The Reaction of 9-(2′,3′-Dideoxy-β-D-*glycero*-pent-2-Enofuranosyl)-adenine Derivatives with Arene- and Alkanesulfenyl Chlorides. An Unusual Ring Opening Reaction of Thiiranium Ions

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A series of arenesulfenyl chlorides and methanesulfenyl chloride were reacted in pyridine solution with 6-*N*-dibenzoyl-9-(2′,3′-dideoxy-β-D-*glycero*-pent-2-enofuranosyl)adenine (*1b*). In each case, the relative abundance of isomeric β-chloroarene/alkane sulfides was estimated and used to assess the relative thermodynamic stabilities of the *lyxo* and *ribo* thiiranium ion intermediates and their steric susceptibilities to attack by a nucleophile (Cl^-). Subsequently, the β-chloroarene/alkane sulfides *8a-d* to *13a-d*, upon alkaline treatment, underwent an unprecedented ylide-mediated β elimination of the intermediary *lyxo* and *ribo* thiiranium ions, to give only 2′-ene-thiol ethers *14–19*.

Compelling evidence has been put forward that the addition of an arene- or an alkanesulfenyl chloride to a double bond proceeds through the intermediacy of a thiiranium ion, followed by the attack of a nucleophile in a *trans* stereospecific manner.[1-3] It was envisioned that such addition reactions of sulfenyl chlorides to the sterically constrained pentofuranose system of a β-D-nucleoside containing a double bond between 2′ and 3′ carbons, as in *1b*, would give rise to four isomeric compounds (*2a-d* to *7a-d*). It was clear that the actual distribution of these isomers would depend upon two factors: firstly, the relative thermodynamic stabilities of the two isomeric thiiranium ions, *A* and *B* (*ribo* and *lyxo*, respectively) and, secondly, upon the steric feasibility of the attack by a nucleophile (Cl^-). It was furthermore possible that such functionalisation of the pentofuranose moiety of a β-D-nucleoside could lead to the preparation of biologically important antimetabolites for viral and cancer chemotherapeutic purposes.[4]

We first needed to find a suitable method of protection for the adenine residue. After trial reactions using phthaloyl[5], monobenzoyl, dibenzoyl, monomesitoyl, 2-nitrobenzenesulfenyl[6] and 2,4-dinitrobenzenesulfenyl for N^6 protection, we chose the N^6,N^6-dibenzoyladenine derivative as being the most suitable for further work. N^6,N^6-dibenzoyl-9-(2′,3′-β-D-glycero-pent-2-enofuranosyl)adenine (*1b*) was best prepared by benzoylation of 9-(2′,5′-di-*O*-acetyl-3′-bromo-3′-deoxy-β-D-xylofuranosyl)adenine followed by reductive elimination[7] (Scheme 1). This compound (*1b*) was reacted with a series of arenesulfenyl chlorides, and with methanesulfenyl chloride in dry pyridine solution at 0 °C, producing a mixture of isomers *2a-d* to *7a-d*, which could be separated only in a few cases. Reaction with 2-nitrobenzene- and 2,4-dinitrobenzenesulfenyl chlorides gave rise to complete depurination of the starting material. After removal of the protecting groups from the 5′-hydroxyl and the exocyclic amino functions from *2a-d* to *7a-d* with methanolic ammonia at 20 °C, the isomeric composition of the mixture could be determined by comparing the

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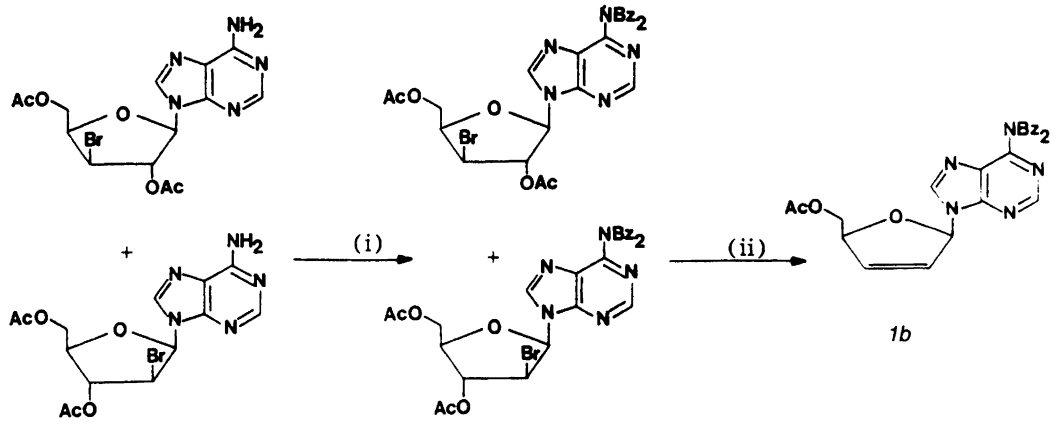
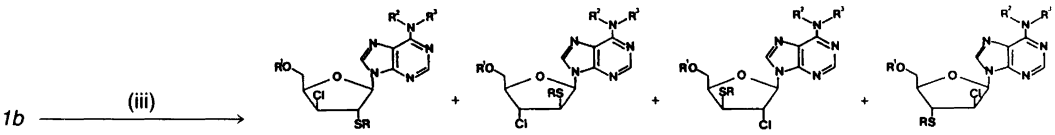


1 *1a* *1b*

(i) Benzoyl chloride (3 eq.) in dry pyridine, 2 h.
(ii) Zinc/acetic acid (10 eq.) in THF/ethanol (9:1, v/v), 30 min.



2a-d; R=C_6H_5; R^1=Ac; R^2=R^3=Bz	*2a*	*2b*	*2c*	*2d*[a]
3a-d; R=4-$CH_3C_6H_4$; R^1=Ac; R^2=R^3=Bz	*3a*	*3b*	*3c*	*3d*[a]
4a-d; R=2-$CH_3C_6H_4$; R^1=Ac; R^2=R^3=Bz	*4a*	*4b*	*4c*	*4d*[a]
5a-d; R=4-ClC_6H_4; R^1=Ac; R^2=R^3=Bz	*5a*	*5b*	*5c*	*5d*[a]
6a-d; R=2-ClC_6H_4; R^1=Ac; R^2=R^3=Bz	*6a*	*6b*	*6c*	*6d*[a]
7a-d; R=CH_3; R^1=Ac; R^2=R^3=Bz	*7a*	*7b*	*7c*	*7d*
8a-d; R=C_6H_5; R^1=R^2=R^3=H	*8a*	*8b*	*8c*	*8d*[a]
9a-d; R=4-$CH_3C_6H_4$; R^1=R^2=R^3=H	*9a*	*9b*	*9c*	*9d*[a]
10a-d; R=2-$CH_3C_6H_4$; R^1=R^2=R^3=H	*10a*	*10b*	*10c*	*10d*[a]
11a-d; R=4-ClC_6H_4; R^1=R^2=R^3=H	*11a*	*11b*	*11c*	*11d*[a]
12a-d; R=2-ClC_6H_4; R^1=R^2=R^3=H	*12a*	*12b*	*12c*	*12d*[a]
13a-d; R=CH_3; R^1=R^2=R^3=H	*13a*	*13b*	*13c*	*13d*

(iii) RS–Cl (10 eq.) in dry pyridine, 0 °C, 24 h. [a]Not found in the reaction mixture.

