times with CH_2Cl_2. The organic solution was dried on anhydrous K_2CO_3 and Na_2SO_4. The solvent was distilled off in low vacuum and the residue was analyzed by GC, IR, and ^{13}C NMR spectroscopy.[19b,25a] The only product was 2-methyl-*exo*-2-norborneol in the case of 2-methyl-2-norbornene and 2-methylenenorbornane and 1-methyl-1-cyclohexanol in the case of 1-methylcyclohexene and methylenecyclohexane.

Ca. 0.5 g of 2-methyl-2-norbornene was also hydrated in 25 cm^3 of 1 mol dm^{-3} $DClO_4(D_2O)$ at room temperature. The product was analyzed by GC, IR, and ^{13}C NMR (in CCl_4) and ^2H NMR (in CCl_4 with $CDCl_3$ as internal standard) spectroscopy (JEOL JNM-GX-400). The product was 3-deuterio-2-methyl-*exo*-2-norborneol, since the C-3 signal (48.1 ppm) split into a triplet in the C–H decoupled ^{13}C NMR spectra. A slight division of the C-2 signal (77.0 ppm) due to partial deuteration of the hydroxylic hydrogen was also observed. According to the ^2H NMR spectra, deuterium was mainly at the exo-3 position (99.4 ± 0.3%) and in minor quantity at the endo-3 position (0.6 ± 0.3%; the integrations were quite rough).

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Registry No. 1, 694-92-8; 2, 497-35-8; 3, 591-49-1; 4, 1192-37-6; deuterium, 7782-39-0.

(Trifluoromethyl)sulfonyl (Triflyl) Migration. Synthesis of 6,3′-Anhydro-3-benzyl-1-(5-chloro-5-deoxy-β-D-xylofuranosyl)barbituric Acid from the 2′-Trifluoromethanesulfonate (Triflate) of 6,5′-Anhydro-3-benzyl-1-β-D-ribofuranosylbarbituric Acid[1]

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The first evidence of (trifluoromethyl)sulfonyl (triflyl) migration is presented. The 2′,3′-*O*-stannylene derivative of 6,5′-anhydro-3-benzyl-1-β-D-ribofuranosylbarbituric acid (**1**) afforded a 9:1 mixture of isomeric 2′- and 3′-triflates **2** and **3** upon treatment with triflyl chloride in *N*,*N*-dimethylformamide. On acetylation, **2** and **3** afforded their corresponding acetyl derivatives **4** and **5**. Compound **4** was converted into 6,2′-anhydro-3-benzyl-1-(3-*O*-acetyl-5-chloro-5-deoxy-β-D-arabinofuranosyl)barbituric acid (**6**) by treatment with LiCl in hexamethylphosphoric triamide (HMPA), whereas **5** afforded the 6,3′-anhydro-xylo isomer **7**. Compounds **6** and **7** were reduced to the 5′-deoxy nucleosides **8** and **9**, respectively. Treatment of both 2′- and 3′-triflates **2** and **3** with LiCl in HMPA afforded, exclusively, the same 6,3′-anhydro-xylo derivative **10**, which was acetylated to **7**. The triflyl group on C-2′ in **2** migrated to C-3′ prior to the formation of the 6,3′-anhydro linkage during the conversion to **10**. A plausible mechanism is discussed.

During the past decade, the trifluoromethanesulfonate (triflate) group has become a useful and widespread reagent in synthetic organic chemistry[2] due to superior leaving ability and low nucleophilicity to conventional leaving groups such as mesylate, tosylate, or halide. We have been using the triflate leaving group extensively in nucleoside interconversion studies.[3-5] Recently, we found evidence for an unexpected (trifluoromethyl)sulfonyl (triflyl) migration. Since the triflyl group is commonly used in organic synthesis, our finding, as described below, should be taken into consideration in studies where a triflyl group neighboring an hydroxyl function is involved.

