fectively with a carbenium ion center at C-4; perhaps this is because bromide ion loss is irreversible, whereas cyclobutane formation is reversible.

Experimental Section

Commercial **ethyl α-cyanoacrylate** (Eastman 910 Adhesive) was distilled from phosphorus pentoxide (bp 43 °C (0.2 mm Hg)).[4]

1,1-Diethoxy-2-bromoethylene (bp 75 °C (8 mm Hg)) was obtained by dehydrobromination of 1,1-dibromo-2,2-diethoxyethane (**4**) as described by McElvain.[5] Dibromide **4** was synthesized by bromination of 2-bromo-1,1-diethoxyethane (**5**) with bromine and calcium carbonate in carbon tetrachloride. The synthesis of **5** is described by Bedoukian[6] starting from vinyl acetate.

Diethyl 1-Cyano-1,2-cyclopropanedicarboxylate (3). 1,1-Diethoxy-2-bromoethylene, 1.9 mL (10 mmol), was dissolved in dichloromethane at 0 °C in the presence of a trace of diphenylpicrylhydrazyl (DPPH) to prevent adventitious polymerization. Freshly distilled ethyl α-cyanoacrylate, 1 mL (10 mmol), was added with stirring, and the mixture was stirred for 1 h. The mixture was distilled. The first fraction contained ethyl bromide, as shown by NMR spectroscopy. Cyclopropane (**3**), 1 g (40–50% yield), was collected at 115–120 °C (1 mm Hg): IR 3100 (cyclopropane), 2250 (CN), 1735 (ester), 856 cm^{-1} (cyclopropane); NMR δ 4.25 (quadruplet, $-COO\mathbf{CH_2}CH_3$), 2.60 (two doublets, >**CH**COO–), 2.2–1.7 (multiplet, $-\mathbf{CH_2}-$), 1.30 (two triplets, $-CH_2\mathbf{CH_3}$); mass spectrum 184 ($-C_2H_3$), 166 ($-H_2O$), 137 (–HCO), 111 (–CN), 83 ($-C_2H_4$).

The IR and NMR correspond to those given by Saegusa and co-workers for dimethyl 1-cyanocyclopropane-1,2-dicarboxylate. The mass spectra further corroborate the assigned structure.[8]

Anal. Calcd: C, 56.86; H, 6.20; N, 6.63. Found: C, 56.74; H, 6.20; N, 6.68.

Ethyl Methyl 1,2-Cyclopropanedicarboxylate. 1,1-Diethoxy-2-bromoethylene, 0.8 mL (5 mmol), was mixed with 2.7 mL (30 mmol) of methyl acrylate in a glass tube. A trace of DPPH was added. The tube was sealed under vacuum and heated at 110 °C for 20 h. The mixture was distilled, and 0.4 g (50% yield) of ethyl methyl 1,2-cyclopropanedicarboxylate, bp 70 °C (0.4 mm Hg), was collected:

Anal. Calcd: C, 55.80; H, 7.03. Found: C, 55.85; H, 7.08.

IR 1735 (ester), 860 cm^{-1} (cyclopropane); NMR δ 4.15 (quadruplet, $-COO\mathbf{CH_2}CH_3$), 3.70 (singlet, $-COO\mathbf{CH_3}$), 2.4–1.5 (multiplet, ring protons), 1.3 (triplet), $-CH_2\mathbf{CH_3}$); mass spectrum 141 (–MeO), 127 (–EtO), 113 (–COOMe), 98 (–Me).

Acknowledgment. We are deeply indebted to the Air Force Office of Scientific Research (Grant No. 74-7426) for support of this work.

Registry No.—**3**, 10432-27-6; **4**, 761-17-1; **5**, 2032-35-1; ethyl α-cyanoacrylate, 7085-85-0; 1,1-diethoxy-2-bromoethylene, 42520-11-6; ethyl methyl 1,2-cyclopropanedicarboxylate, 878-14-8; methyl acrylate, 96-33-3.

