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Fluorinated Alcohol Mediated Displacement of the C_{10} Acetoxy Group of Benzo[*a*]pyrene-7,8,9,10-tetrahydrotetraol Tetraacetates: A New Route to Diol Epoxide−Deoxyguanosine Adducts

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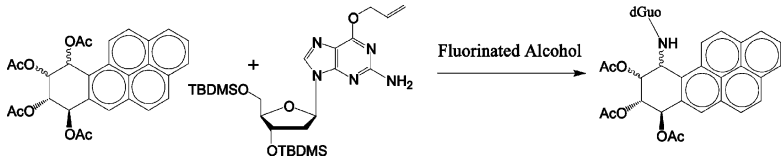

We describe a novel trifluoroethanol (TFE) or hexafluoropropan-2-ol (HFP) mediated substitution reaction of the bay-region C_{10} acetoxy group in four stereoisomeric 7,8,9,10-tetraacetoxy-7,8,9,10-tetrahydrobenzo[*a*]pyrenes (tetraol tetraacetates, two pairs of cis and trans isomers at the 9,10 positions) by the exocyclic N^2-amino group of O^6-allyl-3′,5′-di-*O*-(*tert*-butyldimethylsilyl)-2′-deoxyguanosine (**3**). The tetraacetates are derived from cis and trans hydrolysis of (±)-7*β*,8α-dihydroxy-9*β*,10*β*-epoxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene (B[*a*]P DE-1) and of (±)-7*β*,8α-dihydroxy-9α,10α-epoxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene (B[*a*]P DE-2) at C-10 followed by acetylation. Excellent yields and high regioselectivity were observed. Similar cis/trans product ratios were observed for each set of cis and trans tetraol tetraacetates derived from DE-1 (∼75/25) and from DE-2 (∼67/33) in HFP. This strongly suggests that the substitution proceeds via an S_N1 mechanism involving a carbocation intermediate that is common to the cis and trans tetraacetates. Since it is likely that the cis and trans products from **3** arise from different conformations of the carbocation, its lifetime must be sufficiently long to permit conformational equilibration before its capture by the purine nucleophile. The corresponding reaction of (±)-9α-bromo-7*β*,8α,10*β*-triacetoxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene with **3** in HFP was highly regio- and stereoselective and gave exclusively trans 10*β*-adducts. This newly developed substitution reaction provides an attractive alternative synthetic strategy for the preparation of polycyclic hydrocarbon adducted oligonucleotide building blocks.

Introduction

The polycyclic aromatic hydrocarbon benzo[*a*]pyrene (B[*a*]P) is one of the most prevalent environmental carcinogens to which humans are exposed.[1] It is metabolized in mammals by the combined action of the cytochrome P450 monooxygenase system and epoxide hydrolase to form two enantiomeric pairs of diastereomeric bay-region 7,8-diol 9,10-epoxides (DEs), referred to as DE-1 (**1**; benzylic C-7 hydroxyl group and 9,10-epoxide are cis) and DE-2 (**2**; benzylic C-7 hydroxyl group and 9,10-epoxide are trans).[2] These DEs are thought to initiate cancer by forming stable DNA adducts, primarily at the exocyclic amino groups of deoxyguanosine (dGuo) and deoxyadenosine (dAdo) by cis and trans opening of the epoxide ring.[3] Subsequent error-prone replication by human DNA polymerases and inac-

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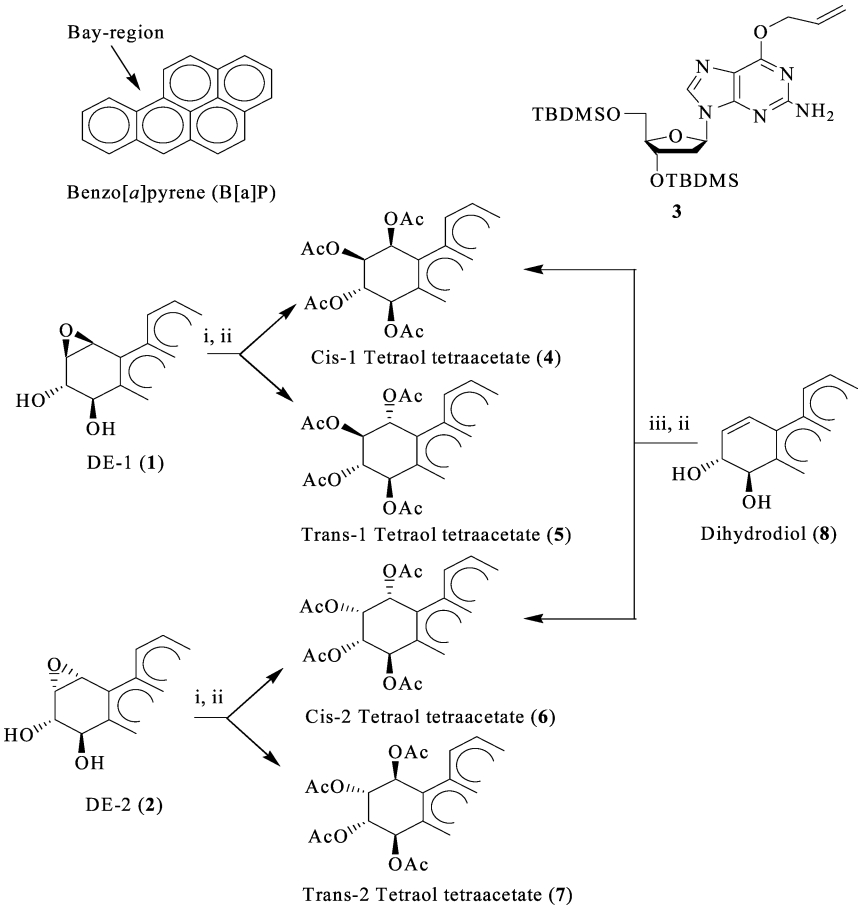
SCHEME 1 [a]