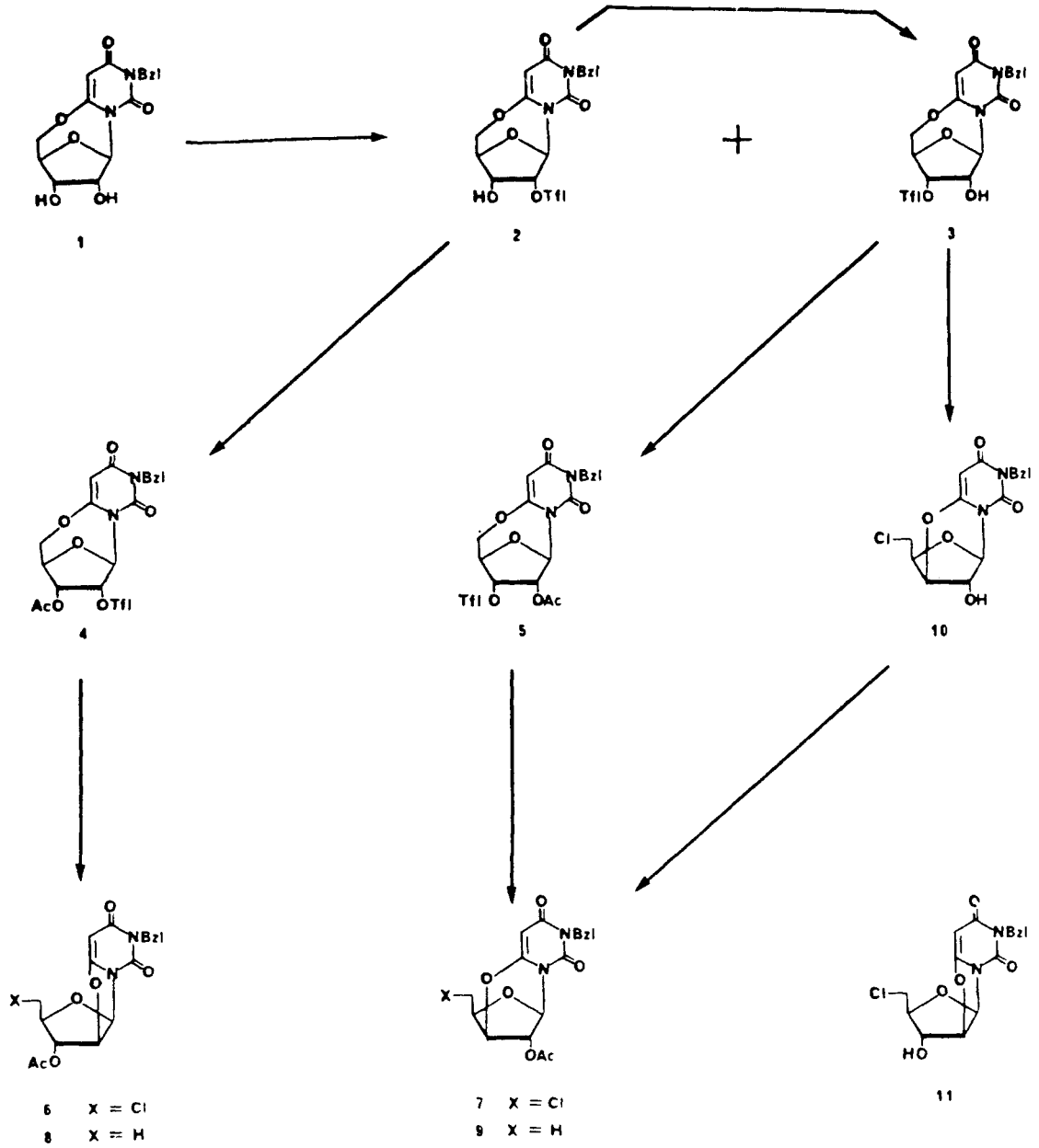
The 2′,3′-*O*-di-*n*-butylstannylene derivative of 6,5′-anhydro-3-benzyl-1-β-D-ribofuranosylbarbituric acid (**1**)[6] afforded a 9:1 mixture of isomeric 2′- and 3′-monotriflates **2** and **3** upon brief treatment with triflyl chloride in *N*,*N*-dimethylformamide (DMF). Compounds **2** and **3** were separated on a silica gel column. The ^1H NMR spectra (Table I) of both products show an AB quartet for H-5′,5″ and one exchangeable doublet, indicating the presence of the intact 6,5′-anhydro linkage and one secondary OH. A multiplet at δ 4.62 in the spectrum of the minor product is readily assigned to H-2′, as it collapsed to a sharp double doublet upon exchanging the dissociable proton with a deuterium, which coupled with H-1′ and H-3′ ($J_{1',2'}$ = 1.4 Hz, $J_{2',3'}$ = 5.8 Hz). These spectral data establish the minor

(1) Nucleosides. 137.
(2) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.
(3) Pankiewicz, K. W.; Watanabe, K. A. *Nucleic Acids Res. Symp. Ser.* **1982**, *11*, 9.
(4) Pankiewicz, K. W.; Kim, J.-H.; Watanabe, K. A. *J. Org. Chem.* **1985**, *50*, 3319.
(5) Pankiewicz, K. W.; Watanabe, K. A.; Takayanagi, H.; Itoh, T.; Ogura, H. *J. Heterocycl. Chem.* **1985**, *22*, 1703.

(6) Compound **1** used in this investigation was prepared from 6,5′-anhydro-1-(2,3-*O*-isopropylidene-β-D-ribofuranosyl)barbituric acid [Otter, B. A.; Falco, E. A.; Fox, J. J. *J. Org. Chem.* **1969**, *34*, 1390] by benzylation with benzyl chloride in the presence of DBU followed by de-O-isopropylidenation with 80% trifluoroacetic acid. Deacetonation prior to benzylation was unsuccessful due to cleavage of the glycosyl bond. Benzylation of 6,5′-anhydro-1-β-D-ribofuranosylbarbituric acid [Lipkin, D.; Cori, C.; Sano, M. *Tetrahedron Lett.* **1968**, 5993. Maruyama, T.; Sato, S.; Honjo, M. *Chem. Pharm. Bull.* **1982**, *30*, 2688] was found to be less advantageous, since synthesis of their starting anhydro nucleoside is inefficient.