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Facile Synthesis of 2′-Amino-2′-deoxyribofuranosyl Purines

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Received December 20, 1978

Analogues of the common ribonucleosides containing an amino group at the 2′ position have valuable potential for the investigation of chemical or biochemical problems in which the 2′ moiety is involved. Derivatization at the amino group can lead to the synthesis of antibiotics[1] and affinity labels.[2] The 2′-amino analogue of guanosine (**5**) has been isolated as an antibiotic[3] from *Enterobacter sp.*

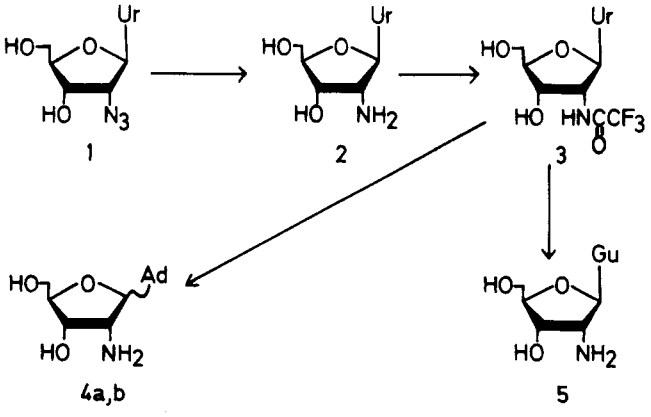
A facile synthesis of 2′-amino-2′-deoxyuridine and -cytidine via a 2,2′-cyclonucleoside has been described.[4] On the other hand, the synthesis of the corresponding purine nucleosides has been fraught with difficulty. The methods of synthesis have involved both transformations of 2′,3′-anhydronucleosides[5] or arabinonucleosides[6,7] as well as condensation of derivatives of a suitable amino sugar with a purine base.[8] All of these methods are rather lengthy and total yields are not satisfactory in most cases.

A more convenient synthesis of 2′-azido-2′-deoxy- and 2′-amino-2′-deoxyribofuranosyl purines from 2′-azido-2′-deoxyuridine,[4] which is readily available from uridine, was recently developed[9] in our laboratory. It utilizes the sugar moiety derived from the pyrimidine nucleoside for condensation with the purine bases. In order to simplify the synthesis further, we were led to investigate a direct transglycosylation reaction with purine bases instead of isolating and condensing the sugar moiety separately. Recently, we reported such transglycosylation reactions using trimethylsilyl trifluoromethanesulfonate[10] (TMSTF) as Friedel–Crafts catalyst for the synthesis of 3′-azido-2′,3′-dideoxyribofuranosyl purines.[11] The utility of the transglycosylation reaction was also demonstrated for the synthesis of unmodified purine ribonucleosides.[11,12]

Here we describe the success of this approach for the synthesis of 2′-amino-2′-deoxyadenosine (**4b**) and -guanosine (**5**) in much better yields than previously obtainable, using 2′-amino-2′-deoxyuridine (**2**) as starting material. An attempted transglycosylation reaction with 2′-azido-2′-deoxyuridine (**1**), on the other hand, failed.

2′-Azido-2′-deoxyuridine[4,9] (**1**) obtained from uridine in a yield of 50% is converted to 2′-amino-2′-deoxyuridine (**2**) by reduction with triphenylphosphine.[13] After purification over a Dowex 50 column, **2** was isolated in a yield of 91%. To protect the 2′-amino function, we selected the trifluoroacetyl group

Scheme I



Ur = uracil-1-yl, Ad = adenin-9-yl, Gu = guanin-9-yl, a = α anomer, b = β anomer.

