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Purines. XXVIII.[1] Preparation of Some 3,7-Dialkyladenines from 3-Alkyladenines by Alkylation: A Subordinate Formation of 3,9-Dialkyladenines

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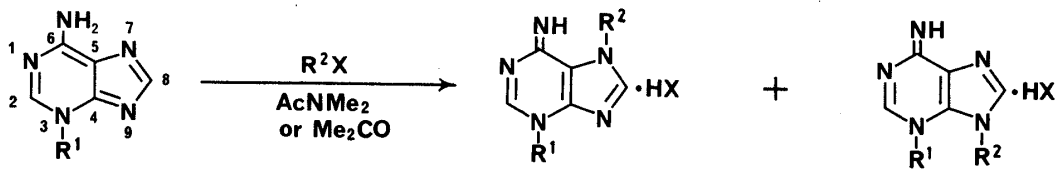
A detailed account is given of the preferential alkylation at the 7-position of 3-alkyladenines (**1**—**3**), which has been effected with MeI, EtI, and $PhCH_2Br$ in $AcNMe_2$ or acetone to prepare the corresponding 3,7-dialkyladenine salts (**4a**—**i**). In the cases of benzylation of 3-methyladenine (**1**) and 3-ethyladenine (**2**) and methylation of 3-benzyladenine (**3**), the 9-position has been found to be another, but much less favored site of alkylation.

Keywords——3-alkyladenine preferential 7-alkylation; 3,7-dialkyladenine synthesis; 3,9-dialkyladenine formation; 3,7-dialkyladenine UV; 3,9-dialkyladenine UV; 3,7-dialkyladenine ^{1}H-NMR; 3,9-dialkyladenine ^{1}H-NMR

In connection with our continuing study on fission and reclosure of the adenine ring,[2] we needed to prepare all the nine 3,7-dialkyladenines (**4a**—**i**) that carry any one of the methyl, ethyl, and benzyl groups at the 3- and 7-positions. It is known that alkylation of 3-alkyladenines (type **1**) with alkyl halide is a ready and convenient access to 3,7-dialkyladenines (type **4**).[3] In the present work, therefore, the necessary compounds **4a**—**i** were prepared from the corresponding 3-alkyladenines (**1**—**3**) according to such a 7-alkylation procedure. Brief accounts of a few of the results recorded here have been published in preliminary form.[3a,e]



1: R^1 = Me
2: R^1 = Et
3: R^1 = $PhCH_2$

4a-i

5c,f,g

a: $R^1=R^2=Me$ **b**: $R^1=Me$; $R^2=Et$ **c**: $R^1=Me$; $R^2=PhCH_2$
d: $R^1=Et$; $R^2=Me$ **e**: $R^1=R^2=Et$ **f**: $R^1=Et$; $R^2=PhCH_2$
g: $R^1=PhCH_2$; $R^2=Me$ **h**: $R^1=PhCH_2$; $R^2=Et$ **i**: $R^1=R^2=PhCH_2$

Chart 1

Alkylations of 3-methyladenine (**1**), 3-ethyladenine (**2**), and 3-benzyladenine (**3**) were effected in most cases in $AcNMe_2$ at 23—80 °C for 1.5—24 h with 3 molar eq of MeI or EtI or with 2 molar eq of $PhCH_2Br$. The main product from each of these alkylations was the ex-