[a] Key: (i) H_3^+O; (ii) Ac_2O/Py; (iii) OsO_4/Py.

curate repair lead to mutant cells, some of which result in tumor formation. The tetrahydrotetraols (Scheme 1) derived from hydrolysis of B[*a*]P DE (**2**) were found to be weaker carcinogens than their parent DE-2.[4] Therefore, the formation of these tetrahydrotetraols is generally considered to be a detoxification process.[4]

For the past several years, the synthesis of oligonucleotides containing site-specific and stereospecific adducts of DEs has become an active area of research. These modified oligonucleotides with a wide variety of sequence contexts have been utilized in structural studies such as NMR solution conformation[5] and X-ray crystallographic analysis.[6] They have also found application in the study of site-specific mutagenicity[7a] and as mechanistic probes for a variety of DNA processing enzymes.[7b,c−12]

Recently, our laboratory developed a convenient method for the synthesis of modified dGuo adducts by direct reaction of O^6-allyl-3′5′-di-*O*-(*tert*-butyldimethylsilyl)-2′-deoxyguanosine (**3**) with B[*a*]P DEs[13−15a] as well as with benzo[*c*]-phenanthrene DEs.[15] Use of the *O*-allyl protection of the O^6-carbonyl group of dGuo not only prevented adduct formation at this position but also increased the nucleophilic reactivity of the N-2 amino group. Choice of the solvent was critical. Dimethylacetamide (DMA)[15a] and fluorinated alcohols were found to be effective solvents for this addition reaction. In particular, fluorinated alcohols such as trifluoroethanol

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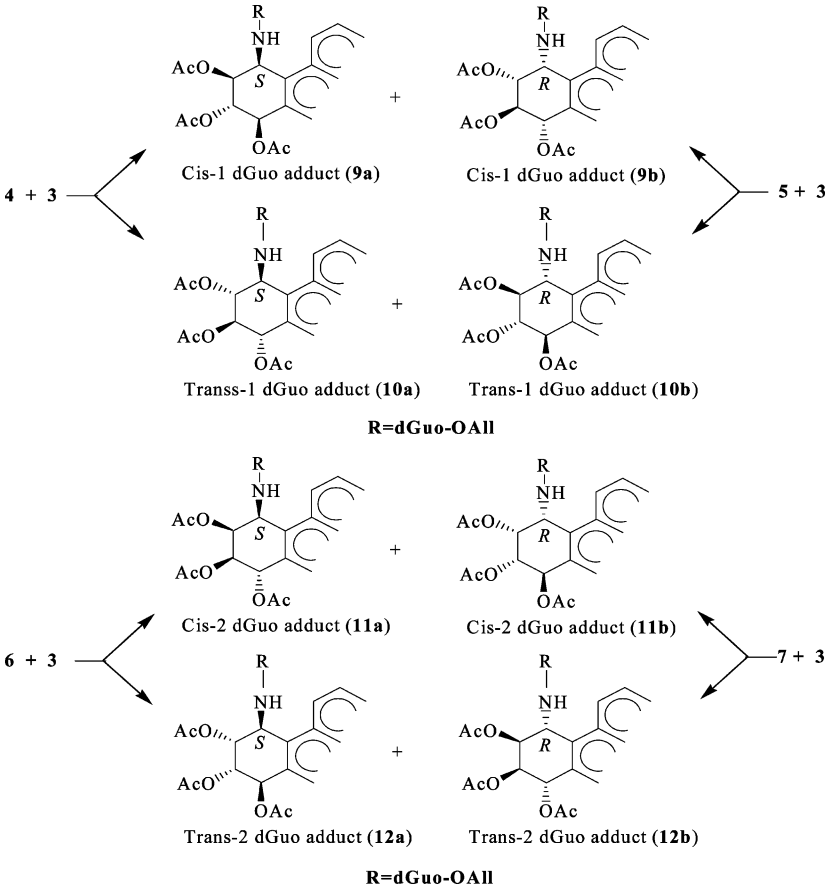
SCHEME 2



(TFE), hexafluoropropan-2-ol (HFP), and perfluoro-*tert*-butanol (PFTB) showed an exceptional ability to catalyze this addition reaction.[13−15b] These alcohols are acidic because of the electron withdrawing nature of fluorine and can catalyze the epoxide opening through their strong hydrogen-bonding capability. Their high polarity, high ionizing power, and low nucleophilicity make them ideal solvents for this type of addition reaction by catalyzing the formation of carbocation intermediates.[16] On the basis of our observations of these fluorinated alcohol-mediated addition reactions of DEs, we envisaged the possibility of regioselective substitution reactions using seemingly inert tetrahydrotetraol derivatives of B[*a*]P. We thought it might be possible to generate a stable carbocation regioselectively at the benzylic C-10 position of the tetrahydrobenzo-ring by introducing a substituent which has a strong ability to hydrogen bond with the fluorinated alcohol. The carbocation formed at the bay-region C-10 benzylic position ($\Delta E_{deloc} = 0.794^{\beta}$) is much more stable and thus more easily formed than the corresponding carbocation at the C-7 benzylic position ($\Delta E_{deloc} = 0.488^{\beta}$).[17] Here we report the first example of such a regioselective substitution reaction between tetrahydrotetraol derivatives of B[*a*]P and the dGuo reactant **3** in fluorinated alcohol solvents.

