Experimental Section

1,3,3-Trimethyl-2-oxyl-2-azabicyclo[2.2.2]octan-5-one (9). Piperitenone (7) was prepared by the method of Beerebom[9] from 178 g of methyl vinyl ketone and 686 g of mesityl oxide, giving 112 g of crude petroleum [90–125 °C bp (10 mm)], which was stirred with 28% aqueous ammonium hydroxide for 120 h at room temperature, saturated with sodium chloride, extracted in ether, extracted with 3 M HCl, dried, and concentrated to a 22% yield (based on MVK) of ca. 90% pure 8. Pulverized 85% potassium hydroxide (20 g) was dissolved in 200 mL of diethylene glycol by heating to 70 °C, and after the solution cooled to 35 °C, 14 g of hydrazine hydrate and 14 g of crude 8 were added. The solution was heated at 230 °C for 3 h and while the distillate produced was collected and cooled to room temperature. After addition of 250 mL of water, the pot solution was extracted three times with 250 mL of ether. Concentration, extraction into 3 M HCl, basification, extraction into ether, drying, concentration, and Kugelrohr distillation gave 2.24 g (19%) 9 as an oil: ^{1}H NMR ($CDCl_3$) δ 0.98 (s), 1.22 (s), 1.50 (s); ^{13}C NMR ($CDCl_3$) δ 23.15, 28.72, 30.90, 32.94, 33.78, 48.52, 51.55; high-resolution mass spectral peak match for $C_{10}H_{19}N$.

Nitroxides 9, 11, 12 and 13 were prepared by use of sodium tungstate dihydrate, hydrogen peroxide oxidation of their amines,[5c] and purification by column chromatography on neutral alumina. All showed the expected ESR spectra.[5-7]

Physical Measurements. The PE, CV, and ^{13}C NMR measurements and data workup have been previously described.[2,4]

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Registry No. 7, 491-09-8; 8, 33069-72-6; 9, 83291-33-2; 11, 34122-41-3; 12, 7123-92-4; 13, 31785-68-9.

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Coupling of Diazopurines, a Curious Steric Effect in a Free Radical Reaction

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The reaction of adenine derivatives with nitrite esters in the presence of arenes was examined and found to give 6-arylpurines in good (83%) to poor (11%) yield. The arylated products consisted only of the meta and para isomers; none of the anticipated ortho isomers were found. The predominance of meta- and para-substituted products is attributed to steric effects. The evidence that the reaction proceeds via a purine radical includes light stimulation, relative insensitivity to electronic factors, and the facile reaction of the purine intermediate with pyridine *N*-oxide. Photolysis of 6-iodo-9-benzylpurine in the presence of anisole gave the same mixture of 6-(*m*-methoxyphenyl)- and 6-(*p*-methoxyphenyl)purine as did diazotization, suggesting that both reactions involve the same purine radical.

The coupling of phenyl diazo compounds with arenes to produce mixed biphenyls is well-known,[1] but coupling of the unstable diazo derivatives of electron-deficient heterocycles[2] has not been reported. Such a reaction would be valuable for it would allow the ready synthesis of unnatural nucleosides, analogues of the antitumor antibiotics like puromycin,[3] and analogues of the postulated endogenous antianxiety substance hypoxanthine.[4] An advantage of using heterocyclic diazo compounds to couple to a benzene, rather than adding phenyl radicals to the heterocycle, is that one can control, a priori, the position of substitution on the heterocyclic ring. Furthermore, a large number of compounds with different substituents and different substitution patterns may be prepared from one intermediate.

The hydrolysis of adenine to hypoxanthine by using aqueous nitrous acid was reported in the last century,[5] but the presumed purinediazonium salt intermediate has never been isolated. Purinediazonium compounds probably have only a transitory existence as few[6] reports exist of their synthetic utility. We report the coupling of the diazo derivatives of N-9-alkylated adenine with other aromatic compounds and discuss possible mechanistic implications arising from the lack of ortho-coupled products in this reaction.