TABLE I. UV Spectra of 3,7- and 3,9-Dialkyladenine Salts

Compound No.	X	UV spectra: Solvent E[a] λ_{max} (nm)	Solvent E $\varepsilon \times 10^{-3}$	Solvent A[b] λ_{max} (nm)	Solvent A $\varepsilon \times 10^{-3}$	Solvent N[c] λ_{max} (nm)	Solvent N $\varepsilon \times 10^{-3}$	Solvent B[d] λ_{max} (nm)	Solvent B $\varepsilon \times 10^{-3}$
4a	I	279	16.2	225	24.2	225	24.4	225	19.5
				277	16.3	277	16.6	282	14.7
4b	I	280	16.1	226	25.8	226	25.0	225	18.4
				278	17.1	278	16.6	282	14.8
4c	Br	281	15.9	224[e]	13.1	224[e]	12.9	285	14.0
				278	16.1	278	16.0		
4d	I	280	17.3	225	24.3	225	24.3	225	18.2
				277	17.1	277	17.1	282	15.1
4e	ClO_4	226	11.1	225	11.2	225	11.6	283	14.8
		280	17.5	277	16.9	277	16.9		
4f	Br	223.5[e]	12.0	222.5[e]	12.5	222.5[e]	12.7	283	13.3
		280	15.8	277	15.3	277	15.3		
4g	ClO_4	226[e]	11.8	223.5[e]	12.7	224[e]	13.3	280	16.2
		281.5	18.0	278	17.6	278	17.5		
4h	ClO_4	226[e]	12.1	225[e]	12.5	225[e]	12.6	282	15.2
		282	18.5	279	17.3	279	17.5		
4i	Br	226[e]	14.9	223.5[e]	14.6	223[e]	15.2	282	13.7
		282	18.5	278.5	17.3	278	17.1		
5c	Br	272.5	17.0	271	17.2	271	17.2	Unstable	
5f	Br	273	16.6	271	17.0	271	17.0	Unstable	
5g	I	273	15.8	271	15.7	271	15.7	Unstable	

a) 95% (v/v) aqueous EtOH. *b*) 0.1 N aqueous HCl (pH 1). *c*) 0.005 M phosphate buffer (pH 7). *d*) 0.1 N aqueous NaOH (pH 13). *e*) Shoulder.

pected 3,7-dialkyladenine, which was isolated (in 50—88% yield) and characterized in the form of an appropriate salt. Benzylation of 3-benzyladenine (**3**) was carried out with *ca.* 6 molar eq of $PhCH_2Br$ in boiling acetone instead of $AcNMe_2$, producing 3,7-dibenzyladenine hydrobromide [**4i** (X=Br)] in 77% yield. Methylation of **3** with MeI in a similar manner afforded 3-benzyl-7-methyladenine hydriodide [**4g** (X=I)] in 79% yield. The 3,7-disubstituted structures of the new compounds **4b—f,h** were supported by their ultraviolet (UV) spectra (Table I) similar to those of the known salts **4g** (X=I) and **4i** (X=Br),[3a,e] which had already been shown to give 7-methyladenine and 7-benzyladenine, respectively, on catalytic hydrogenolysis after conversion into the perchlorate or hydrochloride salts.[3a,e]

In all the above alkylations in $AcNMe_2$, thin-layer chromatographic (TLC) analyses of the reaction mixtures suggested the presence of by-products. Attempts to isolate the minor products were successful only in three cases, giving the 3,9-dialkyladenine salts **5c** (X=Br), **5f** (X=Br), and **5g** (X=I) in 3—9% yields from **1**, **2**, and **3**, respectively. These three salts were converted into the corresponding known perchlorates[4] and identified by direct comparison with authentic samples. It has been reported that methylation of N^6,3-dimethyladenine with MeI in $AcNMe_2$ or $HCONMe_2$ also furnishes the 7-methylated product mainly, but with a considerable amount of the 9-methylated product (15—16% yield).[5] On the other hand, N^6,N^6,3-trimethyladenine has been reported to orient a similar methylation almost exclusively to the 9-position.[6] In the light of the present alkylation results, such alterations in regioselectivity may be attributed to a steric repulsion between the N^6-HMe or N^6-Me_2 and the MeI approaching the 7-position.

In conclusion, the above preparation of the 3,7-dialkyladenine salts has enlarged the

scope of the general 7-alkylation procedure for 3-alkyladenines. It is of particular interest that in a few cases the 9-position of the 3-alkyladenines **1**—**3** has been found to be another, but much less favored site of alkylation.