0022-3263/86/1951-1525$01.50/0

Scheme I



product to be the 3′-triflate **3** and the major product to be the 2′-triflate **2**.

On acetylation, **2** and **3** afforded the corresponding acetyl derivatives **4** and **5** in high yield in crystalline form. The H-2′ signal for the acetate from **3** appeared at δ 5.60 as a double doublet ($J_{1',2'}$ = 1.9 Hz, $J_{2',3'}$ = 5.8 Hz) which is consonant only with the 2′-acetate structure **5**. The well-resolved spectrum of the acetate from the major triflate **2** is fully consistent with the 3′-acetate **4**. The ^{13}C NMR spectra for **2** and **3** or **4** and **5** are quite similar (Table II) and are in agreement with isomeric structures for these nucleoside pairs. All the data are consistent with these four 6,5′-anhydro nucleoside triflates **2**–**5**, and no other structures can be deduced from these data. Compound **4**, when treated with LiCl in hexamethylphosphoric triamide (HMPA), was converted smoothly into 6,2′-anhydro-3-benzyl-1-(3-*O*-acetyl-5-chloro-5-deoxy-β-D-arabinofuranosyl)barbituric acid (**6**). The H-5′,5″ signal of **6** in ^1H NMR is no longer an AB quartet. The large coupling between H-1′ and H-2′ ($J_{1',2'}$ = 5.2 Hz) and the little $J_{2',3'}$ value establish the cis arrangement for H-1′ and H-2′ and trans configuration for H-2′ and H-3′. A large upfield shift of the C-5′ signal in ^{13}C NMR (Table II) also supports the cleavage of the 6,5′-anhydro bond. These data are fully consistent with the 6,2′-anhydro arabino structure **6**. The isomeric 3′-triflate **5** afforded the 6,3′-anhydro isomer **7**. Undetectably small couplings between H-1′ and H-2′ also between H-2′ and H-3′ in ^1H NMR and a large upfield shift of C-5′ in ^{13}C NMR conclusively prove the 6,3′-anhydro-xylo structure **7** for this product. Apparently, nucleophilic attack by the chloride occurred first on C-5′, liberating the 6-oxide ion, which then attacked the triflate group at C-2′ in **4** and C-3′ in **5**, resulting in the formation of the corresponding 5′-chloro-5′-deoxy-6,2′-anhydro-arabino or -6,3′-anhydro-xylo nucleosides **6** and **7** (Scheme I). Both isomers **6** and **7** were reduced to their corresponding 5′-deoxy nucleosides **8** and **9** under Barton's conditions with *n*-Bu_3SnH.[7] The formation of the 5′-deoxy nucleosides **8** and **9** as evidenced by the presence of a high-field methyl doublet (see Table I) is an additional proof for the 5′-chloromethyl structures for **6** and **7** and supports the proposed mechanism of formation of **6** and **7** from **4** and **5**, respectively.

(7) Barton, D. H. R.; Subramanian, L. R. *J. Chem. Soc., Chem. Commun.* **1976**, 867; *J. Chem. Soc., Perkins Trans. 1*, **1977**, 1718.

Table I. ^{1}H NMR Parameters for Anhydro Nucleosides[a]

