UNUSUAL CONVERSION OF AMINOAZIDOFURAZAN INTO 1-HYDROXY-5-CYANOTETRAZOLE SODIUM SALT

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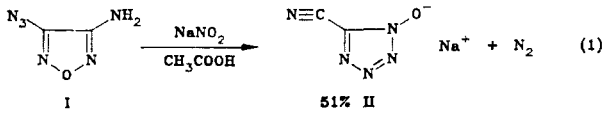
Aminoazidofurazan, on treatment with excess sodium nitrite in acetic acid, is converted into the sodium salt of 1-hydroxy-5-cyanotetrazole, crystals of which have been subjected to x-ray diffraction analysis.

The conversion of furazans into other heterocyclic systems has been described [1], but no case has been reported of the conversion of furazans into tetrazoles.

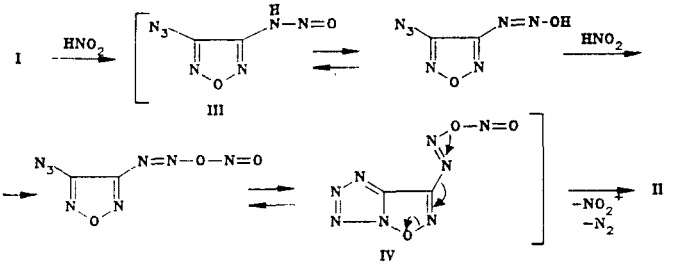
We have observed an unusual transformation of aminoazidofurazan (I) into the sodium salt of 1-hydroxy-5-cyanotetrazole (II):



I 51% II

However, treatment of (I) with one equivalent of sodium nitrite did not result in evolution of nitrogen, and according to TLC the intermediate (III) was formed, which we were unable to isolate and identify. It is probably azido(N-nitrosoamino)furazan.

The reaction may be represented as follows:



The structure of the tetrazole (II) was confirmed by elemental x-ray diffraction analysis of the hydrated crystal $C_2N_5ONa \cdot 2H_2O$ (Fig. 1 and Tables 1-4).

The anion $C_2N_5O^-$ and the cation Na^+ are located on the crystal plane m, and the oxygen atoms and the two water molecules on the second-order rotational axes. The distribution of bond lengths in the tetrazole ring in the anion (II) is approximately the same as in sodium tetrazolate monohydrate [2]. The $N_{(2)}-N_{(3)}$ bond length is somewhat shorter than $N_{(3)}-N_{(4)}$ and $N_{(2)}-N_{(1)}$. The $C_{(5)}C_{(1)}N_{(5)}$ moiety is nearly linear, and the $C_{(1)}N_{(5)}$ bond length corresponds to the C≡N triple bond.

The $N_{(1)}-O_{(1)}$ bond length is greater than the standard value for N → O (1.27 Å [3]). The sodium atom is coordinated at the apices of an irregular seven-pointed star (Table 2) with $N_{(3)}$, $N_{(4)}$, and $N_{(5)}$ of the three $C_2H_5NO^-$ anions, and the oxygen atoms of the four water molecules.

Atom $O_{(1)}$ is involved in hydrogen bonding with two water molecules (Table 2). The remainder of the intermolecular contacts have the van der Waals values.

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TABLE 1. Atom Coordinates in the Tetrazole (II·$2H_2O$) (in cell fractions ·10^4)

Atom	x	y	z	Atom	x	y	z
Na	1088(3)	7301(3)	0	$N_{(5)}$	4541(8)	11155(7)	0
$C_{(1)}$	3848(9)	10099(7)	0	$O_{(1)}$	1639(6)	11274(4)	0
$C_{(5)}$	2957(8)	10151(7)	0	$O_{(w1)}$	0	8074(5)	−2500
$N_{(1)}$	1959(7)	10459(5)	0	$O_{(w2)}$	2500	7500	2360(10)
$N_{(2)}$	1308(7)	9775(6)	0	$H_{(w2)}$	2312	7825	3148
$N_{(3)}$	1888(7)	9061(6)	0	$H_{(w1)}$	367	8384	−3251
$N_{(4)}$	2931(7)	9271(6)	0				

TABLE 2. Distances (Å) in the Coordination Polyhedron of the Sodium Atom

Na—$N_{(3)}$	2,88	Na—$O'_{(w2)}$	2,44
Na—$N_{(4)}$	2,71	Na—$O_{(w1)}$	2,50
Na—$N_{(5)}$	2,64	Na—$O'_{(w1)}$	2,50
Na—$O_{(w2)}$	2,44		