Experimental

General Notes——All melting points are corrected. UV spectra were measured with a Cary model 15 or a Hitachi model 320 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Associates A-60 or a JEOL JNM-FX-100 spectrometer at 24 °C with Me_4Si as an internal standard. Microanalyses were performed by Mr. Yoshitaka Itatani and his associates at Kanazawa University and by Mr. Josef Nemeth and his associates at the University of Illinois. The following abbreviations are used: br = broad, D = signal disappears on exchange with D_2O, m = multiplet, q = quartet, s = singlet, t = triplet.

3,7-Dimethyladenine Hydriodide [4a (X = I)]——A mixture of 3-methyladenine (**1**)[7] (2.54 g, 17 mmol), MeI (7.24 g, 51 mmol), and $AcNMe_2$ (150 ml) was stirred at 27 °C for 5 h. The precipitate that resulted was filtered, washed with EtOH, and dried to give **4a** (X = I) (2.10 g, 42%), mp > 300 °C. A further crop from the mother liquor and ethanolic washings raised the yield of **4a** (X = I) to 3.34 g (67%). For analysis, the first crop of the crystals was recrystallized from EtOH to give colorless prisms, mp > 300 °C (lit.[3c] mp > 300 °C); UV (Table I); NMR (Me_2SO-d_6) δ: 3.95 [3H, s, N(3)-Me], 4.11 [3H, s, N(7)-Me], 8.60 and 8.73 (1H each, s, purine H's), 8.25—8.65 and 9.0—9.35 (1H each, br, D, NH's). *Anal.* Calcd for $C_7H_{10}IN_5$: C, 28.88; H, 3.46; N, 24.06. Found: C, 28.80; H, 3.60; N, 24.02.

7-Ethyl-3-methyladenine Hydriodide [4b (X = I)]——A mixture of **1**[7] (2.68 g, 18 mmol), EtI (8.42 g, 54 mmol), and $AcNMe_2$ (140 ml) was stirred at 50 °C for 7 h. The resulting faintly yellow solution was concentrated *in vacuo*. The residual solid was washed with ether and recrystallized from 70% (v/v) aqueous EtOH to afford **4b** (X = I) (2.76 g, 50%) as colorless prisms, mp 253.5—255.5 °C (dec.). Further recrystallization in the same manner yielded an analytical sample, mp 269.5—271.5 °C (dec.); UV (Table I); NMR (Me_2SO-d_6) δ: 1.39 (3H, t, J = 7 Hz, $NCH_2\underline{Me}$), 3.96 (3H, s, NMe), 4.54 (2H, q, J = 7 Hz, $NC\underline{H}_2Me$), 8.70 and 8.75 (1H each, s, purine H's), 8.3—8.7 and 9.0—9.4 (1H each, br, D, NH's). *Anal.* Calcd for $C_8H_{12}IN_5$: C, 31.49; H, 3.96; N, 22.95. Found: C, 31.32; H, 3.87; N, 23.07.

7-Benzyl-3-methyladenine Hydrobromide [4c (X = Br)] and 9-Benzyl-3-methyladenine Hydrobromide [5c (X = Br)]——A mixture of **1**[7] (5.97 g, 40 mmol) and $AcNMe_2$ (320 ml) was stirred at 80 °C, and a solution of $PhCH_2Br$ (13.69 g, 80 mmol) in $AcNMe_2$ (80 ml) was added dropwise over a period of 17 min. The resulting mixture was stirred at 80 °C for 1.5 h and then cooled in an ice bath. The precipitate that resulted was filtered, washed with a little EtOH, and dried to give **5c** (X = Br) (1.17 g, 9%), mp 265—266.5 °C (dec.). Recrystallization from 80% (v/v) aqueous EtOH produced an analytical sample as colorless scales, mp 267.5—268.5 °C (dec.); UV (Table I); NMR (Me_2SO-d_6) δ: 3.95 (3H, s, NMe), 5.84 (2H, s, $NC\underline{H}_2Ph$), 7.1—7.5 (5H, m, $NCH_2\underline{Ph}$), 8.52 (1H, s, C(8)-H),[8] 8.57 (1H, s, C(2)-H),[8] 9.21 and 9.32 (1H each, br s, NH's). *Anal.* Calcd for $C_{13}H_{14}BrN_5$: C, 48.77; H, 4.41; N, 21.87. Found: C, 48.51; H, 4.30; N, 21.74.

