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Notes

Rearrangement of Cinnamyl Groups from O^6 to C-8 in the Guanine Series

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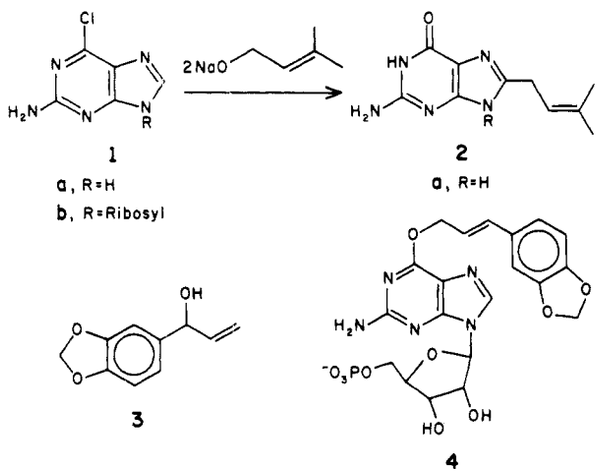
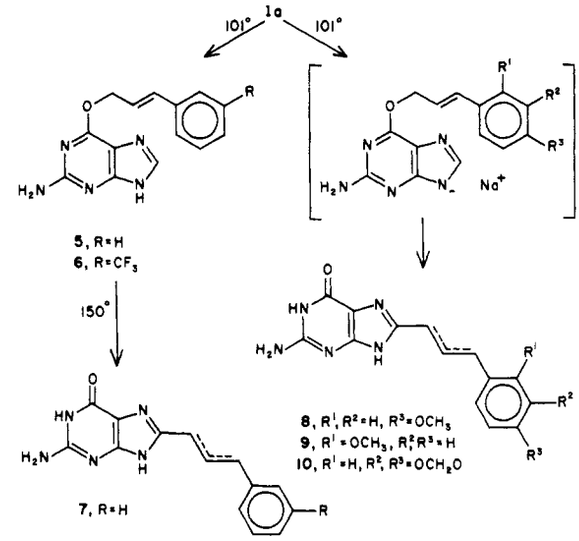
It was established in this Laboratory that displacement reactions of 2-amino-6-chloropurine (**1a**) with the sodium salts of allylic alcohols proceed through an O^6 ether to yield 8-substituted guanines (e.g., **2a**),[2] with the following stipulations: (a) the O^6 to C-8 rearrangement occurs with overall allylic retention and is partially controlled by the degree of methyl substitution of the allylic group and by the temperature, (b) the rearrangement proceeds with greatest facility through anionic species, and (c) it occurs intramolecularly and most logically by two [3,3]sigmatropic shifts via C-5.



Derivatives of allylbenzene and propenylbenzene are widely occurring plant constituents, and many which are present as major components of common spices and flavorings exhibit biological activity.[3] It has been shown that allylbenzene derivatives can be oxidized metabolically to give allylic alcohols.[4,5] More specifically, safrole (3,4-methylenedioxyallylbenzene), which is a hepatotoxin and a hepatocarcinogen, is oxidized in the liver, inter alia, to 1-(3,4-methylenedioxyphenyl)-2-propen-1-ol (**3**), a more potent carcinogen than the parent safrole.[5] Furthermore, a University of Wisconsin group has shown that the synthetic acetate of **3**, as a model for metabolic activation, reacts with guanosine monophosphate to give the O^6-allylic ether **4**. These reports led us to investigate the rearrangement of O^6-cinnamyl ethers of guanine.

Treatment of 2-amino-6-chloropurine (**1a**) with the sodium salt of either cinnamyl alcohol or *m*-trifluoromethylcinnamyl alcohol in refluxing dioxane (101 °C) for 4 h gave the corresponding O^6 ether **5** or **6**, respectively, of guanine. At 101 °C, no rearrangement product was detectable by thin-layer chromatography, even after heating at reflux for 24 h. However, when O^6-cinnamylguanine (**5**) was converted to its sodium salt with 1 equiv of sodium hydride and heated at 150 °C for 24 h in either anhydrous diglyme or dimethylformamide, rearrangement occurred to a mixture of 8-(3-phenyl-1-propenyl)guanine and 8-(3-phenyl-2-propenyl)guanine (**7**). When the *m*-trifluoromethyl compound **6** was treated under the same conditions at 150 °C, guanine was the only purine product that could be detected.