NMR signals for the anomeric, H-8 and H-2 protons (Table 1). It emerged during the studies with these deprotected mixtures *8a-d* to *13a-d* that while benzene-, *p*-toluene-, *o*-toluene-, *p*-chlorobenzene- and *o*-chlorobenzenesulfenyl chlorides, upon reaction with *1b*, gave three of the four possible isomers, methanesulfenyl chloride, in a very similar reaction with *1b*, gave all four isomeric products (Table 1). This distribution of products demonstrated the intermediacy of both *lyxo* and *ribo* thiiranium ions and gave information about their relative ease of formation. It may be noted that it is the intermediacy of the *ribo* thiiranium ion (general formula: *A*) which is most predominant except in the reaction with *o*-chlorobenzenesulfenyl chloride (69 % of *lyxo* thiiranium; general formula: *B*). Furthermore, the distribution of isomers formed suggested that the nucleophilic attack leading to opening of the *lyxo* thiiranium intermediate occurred at both C-2′

Table 1. Distribution of products[a] from the addition reactions of arene/alkane sulfenyl chlorides with *1b*

Arene/Alkane R=	*8–13a* Distribution/% (yield/%)	*8–13b* Distribution/% (yield/%)	*8–13c* Distribution/% (yield/%)	*8–13d* Distribution/% (yield/%)	Total
Benzene	73.4 (65.0)	18.8 (16.6)	7.8 (6.9)	0.0 (0.0)	100 (88.5)
p-Toluene	64.5 (60.0)	12.9 (21.0)	22.6 (21.0)	0.0 (0.0)	100 (93.0)
o-Toluene	66.2 (60.0)	25.8 (23.4)	8.0 (7.3)	0.0 (0.0)	100 (90.7)
p-Chlorobenzene	63.0 (55.4)	28.5 (25.1)	9.5 (9.2)	0.0 (0.0)	100 (89.7)
o-Chlorobenzene	30.5 (28.5)	38.5 (36.0)	31.0 (29.0)	0.0 (0.0)	100 (93.5)
Methane	87.4 (54.1)	3.4 (2.2)	2.3 (1.3)	6.9 (4.2)	100 (61.8)

[a]By NMR.

and C-3′ from the α face without hindrance. However, the nucleophilic attack on the *ribo* thiiranium ion *A* from the β face was quite regiospecific at C-3′ except for one example (reaction of *1b* with methanesulfenyl chloride to give *7a* to *d*), suggesting that the aglycone played some role in the steric hindrance of C-2′. It may be added that no isomerization of these compounds was observed in dry pyridine solution at 20 °C after 6 days. Separation of the isomers *8a-c* to *13a-d* from the deprotected reaction mixtures was carried out by chromatography using silica gel. Although not successful in all cases, sufficient information was obtained to allow us to assign the structures of all isomers.

The structures of the isomers were determined using ^{1}H NMR on the basis of the following criteria: (1) the anomeric proton is paramagnetically shielded if the C-2′ substituent, bearing lone pairs, is *trans* to the aglycone[8–10] (i.e., where either chlorine or sulfur is *cis* to H-1′, "*cis*-shielding"[11]); (2) the chemical shifts of H-2′ and H-3′ are directly dependent on the substituent bound to the same carbon; (3) the chemical shifts of C-2′ and C-3′ and their respective $^1J_{CH}$ are directly dependent upon the electronegativity of the substituent [12,13]. ^{1}H NMR and relevant spin-spin coupling constants are shown in Tables 3 and 4 respectively; ^{13}C NMR chemical shifts and rele-

Table 2. Reaction of *8a-c* to *13a-d* with 0.25 M sodium methoxide

Starting mixture (composition by ^{1}H NMR)	Reaction time (h)	Product	Yield (%)
8a+8b+8c (65:17:7)	36	*14*	88
9a+9b+9c (3:1:2)	24	*15*	44
10a+10b+10c (3:2:1)	48	*16*	75
11a+11c (1:1)	48	*17*	63
11b	48	*17*	71
12a+12b+12c (1:1:1)	48	*18*	78
12a	48	*18*	64
12b	48	*18*	96
12c	200	*18*	36[a]
13a+13b+13c+13d (50:2:1:4)	24	*19*	54

[a]Adenine also isolated.

vant one bond carbon-proton coupling constants are shown in Table 5.

The product mixtures *8* to *13* were then reacted under strongly basic conditions (0.25 *M* sodium methoxide in methanol at 20 °C). In each case, only 2′-ene-thiol ethers *14-19* were isolated from all isomeric mixtures of *trans*-β-chloroarene/alkane sulfides in 70–80 % yields (Table 2). In addition, compounds *12a, b* and *c* were individually treated under the same conditions and all found to give the same product *17*. This suggests that the reaction takes place via two isomeric thiiranium intermediates (Scheme 2) from which the H-2′ is abstracted followed by the cleavage of 3′-carbon-sulfur bond to yield the products *14–19*. The possibility of a *trans* elimination followed by a migration of the 3′,4′-double bond (Scheme 3) has been ruled out by performing the reaction in a deuteriated medium (CD_3OD), and observing no incorporation of deuterium into the product. Further experimental evidence against the migration of a 3′,4′-double bond (Scheme 3) and subsequent epimerisation at C-4′ has been obtained by the conversion of *15a* to *25* which has been found to be identical to an authentic specimen. Previously, it has been shown[1–3] that a thiiranium ion could be opened up by the attack of a suitable nucleophile on either of the cyclic carbons or on sulfur or by an attack on the exocyclic carbon attached to the thiiranium-sulfur. The present work constitutes the first example of a base-induced, ylide mediated β-elimination of intermediate thiiranium ions, generated from *trans*-β-chloro arene/alkane sulfides *8* to *13* to give the thermodynamically stable ene-thiol ethers *14* to *19*, respectively.

Further evidence to support the presence of a thiiranium intermediate is that the chlorine may be exchanged for an acetate group by reaction with sodium acetate (5 equivalents in 95 % monoglyme-water, ~100 °C for 3 h) to give product *20a* which was isolated after acetylation of the 5′-hydroxyl in 33 % yield (Scheme 4); no trace of the corresponding 2′-acetate was detectable under this condition. An unambiguous structural assignment of *20a* was confirmed by its conversion to the corresponding sulfone *20b*.

Subsequently, the pure isomers *13a-d* have been converted to their sulfones *21a-d* in quantitative yields (0.1 *M* aqueous $KMnO_4$ in acetic acid, 3:7, v/v at 20 °C). The isolation and unambiguous spectroscopic characterisation of these sulfones, through the observation of the downfield chemical shift of the sugar proton on the carbon attached to $-SO_2Me$, furthermore corroborated the structures of *8–13(a-d)*. These sulfones, upon brief treatment with a 25 % solution of pyridine in dioxane at 50 °C underwent a *syn* periplanar elimination, upon abstraction of the most acidic ring proton attached to the 2′- or 3′-sulfonyl carbon, to give the 2′- and 3′-ene-sulfone *23* and *24*, respectively in quantitative yields. It should be noted that *22a* even underwent the *cis* elimination in a neutral medium (methanol-d_4 at 30 °C) with a half-life (^1H NMR) of approximately 240 min while *22b, 22c* and *22d* were completely stable under normal conditions of work-up and purification. On the other hand, the half-lives (^1H NMR) of *cis* elimination of *22a, 22b, 22c, 22d* in 30 % pyridine-d_5/deuteriochloroform mixture (v/v) at 20 °C were 60, 75, 60 and 240 min respectively. A comparison of the half-lives of *22a* and *22d*, with the most acidic H-2′ and H-3′ protons on the β face, revealed that it was likely that the former underwent *cis* elimination by intramolecular abstraction of H-2′ by the purine N^3 while the steric proximity or orientation of the N^3 lone pair may have been unfavourable for H-3′ abstraction in *22d*. The extra stability of *22d* could also have been due to steric reasons, that is, that the H-3′ on the β face was less accessible to attack by a base. That *22b* and *22c* underwent *cis* elimination at a very similar rate is due to the fact that the most acidic protons, H-2′ and H-3′, are on the α face and, therefore, equally susceptible to abstraction by a base, as has been observed in the ring opening of a *lyxo* thiiranium ion by Cl^-. It may be added that the ene-sulfone that was obtained from *22a* and *22b* was identical to that of the product *23* obtained by acetylation and oxidation of *19*. Further work is in progress to employ these reactions in synthetic nucleoside chemistry.

