# Nucleoside Synthesis by the Photorearrangement of Ribofuranosyl Enamino Nitriles

J. P. Ferris,* V. Ramachandra Rao, and T. A. Newton

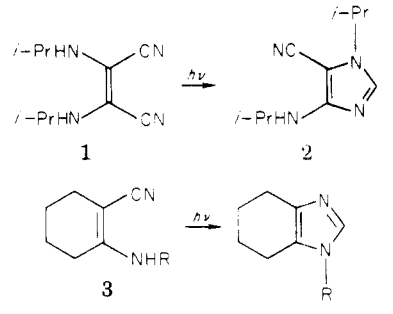
*Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181*

*Received August 9, 1979*

Condensation of 2-oxocyclohexanecarbonitrile (**7**) with 2,3-*O*-isopropylidene-D-ribofuranosylamine (**8**) gave *N*-(2,3-*O*-isopropylidene-α-D-ribofuranosyl)-1-amino-2-cyanocyclohexene (**9a**) (44%) and the corresponding β anomer **9b** (15–20%). An acetonitrile solution of **9a** photorearranged in 80% yield to *N*-(2,3-*O*-isopropylidene-α-D-ribofuranosyl)tetrahydrobenzimidazole (**13a**) which was deblocked in aqueous acetic acid at 100 °C to *N*-(α-D-ribofuranosyl)tetrahydrobenzimidazole (**14a**). Photolysis of **9a** in methanol resulted in **13a** along with a 70% yield of a bleached product which gave a 40% yield of **9b** together with a 30% yield of **9a** on standing in the dark for 60 h. Five repetitive irradiations of a methanol solution of **9a** for 8 h each followed by 60-h dark reactions gave a 2.4:1 ratio of **13b** and **13a**, respectively. The ketal of **13b** was cleaved in aqueous acetic acid at 100 °C to give **14b**. The configuration at C-1′ of the isomers of **9**, **13**, and **14** was established by $^1H$ and $^{13}C$ NMR. The photochemical conversion of (2,3,4-tri-*O*-acetylribopyranosyl)diaminomaleonitrile (**15**) to imidazole nucleosides **16** and **17** proceeds in low yield. No imidazole products were detectable on irradiation of ribopyranosyldiaminomaleonitrile.

The photochemical rearrangement of enamino nitriles is a convenient synthetic route to novel imidazoles.[1] This photorearrangement also proceeds with N-substituted enamino nitriles such as **1**, **3b**, **3c**, and **3d** to yield the corresponding N-substituted imidazoles **2**, **4b**, **4c**, and **4d** (see Scheme I.)[1,2] The starting enamino nitriles are readily prepared by the Thorpe–Ziegler cyclization of dinitriles[3] or by the reaction of a cyano ketone with an amine.[1] The successful photocyclization of the N-substituted enamino nitriles prompted our investigation of the photochemical cyclization of *N*-ribosyl enamino nitriles as a new route to novel imidazole nucleosides. The requisite *N*-ribosyl enamino nitrile starting materials are readily prepared by the reaction of the sugar with the enamino nitrile[4,6] or by the reaction of a ribosylamine derivative with a cyano ketone. Our exploration of these synthetic routes to nucleosides is the subject of this paper.

Scheme I




a, R = H; b, R = $CH_3$; c, R = *t*-Bu; d, R = $PhCH_2$

## Results and Discussion

The synthesis of the ribosyl enamino nitrile **6** from **3a** was investigated first since we had observed that ribose (**5**) reacts readily with simple enamino nitriles[4,5] (see Scheme II). However, **6** was not observed as a reaction product. An alternative synthesis by the condensation of 2-oxocyclohexanecarbonitrile[6] (**7**) and ribosylamine[7] also was not operative. We succeeded in preparing the requisite starting material by the condensation of 2-oxocyclohexanecarbonitrile (**7**) with 2,3-*O*-isopropylidene-D-ribofuranosylamine (**8**).[8] The reaction gave a 60–70% overall yield of a product mixture from which a 44% yield of the crystalline α anomer **9a** and a 15–20% yield of the gummy β anomer **9b** were isolated. The isomeric nature of the reaction products **9a** and **9b** was established by their identical UV spectra and by similar $^1H$ NMR spectra which exhibited characteristic differences in the chemical shifts of H-1′ (see Experimental Section). The assignment of the anomeric configurations at C-1′ in **9a** and **9b** was made with the aid of the $^{13}C$ NMR and $^1H$ NMR studies discussed below.