Electron-donating groups on the phenyl ring facilitated rearrangement. Thus, treatment of **1a** separately with the sodium salts of *p*-methoxycinnamyl alcohol,[6] *o*-methoxycinnamyl alcohol,[6] and 3-(3,4-methylenedioxyphenyl)-2-propen-1-ol[5] in refluxing dioxane (101 °C) gave the corresponding C-8 substituted guanines **8–10**. The product in each case was isolated as an approximately 1:1 mixture of the double-bond isomers. TLC analysis of the progress of the re-

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action showed that the O^6 ether was formed initially and was converted slowly to the C-8 product (**8–10**). At the end of 24 h, no detectable O^6 intermediate remained in the reaction mixture. Assignment of the structure of each C-8 product was based on the absence of an 8-H signal in the NMR and on the upfield shift of the signal for the methylene hydrogens from $\delta \sim 5$ for O^6 substitution to δ 3.4–3.7 for C substitution.

We had noted earlier that γ-methyl substitution on the migrating allylic group facilitates O^6 to C-8 rearrangement.[2] The present results support the hypothesis that γ substituents influence the ease of rearrangement through an electronic rather than a steric factor since there is little difference in bulk between the substituted phenyl rings. On a qualitative basis, these results are similar to those for the ortho Claisen rearrangement of substituted cinnamyl *p*-tolyl ethers, which have a negative ρ and can be correlated to σ^+.[7]

In order to evaluate the possible biological significance of the O^6 to C-8 rearrangement, we extended our investigations to guanosine derivatives. Since O^6-(3-methyl-2-butenyl)-guanine [O^6-(Δ^2-isopentenyl)guanine] rearranges more readily than any other allylic ether tried, we examined the stability of the related O^6-(3-methyl-2-butenyl)guanosine as a control for the effect of 9-ribosyl substitution. Treatment of 2-amino-6-chloro-9-(β-D-ribofuranosyl)purine (**1b**) with sodium 3-methyl-2-butene 1-oxide in 3-methyl-2-buten-1-ol at 115 °C in 5 min gave the corresponding O^6 ether as the sole product. In a typical experiment, O^6-(3-methyl-2-butenyl)-guanosine was treated with 1 equiv of sodium hydride in anhydrous dimethylformamide at 100 °C for 12 h. Hydrolytic removal of the ribose in 1 M HCl and high-performance liquid chromatography of the products failed to show the presence of any detectable amount of 8-(3-methyl-2-butenyl)guanine by comparison of retention time with that of an authentic sample. Similar results were obtained using up to 4 equiv of sodium hydride and raising the temperature to 170 °C.

We have shown that O^6-cinnamyl ethers of guanine can rearrange to C-8 substituted guanines and that this rearrangement is greatly facilitated by electron-donating substituents in the phenyl ring. We did not detect the parallel O^6 to C-8 rearrangement of allylic guanosine derivatives, presumably because the ribosidated nucleus is unable to form an anion. Thus, the event of in vivo O^6-cinnamylation of a guanosine or guanylic unit cannot be excluded as a *sufficient* basis for the observed biological effect, e.g., in the case of safrole.[5] O^6-Alkylation in a DNA template has already been implicated in miscoding operations.[8,9] Were N-7 the alternative site[9] of mutational cinnamylation, the formation of such 7-substituted guanosine units would have to be sufficient to cause deletion or to effect miscoding. The possibility of a subsequent N-7 to C-8 [3,2]sigmatropic shift remains in chemical consideration for 7-allylated guanosines, even though 7-allylated guanines are stable,[2b,10] and these should be explored as special cases of 7-alkylated guanosines.

Experimental Section

All melting points are uncorrected. The ^1H NMR spectra were recorded on Varian Associates A-60, EM-390, or HA-100 spectrometers using tetramethylsilane as an internal standard. The ultraviolet spectra were obtained on a Beckman Acta Model M VI spectrometer. Microanalyses were performed by Mr. Josef Nemeth and associates, who also weighed samples for quantitative electronic absorption spectra. Low-resolution mass spectra were obtained on a Varian MAT CH-5 spectrometer. Field desorption and high-resolution mass spectra were obtained on a Varian MAT 731 spectrometer, coupled with a 620i computer and STATOS recorder.