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TABLE 1. Fluorinated Alcohol Mediated Synthesis of cis- and trans-N^2-dGuo Adducts (yields in %) from Tetraol Tetraacetates Derived from B[*a*]P DE-1 and DE-2 and Bromotriol Triacetate[a]

tetraol tetraacetate	solvent	reaction time (h)	cis-1 adducts **9a** and **9b**		trans-1 adducts **10a**	**10b**
cis-1 (**4**)	HFP	72	76		11	13
trans-1 (**5**)	HFP	16	73		12	14
			cis-2 adducts		trans-2 adducts	
			11a	**11b**	**12a**	**12b**
cis-2 (**6**)	HFP	42	37	31	20	13
	TFE	40	29	25	22	23
trans-2 (**7**)	HFP	14	35	32	18	16
			trans adducts			
			14a		**14b**	
bromotriol triacetate (**13**)	TFE	24	47		53	
	HFP	4	48		52	

[a] The ratio was determined by HPLC (345 nm). Reaction was carried out in a sealed glass tube at 70 °C in a 1:5 molar ratio of the acetate and dGuo reactant (**3**) in fluorinated alcohol (100 molar equiv).

Results and Discussion

Easily accessible tetraol tetraacetates (**4**, **5**, **6**, and **7**) derived from B[*a*]P DE-1(**1**) and DE-2 (**2**) were chosen for the reasons discussed in the Introduction. The cis-1 tetraol tetraacetate **(4)** and the trans-1 tetraol tetraacetate (**5**) were obtained in a ratio of 60:40[18] by acidic hydrolysis of B[*a*]P DE-1 (**1**) followed by acetylation and HPLC separation. The acidic hydrolysis of B[*a*]P DE-2 (**2**) and successive acetylation afforded the cis-2 tetraol tetraacetate (**6**) and trans-2 tetraol tetraacetate (**7**) in a ratio of