Experimental

^1H and ^{13}C NMR spectra were recorded, in δ scale, using a Jeol FX90 Q Spectrometer at 89.5 and 23.5 MHz, respectively, TMS being used as internal standard for ^1H NMR and $CDCl_3$ = 77.14 ppm or DMSO = 39.38 ppm as references for ^{13}C NMR in $CDCl_3$ and DMSO-d_6 respectively. $^1J_{CH}$ were measured using a gated decou-

Table 3. ^{1}H NMR chemical shifts for adenosine derivatives

Compound	Solvent[a]	H-1′	H-2′	H-3′	H-4′	H-5′	Other
1a	C	6.32 (d)	5.77 (m)	4.46 (m)	4.46 (m)	4.46 (m)	8.67 (s, 1H, H-8), 8.61 (s, 1H, H-2), 7.96–7.32 (m, 10H, arom.), 2.14 (s, 3H, OAc), 2.09 (s, 3H, OAc).
1b	C	7.16 (m)	6.15 (m)	6.39 (m)	5.16 (m)	4.27 (d)	8.69 (s, 1H, H-8), 8.24 (s, 1H, H-2), 7.91–7.26 (m, 10H, arom.), 2.01 (s, 3H, OAc).
2a	C	6.27 (d)	4.36 (m)	4.72 (m)	4.45 (m)	4.45 (m)	8.63 (s, 1H, H-8), 8.47 (s, 1H, H-2), 7.91–7.2 (m, 15H, arom.), 2.11 (s, 3H, OAc).
2b	C	6.47 (d)	4.38 (m)	4.38 (m)	4.38 (m)	4.38 (m)	8.53 (s, 1H, H-8), 8.1 (s, 1H, H-2), 7.95–7.03 (m, 15H, arom.), 2.09 (s, 3H, OAc).
3a	C	6.27 (d)	4.45 (m)	4.65 (m)	4.45 (m)	4.45 (m)	8.65 (s, 1H, H-8), 8.47 (s, 1H, H-2), 7.91–7.08 (m, 14H, arom.), 2.31 (s, 3H, methyl), 2.09 (s, 3H, OAc).
3b	C	6.43 (d)	4.27 (m)	4.27 (m)	4.27 (m)	4.27 (m)	8.53 (s, 1H, H-8), 8.08 (s, 1H, H-2), 7.92–7.26 (m, 14H, arom.), 2.25 (s, 3H, methyl), 2.07 (s, 3H, OAc).
4a	C	6.32 (d)	4.51 (m)	4.81 (m)	4.51 (m)	4.51 (m)	8.63 (s, 1H, H-8), 8.45 (s, 1H, H-2), 7.93–7.16 (m, 14H, arom.), 2.42 (s, 3H, methyl), 2.09 (s, 3H, OAc).
4b	C	6.47 (d)	4.19 (m)	4.83 (m)	4.24 (m)	4.24 (m)	8.59 (s, 1H, H-8), 8.08 (s, 1H, H-2), 7.92–7.05 (m, 14H, arom.), 2.19 (s, 3H, methyl), 2.09 (s, 3H, OAc).
5a	C	6.29 (d)	4.5 (m)	4.72 (m)	4.5 (m)	4.5 (m)	8.65 (s, 1H, H-8), 8.51 (s, 1H, H-2), 7.96–7.24 (m, 14H, arom.), 2.11 (s, 3H, OAc).
6a	C	6.35 (d)	4.5 (m)	4.8 (m)	4.5 (m)	4.5 (m)	8.59 (s, 1H, H-8), 8.46 (s, 1H, H-2), 7.91–7.15 (m, 14H, arom.), 2.11 (s, 3H, OAc).
6b	C	6.5 (d)	4.5 (dd)	4.85 (m)	4.5 (m)	4.5 (m)	8.55 (s, 1H, H-8), 8.14 (s, 1H, H-2), 7.92–7.0 (m, 14H, arom.), 2.1 (s, 3H, OAc).
7a	C	6.27 (d)	3.88 (dd)	4.49 (dd)	4.72 (m)	4.54 (m)	8.67 (s, 1H, H-8), 8.49 (s, 1H, H-2), 7.82–7.4 (m, 10H, arom.), 2.33 (s, 3H, SMe), 2.09 (s, 3H, OAc).
7b	C	6.59 (d)	3.8 (dd)	4.44 (m)	4.44 (m)	4.44 (m)	8.67 (s, 1H, H-8), 8.2 (s, 1H, H-2), 7.8–7.4 (m, 10H, arom.), 2.09 (s, 3H, SMe), 1.99 (s, 3H, OAc).