The readily available[7] substituted adenines 1 were diazotized in situ and coupled to an arene which was present

Table I. Partial Rate Factors for the Coupling of Radicals to Substituted Benzenes[a]

	purinyl radical			phenyl radical		
R	ortho	meta	para	ortho	meta	para
OCH3		0.9	5.6	2.4	0.6	1.1
CF3		0.32	0.29	0.6	1.2	2.4
pyridine	0.29	0.14	0.46	1.9	0.9	1.0

[a] The benzene values refer to the coupling of phenyl radicals derived from benzoyl peroxide at 80 °C and are taken from: Walling, Cheves. "Free Radicals in Solution"; Wiley: New York, 1957; p 484.

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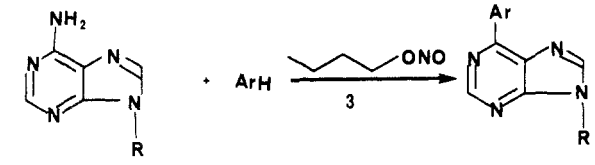


1 a R = CH_3 2 a Ar = C_6H_5 4

b = $CH_2C_6H_5$ b = $C_6H_4CF_3$

c = $C_6H_4OCH_3$

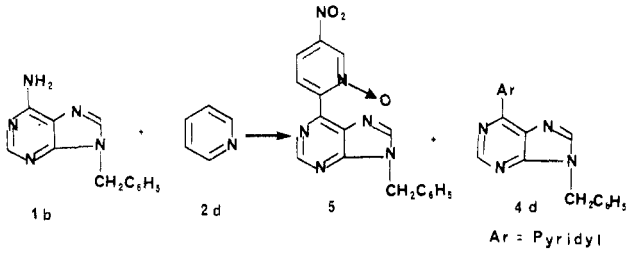
d = Pyridyl

as the solvent. Substituted arenes lead to isomeric mixtures of *m*- and *p*-6-arylpurines which were isolated by HPLC. The structures of the products were assigned by ^1H NMR. Facilitating the assignment of structure was the observation that a proton on the 2′- and 6′-carbon atoms of the newly introduced aromatic ring is shifted 1 ppm downfield by the purine. Complete analysis of the coupling constants of the aromatic protons fully supports the structural assignments.

Phenyl radicals will mainly couple to the ortho position of a monosubstituted benzene derivative. With a strong ortho-directing group such as methoxy, nearly 70% of the biphenyl produced in a coupling reaction will have the ortho orientation. Some partial rate factors for the purine coupling reaction are presented in Table I and are compared to the analogous rate factors for the reaction of phenyl radicals with the same arenes. These partial rate factors were measured by the competition technique.[8]

When **1b** was coupled with pyridine, the expected mixture of α-, β-, and γ-substituted products was isolated. It was then clear that the previous selectivity depended on the steric requirement of the substitutent on the benzene ring involved in the coupling. The other reaction mixtures were carefully examined, and although there were some additional uncharacterized purine products, there was no identifiable amount of ortho isomers.

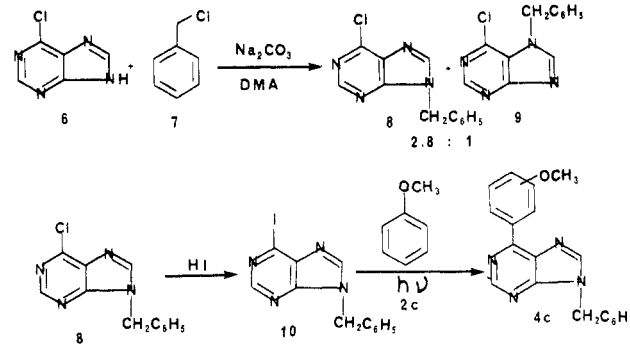
The major product **5** isolated from this pyridine ex-



periment confirmed the radical nature of this reaction. The compound had an elemental composition and mass spectrum corresponding to the empirical formula $C_{17}H_{14}N_6O_3$. This substance possessed a strong amine oxide stretching band in the IR at 1292 cm^{-1} and three pyridine resonances in the ^1H NMR. Decoupling experiments showed that the downfield and upfield pyridine protons were coupled to the third proton with coupling constants of 1.8 and 8.1 Hz but not to each other. This lack of coupling was the critical clue for determining the orientation of substitution, since only the 2- and 5-protons of a pyridine *N*-oxide show no coupling.[9] This product must arise from oxidation of the pyridine, followed by β nitration which is known to occur with nitrites.[10] Arylation at the α-position of an *N*-oxide is known to be enormously accelerated relative to that for benzene.[11]