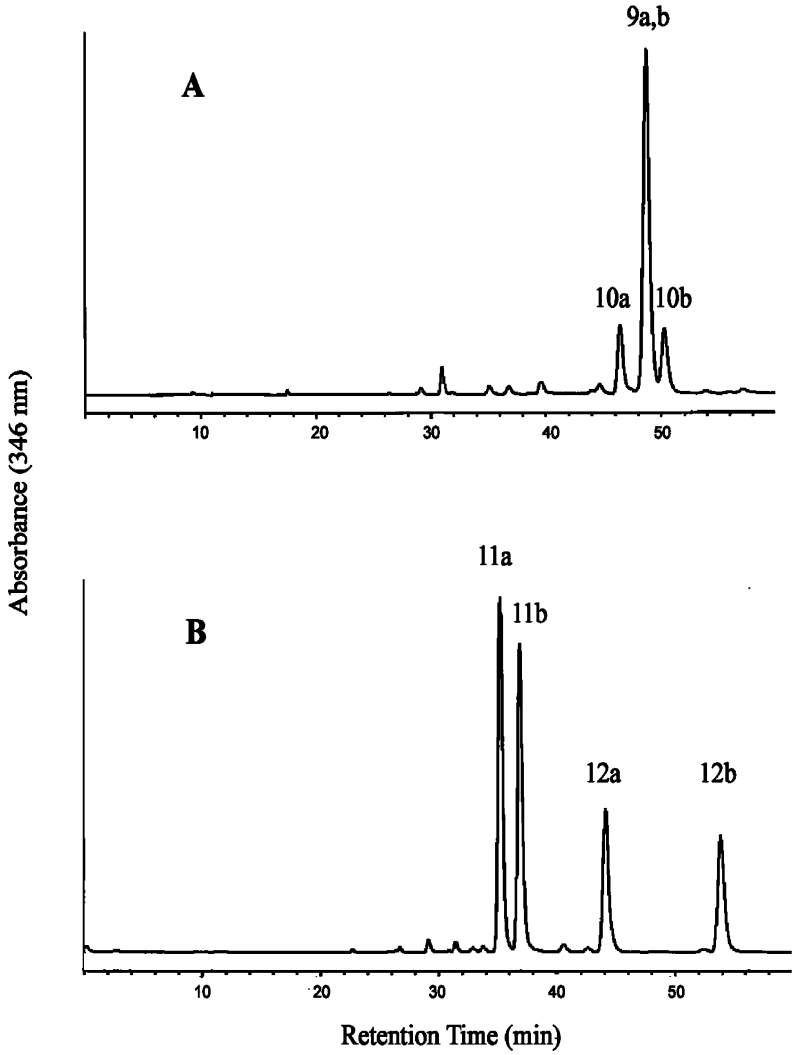

FIGURE 1. HPLC profiles of the products of reaction between O^6-allyl dGuo diTBDMS (**3**) and (±)-trans-1 tetraol tetraacetate **5** (A) or (±)-trans-2 tetraol tetraacetate **7** (B) on three coupled Axxiom Sil columns (9.5 mm × 250 mm) eluted with 14% acetone in *n*-hexane at a flow rate of 5 mL/min (detected at 346 nm). (A) t_R = 46.4 min: (10*S*)-trans-1 dGuo adduct (**10a**); t_R = 48.7 min: (10*S*)- and (10*R*)-cis-1 dGuo adducts (**9a,b**); t_R = 50.3 min: (10*R*)-trans-1 dGuo adduct (**10b**); (B) t_R = 35.2 min: (10*S*)-cis-2 dGuo adduct (**11a**); t_R = 36.9 min: (10*R*)-cis-2 dGuo adduct (**11b**); 44.1 min: (10*S*)-trans-2 dGuo adduct (**12a**); t_R = 53.8 min: (10*R*)-trans-2 dGuo adduct (**12b**).

3:97.[18] The minor cis-2 tetraol tetraacetate (**6**) could also be obtained as a major product (86% yield) together with a minor product, the cis-1 tetraol tetraacetate (**4**; 8.4% yield) from the osmium tetroxide oxidation of B[*a*]P 7,8-dihydrodiol (**8**) followed by acetylation (Scheme 1).

As predicted, fluorinated alcohols have a dramatic catalytic effect on the regioselective substitution reaction at the C-10 acetoxy group for all of the above tetraol tetraacetates (**4**, **5**, **6**, and **7**) with the N^2-amino group of **3**. Reaction of a 5-fold molar excess of **3** with the trans-1 (**5**) and trans-2 tetraol tetraacetate (**7**) was complete within 16 and 14 h, respectively, at 70 °C in the presence of 5 molar equiv of HFP (cf. Table 1). The corresponding reaction for the cis-1 (**4**) and cis-2 tetraol tetraacetate (**6**) required more prolonged heating (72 and ∼40 h, respectively). *The yields for the substitution in all cases were nearly quantitative (>95%).* Unlike the addition reaction of **3** with DEs, no solvent adducts[13,14,15b] were formed. The reactions of the cis-1 (**4**) and trans-1 tetraol tetraacetate (**5**) each afforded a mixture of cis-1 dGuo adducts (**9a** and **9b**) and trans-1 dGuo adducts (**10a** and **10b**) in similar ratios [the total cis-1 dGuo adducts: the total trans-1 dGuo adducts from **4** (76:24) and from **5** (73:27)]. The corresponding ratios of the total cis-2 dGuo adducts (**11a** and **11b**) to the total trans-2 dGuo adducts (**12a** and **12b**) from **6** (68:32) and from **7** (66:34) were also similar to each other (Scheme 2 and Table 1). The corresponding reaction of these tetraacetates in the less acidic TFE required more prolonged heating. Even the trans-2 tetraol tetraacetate (**7**), which was the most reactive isomer under these conditions, required heating at 70 °C for 40 h (∼95% completion). Interestingly, a somewhat different cis/trans ratio (55:45) was observed for the reaction of **7** in TFE compared with those obtained in HFP as shown in Table 1. The reaction rates for the less reactive tetraacetates (**4**, **5**, and **6**) in TFE were too slow to be practical for synthetic purposes. Unlike the addition reaction of **3** with DEs,[13−15] these adduct ratios were insensitive to the molar ratio of solvent to reactants. As shown in Table 1, a small but significant stereoselectivity was observed for the set of diastereomeric adducts formed by the reaction of **6** as well as **7** (e.g., **11a** and **11b** vs **12a** and **12b**). The product dGuo

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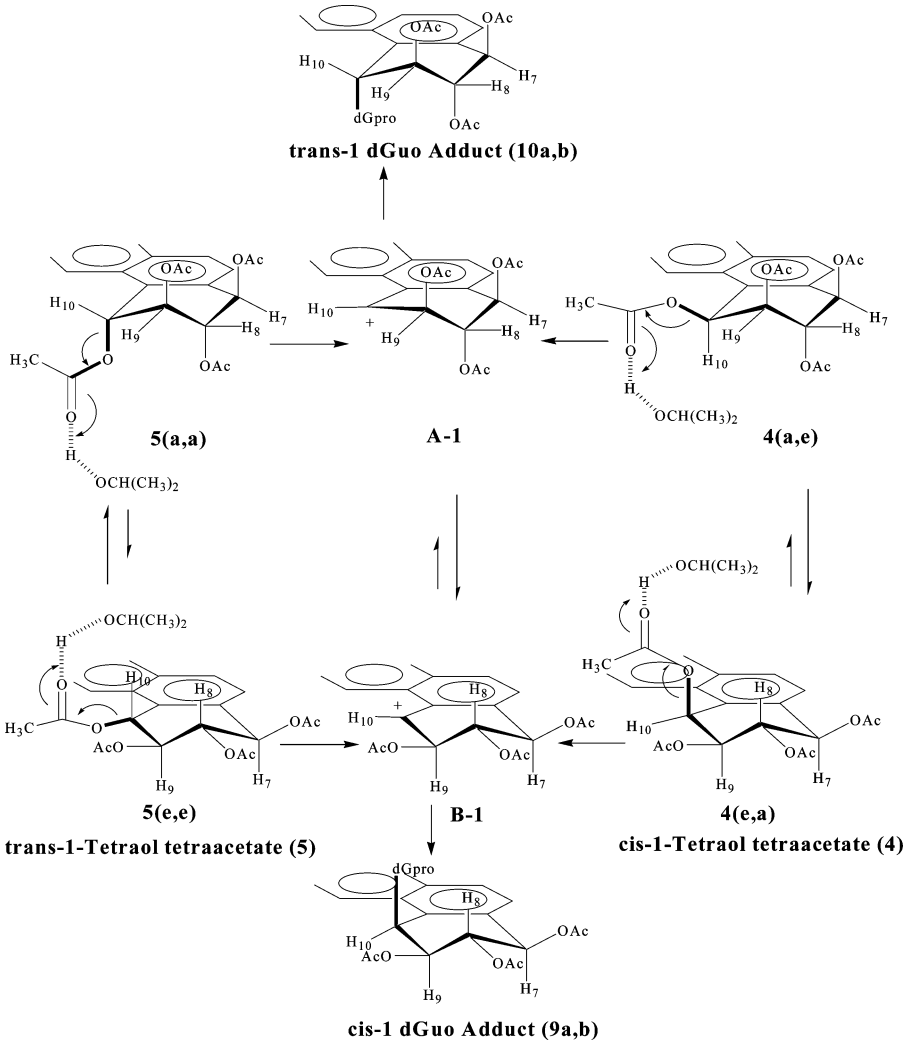
SCHEME 3