***O*⁶-Cinnamylguanine (5).** A suspension of sodium hydride (283 mg of a 50% oil dispersion, 5.90 mmol), dry dioxane (24 mL), and cinnamyl alcohol (791 mg, 5.90 mmol) was stirred under a nitrogen atmosphere. After evolution of hydrogen had ceased, 2-amino-6-chloropurine (**1a**, 500 mg, 2.95 mmol) was added, and the mixture was heated at reflux for 4 h. The solvent was removed in vacuo. The residue was dissolved in water (10 mL) and washed with ether (2 × 10 mL). The water layer was acidified to pH 6 with 20% aqueous acetic acid. After cooling, the solid was removed by filtration. Recrystallization from ethanol gave 440 mg (56%) of tan solid: mp 165–175 °C dec; λ_{max} (0.1 M HCl, EtOH) 281 nm sh (ϵ 10 670), 274 (10 880), 239 (21 760); (EtOH) 282 sh (8530), 272 (11 310), 266 sh (10 990), 236.5 (24 660); (0.1 M NaOH, EtOH) 281 sh (9810), 273 (10 990), 266 sh (10 240), 236.5 (21 420); NMR [$(CD_3)_2SO$] δ 5.16 (d, 2, CH_2), 6.22 (br, 2, NH_2), 6.62–7.05 (m, 2, CH=CH), 7.34 (m, 5, C_6H_5), 7.89 (s, 1, pu-H); field desorption mass spectrum, *m/e* 267 (M^+).

Anal. Calcd for $C_{14}H_{13}N_5O$: C, 62.91; H, 4.90; N, 26.20. Found: C, 62.98; H, 4.90; N, 26.04.

***O*⁶-(*m*-Trifluoromethylcinnamyl)guanine (6).** A suspension of sodium hydride (247 mg of a 50% oil dispersion, 5.15 mmol), dry dioxane (25 mL), and *m*-trifluoromethylcinnamyl alcohol (1.04 g, 5.15 mmol) was stirred under a nitrogen atmosphere for 6 h at 25 °C. To this mixture 2-amino-6-chloropurine (**1a**) was added, and the mixture was heated at reflux for 4 h. After cooling, glacial acetic acid (0.3 mL) was added, and the solid material was removed by filtration. The solvent was removed in vacuo, and the residue was dissolved in ethyl acetate (1 mL). The ethyl acetate solution was applied to an 8-g silica gel column. Elution with ethyl acetate gave a fraction containing 606 mg (72%) of light yellow solid: mp 75–80 °C; λ_{max} (0.1 M HCl, EtOH) 294 nm sh (ϵ 9700), 285 (11 030), 246 (19 500); (EtOH) 282 (10 360), 244.5 (22 590); (0.1 M NaOH, EtOH) 283 (9820), 247 (18 390), 227 (14 660); NMR [$(CD_3)_2SO$] δ 5.10 (s, 2, CH_2), 6.19 (br, 2, NH_2), 6.4–7.0 (m, 2, CH=CH), 7.3–7.88 (m, 4, $C_6H_4CF_3$), 7.81 (s, 1 H, pu-H); field desorption mass spectrum, *m/e* 335 (M^+).

Anal. Calcd for $C_{15}H_{12}F_3N_5O$: C, 53.68; H, 3.58; F, 17.00; N, 20.88. Found: C, 53.67; H, 3.50; F, 16.95; N, 20.65.