We considered the possibility that with a relatively unreactive arene such as pyridine, the purine intermediate might react with the benzyl group of a second purine molecule. There were no products with spectral properties consistent with such a process. Also, in the few cases where the coupling of 9-methyl compounds was examined, there was no dramatic increase in yield.

Photolysis of aryl iodides is a general method for producing aryl radicals. To further support the intermediacy of a 6-purinyl radical from the 6-diazonium compound, we prepared 6-iodo-9-benzylpurine (**10**) by the route shown below and photolyzed it in the presence of anisole. The



6-(methoxyphenyl)purine products were isolated by HPLC, and again only the para and meta isomers were obtained. The product ratios from the iodide photolysis and from the diazotization were nearly identical, suggesting that both reactions proceed through the same intermediate.

It is conceivable that the intermediate in the purine arylation is a heterobenzyne. Similarly, one could imagine that the intermediate has carbene character and that this carbene could insert into the 3–4 carbon double bond of the arene and that the resultant norcaradiene could rearrange to products. We could find no additional products that would support such intermediates. Our results suggest that this reaction of adenines is radical-like for it is relatively insensitive to resonance and inductive effects, it is stimulated by light, and there is ample precedence for the production of radicals from phenyl diazonium compounds. Changing the conditions of the reaction, such as adding trifluoroacetic anhydride or various metal salts or irradiating the reaction mixture, does not alter the product ratios, although it does effect the yield. The measurement of the partial rate factors was done with trifluoroacetic anhydride present so that the reaction mixture was homogeneous.

In summary, we have found that 6-purinyl radicals insert with some regioselectivity into arenes. The products seem to result from a radical substitution reaction with some degree of steric control, and we have not found any products that would support a benzyne- or carbene-type intermediate. Further work on other heterocyclic systems is underway in our laboratory to see if this selectivity is a general phenomenon.

Experimental Section

All melting points were determined in a Thomas-Hoover apparatus and are uncorrected. The elemental analyses were performed by Dr. R. Hargreaves and staff and are within 0.4%. The spectra were determined by Dr. W. Gore and staff. All the liquid reagents were distilled prior to use, and the purines were freshly sublimed. All reactions were carried out in oven-dried glassware under an argon atmosphere.

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Measurement of Partial Rate Factors. The general method is illustrated with the specific example of the trifluoromethyl case. A mixture of 49.9 mg of 9-benzyladenine, 5.95 g of trifluorotoluene, 1.19 g of benzene, and 0.15 mL of trifluoroacetic anhydride was slowly heated to 75 °C (oil bath). A 0.10-mL portion of *n*-butyl nitrate was added to the homogeneous solution, and the reaction mixture was kept at 75 °C for 90 min. The cooled solution was evaporated at reduced pressure and the residue filtered through a Waters Sep-Pak with ethyl acetate. Product ratios were determined by HPLC on a 25 cm × 4.6 mm column packed with 10-μm Si-600 and eluted with 30:70 ethyl acetate/hexane. Base-line separation of the arylpurines was achieved. An LDC spectromonitor III variable-wavelength detector was coupled to a Spectra-Physics System I computing integrator, and detector response to the aryl purines was determined by injection of authentic samples. The partial rate factors reported in Table I are the average of two runs done at different ratios of arene solvent. The corrected product ratios from each of the two runs agreed within 10% or better. This corresponds to an error in the partial rate factors ranging from 0.05 with the 3-pyridyl case to 0.1 with *p*-methoxy.