adducts were separated by HPLC (Figure 1) and were characterized by comparison of ^{1}H NMR, mass, and CD spectra with authentic samples.[13−15]

The similar cis/trans product ratios obtained from each set of the cis- and trans- tetraol tetraacetates strongly suggest the involvement of a common carbocation intermediate. Conformations of the starting tetraol tetraacetates and their intermediate carbocations (Schemes 3 and 4) provide a plausible explanation for the cis/trans product ratios observed. The conformational preferences for these tetraol tetraacetates and the C-10 carbocations derived from them are determined by the following two factors: (i) the acetoxy group at the hindered C-10 position prefers a quasi-axial conformation due to steric hindrance in the bay region,[18] and (ii) the acetoxy groups at the other positions prefer quasi-equatorial conformations[19,20] in the carbocation. On the basis of ^{1}H NMR spectra, **5** has an equal preference for conformation **5(a,a)** and **5(e,e)**, whereas **4** is expected to prefer conformation **4(e,a)**. The conformation of the common carbocation formed from **5(e,e)** and from **4(e,a)** is **B-1 (**with three quasi-equatorial acetoxy groups) which is expected to be the preferred one at equilibrium with **A-1** (with three quasi-axial acetoxy groups). Carbocation formation from **4** most likely proceeds via axial departure (the microscopic reverse of axial attack) of the acetoxy group from **(4e,a)** to give initially carbocation **B-1**. Similarly, axial loss of the acetoxy group from **(5a,a)** would give carbocation **A-1**. Energetically favorable axial attack[20] on **B-1** will lead to cis-1 dGuo adducts **9a** and **9b**, whereas conformation **A-1** should give trans-1 dGuo adducts **10a** and **10b**. Thus if **A-1** and **B-1** are trapped by **3** faster than they equilibrate with each other, **5** would be predicted to give predominantly trans adducts whereas **4** would give predominantly cis adducts. The fact that a similar cis/trans adduct ratio was obtained from both the cis-1 (**4**) and trans-1 tetraol tetraacetate (**5**) regardless of their conformational preference strongly suggests the carbocations **A-1** and **B-1** undergo conformational equilibration at a faster rate than their capture by **3** (Scheme 3).

The preferred conformation of **7** is **7(a,a)**, whereas **6** exists as a mixture of **6(e,a)** and **6(a,e)**. Preferred axial departure of the acetoxy group should initially give cation **A-2** from **6** and **B-2** from **7**. Again, the cis/trans ratios from **6** and **7** are very similar, suggesting that the cation intermediate undergoes conformational equilibration faster than trapping by **3**. The