8-(3-Phenyl-1-propenyl)guanine and 8-(3-Phenyl-2-propenyl)guanine (7). A suspension of O^6-cinnamylguanine (**5**, 100 mg, 0.374 mmol) and sodium hydride (18 mg of a 50% oil dispersion, 0.374 mmol) in dry diglyme (3 mL) was stirred for 2 h at 25 °C. The mixture was heated at 150 °C for 24 h under a nitrogen atmosphere and was then treated with glacial acetic acid (0.3 mL) and ether (50 mL). The solid was filtered and washed with water (5 mL). Recrystallization from 50% aqueous ethanol gave 76 mg (76%) of light tan solid, mp >300 °C. NMR showed a mixture of the double-bond isomers [$(CD_3)_2SO$]: δ 3.48–3.65 (m, 2, CH_2), 6.1–6.85 (m, 4, CH=CH, NH_2), 7.1–7.5 (m, 5, C_6H_5); mass spectrum (10 eV). *m/e* 267 (M^+).

Anal. Calcd for $C_{14}H_{13}N_5O$: C, 62.91; H, 4.90; N, 26.20. Found: C, 62.68; H, 4.92; N, 25.98.

8-[3-(3,4-Methylenedioxyphenyl)-1-propenyl]guanine and 8-[3-(3,4-Methylenedioxyphenyl)-2-propenyl]guanine (10). A suspension of sodium hydride (283 mg of a 50% oil dispersion, 5.90 mmol), dry dioxane (50 mL), and 3-(3,4-methylenedioxyphenyl)-2-propen-1-ol (1.05 g, 5.90 mmol) was stirred at 25 °C under a nitrogen atmosphere. After evolution of hydrogen had ceased (~6 h), 2-amino-6-chloropurine (500 mg, 2.95 mmol) was added, and the mixture was heated at reflux for 24 h. After cooling, the dioxane was removed in vacuo, and ether (50 mL) was added to the residue. Glacial acetic acid (0.5 mL) was added to the mixture with vigorous stirring. The solid was removed by filtration and washed successively with ethanol, water, and ethanol to give 605 mg (66%) of light tan solid. An analytical sample was obtained by suspending 100 mg of the solid in refluxing ethanol and adding water until the solid dissolved. The hot solution was treated with charcoal and filtered through a Celite pad. The volume of the solution was then reduced to ~15 mL by boiling. After cooling, the solid was collected, mp 274–280 °C dec. NMR showed a mixture of the double-bond isomers [$(CD_3)_2SO$]: δ 3.4–3.6 (m, 2, CCH_2C), 5.98 (s, 2, OCH_2O), 6.1–6.74 (m, 4, CH=CH, NH_2), 6.75–7.05 (m, 3, C_6H_3); mass spectrum (10 eV), *m/e* 311 (M^+); high-resolution mass spectrum, *m/e* 311.1015 (calcd for $C_{15}H_{13}N_5O_3$).

Anal. Calcd for $C_{15}H_{13}N_5O_3$: C, 57.87; H, 4.21; N, 22.50. Found: C, 57.78; H, 4.32; N, 22.51.

A similar procedure was used to prepare mixtures of 8-[3-(*p*-methoxyphenyl)-1-propenyl]- and 8-[3-(*p*-methoxyphenyl)-2-propenyl]guanine (**13**) and of 8-[3-(*o*-methoxyphenyl)-1-propenyl]- and 8-[3-(*o*-methoxyphenyl)-2-propenyl]guanine (**14**). Satisfactory ^1H NMR spectra, low-resolution mass spectra, and high-resolution mass spectra were obtained.[11]

***O*⁶-(3-Methyl-2-butenyl)guanosine** was prepared in a manner similar to other O^6-substituted guanosine derivatives:[12] mp 210–215 °C dec; field desorption mass spectrum, *m/e* 351 (M^+).

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equipment were provided by Grants CA 11388 and GM 16864 from the National Institute of Health.

Registry No.—**1a**, 10310-21-1; **5**, 64189-11-3; **6**, 64189-12-4; **7** (2-propenyl isomer), 64189-13-5; **7** (1-propenyl isomer), 64189-14-6; **10** (1-propenyl isomer), 64189-15-7; **10** (2-propenyl isomer), 64189-16-8; cinnamyl alcohol, 104-54-1; *m*-trifluoromethylcinnamyl alcohol, 64189-17-9; 3-(3,4-methylenedioxyphenyl)-2-propen-1-ol, 17581-86-1; O^6-(3-methyl-2-butenyl)guanosine, 64189-18-0.