9-Benzyl-6-phenylpurine. A mixture of 6 g (27.0 mmol) of 9-benzyladenine, 2 mL of *n*-butyl nitrite, 500 mg of cuprous oxide, and 60 mL of benzene was heated at reflux for 2 h. An additional 2 mL of *n*-butyl nitrite was added and the mixture heated overnight. The reaction mixture was diluted with 100 mL of methylene chloride and washed with $NaHCO_3$ solution. This solution was chromatographed directly on a Waters Prep-LC 500 and eluted with 1:1 ethyl acetate/hexane to give 6.33 g (83.0 % yield) of a yellow oil (k = 2.3) which solidified upon standing. Recrystallization from benzene gave the analytical sample: mp 121–123 °C; ^{1}H NMR ($CDCl_3$) δ 9.02 (s, 1 H, H-2), 8.80 (m, 2 H, H-2′), 8.01 (s, 1 H, H-8), 7.52 (m, 3 H), 7.27 (s, 5 H, Bz), 5.35 (s, 2 H, CH_2); ^{13}C NMR ($CDCl_3$) 154.5 (5, C-4), 152.4 (59, C-2), 144.1 (50, C-8), 47.0 (52, CH_2) ppm; IR (KBr) 1580, 1565 cm^{-1}; UV (CH_3OH) 205 nm (ε 4.23), 288 (3.86); MS, m/e (relative intensity) 286 (90, M^+), 285 (100, M – H), 258 (5.5, M – HCN), 91 (83, $C_7H_7^+$).

9-Methyl-6-phenylpurine. A mixture of 1 g (6.7 mmol) of 9-methyladenine, 1 mL of *n*-butyl nitrite, and 25 mL of benzene was heated at reflux for 20 h. An additional 1 mL of *n*-butyl nitrite was added and the mixture heated overnight. The cooled reaction mixture was evaporated at reduced pressure and chromatographed by preparative TLC on silica gel. Elution with ethyl acetate gave 0.22 g (R_f 0.32; 15.6% yield) of a white solid. Recrystallization from chloroform/isopropyl ether gave the analytical sample: mp 110–112 °C ^{1}H NMR ($CDCl_3$) δ 9.00 (s, 1 H, H-2), 8.77 (m, 2 H, H-2′), 8.03 (s, 1 H, H-8), 7.53 (m, 3 H), 3.83 (s, 3 H, CH_3); IR (KBr) 1685, 1675, 1322 cm^{-1}; UV (CH_3OH) 202 nm (ε 4.31), 289 (4.04); MS, m/e (relative intensity) 210 (100, M^+), 195 (33, M – CH_3), 183 (32, M – HCN).

Coupling of 9-Benzyladenine with Anisole. A mixture of 5 g (33.3 mmol) of 9-benzyladenine, 5 mL of trifluoroacetic anhydride, and 150 mL of anisole was stirred at room temperature for 20 h. A 5-mL portion of *n*-butyl nitrite was added and the mixture heated at reflux as it was irradiated with a Hanovia 140-W mercury lamp. The reaction was slower in the absence of light. The irradiation was continued overnight as additional *n*-butyl nitrite was added. The cooled reaction mixture was evaporated at reduced pressure and the residue taken up in 50 mL of methylene chloride. This solution was chromatographed on a Waters Prep-LC 500 and eluted with 2:1 ether/hexane to give 0.78 g (10.9 % yield) of a yellow solid (k = 3.0) identified as 9-benzyl-6-(*m*-methoxyphenyl)purine. Recrystallization from isopropyl ether/ethyl acetate gave the analytical sample: mp 114–116 °C; ^{1}H NMR ($CDCl_3$) δ 9.06 (s, 1 H, H-2), 8.43 (m, $J_{5'-6'}$ = 11 Hz, 1 H, H-6′), 8.39 (m, $J_{2'-6'}$ = 2 Hz, 1 H, H-2′), 8.05 (s, 1 H, H-8), 7.48 (m, $J_{4'-5'}$ = 8 Hz, 1 H, H-4′), 7.33 (s, 5 H), 7.00 (m, 1 H, H-5′), 5.34 (s, 2 H, CH_2), 3.91 (s, 3 H, OCH_3); IR (KBr) 1580, 1568 cm^{-1}; UV (CH_3OH) 300 nm (ε 4.19); MS, m/e (relative intensity) 316 (10, M^+), 315 (10, M – 1), 286 (3, M – CH_2O), 91 (100, C_7H_7).