TABLE 3. Angles (°) in the Sodium Polyhedron

$O_{(w1)}$	Na	$O_{(w2)}$	143,8	$N_{(5)}$	Na	$O_{(w1)}$	83,8
$N_{(3)}$	Na	$N_{(5)}$	152,4	$N_{(4)}$	Na	$O_{(w2)}$	76,6
$N_{(4)}$	Na	$O_{(w1)}$	132,0	$N_{(3)}$	Na	$O_{(w1)}$	76,3
$N_{(5)}$	Na	$O_{(w2)}$	129,8	$N_{(4)}$	Na	$N_{(5)}$	75,8
$O_{(w1)}$	Na	$O'_{(w1)}$	87,0	$N_{(3)}$	Na	$O_{(w2)}$	67,5
$O_{(w1)}$	Na	$O'_{(w2)}$	84,4				

TABLE 4. Intermolecular Hydrogen Bonds (Å) in the Tetrazole Crystal (II·$2H_2O$)

$O_{(1)}\ldots O_{(w1)}$	2,88	$O_{(1)}\ldots H_{(w1)}$	2,08
$O_{(1)}\ldots O_{(w2)}$	2,83	$O_{(1)}\ldots H_{(w2)}$	2,06

The NMR experimental data (see Experimental) do not in themselves prove the structure of (II), although they establish the presence of all the atoms other than oxygen (two signals in the ^{13}C spectrum, and five in the ^{15}N NMR spectrum). The CN group signals were assigned by analogy with nitriles [4]. The signal at −71.66 ppm is attributed to $N_{(1)}$, since this is the only narrow signal seen in the ^{14}N NMR spectrum of (II).

Existing analogies are insufficient to assign the signals in the ^{15}N NMR spectrum for the three other nitrogens [5]. The presence of a narrow signal for $N_{(1)}$ indicates that the N-oxide form makes a large contribution to the structure of (II), since in the ^{14}N NMR spectra of N-alkoxytetrazoles the ^{14}N signal for the $=\overset{|}{N}-OR$ fragment is broadened. At normal temperatures, two of the four ^{15}N signals for the tetrazole ring are significantly broadened, the extent of broadening at half height of the signals with chemical shifts of −12.7 and −52.46 ppm being greater than 15 Hz, whereas at 60°C these signals narrow to the size of the other ^{15}N signals.

Since special calculations show that such marked broadening of the ^{15}N signals cannot be due to spin coupling of the ^{15}N nitrogen with the narrow signal for ^{14}N, it can arise only as a result of an exchange process. Such a process, we believe, could be protonation of the $C_2N_5O^-$ anion in water, taking place selectively at nitrogens $N_{(2)}$ and $N_{(4)}$.

In such a case, the chemical shifts of the $N_{(1)}$, and especially the $N_{(3)}$, atoms (signals at −71.66 and −18.46 ppm, respectively) should not undergo any marked change, since their hybridization remains the same, whereas the other two nitrogens on protonation change their hybridization, and therefore their chemical shifts should undergo considerable changes (see [5]).

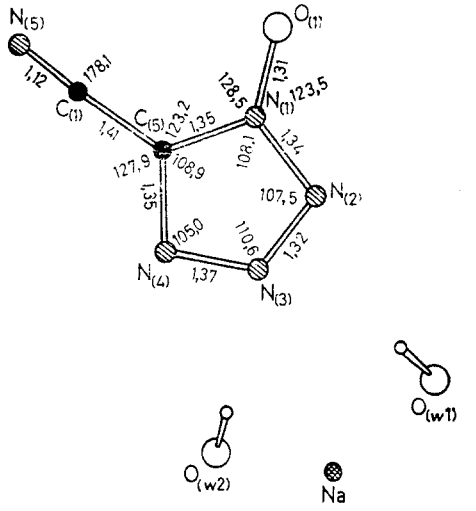

Fig. 1. Bond lengths (Å) and valence angles (°) in the ($II \cdot 2H_2O$) crystal.

It may be mentioned that there has been a report [5] on the broadening of the individual signals in the ^{15} N NMR spectra of polyazoles on protonation.

EXPERIMENTAL

The furazan (I) was obtained as described in [6]. The IR spectrum of (II) was obtained on a Specord 75 IR spectrometer in KBr disks: 760...780, 1220...1250, 1420...1430, 1470, 2200 (sl. br.), 2260 cm^{-1}. ^{13}C, ^{14}N, and ^{15}N NMR spectra of (II) were obtained on a Bruker AM-300 spectrometer (75.43, 21.69, and 30.42 MHz) in D_2O, internal standard acetone. The ^{13}C chemical shifts (relative to TMS) were: 107.79 and 125.11 ppm; ^{14}N and ^{15}N (relative to nitromethane) −75.35 (half-width 230 Hz) and −12.70 (br. at 20°C) −18.46 and −52.46 (br. at 20°C), −71.66 and −106.01 ppm, respectively. The integral intensities of the signals in the ^{15}N NMR spectrum were 1:1:1:1:1. Calculation of the half-width of the ^{15}N signals for $\Delta\nu_{1/2}$ (^{14}N) = 230 Hz, T_2 = 1 Hz, and $^{n}J_{^{14}N^{15}N} \approx 5$ Hz using the QUADRM program* showed that $\Delta\nu_{1/2}$ ^{15}N should not exceed 1.35 Hz. X-ray diffraction analysis of the ($II \cdot 2H_2O$) crystal was carried out on an automatic Hilger diffractometer (λ_{Mo} irradiation), 784 reflections being measured, of which 702 (89.5%) had intensities $I \geq 2\sigma$ (σ is the standard deviation). Calculation of the structure and refinement of the positional and thermal parameters of the atoms was carried out on a Nova-1200 minicomputer using the XTL suite of programs. The final value of the R factor was 0.086, and the accuracy of measurement of the bond lengths ±0.011-0.013 Å, and of the valence angles ±0.45-0.74°.