compd	chemical shifts, δ (mult)								coupling constants, Hz
	H-1′	H-2′	H-3′	H-4′	H-5′	H-5″	H-5	others	
1	6.22 (s)	4.21		4.39 (m)	4.56 (d)	3.96 (d)	5.47 (s)	4.95 (s, 2 H, CH_2), 7.29 (s, 5 H, Ph), 5.21 (d, 1 H, OH), 5.48 (d, 1 H, OH)	$J_{5',5''}$ = 12.6
2	6.60 (s)	5.70 (d)	4.58		4.72 (m)	4.07 (d)	5.57	4.97 (s, 2 H, CH_2), 7.28 (s, 5 H, Ph), 6.40 (d, 1 H, OH)	$J_{2',3'}$ = 6.0, $J_{5',5''}$ = 11.8
3	6.33 (d)	4.64 (dd)	5.71 (d)	4.92 (s)	4.90 (d)	4.08 (d)	5.56 (s)	4.95 (s, 2 H, CH_2), 7.29 (s, 5 H, Ph), 6.73 (d, 1 H, OH)	$J_{2',3'}$ = 5.8, $J_{5',5''}$ = 13.2, $J_{1',2'}$ = 1.4
4	6.68 (s)	5.70 (d)	6.01 (d)	4.87 (s)	4.71 (d)	4.15 (d)	5.61 (s)	4.96 (s, 2 H, CH_2), 7.28 (s, 5 H, Ph), 2.12 (s, 3 H, Ac)	$J_{2',3'}$ = 6.5, $J_{5',5''}$ = 12.3
5	6.46 (d)	5.60 (dd)	6.05 (d)	5.04 (s)	4.74 (d)	4.17 (d)	5.60 (s)	4.94 (d, 2 H, CH_2), 7.28 (s, 5 H, Ph), 2.12 (s, 3 H, Ac)	$J_{1',2'}$ = 1.9, $J_{2',3'}$ = 5.8, $J_{5',5''}$ = 13.1
6	6.38 (d)	5.53 (d)	5.28 (d)	4.54 (m)	3.67	3.74 (m)	5.34 (s)	4.93 (s, 2 H, CH_2), 7.27 (s, 5 H, Ph), 2.11 (s, 3 H, Ac)	$J_{1',2'}$ = 5.2, $J_{3',4'}$ = 3.8
7	6.26 (s)	5.29 (s)	5.62 (d)	4.57 (dt)	3.78		5.29 (s)	4.91 (s, 2 H, CH_2), 7.28 (s, 5 H, Ph), 2.12 (s, 3 H, Ac)	$J_{3',4'}$ = 2.0, $J_{4',5'}$ = 6.8
8	6.30 (d)	5.43 (d)	5.06 (d)	4.40 (dq)			5.34 (s)	4.92 (s, 2 H, CH_2), 7.27 (s, 5 H, Ph), 2.09 (s, 3 H, Ac), 1.15 (d, 3 H, 5′-Me)	$J_{1',2'}$ = 5.5, $J_{3',4'}$ = 1.6
9	6.17 (s)	5.56 (br s)	5.14 (br s)	4.50 (dq)			5.27 (s)	4.91 (s, 2 H, CH_2), 7.28 (s, 5 H, Ph), 2.10 (s, 3 H, Ac), 1.24 (d, 3 H, 5′-Me)	$J_{3',4'}$ = 2.5
10	6.01 (br s)	4.63 (d)	5.02 (br s)	4.53 (dt)	3.75 (d)		5.22 (s)	4.91 (s, 2 H, CH_2), 7.28 (s, 5 H, Ph), 6.44 (d, 1 H, OH)	$J_{3',4'}$ = 2.2, $J_{4',5'}$ = 6.8

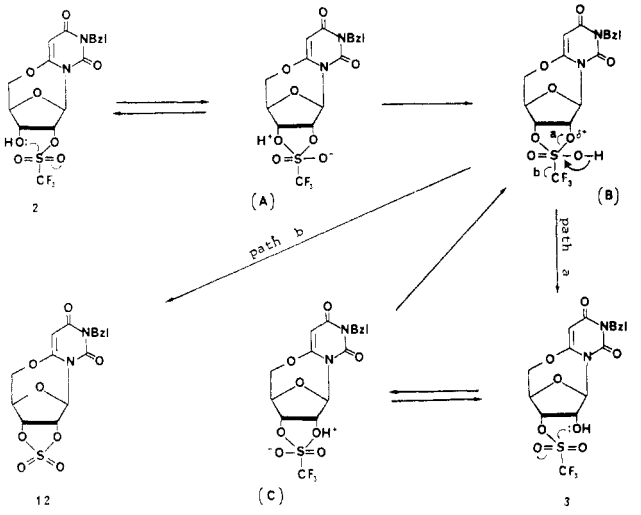
[a] In Me_2SO-d_6: coupling constants are first order: s, singlet; d, doublet; t, triplet; q, quartet; dd, double doublet; dt, double triplet; br s, broad singlet (apparent); m, multiplet.

Table II. ^{13}C NMR Parameters for Anhydro Nucleosides[a]