Compound	Solvent[a]	H-1′	H-2′	H-3′	H-4′	H-5′	Other
7c	C	6.37 (d)	4.9 (dd)	3.6 (dd)	4.85 (m)	4.5 (m)	8.7 (s, 1H, H-8), 8.43 (s, 1H, H-2), 7.8–7.4 (m, 10H, arom.), 2.23 (s, 3H, SMe), 2.11 (s, 3H, OAc).
7d	C	6.59 (d)	4.44 (m)	4.65 (m)	4.44 (m)	4.44 (m)	8.67 (s, 1H, H-8), 8.35 (s, 1H, H-2), 7.82–7.4 (m, 10H, arom.), 2.29 (s, 3H, SMe), 2.09 (s, 3H, OAc).
8a	C	5.93 (d)	4.44 (m)	4.57 (m)	4.36 (m)	4.04 (m)	8.25 (s, 1H, H-8), 8.04 (s, 1H, H-2), 7.23 (m, 5H, arom.)
8b	C	6.66 (d)	4.62 (dd)	4.84 (dd)	4.13 (dt)	3.79 (m)	8.32 (s, 1H, H-8), 8.09 (s, 1H, H-2), 7.25 (m, 5H, arom.)
8c	C	5.83 (d)	5.13 (dd)	3.96 (dd)	4.64 (m)	4.04 (m)	8.33 (s, 1H, H-8), 7.9 (s, 1H, H-2), 7.4–7.15 (m, 5H, arom.)
9a	C	5.88 (d)	4.4 (m)	4.4 (m)	4.4 (m)	4.01 (m)	8.25 (s, 1H, H-8), 8.05 (s, 1H, H-2), 7.33–7.03 (m, 4H, arom.), 2.29 (s, 3H, methyl).
9b	C	6.48 (d)	4.14 (m)	4.8 (dd)	4.14 (m)	4.14 (m)	8.18 (s, 1H, H-8), 8.1 (s, 1H, H-2), 7.03 (m, 4H, arom.), 2.27 (s, 3H, methyl).
9c	C	5.82 (d)	5.07 (dd)	3.88 (dd)	4.62 (m)	4.08 (m)	8.3 (s, 1H, H-8), 7.87 (s, 1H, H-2), 7.4 (m, 4H, arom.), 2.35 (s, 3H, methyl).
10a	D	6.17 (d)	4.76 (m)	4.76 (m)	4.51 (m)	3.9 (m)	8.34 (s, 1H, H-8), 8.18 (s, 1H, H-2), 7.28 (m, 4H, arom.), 2.31 (s, 3H, methyl).
10b	D	6.68 (d)	4.54 (dd)	4.9 (dd)	4.16 (m)	3.9 (m)	8.29 (s, 1H, H-8), 8.13 (s, 1H, H-2), 7.24 (m, 4H, arom.), 2.32 (s, 3H, methyl).
10c	D	6.22 (d)	5.12 (dd)	4.34 (m)	4.71 (m)	3.9 (m)	8.49 (s, 1H, H-8), 8.17 (s, 1H, H-2), 7.39 (m, 4H, arom.), 2.38 (s, 3H, methyl).
11a	C	5.85 (d)	4.32 (dd)	4.6 (m)	4.42 (m)	4.06 (m)	8.27 (s, 1H, H-8), 7.96 (s, 1H, H-2), 7.24 (m, 4H, arom.)
11b	C	6.53 (d)	4.23 (m)	4.74 (dd)	4.15 (m)	3.99 (m)	8.18 (s, 1H, H-8), 8.12 (s, 1H, H-2), 7.16 (m, 4H, arom.)
11c	C	5.78 (d)	5.07 (dd)	4.26 (m)	4.56 (m)	4.05 (m)	8.21 (s, 1H, H-8), 7.9 (s, 1H, H-2), 7.2 (m, 4H, arom.)
12a	C	5.96 (d)	4.76 (m)	4.53 (m)	4.53 (m)	4.04 (m)	8.25 (s, 1H, H-8), 7.98 (s, 1H, H-2), 7.25 (m, 4H, arom.)
12b	C	6.58 (d)	4.4 (m)	4.86 (dd)	4.2 (dt)	4.01 (t)	8.19 (s, 1H, H-8), 8.13 (s, 1H, H-2), 7.25 (m, 4H, arom.)
12c	C	5.89 (d)	5.07 (dd)	3.94 (dd)	4.76 (d)	4.05 (m)	8.31 (s, 1H, H-8), 8.08 (s, 1H, H-2), 7.38 (m, 4H, arom.)

Compound	Solvent[a]	H-1′	H-2′	H-3′	H-4′	H-5′	Other
13a	C	5.95 (d)	4.07 (m)	4.49 (m)	4.49 (m)	4.07 (m)	8.3 (s, 1H, H-8), 8.07 (s, 1H, H-2), 2.17 (s, 3H, SMe).
13b	C	6.53 (d)	3.83 (dd)	4.67 (dd)	4.17 (m)	4.01 (m)	8.27 (s, 1H, H-8), 8.23 (s, 1H, H-2), 2.13 (s, 3H, SMe).
13c	C	5.95 (d)	4.99 (dd)	3.6 (dd)	4.58 (m)	3.95 (m)	8.28 (s, 1H, H-8), 8.08 (s, 1H, H-2), 2.35 (s, 3H, SMe).
13d	C	6.46 (d)	4.7 (dd)	3.75 (dd)	4.0 (m)	4.0 (m)	8.35 (s, 1H, H-8), 8.26 (s, 1H, H-2), 2.31 (s, 3H, SMe).
14	C	6.72 (dd)	–	6.26 (t)	5.12 (dt)	3.99 (dd) 3.8 (dd)	8.14 (s, 1H, H-8), 7.8 (s, 1H, H-2), 7.21 (s, 5H, arom.)
15	C	6.78 (dd)	–	6.26 (dd)	4.98 (m)	3.62 (m)	8.23 (s, 1H, H-8), 8.08 (s, 1H, H-2), 7.14 (s, 4H, arom.) 2.25 (s, 3H, methyl).
16	C	6.68 (dd)	–	6.05 (t)	5.11 (m)	3.95 (m)	8.17 (s, 1H, H-8), 7.87 (s, 1H, H-2), 7.25 (s, 4H, arom.) 2.28 (s, 3H, methyl).
17	C	6.68 (dd)	–	6.36 (t)	5.12 (dt)	4.01 (dd) 3.85 (dd)	8.15 (s, 1H, H-8), 7.91 (s, 1H, H-2), 7.13 (s, 4H, arom.)
18	C	6.66 (dd)	–	6.41 (t)	5.15 (dt)	4.05 (dd) 3.86 (dd)	8.17 (s, 1H, H-8), 7.79 (s, 1H, H-2), 7.12 (m, 4H, arom.)
19	C	6.85 (dd)	–	5.88 (dd)	5.12 (m)	3.94 (dd) 3.76 (dd)	8.23 (s, 1H, H-8), 8.11 (s, 1H, H-2), 2.38 (s, 3H, SMe).
20a	C	6.18 (d)	3.82 (dd)	5.36 (dd)	4.7 (dt)	4.44 (d)	8.37 (s, 1H, H-8), 8.1 (s, 1H, H-2), 2.35 (s, 3H, SMe), 2.12 (s, 3H, OAc), 2.04 (s, 3H, OAc).
20b	C	6.55 (d)	5.15 (dd)	5.6 (dd)	4.46 (m)	4.46 (m)	8.3 (s, 1H, H-8), 7.98 (s, 1H, H-2), 3.28 (s, 3H, $MeSO_2$), 2.19 (s, 3H, OAc), 2.09 (s, 3H, OAc).
21a	C	6.2 (d)	3.91 (dd)	4.48 (dd)	4.71 (m)	4.75 (dd) 4.5 (dd)	8.37 (s, 1H, H-8), 8.22 (s, 1H, H-2), 2.34 (s, 3H, SMe), 2.13 (s, 3H, OAc).
21b	C	6.58 (d)	3.84 (dd)	4.64 (dd)	4.33 (m)	4.60 (dd) 4.43 (dd)	8.3 (s, 1H, H-8), 8.0 (s, 1H, H-2), 2.13 (s, 3H, SMe), 2.09 (s, 3H, OAc).
21c	C	6.26 (d)	5.0 (dd)	3.57 (dd)	4.84 (m)	4.51 (dd) 4.47 (dd)	8.37 (s, 1H, H-8), 8.13 (s, 1H, H-2), 2.24 (s, 3H, SMe), 2.14 (s, 3H, OAc).
21d	C	6.55 (d)	4.72 (dd)	3.65 (dd)	4.15 (m)	4.5 (m)	8.37 (s, 1H, H-8), 8.14 (s, 1H, H-2), 2.31 (s, 3H, SMe), 2.14 (s, 3H, OAc).
22a	C	6.41 (d)	4.6 (dd)	4.89 (dd)	4.35 (m)	4.19 (m)	7.96 (s, 2H, H-8 & H–2), 2.97 (s, 3H $MeSO_2$), 1.78 (s, 3H, OAc).