The α anomer (**9a**) is more stable than the β anomer (**9b**). When a purified sample of **9b** was allowed to stand at room temperature for 1 month in $CDCl_3$, 70% was converted to the α anomer. The proportion of α anomer was still increasing after 1 month, so the equilibrium concentration of **9a** is even greater than 70% of the total concentration of **9**. The greater stability of the α anomers of ribofuranosyl-2′,3′-cyclic ketals has been previously reported.[9,10]

Our successful synthesis of the anomers of **9** prompted our application of the same synthetic procedures for the preparation of the corresponding cyclopentene enamino nitrile derivative **11**. Only trace amounts of the desired enamino nitrile **11** were obtained in the reaction of 2-oxocyclopentanecarbonitrile (**10**)[11] with **8**. The low reactivity of **10** is due to the increased number of conformational interactions in the initial condensation product **12** as compared with the starting material. The synthesis proceeds smoothly in the cyclohexane ring system because there are fewer conformational interactions in the cyclohexane analogue of **12**.[12]

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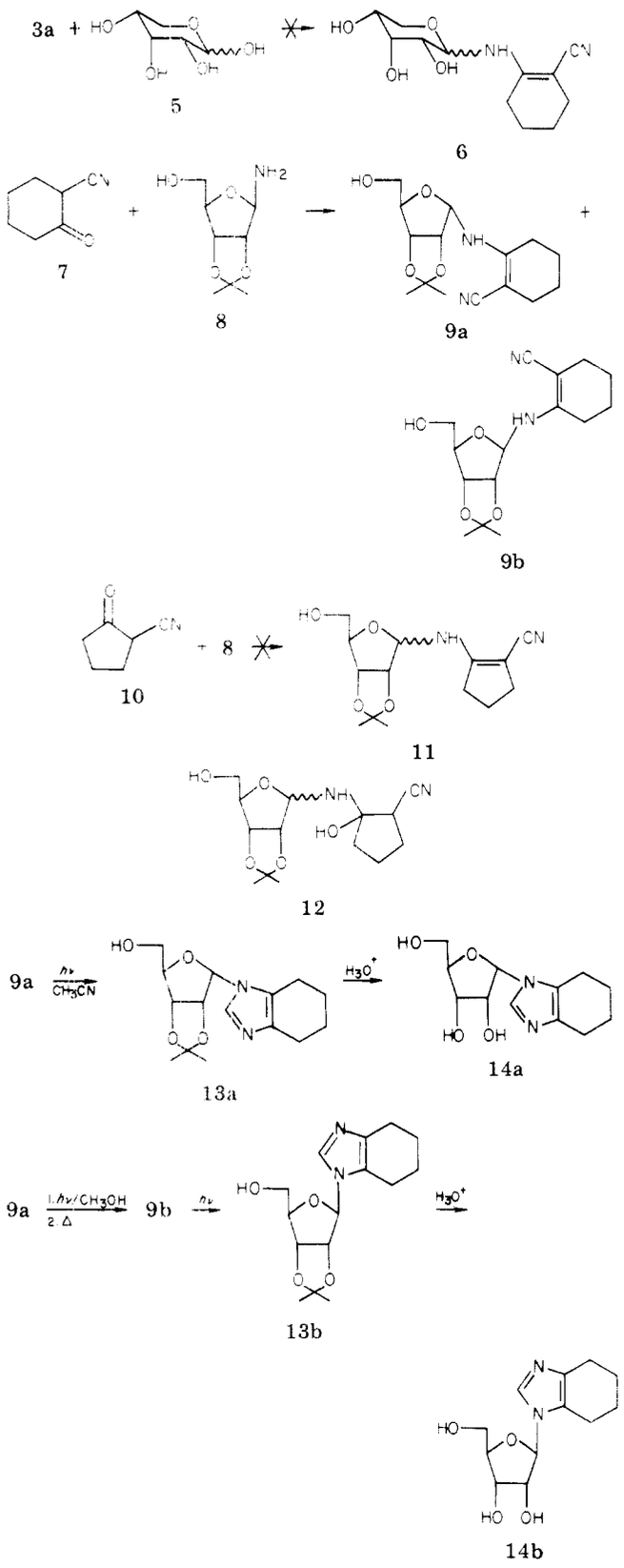
Scheme II