no.	chemical shifts, δ (mult)											coupling constants, Hz					
	C-2	C-4	C-5	C-6	C-1′	C-2′	C-3′	C-4′	C-5′	CH_2	Ph	$J_{C-5,H-5}$	$J_{C-1',H-1'}$	$J_{C-2',H-2'}$	$J_{C-3',H-3'}$	$J_{C-4',H-4'}$	$J_{C-5',H-5'}$
1	150.3 (s)	162.1 (s)	89.2 (d)	160.3 (s)	92.6 (d)	76.5 (d)	77.9 (d)	86.4 (d)	77.4 (t)	43.8 (t)	136.8, 128.2, 127.6, 127.1	177.0	178.2	152.6	147.7	150.1	152.6
2	149.9 (s)	161.9 (s)	90.4 (d)	159.4 (s)	90.0 (d)	87.8 (d)	71.6 (d)	87.2 (d)	77.1 (t)	43.8 (t)	136.6, 128.1, 127.5, 127.1	178.2	162.4	175.8	156.2	153.8	152.0
3	150.2 (s)	161.9 (s)	89.9 (d)	159.7 (s)	91.3 (d)	75.3 (d)	89.1 (d)	83.3 (d)	76.0 (t)	43.9 (t)	136.8, 128.2, 127.7, 127.1	177.0	175.8	152.6	177.0	143.0	152.6
4[b]	149.9 (s)	151.8 (s)	90.2 (d)	159.2 (s)	88.0 (d)	87.6 (d)	72.9 (d)	84.5 (d)	76.6 (t)	43.9 (t)	136.5, 128.1, 127.5, 127.2	178.2	171.0	171.0	162.0	151.4	162.0
5[c]	149.9 (s)	161.9 (s)	89.8 (d)	159.2 (s)	88.1 (d)	76.3 (d)	86.7 (d)	83.7 (d)	75.6 (t)	43.9 (t)	136.3, 128.2, 127.6, 127.1	177.0	177.0	159.3	166.0	166.0	152.5
6[d]	147.2 (s)	161.8 (s)	81.4 (d)	155.0 (s)	76.9 (d)	82.6 (d)	71.5 (d)	80.9 (d)	42.3 (t)	43.6 (t)	136.8, 128.2, 127.6, 127.0	175.8	170.9	186.7	159.7	156.2	141.6
7[e]	147.2 (s)	163.0 (s)	75.8 (d)	160.3 (s)	87.8 (d)	76.2 (d)	83.7 (d)	89.3 (d)	43.0 (t)	43.8 (t)	136.7, 128.1, 127.3, 127.1	178.2	171.0	167.2	181.9	174.5	155.2

[a] In Me_2SO-d_6; coupling constants first order: s, singlet; d, doublet; t, triplet; q, quartet. Assignments for C-2, C-4, and C-6 were made by following: Maruyama, T.; Honjo, M. *Nucleic Acid Res. Symp. Ser.* **1979**, *7*, s7. The C-5 signal appeared as a sharp doublet in relatively high magnetic field, whereas signals for sugar carbons were less sharp due to couplings with their vicinal protons as observed by: Lemieux, R. U.; Nagabhushan, T. L.; Paul, B. *Can. J. Chem.* **1972**, *50*, 773. [b] Acetyl signals at δ 169.2 (s), 20.0 (q). [c] Acetyl signals at δ 169.0 (s), 19.9 (q). [d] Acetyl signals at δ 169.0 (s), 20.4 (q). [e] Acetyl signals at δ 169.5 (s), 20.5 (q).

Scheme II



Treatment of the 2′-*O*-triflyl derivative **2** with LiCl in HMPA, however, did *not* afford the expected 6,2′-anhydro-*arabino* nucleoside **11** but gave in high yield the 6,3′-anhydro-*xylo* nucleoside **10**. The ^{1}H NMR spectrum of **10** (Table I) is very similar to that of 6,3′-anhydro-1-β-D-xylofuranosylbarbituric acid reported by Maruyama et al.[6] The structure of **10** was unambiguously confirmed by conversion to **7** by acetylation. The 3′-*O*-triflyl nucleoside **3** also was converted into the same 6,3′-anhydro-*xylo* nulcoside **10** by similar treatment with LiCl in HMPA. Therefore, the triflyl group on C-2′ in **2** must have migrated to C-3′ prior to the formation of the 6,3′-anhydro linkage in the above reaction. Moreover, the 2′-triflate **2** slowly underwent isomerization to the 3′-triflate **3** at room temperature in solutions of HMPA, Me_2SO, or pyridine. thus, in this system at least, triflyl migration does indeed occur.

A possible mechanism for the migration would be an intramolecular alcoholysis. The process of triflyl migration may be schematically illustrated as shown in Scheme II. Attack of 3′-hydroxyl of **2** on the highly positive sulfur atom would lead to the formation of the zwitterion A, which would be converted into the 1,3,2-dioxathiolane intermediate B by prototropy. Dissociation of the proton from B would result in the selective cleavage of the S–O2′ bond[8] (path a) since O2′ is more electron deficient than O3′, due to the inductive effect of the aglycon. Thus, the migration occurs only from the 2′-triflate **2** to 3′-triflate **3** but not vice versa.

Moreover, we obtained the 2′,3′-O-cyclic sulfonyl nucleoside **12** in 26% yield (Scheme II) by treatment of either **2** or **3** with Amberlyst A 26 (F^-). Apparently, fluoroform was eliminated from intermediate B by the C–S bond fission (path b) by a mechanism similar to the cleavage of the C–C bond in haloform reaction.[9]

This migration[10] is prevented by acetylation of the 3′-OH group. Thus, the 3′-*O*-acetyl nucleoside **4** afforded the 6,2′-anhydro product **6** upon treatment with LiCl. It is well-known that certain *O*-sulfonyl groups undergo solvolysis without changing the configuration.[11] In these instances, alkoxide or hydroxide attacks the sulfur atom in the mesyl group.[11] The sulfur atom in a triflyl group is more positive than that in mesyl, due to the strong inductive effect of CF_3. It is therefore surpirising that such a triflyl migration as is reported herein has not been documented previously.[2,12] The triflyl migration as described herein may occur in systems containing cis vicinal diol under proper conformational and electronic environment. The scope of this migration, using several other systems, is being investigated in our laboratory.