Compound	Solvent[a]	H-1′	H-2′	H-3′	H-4′	H-5′	Other
22b	C	6.75 (d)	4.65 (dd)	5.18 (dd)	4.41 (m)	4.68 (dd) 4.55 (dd)	8.29 (s, 1H, H-8), 8.06 (s, 1H, H-2), 3.04 (s, 3H, $MeSO_2$), 2.18 (s, 3H, OAc).
22c	C	6.26 (d)	5.31 (dd)	4.27 (dd)	4.88 (m)	4.8 (dd) 4.7 (dd)	8.35 (s, 1H, H-8), 8.18 (s, 1H, H-2), 3.2 (s, 3H, $MeSO_2$), 2.12 (s, 3H, OAc).
22d	C	6.46 (d)	5.23 (dd)	4.51 (dd)	4.85 (m)	4.67 (dd) 4.54 (dd)	8.31 (s, 1H, H-8), 8.06 (s, 1H, H-2), 3.21 (s, 3H, $MeSO_2$), 2.15 (s, 3H, OAc).
23	C	7.25 (dd)	–	7.32 (dd)	5.34 (m)	4.55 (dd) 4.43 (dd)	8.32 (s, 1H, H-8), 8.09 (s, 1H, H-2), 2.87 (s, 3H, $MeSO_2$), 2.15 (s, 3H, OAc).
24	C	7.15 (dd)	7.09 (dd)	–	5.45 (m)	4.49 (d)	8.31 (s, 1H, H-8), 8.06 (s, 1H, H-2), 3.19 (s, 3H, $MeSO_2$), 2.04 (s, 3H, OAc).

[a]Solvents: C ($CDCl_3$); D (DMSO–d_6).

Table 4. Spin-spin coupling constants (H_z)

Compound	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{1',3'}$	$J_{1',4'}$	$J_{4',5'a}$	$J_{4',5'b}$	$J_{5'a,5'b}$
8a	6.6							
8b	6.8	10.7	8.1			3.1	3.1	
8c	8.1	10.7	8.6					
9a	7.1							
9b	7.1	10.5	8.8					
9c	7.8	10.8	8.7					
10a	6.1							
10b	6.6	10.9	8.8					
10c	7.1	9.4						
11a	7.3	6.8						
11b	7.3	10.3	8.8					
11c	7.8	10.7						
12a	6.8							
12b	7.3	9.8	8.5			3.2	3.2	
12c	7.6	10.3	8.5					
13a	6.6							
13b	7.1	10.6	9.2			2.0	2.0	12.8
13c	7.7	10.3	8.6			2.0	2.0	
13d	6.0	9.0						
14			1.9	1.7	3.2	2.3	2.7	12.8
15			1.6	1.5	2.7			
16			1.7	1.7	3.4			
17			1.5	1.7	3.4	2.2	2.7	12.2
18			1.7	1.7	3.6	2.2	2.7	13.2
19			1.5	1.5	3.2	2.5	2.5	12.5
20a	2.9	1.6	3.7			5.7	5.7	
20b	4.7	1.2	3.2					

Compound	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{1',3'}$	$J_{1',4'}$	$J_{4',5'a}$	$J_{4',5'b}$	$J_{5'a,5'b}$
21a	3.3	1.8	3.8			4.4	4.9	12.0
21b	7.1	9.5	8.6			2.7	4.8	12.4
21c	4.2	4.6	6.5			3.8	3.8	12.4
21d	5.1	5.3	6.0					
22a	4.7	1.6	3.5					
22b	7.7	9.3	8.8			2.6	5.2	12.5
22c	6.9	7.9	7.3					11.9
22d	5.5	5.7	7.7			2.9	5.5	12.3
23			1.5	1.5	3.2	4.5	3.6	12.3
24	2.9	($J_{2',4'}$=1.8 Hz)				3.3	3.3	

pling sequence. ^{1}H resonances were assigned by homodecoupling, and ^{13}C by selective decoupling. 2D ^{1}H-^{13}C correlation spectra were recorded on a Jeol GX 270 spectrometer using a highly modified Plexus system which was supplied by Jeol AB, Stockholm. UV spectra of all starting materials and reaction products were compared using a Cary/Varian 2200 spectrometer in order to establish that the aglycone was unaltered during the course of the reactions described herein. Molecular ions of all compounds were obtained by chemical ionization spectroscopy using C_4H_{10} as carrier gas. TLC was carried out using precoated silica gel F_{254} plates in the following solvent systems: (a) ethyl acetate/hexane 1:1, v/v; (b) ethyl acetate/hexane 2:1, v/v; (c) ethyl acetate/ethanol 95:5, v/v; (d) chloroform/ethanol 9:1, v/v; (e) chloroform/ethyl acetate 85:15, v/v; (f) 7% ethanol/chloroform, v/v. The short column chromatographic separations were carried out using Merck G60 silica gel with petroleum ether of b.p. 60–80 °C, dichloromethane and chloroform as eluents; stepwise gradients of ethanol in chloroform were used to affect the separations. Pyridine was dried over calcium hydride and stored over activated molecular sieves (4Å). Methanesulfenyl chloride was prepared by chlorination of dimethyl disulfide with chlorine and stored as a 50% solution in dichloromethane at −20 °C. All other sulfenyl chlorides were prepared by chlorination of the corresponding thiol with chlorine gas and stored at 4 °C[12]. 9-(2′,5′-Di-*O*-acetyl-3′-deoxy-3′-bromo-β-D-xylofuranosyladenine was prepared according to Norman and Reese.[13]

6-N-dibenzoyl-9-(2′,5′-di-O-acetyl-3′-deoxy-3′-bromo-β-D-xylofuranosyl)adenine 1a. 9-(2′,5′-Di-*O*-acetyl-3′-deoxy-3′-bromo-β-D-xylofuranosyl)-adenine (4.5 g, 10.8 mmol) was dissolved in dry pyridine (100 ml) and freshly distilled benzoyl chloride (4.6 g, 32.4 mmol) added. The mixture was stirred magnetically for 2 h by which time TLC (system f) showed the reaction to be complete. The mixture was worked up by pouring into a saturated solution of sodium hydrogen carbonate and the products were extracted with dichloromethane (4×50 ml). All solvents were removed by evaporation and the remaining traces of pyridine removed by several coevaporations with toluene. The residue was purified by silica gel chromatography, loading the column with a 1:1 mixture of dichloromethane/petroleum ether, and eluting with dichloromethane and then chloroform. The product *2* was isolated as a chromatographically pure glass in 95% yield (6.4 g) which was recrystallised from ethanol.

6-N-dibenzoyl-9-(5′-O-acetyl-2′,3′-dideoxy-β-D-glycero-pent-2-enofuranosyl)adenine 1b. The dibenzoyl derivative *1a* (4.0 g, 6.4 mmol) was dissolved in tetrahydrofuran (30 ml) and an equal volume of ethanol added and stirred mechanically. Activated zinc (4.4 g, 67 mmol) was added followed by glacial acetic acid (0.88 g, 14.6 mmol). After 1 h, TLC (system a) showed complete reaction, the mixture was filtered through celite, poured into a saturated sodium bicarbonate solution and extracted with dichlormethane (4×50 ml), evaporated to dryness and purified by silica gel chromatography, eluting with dichloro-

