimidine (**3c**(B)). The fact that the C-4 adduct obtained from 5-nitropyrimidine, i.e., **3a** only exists as the 1,4-dihydro tautomer **3a**(B) and the 2-methylthio derivative as a mixture of **3c**(A) and **3c**(B), suggests that the contribution of the mesomeric interaction between the methylthio group at C-2 and the nitrogroup at C-5 in **3c** is of importance to promote the formation of the A tautomer of **3c**. The same conclusions were reached concerning the structure of adduct **3d**. ^{15}N NMR measurements indicate that also **3d** is present as a tautomeric mixture of **3d**(A) and **3d**(B).

In conclusion ^{15}N NMR spectroscopy seems to be a promising tool to establish in which tautomeric structure or structures the σ-adducts formed between azines and liquid ammonia are present.

Experimental Section

The starting materials 5-nitropyrimidine,[13] 4-methoxy-5-nitropyrimidine,[14] 2-(methylthio)-5-nitropyrimidine,[15] and 2-

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(methylsulfonyl)-5-nitropyrimidine[15] were synthesized as described in literature. The ^{15}N NMR spectra were recorded at 30.408 MHz in 15-mm o.d. sample tubes on a Bruker CXP-300 spectrometer equipped with a B-UT 100 variable-temperature controller. For measurements in liquid ammonia, thick wall tubes we reused. In all cases the tubes contained an internal 4-mm capillary containing a 2% solution of $CH_3{}^{15}NO_2$ in CD_3OD. This was used both for the lock signal and as external standard. The chemical shift of CH_3NO_2 in methanol-d_4 (CH_3NO_2/CD_3OD) was 1.97 ppm upfield from pure nitromethane. The latter has a chemical shift of 380.23 ppm downfield from liquid ammonia[16] (δNH_3). The nitrogen chemical shifts measured against nitromethane in the capillary were then converted to liquid ammonia using the following expression:

$$\delta NH_3 = \delta CH_3NO_2/CD_3OD + 378.26 \text{ ppm}$$

Normally the ^{15}N spectra were taken of 0.2–1.0 M solutions. In the DEPT pulse sequence the 90° pulse width for ^{15}N and ^1H was 45 μs and 32 μs, respectively, and the delay between the cycles was 3 s. Typical values for the proton-coupled spectra were a pulse width of 15 μs (30°) for ^{15}N and repetition time of 3 s. The spectral width was 4 kHz (0.24 Hz/point) for **1a–d** in chloroform and/or dimethyl sulfoxide and 15 kHz (0.92 Hz/point) for the measurements in liquid ammonia.

Registry No. **1a**, 14080-32-1; **1b**, 15579-58-5; **1c**, 14001-70-8; **1d**, 65735-65-1; **2a**(A), 84928-78-9; **3a**(B), 84928-80-3; **3c**(A), 84928-82-5; **3d**(A), 84928-84-7; ^{15}N, 14390-96-6; NH_3, 7664-41-7.

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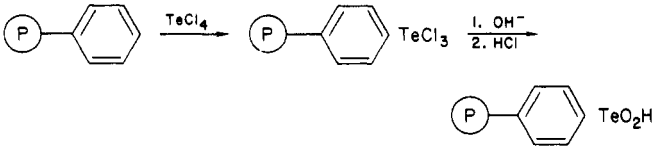
Communications

A Site Isolated Tellurium Oxidation Catalyst Having No Soluble Analogue

Summary: Although other organotellurium compounds have no activity as oxidation catalysts, cross-linked polystyrene tellurinic acid catalyzes the selective epoxidation of olefins with hydrogen peroxide.

Sir: Oxidations catalyzed by tellurium compounds, except for those involving molecular oxygen,[1] are unknown. This is unexpected since there are many examples of oxidation catalysis involving both inorganic[2] and organoselenium compounds.[3] We have been interested in the use of peroxides as selective oxidizing agents and have prepared a catalyst containing tellurium bonded to polystyrene which allows the quantitative epoxidation of olefins with H_2O_2. Similar catalysts having anchored functional groups containing Mn,[4] As,[5] and Se[6] have been reported for H_2O_2 oxidations, but for each catalyst low molecular weight analogues were known to be active.

The anchored tellurium catalyst is readily prepared by condensation of $TeCl_4$ with divinylbenzene–styrene copolymer followed by hydrolysis of the (trichlorotelluro)arene product. Such condensations have been used



for the preparation of arenetellurinic acids which, however, have no catalytic activity.[7] In a typical oxidation, 1 g of solid catalyst prepared from XAD-2 resin is stirred with 20 mL of 1.0 M cyclohexene and 1.0 M H_2O_2 in *tert*-butyl alcohol or dioxane at 60 °C for 24 h to produce a quantiative yield of cyclohexene oxide, based on either reagent. Reaction solutions prepared from 30% H_2O_2 and containing as much as 12% H_2O produce no diol.

Table I. Epoxidation of Olefins with H_2O_2[a]

olefin	rel rate[b]
1-methylcyclohexene	54
cyclohexene	21
3-methylcyclohexene[c]	21
trans-2-butene[d]	15[e]
styrene	10[e]
cis-2-octene[f]	4.3
trans-2-octene[g]	4.2
1-octene	1.0
allyl chloride	0.66[e]
allyl alcohol	0.13 (0.21)[h]

[a] 60 °C, 2 g of catalyst/20 mL of dioxane. [b] By comparison to cyclohexene (k_2 = 1.03 × 10^{-5} L mol^{-1} s^{-1}) using the same XAD-2 supported catalyst unless otherwise noted. [c] 3-Methylcyclohexene oxide is produced with cis:trans = 38:62 compared to 54:46 for *m*-chloroperbenzoic acid. [d] Produces *all-trans*-2,3-butane oxide. [e] Using XAD-4 supported catalyst, k_2 = 12 × 10^{-5} L mol^{-1} s^{-1}. [f] Produces *all-cis*-2,3-octane oxide. [g] Produces *all-trans*-2,3-octane oxide. [h] By competitive rate experiment with cyclohexene.

A study of the reaction kinetics in dioxane shows the oxidation to be cleanly first order in olefin and in H_2O_2 concentration, the rate being directly proportional to the amount of catalyst used. The kinetic behavior holds over a wide range of concentrations and, in fact, may be used to predict the approximate rate of epoxide formation when the reaction solution is passed through a fixed catalyst bed (646 g/L).

The effect of olefin structure on the oxidation rate, shown in Table I, is the same as that found with other electrophilic reagents such as peracids[8] or hydroperoxides;[9] increasing alkyl substitution accelerates the rate. The oxidation is stereospecific, cis–trans geometry being retained in the epoxide product. Results with 3-methylcyclohexene indicate that attack on the least hindered side of the double bond is favored. Allyl alcohol is unexpectedly

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