high extinction coefficient.[13] YI is not formed either in the benzophenone–cyclohexane or in the decafluorobenzophenone–2-propanol system. The I_a effect is apparently related to the efficiency of energy transfer from YI to benzophenone. Triplet sensitization may be the mechanism of energy transfer since YI undergoes intersystem crossing[13] and has triplet energy similar to that of benzophenone.

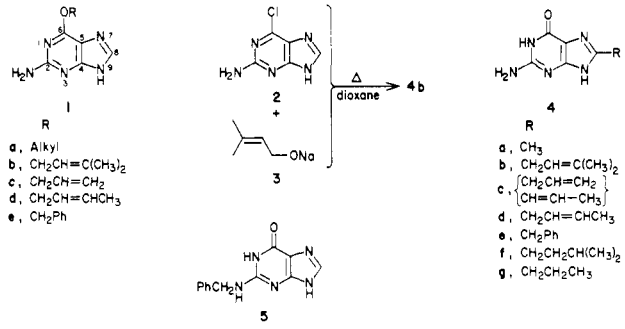
(13) N. Filipescu and F. L. Minn, *J. Amer. Chem. Soc.*, **90**, 1544 (1968).

Jonas Dedinas
Research Laboratories, Eastman Kodak Company
Rochester, New York 14650
Received May 21, 1973

Allylic Rearrangement from O^6 to C-8 in the Guanine Series

Sir:

Because of our interest in fluorescent derivatives of the nucleic acid bases[1-3] we sought to obtain a variety of O^6-substituted guanines (**1**), which are described as strongly fluorescent in the case of O^6-alkyl substituents.[4,5] When we attempted to extend the method of synthesis of O^6-alkylguanines (**1a**)[6] to the allylic and benzylic analogs, some unexpected products resulted. For example, when 2-amino-6-chloropurine (**2**) was caused to react with sodium 3-methyl-2-buten-1-oxide (**3**) (2 equiv) in dioxane at reflux (heterogeneous)



for 24 hr, none of the expected O^6-substituted guanine derivative could be detected. Instead, an isomeric product, $C_{10}H_{13}N_5O$, was isolated in 74% yield.[7] This product exhibited the following properties: (a) the nmr spectrum showed the presence of the 3-methyl-2-buten-1-yl side chain but the absence of an 8 proton; (b) no cleavage of the side chain resulted when the product was heated at 100° in 1 *N* HCl for 24 hr, indicating that it was not an O^6-substituted purine; (c) the mass spectrum showed major peaks at *m/e* 219 $(M)^+$, 204 $(M - CH_3)^+$, 178 $(M - C_3H_5)^+$, 165 $(M - C_4H_6)^+$, and 140 $(M - C_6H_7)^+$, and no appreciable fragment ion of *m/e* 151 $(M - C_5H_8)^+$, indicating *C*-rather than *O*- or *N*-dimethylallyl substitution; (d) the uv spectrum showed $\lambda_{max}^{H_2O}$ (pH 1) 248 nm (ε 12,400), 276 (8210); (pH 7) 246 (9940), 278 (7420); (pH 13) 276 (9450), indicating an 8-substituted guanine, *e.g.*, **4a**.[8] The structure of the product of the reaction of **2** with **3** was established thereby as 8-(3-methyl-2-buten-1-yl)guanine (**4b**).[9] Corroboration of the assigned structure was obtained by catalytic reduction of **4b** to 8-(3-methylbut-1-yl)guanine (**4f**) and comparison with a sample of **4f**[9] obtained by unequivocal synthesis: condensation of 4-methylvaleryl chloride with 6-hydroxy-2,4,5-triaminopyrimidine, followed by ring closure of the sodium salt of the amide intermediate (55% overall yield).

The unusual reaction of **2** + **3** to produce **4b** obviously requires an initial displacement step that places the oxygen of the alkoxide **3** at the 6 position of the purine ring and subsequent allylic C–O bond cleavage. In the only previous example of an allylic rearrangement in the purine series the allyl group moved from an exocyclic oxygen to a neighboring ring nitrogen, specifically, 2,6-diallyloxy-7-methylpurine, when heated at 150°, to 1,3-diallyl-2,6-dioxo-7-methylpurine.[10] Rearrangement from an exocyclic oxygen to a ring carbon is unknown with purines, although two examples of a Claisen-type rearrangement from O to C have been reported with pyrimidines.[11-13] The only example of C-8 alkylation of 8-unsubstituted purines is the reaction of sodium theophyllinate with 2-butenyl bromide and benzyl chloride.[14] There is no precedent in the purine system for the observed rearrangement of the allylic side chain from O^6 to C-8. One formal intramolecular route for visualizing the overall result is a combined Claisen–Cope rearrangement *via* C-5 involving two [3*s*,3*s*] sigmatropic shifts.[15-17]