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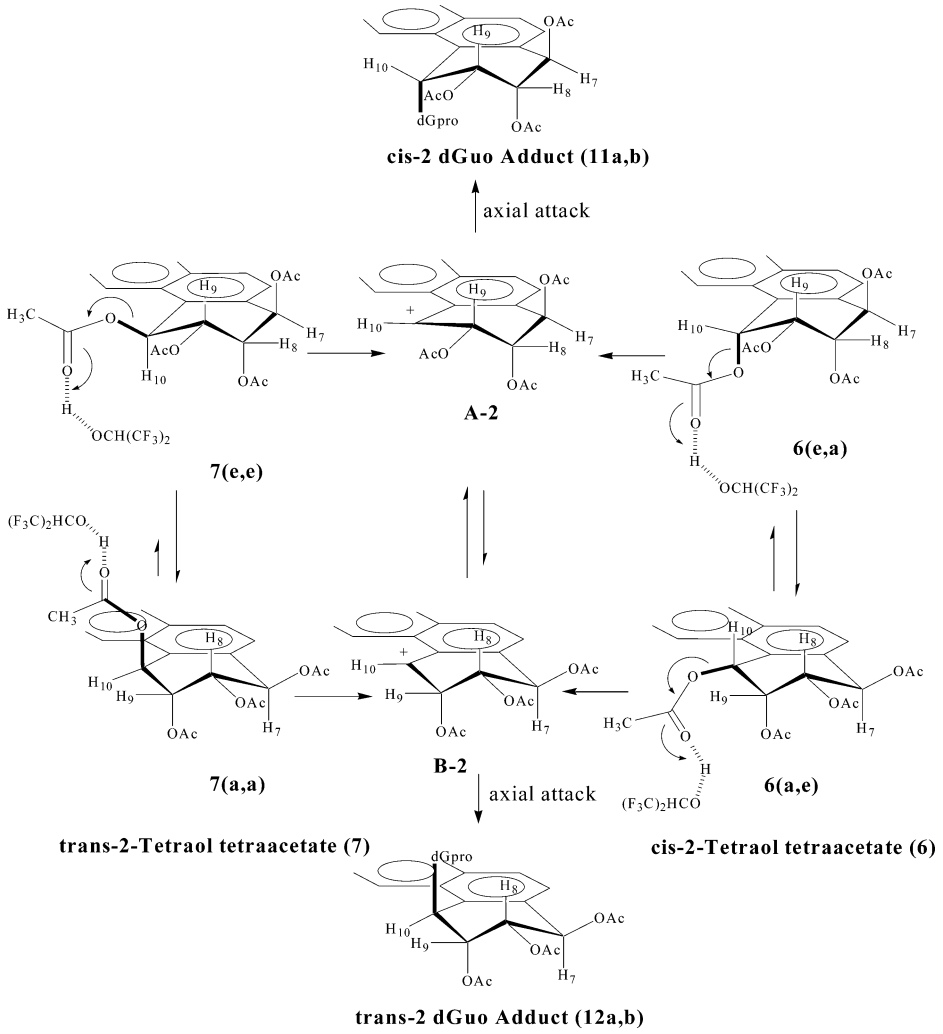
(20) (a) Sayer, J. M.; Yagi, H.; Silverton, J. V.; Friedman, S. L.; Whalen, D. L.; Jerina, D. M. *J. Am. Chem. Soc.* **1982**, *104*, 1972−1978. (b) Goering, H. L.; Josephson, R. R. *J. Am. Chem. Soc.* **1962**, *84*, 2779−2785. (c) Goering, H. L.; Vlazny, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1972−1978.

SCHEME 4



energy difference between **A-2** (with two quasi-axial acetoxy groups) and **B-2** (with one quasi-axial acetoxy) is expected to be slightly smaller than that between **A-1** (with all quasi-equatorial acetoxy groups) and **B-1** (with three quasi-axial acetoxy groups).[20] Accordingly, the preference for cis adduct formation from **6** or **7** in the DE-2 series is slightly less pronounced (~67%) than from **4** or **5** in the DE-1 series (~75%).

Interestingly, the corresponding reaction of the bromotriol triacetate (**13**) with **3** in TFE or in HFP was highly regio- and stereoselective affording exclusively the trans-dGuo adduct diastereomers (**14a** and **14b**) (Scheme 5 and Table 1). In this case, due to the steric hindrance of the bulky bromine substituent at the C-9 position, **13** is almost locked in the conformation **13(a,a)**. Furthermore, the rate of capture of carbocation **A-3** derived from **13(e,e)** by the dGuo reactant **3** is expected to be much slower than that for the capture of carbocation **B-3** due to steric hindrance as well as electronic repulsion between the adjacent cis equatorial bromine in **A-3** at the C-9 position and the incoming dGuo reactant (**3**). The 1,3 diaxial interaction between the C-8 acetoxy group and the incoming **3** should also retard the rate of the cis adduct formation.

Assignment of trans stereochemistry for **14a and 14b** was on the basis of the observed coupling constants of the tetrahydro benzo-ring methine protons ($J_{7,8} = 8.7$; $J_{8,9} = 2.9$; $J_{9,10} = 2.9$ Hz) and the chemical shift of H-10 (6.50 and 6.44 ppm), which were close to those of the trans-2 dGuo adducts (**12a and 12b**).[15a] Absolute configurations of **14a and 14b** were assigned on the basis of comparison of their CD spectra (cf. Figure 2, Experimental Section) with those of the trans-2 dGuo adducts