0022-3263/79/1944-2039$01.00/0

which can easily be removed. This group has also been employed in the synthesis of nucleosides of 2′-amino-2-deoxyaldoses by the usual condensation methods, affording the products in high yield and with high stereospecificity.[14]

A synthesis of 2′-(trifluoroacetamido)-2′-deoxyuridine (**3**) has been reported by Sharma et al.[1a] in which **2** was treated with excess trifluoroacetic anhydride and the *O*-trifluoroacetyl groups were removed with methanol containing a few drops of aqueous ammonia. In the present investigation the introduction of the *N*-trifluoroacetyl group into **2** was accomplished in a yield of 88% by selective acylation of the amino group with *S*-ethyl trifluorothioacetate. This reagent has previously been employed for the introduction of the *N*-trifluoroacetyl group into unprotected amino sugars.[14a] The melting point of our sample of **3** was 5–6 °C higher than that reported. However, the elemental analysis was consistent with the monotrifluoroacetylated derivative and the chemical shift (δ 4.54) of H-2′ in the NMR spectrum was about 0.5 ppm lower than in **2** (δ 4.03), indicating that trifluoroacetylation had occurred on the 2′-amino group.

Compound **3** was used for a one-pot silylation–transglycosylation reaction[11] with N^6-octanoyladenine, yielding 2′-amino-2′-deoxyadenosine (**4b**) as the main product together with its α anomer **4a**. Thus **3** and 1.8 equiv of N^6-octanoyladenine were silylated with bis(trimethylsilyl)acetamide (BSA) in acetonitrile and the solution was used without workup for the transglycosylation reaction catalyzed by 1.3 equiv of TMSTF. Following deacylation with methanolic ammonia, the mixture was separated on a Dowex 1X4 (OH^-) column according to the method of Dekker.[15] Further purification with a Dowex 50WX8 (NH_4^+) column afforded **4b** (34%) and **4a** (7%), which were found to be identical in all respects with authentic samples.[9]

N^6-Octanoyladenine was replaced by N^2-palmitoylguanine in the above reaction to afford the guanine nucleoside derivative. After deacylation the mixture of bases and nucleosides was separated on a Dowex 1X4 (HCO_3^-) column with a linear gradient of triethylammonium bicarbonate (pH 9.6) and ethanol. The required fractions were further purified on a column of Dowex 50WX8 (NH_4^+) to afford crystalline **5** (60%). Although the melting point of our sample (238–240 °C) was lower than that reported by Nakanishi et al.[3] (252–254 °C) and Ikehara et al.[6] (250–252 °C), the structure was confirmed by direct comparison with an authentic sample.[9] The NMR spectrum was identical with that reported.[6,9] Neither a 9α isomer nor 7 isomers were detected in the mother liquor or other fractions.

The synthetic method described here affords products **4b** and **5** in overall yields of 14 and 24%, respectively, based on uridine as starting material, and represents an improvement both in yield and the number of intermediates over the syntheses previously described for these compounds.

Experimental Section

Melting points are uncorrected. UV spectra were recorded on a Shimadzu Model UV 200 and a Zeiss PMQ III spectrometer. NMR spectra were recorded on a Bruker HFX 60 spectrometer, and CD spectra on a Cary 61 spectrometer. Chemical shifts are reported in δ units (parts per million) downfield from internal tetramethylsilane.

Thin-layer chromatography was performed on Merck Kieselgel 60 F 254, 0.2-mm layer thickness, in solvent system A [ethanol–1 M triethylammonium bicarbonate, 3:1 (v/v)] or B [methanol–chloroform, 2:8 (v/v)].

Elemental analyses were performed by Mykroanalytisches Labor Beller, Göttingen.

2′-Amino-2′-deoxyuridine (2). 2′-Azido-2′-deoxyuridine[4,9] (8.46 g, 31.4 mmol) was dissolved in dioxane (150 mL) and concentrated aqueous ammonia solution (120 mL) and triphenylphosphine (14.0 g, 53.4 mmol) was added. The flask was stoppered securely and the mixture was stirred at room temperature. After 1 day, TLC in system A showed the reaction to be complete with one new product (R_f 0.53) being formed. The solvents were evaporated and the residue was partitioned between benzene and water (each 300 mL). The aqueous layer was separated, concentrated to about half the volume, and applied to a column of Dowex 50WX8 (H^+) (60 mL). The column was washed with 500 mL of 30% methanol–water. On elution with 2 M aqueous ammonia **2** was obtained. The solution was evaporated and the residue crystallized from 95% ethanol (6.98 g, 91%): mp 197–199 °C (lit.[5] 197–198 °C).