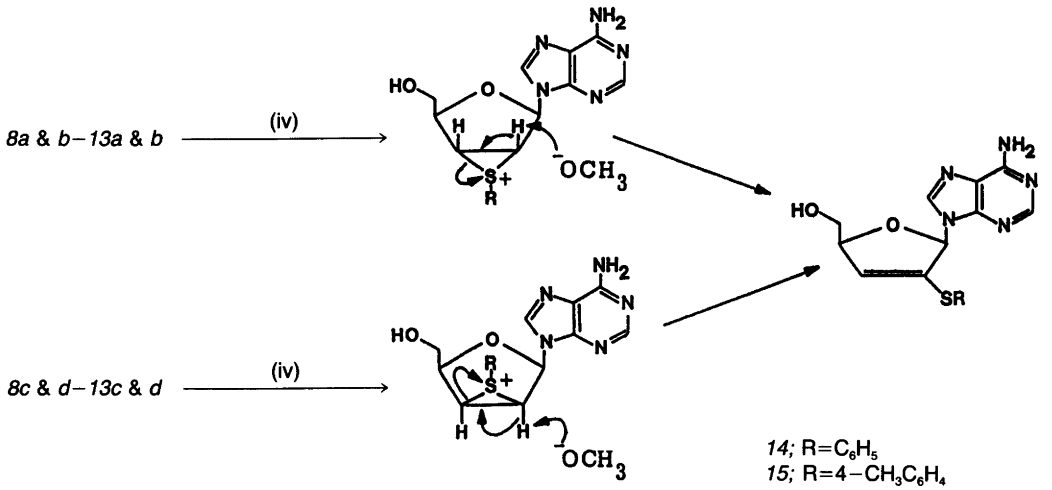
Table 5. ^{13}C NMR chemical shifts of adenosine derivatives ($^{1}J_{CH}$ in Hz)[a]

Compound	C-1′	C-2′	C-3′	C-4′	C-5′
1b	88.8 (170)	126.2 (177)	133.9 (174)	85.4 (151)	64.7 (150)
2a	87.6	–	–	79.2	63.2
2b	85.4 (168)	60.3 (148)	57.3 (161)	83.1 (154)	61.8 (150)
3a	87.7 (170)	60.0 (153)	61.2 (164)	79.1 (152)	63.4 (151)
3b	85.9 (168)	60.5 (150)	57.5 (163)	83.4 (156)	62.1 (149)
4a	88.3 (171)	58.9 (156)	61.6 (164)	79.4 (150)	63.2 (151)
4b	85.7 (168)	59.2 (150)	57.9 (171)	83.3 (151)	62.1 (152)
5a	87.6 (168)	59.9 (154)	61.2 (166)	79.2 (152)	63.3 (150)
6b	85.4 (168)	58.3 (149)	58.1 (160)	83.3 (157)	62.0 (151)
8a	88.4 (169)	57.0 (151)	58.9 (160)	81.1 (149)	62.1 (143)
8b	83.7 (173)	58.0 (148)	57.5 (158)	84.7 (150)	59.1 (140)
9a	85.9 (167)	56.9 (153)	60.3 (166)	80.2 (150)	60.9 (144)
9b	85.7 (168)	60.5 (146)	55.9 (154)	85.8 (151)	58.9 (144)
9c	91.0 (166)	62.0 (162)	57.5 (144)	82.5 (151)	62.8 (143)
10a	86.6 (170)	56.5 (153)	61.1 (165)	80.5 (152)	61.1 (142)
10b	83.6 (171)	58.1 (148)	57.7 (158)	84.8 (151)	59.2 (141)
10c	87.5 (169)	62.4 (171)	54.1 (148)	80.7 (146)	61.8 (143)
11a	88.1 (170)	57.2 (150)	58.6 (160)	80.9 (149)	61.8 (140)
11b	85.6 (170)	56.8 (149)	60.7 (158)	86.2 (148)	59.4 (144)
12a	89.0 (166)	56.0 (143)	61.1 (164)	81.0 (148)	61.4 (150)
12b	82.3 (171)	56.3 (145)	57.3 (158)	84.7 (151)	59.2 (143)
12c	87.3 (168)	62.1 (167)	52.8 (152)	80.3 (155)	61.7 (142)
13a	86.2 (166)	55.8 (149)	61.0 (164)	80.8 (151)	61.0 (143)
13b	85.9 (170)	58.9	57.1	86.6 (151)	58.9
13c	90.9 (165)	63.2 (165)	54.8 (143)	82.4 (145)	62.6 (141)
14	90.0 (169)	–	129.2	88.6 (148)	63.3 (142)
15	87.8	138.3	130.9 (175)	87.8	62.5
16	90.2 (170)	–	129.1	88.6 (146)	63.3 (143)
17	91.3	–	133.2	88.2	66.3
18	90.2 (169)	–	133.0	88.0 (150)	62.9 (143)
19	89.8	135.3	122.1	88.4	63.1
20a	88.9	55.7	76.7	78.9	61.6
21a	88.8	59.6	61.9	79.4	63.5
21b	85.0 (169)	58.2 (145)	58.7 (155)	83.2 (150)	62.0 (150)
21c	90.9 (172)	63.8 (168)	55.4 (152)	79.4 (152)	64.1 (148)
22a	82.6	74.3	56.2	80.4	62.7
22b	81.8 (168)	69.7 (146)	53.2 (159)	83.2 (154)	61.3 (148)
22c	89.1	57.7	69.2	–	62.8
22d	86.0	57.7	69.1	75.3	64.3
23	85.7 (172)	138.3	144.1 (180)	83.7 (154)	63.8 (150)

[a]Spectra were recorded in the same solvent as for ^{1}H NMR except for *8b, 9a, 12a, 12c, 13d* and *23* which were recorded in DMSO–d_6.

methane/chloroform mixture, 1:1, v/v. Recrystallisation from ethanol gave the product *1b* in 93 % yield (2.9 g).

Reaction of (1b) with sulfenyl chlorides (general procedure). Compound *1b* (1 g, 2.07 mmol) was coevaporated to dryness with pyridine and then dissolved in pyridine (20 ml). The solution was cooled to 0 °C and the appropriate sulfenyl chloride (10 equivalents) added. The reactions were monitored by TLC (system b), and were complete after 8 to 20 h at 0 °C. The reactions were

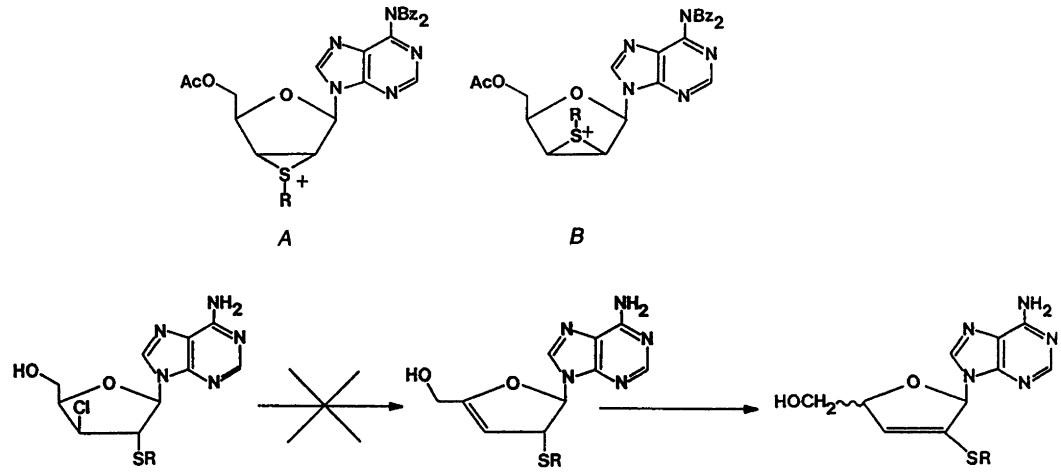


(iv) NaOMe (5 eq. 0.25 M) in methanol, 20 °C, 24 h.