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Stereochemistry of the Furan–Maleic Anhydride Cycloaddition

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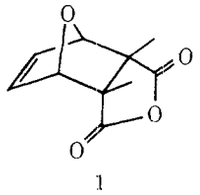
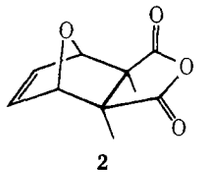
The crystalline product from the Diels–Alder reaction of furan (F) with maleic anhydride (M) was originally formulated as endo adduct **1**.[2] Woodward and Baer showed that the adduct actually has the exo configuration **2**.[3] Anet has stated[4]



1



2

that the exo isomer is initially formed about twice as fast as the endo isomer, and that the endo compound initially produced quickly disappears from the reaction mixture at room temperature.

The kinetically favored formation of the exo compound is a very unusual circumstance and constitutes the only known exception to the rule of predominant endo addition[5] in reactions where dienophiles and/or dienes are not heavily substituted.[6] We also find that all of the usual grounds for explaining endo selectivity (maximum accumulation of unsaturation,[7] secondary orbital interactions,[8] primary overlap at the reaction sites,[9] attractive dipole–dipole interactions, and dispersion forces[10]) are fulfilled in the furan–maleic anhydride cycloaddition. Consequently, we have reinvestigated this reaction using nuclear magnetic resonance spectroscopy.

In agreement with the previous work, the reaction of maleic anhydride with furan gives rise to the exo adduct **2**: mp 125–126 °C; NMR bands at δ 6.5 (2 H, multiplet), 5.3 (2 H, multiplet), 3.2 (2 H, singlet). In acetonitrile solution at 40 °C, initial concentrations of reactants both equal to 1.50 M, a small amount of *endo*-**1** is initially formed and identified by its NMR spectrum: δ 6.5 (multiplet), 5.4 (multiplet), 3.9 (multiplet). *However, the initial rate of formation of endo-***1** *is found to be larger than that for the formation of* **2**. At the end of 24 min the concentrations of **1** and **2** are the same, and the concentration of **2** exceeds that of **1** after that point. Endo adduct has essentially disappeared after 48 h, and the final concentration ratio of product to reactants is $[exo\text{-}2]/[M] = 1.83$ and $K = [M][F]/[2] = 0.289$ L mol^{-1}. Pure exo adduct decomposes to give only the addends. With the initial concentration of **2** equal to 0.120 M, the equilibrium concentration ratio is 0.348 and $K = 0.256$ L mol^{-1}.

At lower initial concentrations of reactants, the only initially discernable product is the endo adduct. With $[M_0] = [F_0] = 0.50$ M, 8% of the reactants are converted to **1** after 310 s, and the concentration of **1** slowly decreases after that time. Exo adduct **2** is only evident in the reaction mixture after 3000 s of reaction time. Several repetitions of all of these experiments gave congruent results.

Using the differential rate expressions directly[11] we find that our data yield the rate constants shown. The rate constant for formation of the endo adduct is actually almost 500 times larger than the exo adduct formation rate constant. Assuming comparable entropies of activation, this rate constant difference corresponds to an activation energy difference of 3.8 kcal favoring the endo adduct. The exo adduct is, however, 1.9 kcal/mol more stable than the endo adduct. Since the formations of both adducts are reversible, the exo adduct is eventually the final isolated product.

$$M + F \underset{4.37 \times 10^{-2}\ s^{-1}}{\overset{7.29 \times 10^{-3}\ L\ m^{-1}\ s^{-1}}{\rightleftharpoons}} \textit{endo}\text{-}1$$

$$M + F \underset{4.40 \times 10^{-6}\ s^{-1}}{\overset{1.60 \times 10^{-5}\ L\ m^{-1}\ s^{-1}}{\rightleftharpoons}} \textit{exo}\text{-}2$$

With these results, the furan–maleic anhydride reaction can be placed within the typical kinetic and thermodynamic pattern for Diels–Alder reactions.[5,12]

Acknowledgment. The financial support of the Robert A. Welch Foundation is greatly appreciated.

Registry No.—**1**, 64113-63-9; **2**, 64161-68-8; maleic anhydride, 108-31-6; furan, 110-00-9.

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