2′-(Trifluoroacetamido)-2′-deoxyuridine (3). 2′-Amino-2′-deoxyuridine (6.32 g, 26 mmol) was suspended in methanol (520 mL) and *S*-ethyl trifluorothioacetate (5.1 mL, 40 mmol) was added with stirring. The resulting clear solution was kept at room temperature for 1 day. After bubbling nitrogen gas through the solution, the solvent was evaporated and the residue crystallized from methanol–chloroform (7.76 g, 88%), giving a single spot on TLC in system B: R_f 0.50; mp 218–220 °C (lit.[1a] 213–214 °C); UV λ_{max} (MeOH) 259.5 nm (ϵ 9700); NMR (Me_2SO-d_6) δ 3.64 (m, 2 H, H-5′a,b), 3.97 (m, 1 H, H-4′), 4.22 (dd, 1 H, $J_{2',3'}$ = 6.1 Hz, $J_{3',4'}$ = 2.4 Hz, H-3′), 4.54 (t, 1 H, H-2′), 5.70 (d, 1 H, $J_{5,6}$ = 8.2 Hz, H-5), 6.06 (d, 1 H, $J_{1',2'}$ = 7.3 Hz, H-1′), 7.90 (d, 1 H, H-6).

Anal. Calcd for $C_{11}H_{12}N_3O_6F_3$: C, 38.95; H, 3.57; N, 12.39. Found: C, 38.89; H, 3.67; N, 12.29.

9-(2-Amino-2-deoxy-α-D-ribofuranosyl)adenine and 9-(2-Amino-2-deoxy-β-D-ribofuranosyl)adenine (4a and 4b). 2′-(Trifluoroacetamido)-2′-deoxyuridine (**3**) (1.36 g, 4.0 mmol) and N^6-octanoyladenine[16] (1.90 g, 7.4 mmol) were suspended in acetonitrile (24 mL) and BSA (7.0 mL, 28 mmol) was added. The mixture was treated at reflux temperature for 15 min. To the clear solution TMSTF (0.88 mL, 5.2 mmol) was added. After heating at reflux temperature for 2 h, the reaction mixture was poured into 120 mL of saturated methanolic ammonia. After 1 day at room temperature, the solution was evaporated and the residue partitioned between 300 mL each of 0.1 M aqueous triethylamine and chloroform. The water layer was concentrated to about half the volume and applied to a column (3.1 × 30 cm) of Dowex 1X4 (OH^-), which was washed with 800 mL of 10% methanol–water. The products were eluted as two separate peaks with 1500 mL of 20% methanol–water as reported earlier.[8]

The fractions of the first peak were combined and evaporated. The crude product was dissolved in water, and the pH was adjusted to 4.5 with acetic acid. This solution was applied to a column of Dowex 50WX8 (NH_4^+) (2 mL) which was washed with 100 mL of 30% methanol–water. The product was eluted with 2 M ammonia in 30% methanol–water. The eluates were evaporated and the residue was treated with ethanol to afford crystals of **4a** (72 mg, 7%), giving a single spot on TLC in system A (R_f 0.47), mp 147–149 °C (lit.[8] 149–151 °C). Direct comparison with an authentic sample[9] showed complete identity by TLC and NMR spectroscopy in D_2O.