To answer the question of the generality of this rearrangement, we selected other examples representative of allyl, crotyl, alkyl, and benzyl substitution. Reaction of 2-amino-6-chloropurine (**2**) with sodium allyloxide (2–10 equiv) at reflux in either allyl alcohol (97°) or dioxane (101°) for 24 hr yielded O^6-allylguanine (**1c**),[9] with a characteristic uv spectrum for O^6-alkyl substitution: $\lambda_{max}^{H_2O}$ (pH 1) 230 nm (sh) (ε 6000), 285 (11,000); (pH 7) 239 (7900), 281 (8400); (pH 13) 245 (sh) (4900), 283 (8800). When a higher boiling solvent, *e.g.*, diglyme (150°), was used, the

(1) J. A. Secrist III, J. R. Barrio, and N. J. Leonard, *Biochem. Biophys. Res. Commun.*, **45**, 1262 (1971).
(2) J. A. Secrist III, J. R. Barrio, N. J. Leonard, and G. Weber, *Biochemistry*, **11**, 3499 (1972).
(3) J. R. Barrio and N. J. Leonard, *J. Amer. Chem. Soc.*, **95**, 1323 (1973).
(4) A. Loveless, *Nature (London)*, **223**, 206 (1969).
(5) B. Singer, *Biochemistry*, **11**, 3939 (1972).
(6) R. W. Balsiger and J. A. Montgomery, *J. Org. Chem.*, **25**, 1573 (1960).
(7) The reported yields are of analytically pure samples. The crude yields in the displacement reactions were between 90 and 95%, and on thin layer chromatography on silica gel in three different solvent systems these showed uv-absorbing spots with R_f values corresponding to the products here reported; no other spots were observed.
(8) G. D. Davies, C. W. Noell, R. K. Robins, H. C. Koeppel, and A. G. Beeman, *J. Amer. Chem. Soc.*, **82**, 2633 (1960).
(9) The microanalytical data (C, H, N) obtained for all of the new compounds described herein were correct within acceptable limits (±0.30%) of those calculated according to the respective molecular formulas. Since, in general, the guanine derivatives decompose on heating and 8-substituted guanines melt at >300°, melting points do not offer meaningful criteria of purity in this series.
(10) E. Bergmann and H. Heimhold, *J. Chem. Soc.*, 1365 (1935).
(11) H. J. Minnemeyer, P. B. Clarke, and H. Tieckelmann, *J. Org. Chem.*, **31**, 406 (1966).
(12) B. S. Thyagarajan, *Advan. Heterocycl. Chem.*, **8**, 143 (1967).
(13) B. A. Otter, A. Taube, and J. J. Fox, *J. Org. Chem.*, **36**, 1251 (1971).
(14) J. H. Lister in "Fused Pyrimidines, Part II," D. J. Brown, Ed., Wiley-Interscience, New York, N. Y., 1971, p 123.
(15) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, GmbH, Weinheim/Bergstr., 1970, p 120 ff.
(16) J. Borgulya, R. Madeja, P. Fahrni, H.-J. Hansen, H. Schmid, and R. Barner, *Helv. Chim. Acta*, **56**, 14 (1973).
(17) U. Widmer, J. Zsindely, H.-J. Hansen, and H. Schmid, *ibid.*, **56**, 75 (1973).

product isolated (63%) was a mixture of 8-allylguanine and 8-propenylguanine (**4c**). When the sodium salt of **1c** was heated in diglyme for 24 hr at 150°, **4c** was also produced in 65% yield. The structure of the **4c** mixture was established by hydrogenation over palladium on charcoal to 8-propylguanine (**4g**) (82% yield) and comparison with a sample synthesized (45%) in a procedure similar to that for **4f** but employing butyryl chloride and 6-hydroxy-2,4,5-triaminopyrimidine. Since the rearrangement of **1c** without added base required a higher temperature (170°, triglyme) and gave a mixture which contained *ca.* 50% of **4c** plus four other products, it is apparent that the rearrangement is favored by proceeding through anionic species.

The crotyl case gave results intermediate between those for allyl and dimethylallyl in ease of rearrangement. The reaction of 2-amino-6-chloropurine (**2**) with sodium 2-buten-1-oxide (2 equiv) at 100° in either 2-buten-1-ol or dioxane yielded a mixture of O^6-(2-buten-1-yl)guanine (**1d**) and 8-(2-buten-1-yl)guanine (**4d**). The ratio of products was sensitive to the time of heating (**1d**:**4d** = 80:20 (74% yield) for 5 hr to 10:90 (59% yield) for 48 hr) and the temperature (0:100 (70% yield) for 5 hr at 150°). The sodium salt of **1d** was converted at 150° in diglyme in 73% yield[7] during 5 hr to **4d** as the only isolated product. The arrangement is thus facilitated by methyl groups at the γ position. No allylic inversion products, *i.e.*, 8-α-methylallylic products, were formed in the rearrangement of the crotyl and dimethylallyl compounds.