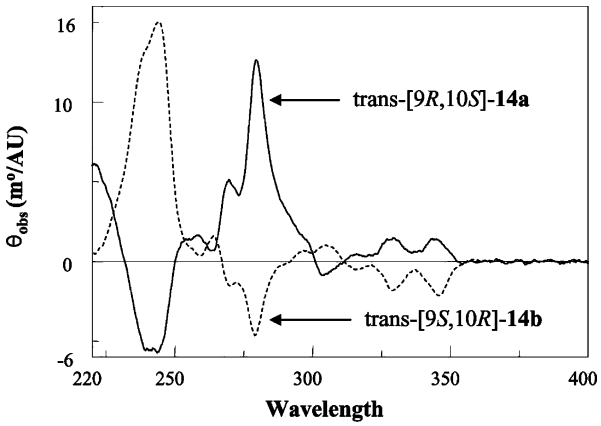
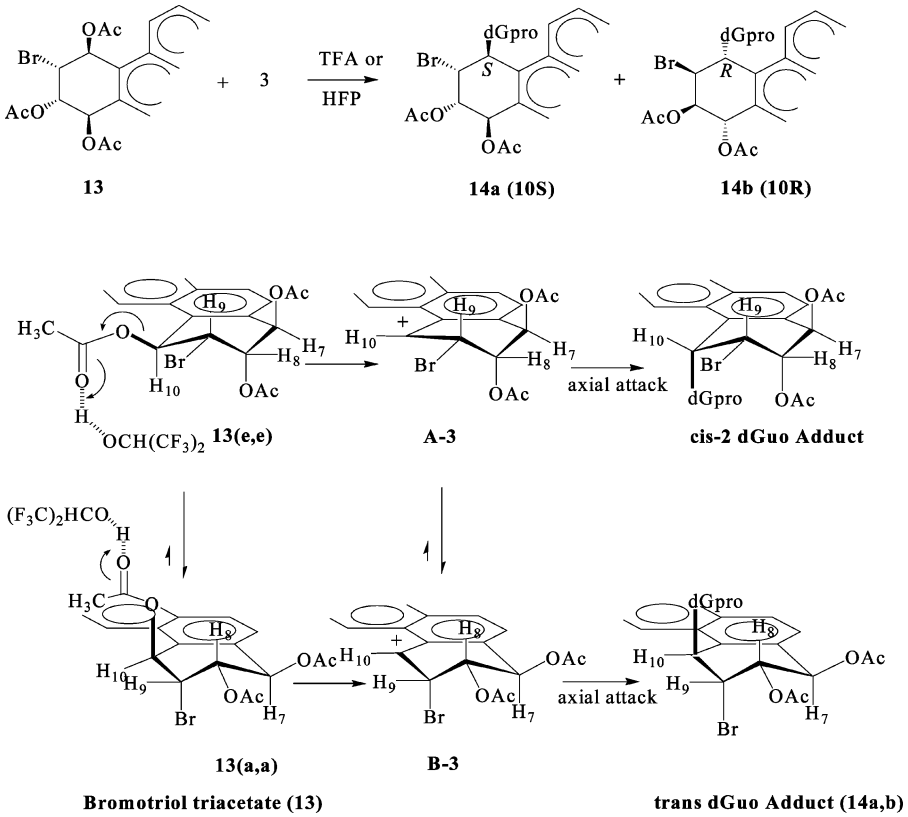


FIGURE 2. CD spectra (normalized to 1 absorbance unit at 8_{max} in methanol) of the trans-N^2-dG adducts (**14a** and **14b**).

(21) See: Johnson, F.; Bonala, R.; Tawde, D.; Torres, M. C.; Iden, C. R. *Chem. Res. Toxicol*. **2002**, *15*, 1489−1494. Lakshman, M. K.; Gunda, P. *Org. Lett*. **2003**, *5*, 39−42. Champeil, E; Pradhan, P.; Lakshman, M. K. *J. Org. Chem*. **2007**, *72*, 5035−5045 and references theirin.

SCHEME 5



(**12a and 12b**) whose absolute configurations were previously determined.[15a]

In summary, a novel and highly efficient, regioselective substitution reaction occurs between the O^6-allyl protected dGuo derivative (**3**) and the tetraol tetraacetates derived from B[*a*]P DEs. The present method compares very favorably with earlier approaches (reviewed in ref 15a) as well as to more recent palladium catalyzed C−N bond forming reactions.[21] For practical synthetic purposes, it is unnecessary to separate the cis/trans mixture of tetraol tetraacetates from either DE-1 or DE-2 in the present approach because the cis and trans tetraol tetraacetates yield the same mixture of dGuo adducts (see Table 1). Compared to the direct solvent assisted reaction of the DEs with **3**, the protected dGuo adducts obtained in this study provide an attractive alternate route for the synthesis of the O^6-allyl-protected N^2-dGuo phosphoramidites which can be incorporated into oligonucleotides with selectable sequence contexts.

Experimental Section

Caution: ***Benzo[a]pyrene 7,8-dihydrodiol and diol epoxides DE-1 and DE-2 are mutagenic and carcinogenic and must be handled carefully in accordance with NIH guidelines.***[22]

General Procedures for the Reaction of B[*a*]P Tetraol Tetraacetates (4, 5, 6, or 7) with O^6-Allyl-dGuo Di-TBDMS Ether (3). To a solution of **3** (548 mg, 1.02 mmol, 5 molar equiv) in TFE (1.5 mL, 20.4 mmol, 100 molar equiv) or HFP (2.1 mL, 20.4 mmol, 100 molar equiv) was added the tetraol tetraacetate (100 mg, 0.204 mmol, 1 molar equiv), and the mixture was stirred at 70 °C (bath temperature) in a sealed glass tube (see Table 1 for reaction time). After completion of the reaction, the solvent was evaporated, and the residue was subjected to HPLC purification (Figure 1). The combined yields of the adducts in all cases were nearly quantitative (>95%). The structures of these adducts (**9a**, **9b**, **10a**, **10b**, **11a**, **11b**, **12a**, and **12b**) were confirmed by comparison of their ^{1}H NMR, CD, and mass spectra with those of authentic samples.[15a]

(±)-9α-Bromo-7*β*,8α,10*β*-triacetoxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene (13). Acetylation of (±)-9α-bromo-7*β*,8α,10*β*,-trihydroxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene[18] was carried out by standard procedures in 93% yield; mp 166−168 °C (EtOAc−*n*-hexane); ^{1}HNMR ($CDCl_3$) δ: 2.17, 2.23, and 2.32 (each s, each 3H, CH_3CO), 4.89 (t, 1H, H_9, J = 3.1 Hz), 5.75 (dd, 1H, H_8, J = 8.7, 3.4 Hz), 6.92 (d, 1H, H_7, J = 8.7 Hz), 7.20 (d, 1H, H_{10}, J = 3.1 Hz), 8.00−8.30 (m, 8 pyrene aromatic protons). $C_{26}H_{21}BrO_6$: C, 61.13; H, 4.16. Found: C, 61.22; H, 4.06.