A second fraction (k = 4.0) of 2.15 g (30.5 % yield) of white solid, identified as 9-benzyl-6-(*p*-methoxyphenyl)purine, was also obtained. Recrystallization from isopropyl ether/ethyl acetate gave the analytical sample: mp 148–151 °C; ^{1}H NMR ($CDCl_3$) δ 8.90 (s, 1 H, H-2), 8.73 (d, $J_{2'-3'}$ = 10 Hz, 2 H, H-2′), 7.95 (s, 1 H, H-8), 7.23 (s, 5 H), 6.96 (d, 2 H, H-3′), 5.36 (s, 2 H, CH_2), 3.80 (s, 3 H, OCH_3); IR (KBr) 1608, 1580 cm^{-1}; UV (CH_3OH) 202 nm (ε 4.60), 311 (4.32); MS, m/e (relative intensity) 316 (100, M^+), 315 (71, M – H), 300 (2.5), 225 (49, M – C_7H_7), 91 (100, $C_7H_7^+$).

Coupling of 9-Benzyladenine with Trifluorotoluene. A mixture of 4.5 g (20.0 mmol) of 9-benzyladenine, 5 mL of *n*-butyl nitrite, 150 mg of cuprous oxide, and 100 mL of trifluorotoluene was heated at reflux for 16 h. An additional 5 mL of *n*-butyl nitrite was added and the mixture heated for an additional 24 h. The cooled reaction mixture was evaporated at reduced pressure and the residue chromatographed on a 2 ft × $^5/_{16}$ in. column packed with 25–40-μm silica gel and eluted with 2:3 ethyl acetate/hexane to give 0.15 g (2.1% yield) of a white solid (k = 2.5; mp 125–131 °C) identified as 9-benzyl-6-[*p*-(trifluoromethyl)phenyl]purine. Recrystallization from toluene/heptane gave the analytical sample: ^{1}H NMR ($CDCl_3$) δ 9.04 (s, 1 H, H-2), 8.90 (d, $J_{2'-3'}$ = 8.5 Hz, 2 H, H-2′), 8.09 (s, 1 H, H-8), 7.76 (d, 2 H, H-3′), 7.33 (s, 5 H, Bz), 5.57 (s, 2 H, CH2); IR (KBr) 1580, 1565, 1325 cm^{-1}; UV (CH_3OH) 240 nm (ε 3.98), 290 (4.25); MS, m/e (relative intensity) 354 (40, M^+), 353 (39, M – H), 335 (2, M – F), 91 (100, $C_7H_7^+$).

A second fraction (k = 2.8) of 0.63 g (8.9% yield) of white solid (mp 106–111 °C), identified as 9-benzyl-6-[*m*-(trifluoromethyl)-phenyl]purine, was also obtained. Recrystallization from toluene/hexane gave the analytical sample: ^{1}H NMR ($CDCl_3$) δ 9.03 (s, 1 H, H-2), 8.98 (m, 2 H, H-2′, H-6′), 8.07 (s, 1 H, H-8), 7.68 (m, 2 H, H-4′, H-5′), 7.30 (s, 5 H), 5.42 (s, 2 H, CH_2); IR (KBr) 1610, 1575, 1325 cm^{-1}; UV (CH_3OH) 205 nm (ε 4.77), 240 (4.03), 289 (4.34); MS, m/e (relative intensity) 354 (72, M^+), 353 (83, M – H), 335 (3, M – F), 91 (72, $C_7H_7^+$).