The fractions of the second peak which contained the β anomer **4b** were evaporated and applied to a column of Dowex 50WX8 (NH_4^+) (10 mL) as described above. The eluate obtained with 2 M ammonia in 30% methanol–water was evaporated and the residue was crystallized from ethanol to give **4b** (361 mg, 34%), giving a single spot on TLC in system A (R_f 0.45), mp 194–196 °C (lit.[8] 194–196 °C). Direct comparison with an authentic sample[9] showed complete identity by TLC and by NMR spectroscopy in D_2O.

9-(2-Amino-2-deoxy-β-D-ribofuranosyl)guanine (5). 2′-(Trifluoroacetamido)-2′-deoxyuridine (**3**) (0.74 g, 2.2 mmol) and N^2-palmitoylguanine[16] (1.53 g, 3.9 mmol) were reacted in acetonitrile (13 mL) with BSA (4.6 mL, 18.8 mmol) and TMSTF (0.48 mL, 2.8 mmol) as described above for **4a** and **4b**. After removal of the protecting groups by methanolic ammonia and extraction with chloroform as described for **4a** and **4b** the pH of the aqueous phase was brought to 10.0 after removal of a trace of chloroform by evaporation. The solution was then applied to a column (3.1 × 23 cm) of Dowex 1X4 (HCO_3^-) made up in 0.02 M triethylammonium bicarbonate (pH 9.6). The products were eluted with 4.0 L of a linear gradient of triethylammonium bicarbonate and ethanol [mixer, 0.05 M triethylammonium bicarbonate (pH 9.6); reservoir, 0.8 M triethylammonium bicarbonate (pH 9.6–ethanol, 1:1 (v/v)], collecting 18-mL fractions. Fractions 167–187 contained material which gave a single spot on TLC in system A (R_f 0.38). These fractions were combined and evaporated to dryness. Crude **5** was dissolved in water and the pH was adjusted to 4.5 with acetic acid. This solution was applied to a column of Dowex 50WX8 (NH_4^+) (6 mL), which was washed with 300 mL of 30% methanol–water, and **5** was eluted with 2 M ammonia in 30% methanol–water. The eluate was evaporated and the residue was crystallized from hot water to give analytically pure microcrystalline plates of **5** (366 mg, 60%), mp 236–238 °C. Direct comparison with an authentic sample[9,17] showed complete identity in spectroscopic properties and

by melting point.

Anal. Calcd for $C_{10}H_{14}N_6O_4$: C, 42.55; H, 5.00; N, 29.78. Found: C, 42.36; H, 5.12; N, 29.72.

Recrystallization from H_2O gave a sample of mp 238–240 °C [lit.[3] 252–254 °C (hydrate); lit.[6] 250–252 °C]. Further recrystallization did not increase the melting point.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft for financial support. The measurement of the NMR spectra by Mr. B. Seeger is gratefully acknowledged.

Registry No.—1, 26929-65-7; 2, 489-59-8; 3, 51989-21-0; 4a, 10407-64-4; 4b, 10414-81-0; 5, 60966-26-9; N^6-octanoyladenine, 52854-12-3; N^2-palmitoylguanine, 21047-87-0.

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(17) The difficulty of obtaining an analytically pure sample of **5** as reported in ref 9 has been overcome by using a Dowex 50 column.

Communications

Nitrogen-15–Carbon-13 Spin–Spin Coupling Constants of *cis*- and *trans*-1-Alkyl-2-aryl-3-benzoylaziridines

Summary: The ^{15}N–^{13}C spin–spin coupling constants are reported for *cis*- and *trans*-1-cyclohexyl-2-phenyl-3-benzoylaziridines. The one-bond coupling constants are in good agreement with the predictions of Wasylishen, based on INDO–MO calculations. Here the ^1J-(^{15}N,^{13}C) values are in good agreement with the supposition that endocyclic N–C bonds have high p character.