Reaction of Bromotriol Triacetate (13) with O^6-Allyl-dGuo Di-TBDMS Ether (3). To a solution of **3** (268 mg; 5 molar equiv) in TFE or HFP (100 molar equiv) was added the bromotriol triacetate (51 mg, 0.1 mmol; 1 molar equiv), and the mixture was stirred at 70 °C (bath temperature) in a sealed glass tube (see Table 1 for the reaction time). After completion of the reaction, the solvent was evaporated, and the residue was subjected to HPLC purification on a silica column using 20% EtOAc in *n*-hexane at a flow rate of 10 mL/min (detected at 280 and 346 nm). Evaporation of the fraction corresponding to the peak at t_R = 16.9 min afforded the unused **3** (200 mg, 75% recovery).

Evaporation of the fraction corresponding to the peak at t_R = 18.4 min afforded ***N*^{2}-[10*S*-(9*R*-bromo-7*R*,8*S*-dihydroxy-7,8,9,-10-tetrahydrobenzo[*a*]pyrenyl)]-*O*^{6}-allyl-3′,5′-di-*O*-(*tert*-butyldimethylsilyl)-2′-deoxyguanosine (14a)** as a colorless solid (36 mg, 39% yield for the reaction in HFP); ^{1}H NMR ($CDCl_3$−CD_3OD) δ: 0.01−0.12 (br. m, 6H, Si bonded methyls), 0.80−0.94 (br. m, 18H, *tert*-butyl methyls), 2.20 and 2.29 (each s, each 3H, CH_3CO), 2.40

(22) *NIH Guidelines for the Laboratory Use of Chemical Carcinogens*; NIH publication No. 81-2385; U.S. Government Printing Office: Washington, DC, 1981.

(m, 1H, $H_{2''}$), 2.62 (m, 1H, $H_{2'}$), 3.78 (m, 2H, $H_{5',5''}$), 4.0 (m, 1H, $H_{4'}$), 4.56 (m, 1H, $H_{3'}$), 5.06 (m, 2H, allyl CH_2), 5.16 (t, 1H, H_9, J = 2.9 Hz), 5.2−5.58 (m, 2H, H_c and H_t), 5.95 (dd, 1H, H_8, J = 8.7, 2.9 Hz), 6.14 (m, 1H, H_v), 6.50 (d, 1H, H_{10}, J = 2.9 Hz), 6.80 (d, 1H, H_7, J = 8.7 Hz), 8.00−8.25 (m, 9H, 8 pyrene aromatic protons and H_{8G}). HRMS (FAB+) calcd for $C_{49}H_{62}O_8N_5BrCs$: 1116.2375 (^{79}Br); 1118.2354 (^{81}Br). Found: 1116.2352 (^{79}Br); 1118.2384 (^{81}Br). The CD spectrum (Figure 2) was similar to that of the *trans*-(10*S*)-**12a**.

Evaporation of the fraction corresponding to the peak at t_R = 20.1 min afforded ***N*²-[10*R*-(9*S*-bromo-7*S*,8*R*-dihydroxy-7,8,9,-10-tetrahydrobenzo[*a*]pyrenyl)]-*O*⁶-allyl-3′,5′-di-*O*-(*tert*-butyldimethylsilyl)-2′-deoxyguanosine (14b)** as a colorless solid (40 mg, 43.4% yield for the reaction in HFP); ^{1}H NMR ($CDCl_3$−CD_3OD) δ: 0.01−0.12 (br. m, 6H, Si bonded methyls), 0.80−0.94 (br. m, 18H, *tert*-butyl methyls), 2.21 and 2.29 (each s, each 3H, CH_3-CO), 2.42 (m, 1H, $H_{2''}$), 2.62 (m, 1H, $H_{2'}$), 3.80 (m, 2H, $H_{5',5''}$), 3.99 (m, 1H, $H_{4'}$), 4.58 (m, 1H, $H_{3'}$), 5.10 (m, 2H, allyl CH_2), 5.19 (t, 1H, H_9, J = 2.9 Hz), 5.2−5.58 (m, 2H, H_c and H_t), 5.94 (dd, 1H, H_8, J = 8.7, 2.9 Hz), 6.14 (m, 1H, H_v), 6.44 (d, 1H, H_{10}, J = 2.9 Hz), 6.81 (d, 1H, H_7, J = 8.7 Hz), 8.00−8.25 (m, 9H, 8 pyrene aromatic protons and H_{8G}). HRMS (FAB+) calcd for $C_{49}H_{62}O_8N_5BrCs$: 1116.2375 (^{79}Br); 1118.2354 (^{81}Br). Found: 1116.2368 (^{79}Br); 1118.2324 (^{81}Br). The CD spectrum (Figure 2) was similar to that of the *trans*-(10*R*)-**12b**. Yields of **14a** and **14b** for the reaction in TFE were similar to those in HFP.

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Supporting Information Available: Synthetic procedures for the reactions of the 7,8-dihydrodiol (**8**) with osmium tetroxide and the hydrolysis of B[*a*]P DE-1 and DE-2 to tetraols under acidic conditions are presented as well as proton NMR spectra of the new compounds **13**, **14a**, and **14b** are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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