An 80% yield of *N*-(2,3-*O*-isopropylidene-α-D-ribofuranosyl)tetrahydrobenzimidazole (**13a**) was obtained on irradiation of a degassed acetonitrile solution of **9a** ($7.1 \times 10^{-3}$ M) for 20 h. The synthesis of **14a** was completed by heating **13a** at 100 °C in 15% acetic acid for 13 h. The vigorous acid hydrolysis conditions are required because protonation of the basic imidazole ring inhibits the initial protonation step in the specific acid-catalyzed hydrolysis of the cyclic ketal.[13]

An entirely different photoproduct was obtained when methanol was substituted for acetonitrile as the reaction solvent. When a $10^{-4}$ M solution of **9a** was irradiated for 4 min, the absorbance at 264 nm decreased from 1.52 to 0.1. An increase in absorbance at 230 nm due to the partial formation of **13** was also observed. When the irradiated solution was allowed to stand in the dark at room temperature, the absorbance at 264 nm gradually increased until it reached a maximum of 1.14 after 60 h. The bleaching and regeneration of the enamino nitrile was not observed when the photolysis was performed in acetonitrile solution.

The β anomer **9b** was the principal photoproduct of **9a** in methanol. A 40% yield of **9b** was isolated after irradiating a $10^{-2}$ M solution of **9a** in methanol for 12 h and then allowing the photolysate to stand at room temperature for 60 h. This isomerization provided a convenient synthesis of the β anomer **13b**, starting from the α anomer **9a**. A $10^{-2}$ M solution of **9a** in methanol was irradiated for 8 h and allowed to stand in the dark for 60 h, and the cycle was repeated until the total irradiation period was 40 h (5 cycles). A 70% yield of the imidazole nucleosides **13b** and **13a** was isolated from the reaction mixture in a 2.4:1 ratio. The α anomer was separated from the mixture by fractional crystallization but the β anomer which remained in the filtrates could not be obtained crystalline. The ketal blocking group of **13b** was cleaved by heating at 100 °C with aqueous acetic acid for 6 h to give **14b** as a gum. Since it was not possible to obtain crystalline samples of the β anomers **9b**, **13b**, and **14b**, their structure analyses depended in part on similarities of the IR, NMR, and mass spectra and on the identity of the UV spectra with the corresponding α anomers (see Experimental Section).

The photolysis of the β anomer **9b** in acetonitrile yielded the β anomer **13b**. The exact yields were not determined because both the reactant and product are not crystalline and were therefore difficult to analyze quantitatively. It was possible to establish by TLC and NMR that the α anomer **13a** was not formed. The **13b** prepared by this route was identical with that prepared by the photolysis of **9a** in methanol, and it could be cleanly hydrolyzed to **14b**.

The anomeric configurations of the isomers of **9**, **13**, and **14** were assigned on the basis of $^1$H and $^{13}$C NMR data. Preliminary assignments were based on the observation that the chemical shift of H-1′ is at higher field in the β anomer than it is in the α anomer.[14] This configurational assignment is consistent with that assigned by the difference in the chemical shifts of the isopropylidene ketal methyl groups of **13a** (0.06 ppm) and **13b** (0.23 ppm).[15] The chemical shift differences between the methyl groups of **9a** and **9b** (0.21 and 0.30 ppm, respectively) were much less, but they were consistent with the configurations assigned at C-1′. The configurational assignments in **9a** and **9b** were confirmed by investigation of their $^{13}$C NMR spectra. The signals for C-1′, C-2′, and C-3′ are at higher field in the α anomer than in the β anomer.[10,16] This result agrees with the configurational assignments determined

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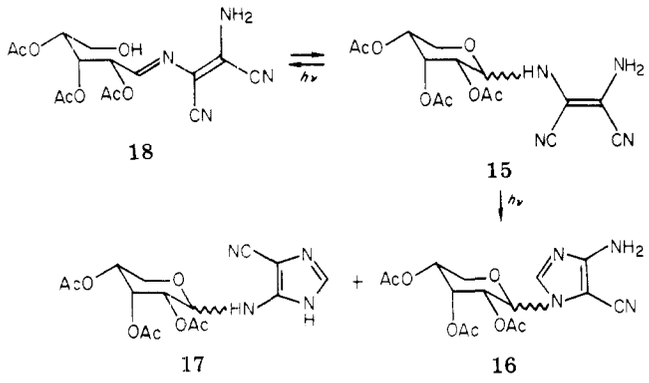
Scheme III



in this series of compounds by the $^1H$ NMR studies discussed above.