Coupling of 9-Benzyladenine with Pyridine. A mixture of 10 g (44.4 mmol) of 9-benzyladenine, 5 mL of *n*-butyl nitrite, 13 mL of trifluoroacetic anhydride, and 300 mL of pyridine was heated at 75 °C for 20 h. An additional 5 mL of *n*-butyl nitrite was added and the mixture heated overnight. This process was repeated twice more, and then the cooled reaction mixture was evaporated at reduced pressure. This residue was chromatographed on a Waters Prep-LC 500 and eluted with 2:1 acetone/hexane to give 1.4 g (9.0% yield) of a yellow solid (k = 1.7) identified as 9-benzyl-6-(5′-nitro-2′-pyridyl)-9*H*-purine 1′-oxide. Recrystallization from chloroform/ethanol gave the analytical sample: mp 216–218 °C; ^{1}H NMR ($CDCl_3$) δ 10.52 (d, $J_{4'-6'}$ = 1.8 Hz, 1 H, H-6′), 9.38 (dd, J = 8.1, 1.8 Hz, 1 H, H-4′), 8.83 (s, 1 H, H-2), 8.13 (s, 1 H, H-8), 7.31 (s, 5 H, Bz), 6.76 (d, $J_{3'-4'}$ = 8.1 Hz, 1 H, H-3′), 5.44 (s, 2 H, CH_2); IR (KBr) 1670, 1570, 1330, 1292 cm^{-1}; UV (CH_3OH) 208 nm (ε 4.54), 300 (4.39); MS, m/e (relative intensity) 348 (44, M^+), 209 (1.5, M – $C_5H_3N_2O_3$), 91 (100, $C_7H_7^+$).

A second fraction (k = 7.0) of 1.40 g (13.9% yield) of white solid (mp 288–291 °C), identified as 9-benzylhypoxanthine (lit.[12] mp 295–297 °C), was also obtained.

A third fraction (k = 2.4) of 1.30 g was rechromatographed on a 9.4 mm × 50 cm Partisil 10 column and eluted with 70:30 toluene/acetone to give a first fraction (k = 4.5) of 0.24 g (1.9% yield) of a tan solid identified as 9-benzyl-6-(3-pyridyl)purine. Recrystallization from ethyl acetate/hexane gave the analytical sample: mp 145–147 °C; ^{1}H NMR ($CDCl_3$) δ 9.83 (s, 1 H, H-2′), 9.00 (br, 1 H, H-4′), 8.92 (s, 1 H, H-2), 8.60 (d, $J_{5'-6'}$ = 5 Hz, 1 H, H-6′), 7.99 (s, 1 H, H-8), 7.34 (m, 1 H, H-5′), 7.22 (s, 5 H, Bz), 5.34 (s, 2 H, CH_2); IR (KBr) 1590 (m), 1575, 1565 (m), 1320 cm^{-1}; UV (CH_3OH) 234 nm (ε 3.60), 291 (3.90); MS, m/e (relative intensity) 287 (39, M^+), 259 (4, M – CH_2N), 231 (3, M – $C_2H_4N_2$), 91 (100, $C_7H_7^+$).

A second fraction (k = 6.2) of 0.68 g (5.3% yield of tan solid, identified as 9-benzyl-6-(2-pyridyl)purine, was obtained. Recrystallization from chloroform/hexane gave the analytical sample: mp 134–137 °C; ^{1}H NMR ($CDCl_3$) δ 10.03 (br, 1 H, H-3′), 9.28 (d, $J_{5'-6'}$ = 7.5 Hz, 1 H, H-6′), 8.93 (s, 1 H, H-2), 8.74 (d, $J_{4'-5'}$ = 5, 1 H, H-4′), 8.06 (s, 1 H, H-8), 7.58 (m, 1 H, H-5′), 7.26 (s, 5 H), 5.50 (s, 2 H, CH_2); IR (KBr) 1580, 1565 (m), 1320 cm^{-1}; UV (CH_3OH) 234 nm (ε 3.91), 291 (4.17); MS, m/e (relative intensity) 287 (40, M^+), 259 (4, M - CH_2N), 196 (32, M - C_7H_7), 91 (100, $C_7H_7^+$).