For isolation of **4c**, the filtrate and washings, which were obtained when the crude **5c** (X = Br) was separated from the reaction mixture, were combined and concentrated *in vacuo*. The residue was washed with three 100-ml portions of ether and treated with boiling EtOH (400 ml). The ethanolic mixture was filtered while hot in order to remove a small amount of the insoluble solid, and the filtrate was kept in a refrigerator. The crystals that deposited were filtered, washed with a little EtOH, and dried to give **4c** (X = Br) (5.45 g, 43%), mp 251—253 °C (dec.). A further crop from the ethanolic mother liquor and washings raised the yield of **4c** (X = Br) to 7.79 g (61%). For analysis, the crude **4c** (X = Br) was recrystallized from EtOH to provide colorless needles, mp 257—258 °C (dec.); UV (Table I); NMR (Me_2SO-d_6) δ: 3.99 (3H, s, NMe), 5.83 (2H, s, $NC\underline{H}_2Ph$), 7.1—7.5 (5H, m, $NCH_2\underline{Ph}$), 8.67 and 8.78 (1H each, s, purine H's), 8.0—8.45 and 8.9—9.25 (1H each, br, D, NH's). *Anal.* Calcd for $C_{13}H_{14}BrN_5$: C, 48.77; H, 4.41; N, 21.87. Found: C, 48.47; H, 4.36; N, 22.05.

9-Benzyl-3-methyladenine Perchlorate [5c (X = ClO_4)]——To a solution of **5c** (X = Br) (100 mg, 0.31 mmol) in warm H_2O (5 ml) was added $NaClO_4$ (76 mg, 0.62 mmol) in one portion. The precipitate that resulted was filtered, washed with a little H_2O, and dried to give a colorless solid (52 mg, 49%). Recrystallization of the solid from MeOH furnished **5c** (X = ClO_4) as colorless needles, mp 248—250 °C (dec.) [lit.[4] mp 248—249 °C (dec.)]. This sample was identical [by mixture melting point test and comparison of infrared (IR) spectrum and TLC mobility] with an authentic sample.[4]

3-Ethyl-7-methyladenine Hydriodide [4d (X = I)]——A mixture of 3-ethyladenine (**2**)[9] (3.26 g, 20 mmol) and MeI (8.52 g, 60 mmol) in $AcNMe_2$ (200 ml) was stirred at 30 °C for 6 h. The resulting yellow solution was concentrated *in vacuo*, and the residual solid was recrystallized from 70% (v/v) aqueous EtOH to give **4d** (X = I) (4.51 g, 74%) as colorless needles, mp 289—291 °C (dec.); UV (Table I); NMR (Me_2SO-d_6) δ: 1.46 (3H, t, J = 7.1 Hz, $NCH_2\underline{Me}$), 4.10 (3H, s, NMe), 4.42 (2H, q, J = 7.1 Hz, $NC\underline{H}_2Me$), 8.61 and 8.80 (1H each, s, purine H's), 8.25—8.8 and 9.0—9.5 (1H each, br, D, NH's). *Anal.* Calcd for $C_8H_{12}IN_5$: C, 31.49; H, 3.96; N, 22.95. Found: C, 31.58; H, 3.98; N, 22.86.

3,7-Diethyladenine Perchlorate [4e (X = ClO_4)]——A mixture of **2**[9] (3.26 g, 20 mmol) and EtI (9.36 g, 60 mmol) in $AcNMe_2$ (200 ml) was stirred at 50 °C for 24 h. The resulting yellowish orange solution was concentrated *in vacuo*.