Experimental Section

General Methods. Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL FT90Q spectrometer using Me_2SO-d_6 as the solvent and Me_4Si as the internal standard. Chemical shifts are reported in parts per million (δ). Apparent shapes of signals are described as s (singlet), d (doublet), t (triplet), q (quartet), dd (double doublet), m (multiplet), br s (broad singlet). Values given for coupling constants are first order. TLC was performed on Uniplates (Analtech Co., Newark, DE) and column chromatography on Woelm silica gel (70–230 mesh). Microanalyses were performed by Galbraith Laboratories, Inc., or by M.H.W. Laboratories. Mass spectral data were collected at Rockefeller University, Mass Spectrometric Biotechnology Resource, by F. A. Bencsath.

6,5′-Anhydro-3-benzyl-1-(2,3-*O*-isopropylidene-β-D-ribofuranosyl)barbituric Acid. A mixture of 6,5′-anhydro-1-(2,3-*O*-isopropylidene-β-D-ribofuranosyl)barbituric acid[6] (2.82 g, 0.01 mol) and DBU (3.04 g, 0.02 mol) in DMF (50 mL) was stirred for 5 h at room temperature. The mixture was concentrated in vacuo and the residue was chromatographed on a silica gel column with $CHCl_3$–Me_2CO (10:1 v/v) as the eluent to give the title product (3.1 g, 83%) as a foam: ^{1}H NMR δ 1.28 (3 H, s, CMe), 1.42 (3 H, s, CMe), 4.06 (1 H, d, H-5′, $J_{5',5''}$ = 12.3 Hz), 4.62 (1 H, d, H-5″, $J_{5',5''}$ = 12.3 Hz), 4.62 (1 H, s, H-4′), 4.96 (4 H, s, H-2′,3′, PhCH_2), 5.48 (1 H, s, H-5), 6.23 (1 H, s, H-1′), 7.28 (5 H, s, Ph).

Anal. Calcd for $C_{19}H_{20}N_2O_6$: C, 61.28; H, 5.41; N, 7.52. Found: C, 60.98; H, 5.28; N, 7.23.

6,5′-Anhydro-3-benzyl-1-β-D-ribofuranosylbarbituric Acid (1). The above compound (3.72 g, 0.01 mol) was dissolved in 80% CF_3CO_2H (40 mL), the mixture stirred for 2 h and concentrated in vacuo, and the residue chromatographed over a silica gel column with $CHCl_3$–Me_2CO (5:1 v/v) as the eluent to give crystalline **1**, which was recrystallized from MeOH (2.25 g, 88%), mp 144–145 °C. For ^{1}H NMR and ^{13}C NMR parameters, see Tables I and II.

Anal. Calcd for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43. Found: C, 57.68; H, 4.70; N, 8.27.

6,5′-Anhydro-3-benzyl-1-(2-*O*-triflyl-β-D-ribofuranosyl)-barbituric Acid (2) and 6,5′-Anhydro-3-benzyl-1-(3-*O*-triflyl-β-D-ribofuranosyl)barbituric Acid (3). A mixture of **1** (3.32 g, 0.01 mol) and *n*-Bu_2SnO (2.49 g, 0.01 mol) in MeOH (200 mL) was heated at reflux until a clear solution was obtained. The solvent was removed in vacuo, and the solid residue was dissolved in DMF (70 mL) and treated with CF_3SO_2Cl for 2 h at room temperature. The mixture was concentrated in vacuo, and the semisolid residue was washed with *n*-hexane (200 mL) and was triturated with $CHCl_3$ to give crystalline **2**, which was collected by filtration (2.1 g, 45.3%), mp 195–196 °C. The ^{1}H and ^{13}C NMR parameters are listed in Tables I and II.

Anal. Calcd for $C_{17}H_{15}F_3N_2O_8S$: C, 43.97; H, 3.25; N, 6.03; S, 6.90. Found: C, 43.69; H, 3.34; N, 5.93; S, 7.20.

(8) There is a precedent for S–O bond cleavage in triflates: Subramanian, L. R.; Hanack, M.; Chang, L. W. K.; Imhoff, M. A.; Schleyer, P. V. R.; Effenberger, F.; Kurtz, W.; Stang, P. J.; Dueber, T. E. *J. Org. Chem.* **1976**, *41*, 4099.

(9) March, J. *Advanced Organic Chemistry. Reactions, Mechanisms and Structure*, 2nd ed.; McGraw-Hill: New York, 1977; p 574.

(10) This mechanism is quite different from that of acyl migration reactions in which the acyl carbonyl oxygen plays a role as a nucleophile and proceeds through ortho acid (or cyclic carboxonium ion) intermediates: Hains, A. H. *Adv. Carbohydr. Chem. Biochem.* **1976**, *33*, 11. Paulsen, H.; Behre, H.; Herold, C. P. *Fortschr. Chem. Forsch.* **1970**, *14*, 472.