A third fraction (k = 7.8) of 0.35 g (2.8% yield) of tan solid, identified as 9-benzyl-6-(4-pyridyl)purine, was obtained. Re-

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crystallization from ethanol gave the analytical sample: mp 138-144 °C; ^{1}H NMR ($CDCl_3$) δ 8.94 (s, 1 H, H-2), 8.69 (s, 4 H, pyr), 8.12 (s, 1 H, H-8), 7.20 (s, 5 H, Bz), 5.40 (s, 2 H, CH_2); IR (KBr) 1640 (m), 1580, 1325 cm^{-1}; UV (CH_3OH) 216 nm (ϵ 4.30), 290 (4.13); MS, m/e (relative intensity) 287 (61, M^+), 259 (6, M - CH_2N), 210 (8, M - C_6H_5), 91 (100, $C_7H_7^+$).

9-Benzyl-6-chloropurine was made by a modification of the procedure of Montgomery.[13] A mixture of 23.3 g (0.15 mol) of 6-chloropurine and 16.25 g of sodium carbonate in 200 mL of dimethylacetamide was stirred at room temperature as 17.5 mL of benzyl chloride was added. After 1 day a second portion of 17.5 mL of benzyl chloride was added, and the stirring was continued for an additional 2 days. The reaction mixture was poured into 2 L of water and the aqueous phase decanted from the gummy solid which formed. This solid was dissolved in 400 mL of methylene chloride, and this solution was chromatographed on a Waters Prep-LC 500 and eluted with 3:2 ethyl acetate/hexane to give 18.67 g (50.9% yield) of a tan solid (k = 2.2) identified as 9-benzyl-6-chloropurine, mp 93-95 °C (lit.[14] mp 84-8.5 °C). A second fraction (k = 6.0) of 6.69 g (18.2 % yield) of white solid (mp 148-149 °C), identified as 7-benzyl-6-chloropurine (lit.[13] mp 152-153 °C), was also obtained.

9-Benzyl-6-iodopurine was made by standard methods.[15] Five grams (20.4 mmol) of 9-benzyl-6-chloropurine was added in portions over 20 min to 25 mL of mechanically stirred, ice cold, 55% aqueous HI. The bright yellow slurry was stirred for an additional 90 min, and the temperature was kept below -5 °C. The slurry was filtered, washed with a little cold water, and then washed with acetone. The air-dried solid residue was suspended in 50 mL of water and cooled to 10 °C, and the pH was adjusted to 8.1. Filtration and drying gave 6.19 g (90.3% yield) of a yellow powder. Recrystallization from toluene/acetone gave the analytical sample: mp 152-154 °C; ^{1}H NMR ($CDCl_3$) δ 8.56 (s, 1 H, H-2), 8.06 (s, 1 H, H-8), 7.30 (s, 5 H, Bz), 5.37 (s, 2 H, CH_2); UV (CH_3OH) 275 nm (ϵ 4.06), 295 (2.97); MS, m/e (relative intensity) 336 (15, M^+), 209 (16, M - I), 91 (100, $C_7H_7^+$).

Photolysis of 9-Benzyl-6-iodopurine. A mixture of 0.5 g (1.49 mmol) of the iodopurine, 0.15 g of sodium bicarbonate, a trace of sodium thiosulfate, and 50 mL of anisole in 300 mL of acetone was placed in a quartz photochemical reactor. The mixture was irradiated for 1 h with a 450-W medium-pressure mercury lamp fitted with a Vycor sleeve. Filtration and evaporation gave 0.69 g of brown gum which was chromatographed to give 0.03 g (6.4% yield) of 9-benzyl-6-(3-methoxyphenyl)purine (mp 110-113 °C) and 0.8 g (17.0% yield) of 9-benzyl-6-(4-methoxyphenyl)purine, mp 150-153 °C. Also obtained were 0.08 g of unreacted starting material and an additional 0.08 g of an uncharacterized non-anisole-containing purine.