The crystals of the salt ($II \cdot 2H_2O$) were of rhombic habit, space group C_{ccm}, and the number of formula units (Z) was 8. The elementary cell parameters were: a = 12.735 ± 0.001 Å; b = 15.302 ± 0.001 Å; c= 6.8614 ± 0.0007 Å, V = 1337.2 ± 0.2 $Å^3$ and ρ = 1.676 g/cm^3.

1-Hydroxy-5-cyanotetrazole Sodium Salt. To a solution of 1 g (7.94 mmoles) of aminoazidofurazan in a mixture of 20 ml of acetic acid and 15 ml of dry ether was added with stirring at −5°C 1.65 g (24 mmoles) of sodium nitrite. The temperature of the mixture was raised to +5°C over 1 h, then stirred for a further 30 min at ~20°C. The gas which was evolved was nitrogen (GC [7]). The mixture was diluted with ether to a volume of 150 ml, the sodium acetate which separated filtered off and washed with ether, and the filtrate evaporated under reduced pressure to a volume of 30 ml, and the remaining acetic acid distilled off in vacuo as the azeotrope with heptane (bath temperature 35°C). The solid residue was purified by column chromatography on silica gel (eluted successively with ethyl acetate and acetone), and dried over P_2O_5. Yield of salt II 0.54 g (51%) mp 255°C (decomp.). A monocrystal for the x-ray analysis was grown from a concentrated aqueous solution. Found, %: C 18.2, N 52.4; Na 17.4. C_2N_5ONa. Calculated, %: C 18.0; N 52.6; Na 17.3.

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4H-3,1-BENZOXAZOLES.

4.* EXAMINATION OF THE FORMATION OF 1,2-DIHYDRO-4H-3,1-BENZOXAZINES USING TAGGED ATOMS

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A mechanism is proposed for the formation of 4,4-diphenyl-1,2-dihydro-4H-3,1-benzoxazines, which has been proved by introducing a $^{17}O/^{18}O$ isotopic label into the starting 2-aminophenyldiphenylmethanols and carbonyl compounds. ^{17}O NMR and mass spectrometry show that the 3,1-benzoxazine ring contains the oxygen atom from the alcohol group in the starting 2-aminophenyldiphenylmethanol.

We have previously examined the reaction of 2-aminophenyldiphenylmethanol (APM) with carbonyl compounds in acidic media [1, 2], and shown that 4,4-diphenyl-1,2-dihydro-4H-3,1-benzoxazines are formed. It was of interest to examine the mechanism of this reaction. It has been reported [3] that the closure of the 3,1-oxazine ring on reaction of APM with aldehydes may follow two courses. In one of these, the carbonyl carbon attacks the amino-group in the starting APM, followed by elimination of a molecule of water and heterocyclization to 1,2-dihydro-4H-3,1-benzoxazine. In the other, the o-aminophenyldiphenylcarbenium cation initially formed in the acidic medium attacks the oxygen atom of the carbonyl group in the oxo-compound [3, 4].

In order to determine the mode of closure of the heterocycle in the acid-catalyzed synthesis of 1,2-dihydro-4H-3,1-benzoxazines, the products (II*) were obtained from compounds tagged with labeled oxygen isotopes $^{17}O/^{18}O$ (Scheme 1). The compounds were analyzed by ^{17}O NMR and mass spectrometry. The starting material used was benzaldehyde enriched in isotopes $^{17}O/^{18}O$ [5], the ^{17}O NMR spectrum of which showed it to contain 7.6% of ^{17}O. In the ^{17}O spectrum of the product of reaction of APM hydrochloride with enriched benzaldehyde, no signal for ^{17}O was seen, showing that the oxygen atom of the APM hydroxyl group had been retained in (II) (Scheme 1).

2,4,4-Triphenyl-1,2-dihydro-4H-3,1-benzoxazine (II*) was obtained by direct synthesis from $^{17}O/^{18}O$-enriched APM hydrochloride (I*). The presence of a signal for ^{17}O in the spectra of the products (II*) (δ 67 ppm) showed that the C—^{17}O bond in the APM had been retained. This provides further confirmation that the reaction of APM with carbonyl compounds occurs by the first of these mechanisms.

*For Communication 3, see [1].

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