(11) Formation of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside from 4,6-*O*-benzylidene-2,3-di-*O*-tosyl-α-D-glucopyranoside (discovered in 1935 by: Robertson, G. R.; Griffice, C. F. *J. Chem. Soc.* **1935**, 1193) proceeds by hydrolysis of 2-*O*-tosyl to generate 2-alkoxide, which attacks C-3 to liberate a tosylate with simultaneous formation of the 2,3-anhydroalloside. For more recent examples, see: Sinclair, H. B. *J. Org. Chem.* **1981**, *46*, 2450. D'Rosario, P.; Smyth, R. L.; Williams, A. *J. Am. Chem. Soc.* **1984**, *105*, 5027.

(12) Binkley, R. W.; Ambrose, M. G. *J. Carbohydr. Chem.* **1984**, *3*, 1.

The filtrate was concentrated in vacuo, and the residue was chromatographed on a silica gel column with $CHCl_3$–Me_2CO (10:1 v/v) as the eluent to give two nucleoside-containing fractions. After evaporation of the first fraction and trituration of the residue with *n*-hexane, **3** (400 mg, 8.7%) was obtained, mp 170–172 °C. The ^1H and ^{13}C NMR data are given in Tables I and II.

Anal. Calcd for $C_{17}H_{15}F_3N_2O_9S$: C, 43.97; H, 3.25; N, 6.03; S, 6.90. Found: C, 43.77; H, 3.51; N, 5.93; S, 6.94.

From the second fraction, 1.9 g of **2** was obtained, giving a total yield of 87%.

2′-*O*- to 3′-*O*-Triflyl Migration. A solution of **2** (200 mg) in pyridine (5 mL) was kept standing at room temperature for 3 days and then concentrated to dryness in vacuo. Traces of pyridine were removed by coevaporation with toluene and EtOH. The ^1H NMR spectrum of the residue (200 mg) was identical with that of **3**.

6,5′-Anhydro-3-benzyl-1-(3-*O*-acetyl-2-*O*-triflyl-β-D-ribofuranosyl)barbituric Acid (4). A mixture of **2** (900 mg, 1.94 mmol) and Ac_2O (1 mL) in pyridine (15 mL) was stirred at room temperature for 1 h. The reaction was quenched by addition of EtOH (5 mL), and the mixture was concentrated in vacuo. The residue was coevaporated several times with EtOH until crystallization occurred. The crystalline residue was washed with a small volume of cold EtOH to give 980 mg (quantitative yield) of **4**, mp 153–154 °C. The ^1H and ^{13}C NMR characteristics of **4** are listed in Tables I and II.

Anal. Calcd for $C_{19}H_{17}F_3N_2O_9S$: C, 45.06; H, 3.38; N, 5.53; S, 6.33. Found: C, 44.96; H, 3.54; N, 5.52; S, 6.54.

In a similar manner, **6,5′-anhydro-3-benzyl-1-(2-*O*-acetyl-3-*O*-triflyl-β-D-ribofuranosyl)barbituric acid (5),** mp 190–191 °C was obtained from **3**. See Tables I and II for ^1H and ^{13}C NMR parameters of **5**.

Anal. Calcd for $C_{19}H_{17}F_3N_2O_9S$: C, 45.06; H, 3.38; N, 5.53; S, 6.33. Found: C, 45.02; H, 3.42; N, 5.52; S, 6.67.

6,2′-Anhydro-3-benzyl-1-(3-*O*-acetyl-5-chloro-5-deoxy-β-D-arabinofuranosyl)barbituric Acid (6). A mixture of **4** (506 mg, 1 mmol) and LiCl (430 mg, 10 mmol) in HMPA (15 mL) was stirred at room temperature for 4 days and then partitioned between EtOAc (200 mL) and water (100 mL). The organic layer was separated, washed with water (4 × 70 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified on a silica gel column with CCl_4–EtOAc (5:3 v/v) as the eluent to give 353 mg (90%) of **6** as a foam. The ^1H and ^{13}C NMR parameters are given in Tables I and II.

Anal. Calcd for $C_{18}H_{17}N_2O_6$: C, 55.04; H, 4.36; Cl 9.02; N, 7.13. Found: C, 55.35; H, 4.69; Cl, 8.76; N, 6.94.

In a similar manner, **5** (506 mg, 1 mmol) was converted into **6,3′-anhydro-3-benzyl-1-(2-*O*-acetyl-5-chloro-5-deoxy-β-D-xylofuranosyl)barbituric acid (7)** (320 mg, 82%) which was obtained as a foam. Tables I and II list the ^1H and ^{13}C NMR parameters of **7**.

Anal. Calcd for $C_{18}H_{17}ClN_2O_6$: C, 55.04; H, 4.36; Cl, 9.02; N, 7.13. Found: C, 55.41; H, 4.28; Cl, 8.74; N, 6.94.