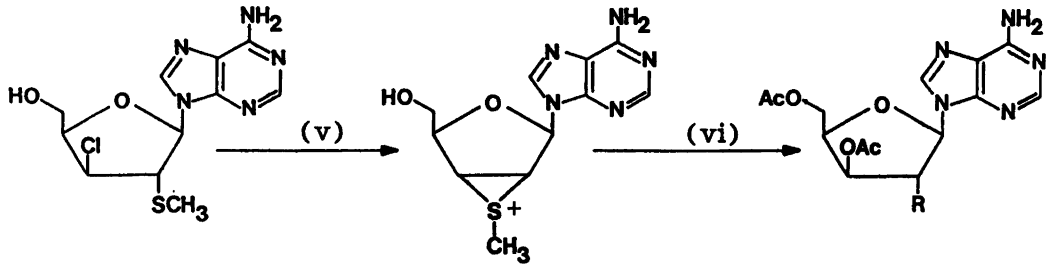
Scheme 2.

quenched by pouring into a saturated solution of sodium hydrogen carbonate, and the products extracted with dichloromethane (4×50 ml). The organic layers were pooled and all solvents removed, the remaining traces of pyridine being removed by coevaporation with toluene.

The product mixtures were isolated by chromatography on silica gel, the column being prepared with dichloromethane and prewashed with petroleum ether. The mixture was applied to the column as a solution in dichloromethane/petroleum ether mixture (1:1, v/v) and the lipophilic by-products were eluted with this solvent mixture. The product mixtures was then eluted with pure dichloromethane and finally a 1:1 mixture (v/v) of dichloromethane and chloroform. The product mixtures were analysed by NMR and used directly for further investigation. Attempts



Scheme 3.



13a

20a; R=SCH_3
20b; R=SO_2CH_3

(v) NaOAc (5 eq.) in monoglyme/water (95:5, v/v) 100 °C, 3 h.
(vi) Acetic anhydride (3 eq.) in dry pyridine, 2 h.

Scheme 4.

were made to separate individual components, but were unsuccessful in all but a few cases.

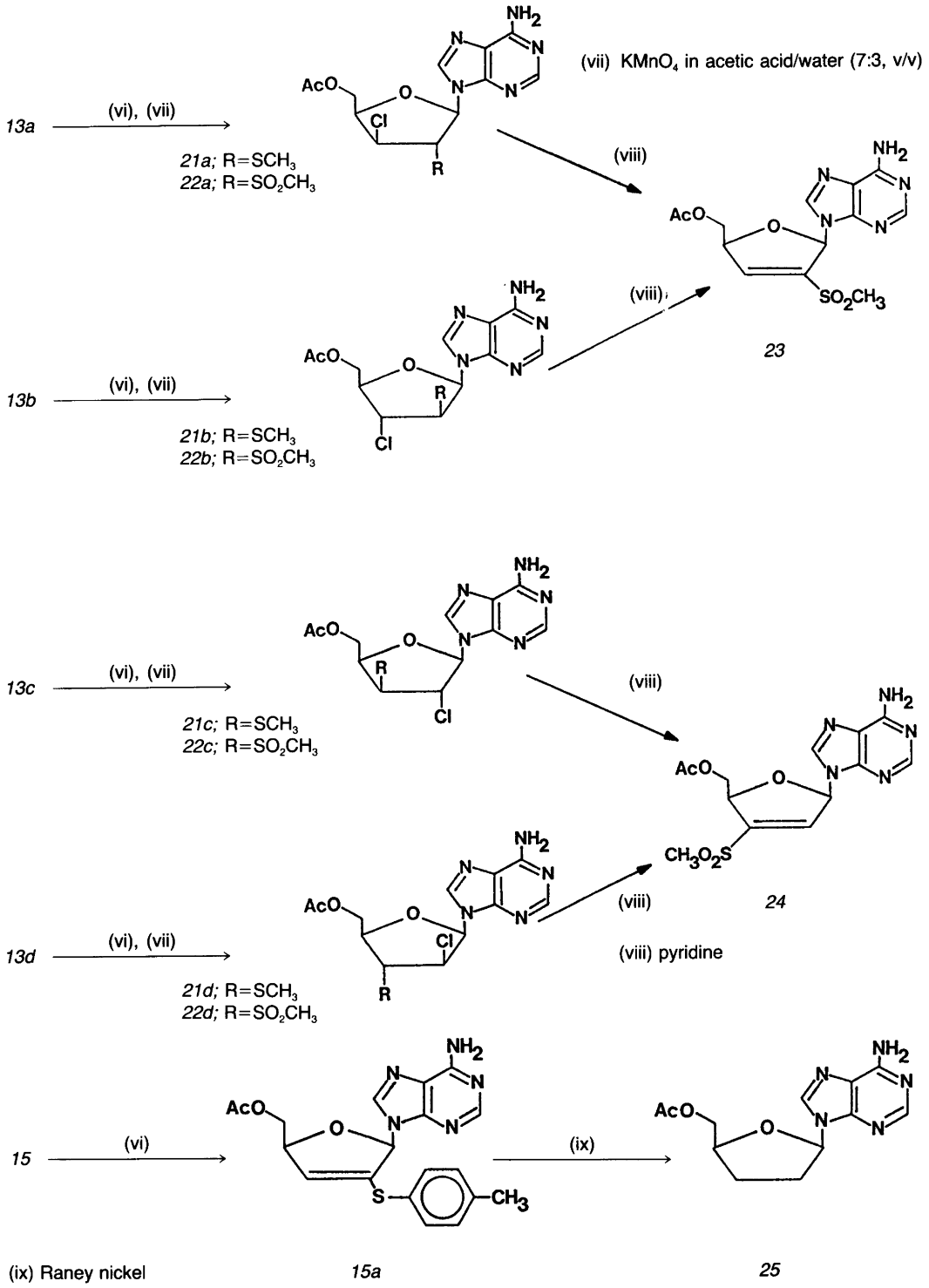
Reactions of *1b* with benzene, *p*-toluene, *o*-toluene, *p*-chlorobenzene, *o*-chlorobenzene and methanesulfenyl chlorides gave a mixture of *2a-c*, *3a-c*, *4a-c*, *5a-c*, *6a-c* and *7a-d* in 93, 87, 90, 88, 91 and 89 % yields respectively.

Deprotection of reaction mixtures 2 to 7 (general procedure). The mixtures of addition products obtained from the reaction of *1b* (2.07 mmol) with the sulfenyl chloride were dissolved in methanol (20 ml) and methanolic ammonia solution (20 equivalents) added. The mixture was stirred at 20 °C until TLC (system d) showed the reaction to be complete. The mixture was then evaporated to dryness and the mixture of products isolated by chromatography, loading the column using 2 % ethanol/chloroform mixture. After removal of the lipophilic by-products and benzamide with 3 % ethanol in chloroform, the desired mixture was eluted with 8 % ethanol in chloroform. The mixtures were examined by NMR for their composition then further separation was attempted by column chromatography. Columns were prepared using 2 % ethanol in chloroform, the products being separated by stepwise increase in the polarity of the solvent from 2 % ethanol to 8 % ethanol in chloroform by 0.5 % increments. The appropriate fractions were pooled and evaporated to dryness. The yields and relative abundancies of the products are shown in Table 1.