The photochemical conversion of (2,3,4-tri-*O*-acetylribopyranosyl)diaminomaleonitrile (**15**) to the corresponding imidazoles (**16** and **17**) is not a synthetically useful reaction (see Scheme III). Irradiation of degassed solutions of **15**[5] in $CH_3OH$ or $CH_3CN$ by using 300- or 350-nm light sources resulted in the formation of only 5–10% yields of substances with UV absorption consistent with structures **16** and **17**. At least five other products were detectable by TLC. Irradiation of ribopyranosyldiaminomaleonitrile gave dark reaction solutions and colored precipitates, but only starting material was detectable on UV analysis of the irradiated solution.

The poor yields observed in the photoconversion of **15** to **16** and **17** are surprising since diaminomaleonitrile is converted to the corresponding imidazole [4-(aminoimidazole)-5-carbonitrile] in greater than 90% yield[17,18] and *N*-isopropyldiaminomaleonitrile is converted to the isomeric *N*-isopropyl-4-(aminoimidazole)-5-carbonitriles in greater than 10% yield.[1] The variety of products observed from **15** must reflect side reactions due to the triacetylribopyranosyl group. One possible side reaction is the photochemical opening of the ribopyranose to **18**, a compound which may undergo further photochemical reactions.

## Experimental Section

The general experimental procedures were described previously.[1] All solutions were degassed by three to five freeze–pump–thaw cycles prior to photolysis in quartz vessels. A Rayonet photochemical reactor equipped with 254-nm lamps was used unless otherwise noted. The $^{13}C$ NMR spectra of **9a** and **9b** were determined by Dr. E. A. Williams of the General Electric Research and Development Center on a Varian CFT-20 spectrometer. The mass spectra of **14a** and **14b** were also obtained with the assistance of Dr. Williams and were measured on a Du Pont 21-104 spectrometer.

***N*-(2,3-*O*-Isopropylidene-D-ribofuranosyl)-1-amino-2-cyanocyclohexene (9).** A suspension of 2,3-*O*-isopropylidene-D-ribofuranosylamine *p*-toluenesulfonate (**8**; 28.9 g, 80 mmol),[8] 2-oxocyclohexanecarbonitrile (**7**; 9.95 g, 80 mmol),[6] and triethylamine (8.1 g, 80 mmol) was prepared in 100 mL of benzene and heated to reflux for 4 h. The water liberated was collected in a Dean–Stark trap. The reaction mixture was diluted with 400 mL of benzene, washed with 30 mL of 1 N NaOH and four 25-mL portions of saturated NaCl solution, and dried over sodium sulfate. The benzene solution was concentrated to 80 mL, and 10.5 g (44%) of **9a** was obtained. Crystallization from ether or absolute ethanol gave the pure product: mp 151–152 °C; UV max ($CH_3OH$) 265 nm ($\epsilon$ 13 800); IR ($CHCl_3$) 3510, 3390, 2990, 2210, 1610, 1545 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.39 (s, 3, $CH_3$), 1.60 (s, 3, $CH_3$), 1.60 (m, 4, 2 $CH_2$), 2.28 (m, 4, 2 $CH_2$), 2.93 (t, 1, OH), 3.68 (t, 2, $CH_2$), 4.14 (t, 1, CH), 4.77 (m, 2, 2 CH), 5.63 (m, CH, NH); $^{13}C$ NMR ($CDCl_3$) $\delta$ 155.12 (C-2), 121.04 (CN), 113.28 (>$CO_2$), 83.35 (C-1′), 82.11 (C-2′, C-4′), 79.66 (C-3′), 76.12 (C-1), 63.55 (C-5′), 26.21, 25.29, 24.96, 21.89, 21.58 (aliphatic carbons).

Anal. Calcd for $C_{15}H_{22}N_2O_4$: C, 61.22; H, 7.54; N, 9.22. Found: C, 61.57; H, 7.71; N, 9.51.

The filtrate contained a 15–20% yield of **9b** which was obtained as a gum. Its NMR spectrum was comparable to that of **9b** obtained by the photolysis of **9a** in $CH_3OH$.