Registry No. **1a**, 700-00-5; **1b**, 4261-14-7; **2a**, 71-43-2; **2b**, 98-08-8; **2c**, 100-66-3; **2d**, 110-86-1; **4** (Ar = C_6H_5; R = $CH_2C_6H_5$), 83135-02-8; **4** (Ar = C_6H_5; R = CH_3), 83135-03-9; **4** (Ar = m-$CH_3OC_6H_4$; R = $CH_2C_6H_5$), 83135-04-0; **4** (Ar = p-$CH_3OC_6H_4$; R = $CH_2C_6H_5$), 83135-05-1; **4** (Ar = p-$CF_3OC_6H_4$; R = $CH_2C_6H_5$), 83135-06-2; **4** (Ar = m-$CF_3C_6H_4$; R = $CH_2C_6H_5$), 83135-07-3; **4** (Ar = 5-nitro-2-pyridyl; R = $CH_2C_6H_5$), 83135-08-4; **4** (Ar = 3-pyridyl; R = $CH_2C_6H_5$), 83135-09-5; **4** (Ar = 2-pyridyl; R = $CH_2C_6H_5$), 83135-10-8; **4** (Ar = 4-pyridyl; R = $CH_2C_6H_5$), 83135-11-9; **5**, 83135-12-0; **6**, 87-42-3; **8**, 1928-76-3; **9**, 1928-77-4; **10**, 83135-13-1; 9-benzylhypoxanthine, 14013-11-7.

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Reactions of (Organostannyl)- and (Organogermyl)lithium Reagents with Some (Allylic) Cyclohex-2-enyl Chlorides

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The stereo- and regiochemistries of the reactions between (trimethylgermyl)lithium, (triphenylstannyl)lithium, and (trimethylstannyl)lithium and *cis*- and *trans*-5-methyl-2-cyclohexenyl chlorides, 3,5-dimethyl-2-cyclohexenyl chlorides, and some deuterated derivatives have been investigated utilizing ^{1}H, ^{2}H, ^{13}C, and ^{119}Sn nuclear magnetic resonance spectroscopy. The major substitution pathway (forming the allylic organometallic) involves configurational inversion at carbon and is accompanied by an insignificant level of ^{2}H relocation between the allylic positions. The S_N2 mechanism is strongly implicated. Serious side reactions accompany the reactions of (trimethylgermyl)lithium generated in hexamethylphosphoric triamide (HMPA), and significant amounts of digermanes and cyclohexenyldimethylamines form. The latter almost certainly result from chloride displacement by dimethylamide ($(CH_3)_2N^-$, formed by alkali metal cleavage of HMPA), such displacement proceeding regio- and stereospecifically in accord with the S_N2 pathway. Pentamethyl(cyclohex-2-enyl)digermanes which are formed stereospecifically, are considered to result from chloride displacement by (pentamethyldigermyl)lithium, formed by dimethylgermylene insertion into (trimethylgermyl)lithium itself. Certain redistribution reactions of the pentamethyl(cyclohex-2-enyl)digermanes have been observed.

Substantial progress has been made in understanding the diverse reaction pathways of organometal anions with organic substrates, and much of this attention has been directed to the reactions of organotin alkalis with alkyl halides. Organogermyl alkalis have also been examined, and much of the available information is available in key papers.[1-5]

Some of our studies necessitated the synthesis of certain allylic germanium and tin compounds, desirably with a high level of stereo- and regiocontrol in the carbon-metal bond formation step. Information available indicated that toward secondary (cycloalkyl) bromides, $(C_6H_5)_3SnLi$ displayed "S_N2" behavior, whereas $(CH_3)_3SnLi$ and $(CH_3)_3GeLi$ reacted by free-radical routes, with associated loss of stereocontrol.[1-5] Cycloalkyl chlorides were less susceptible to electron transfer from the organotin alkalis, with an increased tendency toward stereocontrol (inver-

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