Preparation of 20a. Compound *13a* (113 mg, 0.36 mmol) and sodium acetate (200 mg) were dissolved in 95 % aqueous 2-methoxyethanol (monoglyme) (10 ml) and the reaction mixture was heated at 100–110 °C for 3 h. Then the reaction mixture was evaporated *in vacuo* coevaporated with water and the residue extracted several times with hot ethyl acetate. Evaporation of these extracts gave a syrup which was coevaporated with dry pyridine (3×5 ml). The residue was again dissolved in pyridine (5 ml), acetic anhydride (0.26 ml) was added and the mixture kept stirring for 3 h. The reaction was subsequently worked up in the usual way. Purification over a short column of silica gel gave *20a*, 40 mg (29 % yield).

Preparation of 20b. Compound *20a* (10 mg, 0.026 mmol) was dissolved in acetic acid solution (2 ml, 7:3, v/v) and potassium permanganate (12.4 mg, 3.3 equivalents) was added. The reaction was worked up using a procedure as described for the preparation of *22a*. The product was subsequently purified over a short column of silica gel giving 2.7 mg of *20b* (25 % yield) and 6 mg of a substance identical to *23*.

Conversion of 15a to 25. Compound *15a* (50 mg, 0.09 mmol) was dissolved in ethanol (20 ml) and freshly prepared Raney nickel (50 mg) was added; after stirring for 6 h, an additional lot (50 mg) was added and then the reaction mixture was refluxed for 3 h. It was then filtered through cel-


13a
(vi), (vii)
21a; R=SCH3
22a; R=SO2CH3
(vii) KMnO4 in acetic acid/water (7:3, v/v)
(viii)
13b
(vi), (vii)
21b; R=SCH3
22b; R=SO2CH3
(viii)
23
13c
(vi), (vii)
21c; R=SCH3
22c; R=SO2CH3
(viii)
13d
(vi), (vii)
21d; R=SCH3
22d; R=SO2CH3
(viii)
24
(viii) pyridine
15
(vi)
(ix)
(ix) Raney nickel
15a
25

ite and the solvents evaporated *in vacuo*. The residue was subsequently loaded on a preparative TLC (chloroform/methanol, 9:1, v/v). The major band was excised and extracted to yield 12 mg (48 %) of *25* which was identical to an authentic specimen, m.p.: 163–164 °C; $[\alpha]_D^{20} = -7°$ (*c* 0.5, ethanol). ^{1}H NMR ($CDCl_3$ + CD_3OD): 8.35 (*s*, 1H) H-8; 8.09 (*s*, 1H) H-2; 6.31 (*t*, 1H, $J_{1',2'} = 4.8$ Hz); 4.34 (*m*, 3H) H-4', H-5'a and H-5'b; 2.60 (*m*, 2H) H-2'a and 2'b; 2.16 (*m*, 2H) H-3'a and 3'b; 2.09 (*s*, 3H) acetate. U.V.: λmax 255 nm (= 12300) (pH 7), 253 (pH 2), 255 (pH 12).

Reaction of compounds 8a-d to 13a-d with sodium methoxide (general procedure). The mixtures of isomers (1 mmol when combined) were dissolved in dry methanol (7.5 ml), and 2 *M* sodium methoxide in dry methanol (5 equivalents) was added, giving a final concentration of 0.25 *M*. The reaction was kept free of moisture and stirred for between 24 and 48 h. Compound *12c* required 8 days for complete reaction when treated with sodium methoxide. The product was obtained in 36 % yield and adenine was also isolated from this reaction mixture as the depurination product. Elevating the temperature to 60 °C reduced the reaction time to 6 h. When the reactions were complete, as judged by TLC (system c), the pH was adjusted to 6.5 using acetic acid, and the mixture then evaporated to dryness, and coevaporated with methanol. The nonvolatile residues were then suspended in 5 % ethanolic chloroform and applied to a short silica gel column. The products were isolated by eluting with 5–10 % ethanolic chloroform. After evaporation to dryness and precipitation from petroleum ether, they were characterised by NMR. Yields for these reactions are reported in Table 2.

Conversion of 13a to 21a. Compound *13a* (730 mg, 2.3 mmol) was coevaporated with dry pyridine (2×10 ml), the residue was dissolved in pyridine (25 ml) and acetic anhydride (0.32 ml) was added. The reaction mixture was stirred at 20 °C for 3 h. Then methanol (2 ml) was added and, after 15 min, the reaction mixture was poured into saturated sodium hydrogen carbonate solution and extracted with chloroform (3×40 ml). The organic layer was evaporated *in vacuo* and the residue was coevaporated with toluene. The residue was purified by short column chromatography using chloroform and then with a 3 % methanol/chloroform mixture as eluent. The appropriate fractions were collected and evaporated to give a white foam. Crystallisation from ethyl acetate/hexane mixture (ca. 2:3, v/v) gave 705 mg (85 % yield) of *21a* m.p. 137–138 °C.

Preparation of 21b and 21d. A mixture of *13b* and *d* in 8:2 ratio (by NMR) (85 mg, 0.21 mmol) was acetylated, using conditions as described for the preparation of *21a*, to give a mixture of *21b* and *21d*, 90 mg (96 % yield).

Preparation of 21c. Compound *13c* (16 mg, 0.05 mmol) was acetylated using conditions as described for the preparation of *21a* to give 12 mg of *21c* (66 % yield).

Conversion of 21a to 22a. Compound *21a* (243 mg, 0.63 mmol) was dissolved in acetic acid solution (5 ml, 7:3, v/v) and an aqueous solution (5 ml) of potassium permanganate (177 mg, 1.6 equivalents) was added at 20 °C whilst stirring. The purple colour was immediatly discharged. After 15 min, ethanol (5 ml) was added and the reaction mixture was concentrated under vaccum at the *lowest temperature possible*. The residues were coevaporated two times with an acetonitrile/toluene mixture. The residue was diluted with an acetonitrile/chloroform mixture and washed with dilute sodium hydrogen carbonate solution containing ~5 % EDTA. The organic layer was then evaporated to dryness and the residue was purified using a short column of silica gel with dichloromethane and then 5 % methanol/chloroform mixture as eluant, giving *22a* in a quantitative yield as a white powder which was crystallised from methanol. Compound *22a* was unstable and had to be stored at −20 °C. In solution, it was spontaneously converted to *23*.

Preparation of 22b and 22d. A mixture of acetylated compounds, *21b* and *21d*, (58 mg, 0.16 mmol) was oxidised by potassium permanganate (32 mg, 1.25 equivalents). Column chromatographic separation using a gradient 2 % methanol/chloroform to 5 % methanol/chloroform gave two fractions containing 4 mg of *22d* (7 %) and 50 mg of *22b* (87 %).

Compound 22c. Compound *21c* (8 mg, 0.022 mmol) was oxidised by potassium permanganate (4.5 mg), using the conditions described for the preparation of *22a*, to give 4 mg (47 %) of *22c*.

Preparation of 23. Compound *21a* (203 mg, 0.52 mmol) was heated overnight at 60 °C in a mixture of dioxane/pyridine (4 ml, 8:2, v/v). All solvents were then removed *in vacuo* and the residue purified by silica gel filtration with dichloromethane and then with 5 % methanol in chloroform to give 152 mg (75 % yield) of *23* which was recrystalised from methanol; mp 173 °C.

Preparation of 24. Compound *22c* (4 mg) and *22d* (2 mg) were converted individually to *24* in 96 and 95 % yield, respectively, using conditions described for the preparation of *23*. Product *24* was crystallized from methanol. mp 164–165 °C.

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