***N*-(2,3-*O*-Isopropylidene-α-D-ribofuranosyl)tetrahydrobenzimidazole (13a).** A solution of **9a** (2.1 g, 7.1 mmol) in 700 mL of acetonitrile was irradiated in 100-mL portions for 20 h. The combined photolysates were concentrated and chromatographed on silica gel. Elution with chloroform yielded 300 mg of **9a**. Further elution with chloroform–methanol (50:1) yielded 1.68 g (80%) of *N*-(2,3-*O*-isopropylidene-α-D-ribofuranosyl)tetrahydrobenzimidazole (**13a**). Compound **13a** was further purified by crystallization from benzene–petroleum ether: mp 128–129 °C; UV max ($CH_3OH$) 225 nm ($\epsilon$ 2120); IR ($CHCl_3$) 3165, 2976, 1595, 1470, 1370, 1110, 1070 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.30 (s, 3, $CH_3$), 1.36 (s, 3, $CH_3$), 1.77 (br s, 4, 2 $CH_2$), 2.48 (br s, 4, 2 $CH_2$), 3.8 (br s, 2, $CH_2$), 4.32 (m, 1 CH), 4.87 (m, 2, 2 CH), 5.98 (d, 1, $J$ = 4 Hz, CH), 6.37 (br s, 1, OH), 7.65 (s, 1, CH); mass spectrum (70 eV), *m/e* 294, 279, 205, 189, 177, 173, 164, 162, 151, 150, 148, 129, 123, 122, 121, 101, 94.

Anal. Calcd for $C_{15}H_{22}N_2O_4$: C, 61.22; H, 7.54. Found: C, 61.37; H, 7.43.

***N*-(2,3-*O*-Isopropylidene-β-D-ribofuranosyl)tetrahydrobenzimidazole (13b).** A solution of **9a** (300 mg, 1.0 mmol) in 100 mL of methanol was irradiated for 8 h. The photolysate was allowed to stand in the dark for 60 h. This procedure was repeated four more times for a total irradiation period of 40 h. The photolysate was concentrated to an oil and chromatographed on silica gel. Elution with $CHCl_3$:$CH_3OH$ (50:1) gave 210 mg (70%) of a mixture of α and β nucleosides. Crystallization from benzene–petroleum ether resulted in 90 mg (30%) of **13a**. The β anomer (**13b**; 120 mg, 40%) was purified by preparative TLC (9:1 $CHCl_3$:$CH_3OH$) since it could not be crystallized: UV max ($CH_3OH$) 225 nm; $^1H$ NMR ($CDCl_3$) $\delta$ 1.35 (s, 3, $CH_3$), 1.58 (s, 3, $CH_3$), 1.77 (m, 4, 2 $CH_2$), 2.53 (m, 4, 2 $CH_2$), 3.80 (m, 2, $CH_2$), 4.35 (m, 1, CH), 4.87 (m, 2, 2 CH), 5.60 (d, 1, $J$ = 3 Hz, CH), 6.17 (br s, 1, OH), 7.80 (s, 1, CH); IR ($CHCl_3$) 3170, 2980, 1610, 1475, 1440, 1375 $cm^{-1}$.

Anal. Calcd for $C_{15}H_{22}N_2O_4$: C, 61.22; H, 7.54. Found: C, 60.84; H, 7.55.

***N*-(2,3-*O*-Isopropylidene-β-D-ribofuranosyl)-1-amino-2-cyanocyclohexene (9b).** A solution of **9a** (300 mg, 1.0 mmol) in 100 mL of $CH_3OH$ was irradiated for 12 h. The photolysate was allowed to stand in the dark for 60 h, the solvent evaporated, and the residue purified by preparative TLC on silica gel using $CHCl_3$:$CH_3OH$ (9:1). Extraction of the band of $R_f$ 0.73 yielded 140 mg (46%) of **9b** as a gum: UV max ($CH_3OH$) 267 nm; $^1H$ NMR ($CDCl_3$) $\delta$ 1.33 (s, 3, $CH_3$), 1.52 (s, 3, $CH_3$), 1.63 (t, $J$ = 3 Hz, 4, 2 $CH_2$), 2.30 (m, 4, 2 $CH_2$), 3.43 (s, 1, OH), 3.73 (d, $J$ = 2 Hz, 2, $CH_2$), 4.27 (m, 1, CH), 4.6 (dd, $J$ = 7, 2 Hz, 1, CH), 4.82 (d, $J$ = 7 Hz, 1, CH), 5.28 (dd, $J$ = 2, 11 Hz, 1, CH), 6.4 (d, $J$ = 11 Hz, 1, NH); $^{13}C$ NMR ($CDCl_3$) $\delta$ 156.78 (C-2), 121.06 (CN), 112.53 (>$CO_2$), 90.68 (C-1′), 86.3 (C-4′), 85.30 (C-2′), 82.40 (C-3′), 77.10 (C-1), 63.44 (C-5′), 26.70, 25.00 (2), 24.87, 21.82, 21.58 (aliphatic carbons).