6,2′-Anhydro-3-benzyl-1-(3-*O*-acetyl-5-deoxy-β-D-arabinofuranosyl)barbituric Acid (8). A mixture of 2,2′-azobis(2-methylpropionitrile) (50 mg) and *n*-Bu_3SnH (152 mg, 0.52 mmol) in toluene (2 mL) was added dropwise to a refluxing solution of **6** (100 mg, 0.26 mmol) in toluene. The mixture was heated under reflux for 30 min, the solvent was then removed in vacuo, and the residue was chromatographed on a silica gel column with CCl_4–EtOAc (5:3 v/v) to give **8** (50 mg, 55%) as a foam.

Anal. Calcd for $C_{18}H_{18}N_2O_6$: C, 60.33; H, 5.06; N, 7.82. Found: C, 59.94; H, 5.09; N, 7.24.

Though the result of nitrogen analysis is low, the ^1H NMR spectrum of this sample is consistent with the 5′-deoxy structure **8**.

By following the same procedure but with **7**, **6,3′-anhydro-3-benzyl-1-(2-*O*-acetyl-5-deoxy-β-D-xylofuranosyl)barbituric acid (9)** was prepared in 60% yield as a foam. The ^1H NMR data are given in Table I.

Anal. Calcd for $C_{18}H_{18}N_2O_6$: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.21; H, 5.10; N, 7.62.

6,3′-Anhydro-3-benzyl-1-(5-chloro-5-deoxy-β-D-ribofuranosyl)barbituric Acid (10). A mixture of **2** (464 mg. 1 mmol) and LiCl (430 mg, 10 mmol) in HMPA (15 mL) was stirred at room temperature for 4 days and then partitioned between EtOAc (200 mL) and water (100 mL). The organic layer was washed with water (4 × 70 mL), dried (Na_2SO_4), and concentrated in vacuo; the residue was chromatographed on a silica gel column with $CHCl_3$–Me_2CO (5:1 v/v) to give **10** (330 mg, 94%), mp 210–211 °C, after recrystallization from EtOH. Tables I and II list the ^1H and ^{13}C NMR parameters of **10**.

Anal. Calcd for $C_{16}H_{15}ClN_2O_5$: C, 54.79; H, 4.31; Cl, 10.11; N, 7.98. Found: C, 54.54; H, 4.24; Cl, 10.46; N, 7.64.

Similar treatment of **3** with LiCl also afforded **10** in 94% yield.

6,5′-Anhydro-3-benzyl-1-β-D-ribofuranosylbarbituric Acid 2′,3′-Sulfate (12). A mixture of **2** (222 mg, 0.5 mmol) and Amberlyst A-26(F^-) (666 mg, 2.26 meq) in dry MeCN (15 mL) was heated at reflux overnight. The resin was filtered and washed with MeCN. The combined filtrate and washings were concentrated in vacuo, and the residue was crystallized from Et_2O to give 105 mg (26%) of **12**, mp 218–220 °C: ^1H NMR δ 4.22 (1 H, d, H-5′, $J_{5',5''}$ = 12.6 Hz), 4.72 (1 H, dd, H-5″, $J_{4',5''}$ = 1.4 Hz, $J_{5',5''}$ = 12.6 Hz), 4.96 (2 H, s, PhCH_2), 5.01 (1 H, d, H-4′, $J_{3',4'}$ = 0Hz, $J_{4',5''}$ = 1.4 Hz), 5.59 (1 H, s, H-5), 6.12 (2 H, s, H-2′,3′), 6.58 (1 H, s, H-1′), 7.50 (5 H, s, Ph); ^{13}C NMR δ 44.0 (t, $PhCH_2$), 76.2 (t, C-5′, $J_{C-5',H-5'} = J_{C-5',H-5''}$ = 156.2 Hz), 82.8 (d, C-4′, $J_{C-4',H-4'}$ = 166.0 Hz), 85.9 (d, C-3′, $J_{C-3',H-3'}$ = 165.2 Hz), 87.5 (d, C-2′, $J_{C-2',H-2'}$ = 175.7 Hz), 87.7 (d, C-1′, $J_{C-1',H-1'}$ = 175.7 Hz), 89.6 (d, C-5, $J_{C-5,H-5}$ = 177.0 Hz), 127.1, 127.7, 128.2, 136.5 (d, Ph), 150.0 (s, C-2), 158.9 (s, C-4), 161.9 (s, C-6); MS (CI), *m/e* 395 (MH), 315 (M – SO_3 + H), 219 (3-benzylbarbituric acid + H).

Anal. Calcd for $C_{16}H_{14}N_2O_8 \cdot {}^1/_2H_2O$: C, 47.64; H, 3.72; N, 6.95; S, 7.94. Found: C, 47.62; H, 3.53; N, 6.82; S, 8.47.

The presence of a half molecule of water of crystallization in the sample was also determined by ^1H NMR spectroscopy. Although the analytical value of sulfur was off by 0.53%, spectral data (NMR and MS) are fully consistent with structure **12**.

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