Sir: We wish to report here the $^nJ(^{15}N$–$^{13}C)$ values (where $n \leq 2$) for *cis*- and *trans*-1-cyclohexyl-2-phenyl-3-benzoylaziridines (**1** and **2**). The $^1J(^{15}N,^{13}C)$ values appear in good agreement with recent INDO–FPT calculations on ethylene imine itself, which thereby allows the N(s)–C(s) bond order to be accurately approximated.[1] Our $^1J(^{15}N,^{13}C)$ values are in good agreement with the supposition that endocyclic N–C bonds have high p characters. The magnitude of $^2J(^{15}N,^{13}C)$ and $^2J(^{15}N,H)$ values are related to nitrogen lone pair proximity wherein the syn orientation imparts a positive increment to the absolute value of the coupling constant.[2]

The stereoelectronic properties of small-ring compounds have remained topics of widespread interest.[3] Many chemical reactions and physical properties of cyclopropanes can be explained by the "bent bonds" of the ring, which have a high degree of p character.[4,5] The exocyclic bonds have a correspondingly higher degree of s character as revealed by enhancement of C–H bond acidity[6] and the fact that $^1J(^{13}C,H)$ values increase in magnitude as ring size decreases, indicative of higher percent s character in the C–H bonds.[7] For small ring heterocycles, hybridization values of endocyclic bonds are less well established.[6] Even though the first linear relationship between s character and $^1J(^{15}N,^{13}C)$ couplings was established by Binsch et al.[8] and supported by Schulman,[9] latter work has seriously questioned its validity.[10,11] Hence, the Fermi contact mechanism upon which $^1J(^{15}N$–$^{13}C)$ coupling is based appears inadequate in this instance.[12]

In other work, Schulman and Newton showed other coupling mechanisms than the Fermi contact mechanism were of importance in small ring compounds.[12] Marshall and coworkers have presented strong evidence that the observed coupling constant represents the sum of coupling through all paths.[13] This should be particularly important in three-ring molecules such as aziridines, where the coupling between nitrogen and adjacent carbon is the sum of one-bond and two-bond paths, both of which may be sizable.

To the best of our knowledge, the only data available for small ring nitrogen compounds comes from the work reported by Jennings[14] on (*Z*)-*cis*- and (*E*)-*trans*-oxaziridines (**3** and **4**) (Figure 1). Our data on the N-15 isotopically enriched aziridines **1** and **2** are also presented in Figure 1.[15,16] Of great importance in our work was the assessment of signs for the $^1J(^{15}N,^{13}C)$ and $^2J(^{15}N,^{13}C)$ couplings (Figure 1), which appears consistent with contemporary work in this field.[17–19] For the oxaziridines, the ring oxygen in **3** and **4** increases $^1J(^{15}N,^{13}C)$ couplings based on the data in Figure 1,[20] relative to the aziridines.

The $^1J(^{15}N,^{13}C)$ values for **1** and **2** are in good agreement

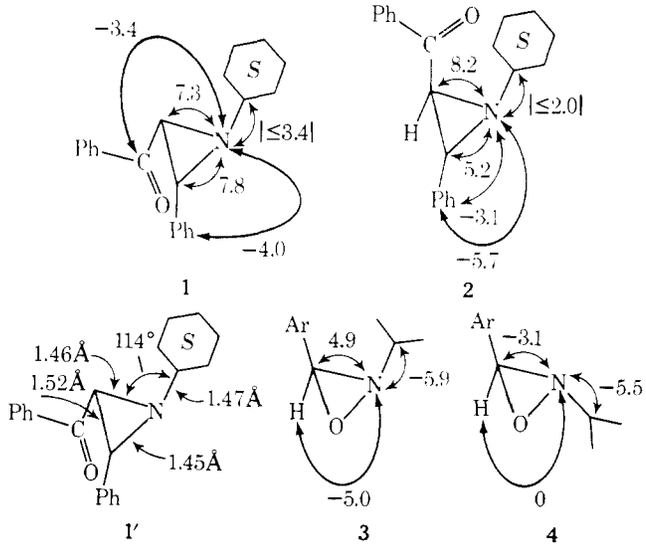

Figure 1.

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