***N*-(α-D-Ribofuranosyl)tetrahydrobenzimidazole (14a).** A solution of **13a** (1.1 g, 3.7 mmol) in 25 mL of aqueous 15% acetic acid was heated at 100 °C for 13 h. The hydrolysate was concentrated to an oil which was dissolved three times in 20 mL of $H_2O$, concentrated to dryness, dissolved twice in 20 mL of ethanol, and concentrated to dryness. The residual gum was chromatographed on silica gel and eluted with $CHCl_3$:$CH_3OH$ (9:1) to give 0.69 g (63%) of **14a** which was purified by crystallization from $CH_3OH$:$CH_3CN$: mp 185 °C; UV max ($CH_3OH$) 225 nm ($\epsilon$ 2540); IR (KBr) 3344, 2890, 1644, 1597, 1468, 1435, 1355, 1310, 1290, 1210, 1100, 1085 $cm^{-1}$; $^1H$ NMR ($Me_2SO$-$d_6$) $\delta$ 1.73 (m, 4, 2 $CH_2$, 2.5 (m, 4, 2 $CH_2$), 3.5 (m, 2, $CH_2$), 4.08 (m, 3, 3 CH), 4.75 (br s, 3, 3 OH), 5.68 (m, 1, CH), 7.68 (s, 1, CH); mass spectrum (70 eV), *m/e* (rel intensity) 254 (20), 123 (36), 121 (13), 95 (11), 94 (100),

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73 (25), 69 (19), 67 (15), 61 (20), 57 (35), 55 (17), 53 (12), 45 (26).

Anal. Calcd for $C_{12}H_{18}N_2O_4$: C, 56.68; H, 7.14; N, 11.02. Found: C, 56.69; H, 6.91; N, 10.95.

**N-(β-D-Ribofuranosyl)tetrahydrobenzimidazole (14b).** A solution of **13b** (160 mg, 0.52 mmol) in 2 mL of 10% aqueous acetic acid was heated for 6 h at 100 °C. The solution was concentrated to an oil, and the oil was dissolved twice in 2 mL of $H_2O$ and twice in 2 mL of ethanol and concentrated to dryness each time. The residual gum was chromatographed on silica gel and eluted with $CHCl_3$:$CH_3OH$ (9:1) to give 70 mg (50%) of **14b** which could not be obtained crystalline: UV max ($CH_3OH$) 225 nm; $^1H$ NMR ($Me_2SO$-$d_6$) δ 1.72 (m, 4, 2 $CH_2$), 2.50 (m, 4, 2 $CH_2$), 3.57 (d, 2, $CH_2$), 4.03 (m, 3, 3 CH), 5.05 (br s, 3, 3 OH), 5.42 (d, 1, $J$ = 6 Hz, CH), 7.77 (s, 1, CH); mass spectrum (70 eV), $m/e$ (rel intensity) 254 (10), 149 (19), 123 (23), 122 (97), 121 (11), 94 (87), 73 (23), 69 (10), 67 (15), 61 (15), 60 (57), 57 (24), 55 (15), 46 (13), 45 (100).

**Photolysis of (2,3,4-Tri-O-acetylribopyranosyl)diaminomaleonitrile (15) and Ribopyranosyldiaminomaleonitrile.**[5] A $2 \times 10^{-3}$ M solution of **15** (90 mg) in acetonitrile was irradiated with a 300-nm light source in a Pyrex vessel for 41 h. The solvent was removed on a rotary evaporator, and the products were separated by preparative TLC using 5:1 benzene:ethyl acetate. Seven UV-absorbing areas could be detected on the TLC plate. The bands were eluted and their UV spectra were measured in $CH_3OH$. One of the substances (6 mg) was tentatively identified as **16** on the basis of the comparison of its UV maxima (264 and 225 nm) with those of 1-isopropyl-4-(aminoimidazole)-5-carbonitrile: UV max ($CH_3OH$) 265, 227 nm.[1] A second substance (6 mg) was tentatively identified as **17** on the basis of the similarity of its UV maxima (257, 228 nm) with those of **16** above. The same compounds were observed in about the same yield when the photolysis was performed with a 350-nm light source in a Pyrex vessel for 144 h. No products with UV absorption in the 250–270-nm region could be detected on irradiating ribosyldiaminomaleonitrile[5] with 300- or 350-nm light sources in a Pyrex vessel. Colored solutions and precipitates were formed, but the UV spectrum of the solution indicated only the presence of starting material.