The sodium salts of both O^6-methylguanine and O^6-ethylguanine (**1a**)[6] were stable at 162° in diglyme for 24 hr. The sodium salt of O^6-benzylguanine (**1e**) was likewise stable under these conditions. The reaction of **2** with sodium benzyloxide (3 equiv) in benzyl alcohol at 130° for 5 hr followed a different course from the allyl types in that the product was not the expected O^6-benzylguanine, but N^2-benzylguanine (**5**), mp 275–276°.[18] The formation of N^2-benzylguanine requires at least 3 equiv of sodium benzyloxide and a trace of benzaldehyde to be present.[19-21] O^6-Benzylguanine (**1e**), mp 202–203°, prepared from **2** using 2 equiv of sodium benzyloxide with the exclusion of benzaldehyde, was convertible to N^2-benzylguanine when heated with 2 equiv of sodium benzyloxide and a trace of benzaldehyde, while N^2-benzylguanine was stable to such treatment.

This study has disclosed an allylic rearrangement from the O^6 to the C-8 position of guanine that occurs without overall allylic inversion, is partially controlled by the degree of methyl substitution on the allylic group and by the temperature, and proceeds with greatest facility through anionic species. Investigation of the mechanistic details is in progress.

Acknowledgment. This work was supported by Research Grant GM 05829 from the National Institutes of Health.

Charles R. Frihart, Nelson J. Leonard*
Roger Adams Laboratory, School of Chemical Sciences
University of Illinois
Urbana, Illinois 61801
Received August 1, 1973

(18) R. Shapiro, B. I. Cohen, S.-J. Shivey, and H. Maurer, *Biochemistry*, **8**, 238 (1969).

(19) In order to obtain O^6-benzylguanine as the product using the following reference, the 30 g of sodium stated in the procedure should be changed to 3.0 g: W. A. Bowles, F. H. Schneider, L. R. Lewis, and R. K. Robins, *J. Med. Chem.*, **6**, 471 (1963).

(20) The mechanism of alkylation of aromatic amines by benzyl alcohol is covered in C. A. Buehler and D. E. Pearson, "Survey of Organic Synthesis," Wiley-Interscience, New York, N. Y., 1970, p 455.

(21) K. J. Andrews, N. Anand, A. R. Todd, and A. Topham, *J. Chem. Soc.*, 2490 (1949), found that 6-amino-9-methyl-2-methylsulfonylpurine with 1 equiv of sodium benzyloxide gave the expected 6-amino-2-benzyloxy-9-methylpurine (66%) and, with 3 equiv, gave the unexpected 6-benzylamino-2-benzyloxy-9-methylpurine (55%).

Photoelectron Spectrum of HBS

Sir:

Molecular photoelectron spectroscopy provides information on the electronic structures of ions and molecules.[1] Intercomparison of a series of isoelectronic species enhances the general usefulness of photoelectron spectra and facilitates their interpretation. However, many interesting members of such series are unstable or reactive and require specialized conditions for observation. Here we report the spectrum of one such species, the HBS molecule. HBS is a linear triatomic molecule with ten valence electrons.[2]

The 127° sector photoelectron spectrometer with electron retardation used in this work has been described previously.[3] By reducing the length of the analyzer entrance slit to 1 cm and by placing a grounded 1 × 4 mm slit between the ionization chamber slit and the analyzer entrance slit, the resolution was improved and the scattered electron intensity reduced. The resolution and sensitivity deteriorated somewhat in the presence of HBS although both could be restored by cleaning the ionization chamber. The spectra reported here were obtained with a resolution of *ca.* 40 meV for argon (FWHM) during the production of HBS.

HBS was continuously prepared by flowing H_2S (Matheson) over pure boron (Koch-Light) in an 8-mm i.d. quartz tube heated to a temperature ranging between 1100 and 1150° as described by Kirk and Timms.[4] The efflux of the reactor was admitted directly to the collision chamber of the spectrometer *via* a 1-cm length of 1-mm i.d. tubing. The pressure in the reactor was estimated to be 0.1 Torr while that in the analyzer was less than 5×10^{-5} Torr. Calibration was carried out using Ar, H_2, and H_2S as internal standards.

Typical photoelectron spectra observed as a function of boron temperature are illustrated in Figure 1. At the higher temperature the production of hydrogen is evidenced by the band beginning at 15.42 eV. In addition, at least two new bands appear. These bands increase with increasing boron temperature and depend on the H_2S mass flow. The ratio of the intensities of the two new bands at lowest ionization potential is independent of temperature and mole fraction of H_2S. As it has been shown previously that HBS and H_2 are the major constituents of the reactor efflux,[2,4] we assign

(1) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, New York, N. Y., 1970.

(2) E. F. Pearson and R. V. McCormick, *J. Chem. Phys.*, **58**, 1619 (1973).

(3) S. Evans, A. F. Orchard, and D. W. Turner, *Int. J. Mass Spectrom. Ion Phys.*, 7, 261 (1971).

(4) R. W. Kirk and P. L. Timms, *Chem. Commun.*, 18 (1967)