**Acknowledgment.** We thank Dr. E. A. Williams for measuring the $^{13}C$ NMR spectra of **9a** and **9b** and Mr. G. Brooks for technical assistance. This work was supported by Grant No. CA 14511 from the National Cancer Institute and a Project Seed Grant from the American Chemical Society to G. Brooks.

**Registry No.** **7**, 4513-77-3; **8**, 46167-41-3; **9a**, 71734-86-6; **9b**, 71734-87-7; **13a**, 71734-88-8; **13b**, 71734-89-9; **14a**, 71734-90-2; **14b**, 71734-91-3; **15**, 70042-25-0; **16**, 71734-92-4; **17**, 71734-93-5; ribopyranosyldiaminomaleonitrile, 71772-49-1.

# Mechanism of the Photochemical Bleaching of Cyclic Enamino Nitriles

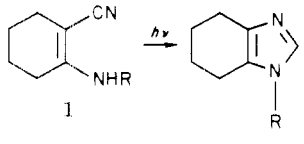
J. P. Ferris,* V. Ramachandra Rao, and T. A. Newton

*Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181*

*Received August 9, 1979*

Photolysis of enamino nitriles in alcohol solution results in the formation of adducts with no UV absorption. These bleached products are thermally labile and regenerate the enamino nitrile grouping. Photolysis of *N*-(2,3-*O*-isopropylidene-α-D-ribofuranosyl)-1-amino-2-cyanocyclohexene (**3a**) yields isomers of the methyl ether **6**. Ether **6** loses methanol at room temperature to regenerate **3a** and its C-1′ isomer **3b**. The presence of isomers of **6** was established by the presence of four overlapping methoxyl peaks in the $^1H$ NMR spectrum of the photolysate. The anomerization at C-1′ is a thermal reaction which proceeds after **6a** is formed. The presence of compounds isomeric at C-1 was established by the formation of only **3a** and **3b** as a result of elimination of methanol from the isomers of **6**. The methanol addition reaction is not catalyzed by acid or base but does proceed from the triplet excited state as shown by triphenylene-sensitized formation of **6**. The absence of methanol addition to the acyclic β-aminocrotononitrile (**10**) is consistent with the high-energy triplets of the cyclic enamino nitriles **1** and **3** as the intermediates leading to the alcohol addition products. The detection of the ketenimine chromophore at 2030 $cm^{-1}$ on irradiation of **1d** under conditions where rapid alcohol addition to the triplet is observed suggests that the ketenimine is formed via the singlet excited state. Since the photochemical rearrangement of enamino nitriles to imidazoles proceeds from the singlet excited state, these data provide further support for the proposal that an iminoketenimine (e.g., **5a**) is the initial product formed from the singlet enamino nitrile. This ketenimine undergoes thermal transformations to yield the rearranged imidazoles.

The photorearrangement of enamino nitriles is a key step in one of the pathways proposed for prebiological purine synthesis from HCN,[1] and it is an efficient synthetic route to imidazoles (e.g., **1** → **2**)[2] and some imidazole nucleosides (e.g., **3a** → **4a**).[3] In the course of our investigation of the photolysis of *N*-(2,3-*O*-isopropylidene-α-D-ribofuranosyl)-1-amino-2-cyanocyclohexene (**3a**) we observed that its UV absorption at 265 nm was rapidly bleached when it was irradiated with a 254-nm light source in methanol solution.[3] This enamino nitrile absorption gradually returned when the bleached solution was allowed to stand in the dark for 60 h. The elucidation of the structure and mechanism of formation of this bleached product is the subject of this report.




1 2

a, R = H; b, R = $CH_3$; c, R = $PhCH_2$; d, R = $(CH_3)_3C$

Initially we assumed that bleaching involved an intramolecular reaction between the 5′-hydroxyl group on the ribose moiety and the excited state of the enamino nitrile chromophore[4] because this bleaching phenomenon had not been detected previously when **1a**, **1b**, **1d**, or other enamino nitriles were irradiated in methanol solution. An intramo-

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