The residual solid was dissolved in hot H_2O (25 ml) and the aqueous solution was cooled after addition of a solution of $NaClO_4$ (4.90 g, 40 mmol) in H_2O (5 ml). The precipitate that resulted was filtered and recrystallized from 70% (v/v) aqueous EtOH (60 ml) to yield **4e** (X = ClO_4) (4.29 g, 74%), mp 256.5—264.5 °C (dec.). Further recrystallization in the same way gave an analytical sample as colorless needles, mp 268.5—270 °C (dec.); UV (Table I); NMR (Me_2SO-d_6) δ: 1.40 [3H, t, J = 7 Hz, N(7)-CH_2Me], 1.47 [3H, t, J = 7 Hz, N(3)-CH_2Me], 4.43 [2H, q, J = 7 Hz, N(3)-CH_2Me], 4.53 [2H, q, J = 7 Hz, N(7)-CH_2Me], 8.69 and 8.80 (1H each, s, purine H's), 8.2—8.7 and 9.0—9.45 (1H each, br, D, NH's). *Anal.* Calcd for $C_9H_{14}ClN_5O_4$: C, 37.06; H, 4.84; N, 24.01. Found: C, 36.88; H, 4.92; N, 24.04.

7-Benzyl-3-ethyladenine Hydrobromide [4f (X = Br)] and 9-Benzyl-3-ethyladenine Hydrobromide [5f (X = Br)]——A mixture of **2**[9] (4.90 g, 30 mmol) and $PhCH_2Br$ (10.26 g, 60 mmol) in $AcNMe_2$ (150 ml) was stirred at 75—80 °C for 3 h. The reaction solution was concentrated *in vacuo* to leave an oil, which was washed with ether and dissolved in boiling EtOH (60 ml). The resulting ethanolic solution was kept in a refrigerator, and the crystals that deposited were filtered and washed with EtOH (20 ml). Recrystallization of the crude crystals (5.03 g) from 90% (v/v) aqueous EtOH (9 ml) furnished **4f** (X = Br) (4.27 g, 43%) as colorless prisms, mp 219—220 °C (dec.). Concentration of the mother liquor of this recrystallization to a volume of *ca.* 3 ml gave a second crop (386 mg, 4%) of **4f** (X = Br). An analytical sample of **4f** (X = Br) was obtained by further recrystallization [from 90% (v/v) aqueous EtOH] as colorless prisms, mp 220—221 °C (dec.); UV (Table I); NMR (Me_2SO-d_6) δ: 1.49 (3H, t, J = 7 Hz, NCH_2Me), 4.44 (2H, q, J = 7 Hz, NCH_2Me), 5.85 (2H, s, NCH_2Ph), 7.1—7.5 (5H, m, NCH_2Ph), 8.84 and 8.85 (1H each, s, purine H's), 8.0—8.7 and 9.0—9.5 (1H each, br, D, NH's). *Anal.* Calcd for $C_{14}H_{16}BrN_5$: C, 50.31; H, 4.83; N, 20.95. Found: C, 50.03; H, 4.96; N, 20.94.

For isolation of **5f**, concentration of the ethanolic filtrate and washings, which were obtained when the initial crude crystals (5.03 g) were isolated, under reduced pressure left a viscous oil. The oil was washed with ether (50 ml) and dissolved in boiling EtOH (20 ml). The resulting ethanolic solution was kept at room temperature, and the crystals that resulted were filtered and recrystallized from EtOH to give **5f** (X = Br) (281 mg, 3%) as colorless needles, mp 235—236 °C (dec.); UV (Table I); NMR (Me_2SO-d_6) δ: 1.22 (3H, t, J = 7.3 Hz, NCH_2Me), 4.32 (2H, q, J = 7.3 Hz, NCH_2Me), 5.76 (2H, s, NCH_2Ph), 7.1—7.5 (5H, m, NCH_2Ph), 8.52 [1H, s, C(8)-H],[8] 8.66 [1H, s, C(2)-H],[8] 9.24 and 9.34 (1H each, br s, NH's). *Anal.* Calcd for $C_{14}H_{16}BrN_5$: C, 50.31; H, 4.83; N, 20.95. Found: C, 50.22; H, 4.80; N, 21.06.

Concentration of the ethanolic mother liquor (20 ml), obtained when the crude **5f** (X = Br) was isolated, under reduced pressure and recrystallization of the residue from 90% (v/v) aqueous EtOH (6 ml) afforded a third crop (2.43 g) of **4f** (X = Br), raising its total yield to 7.09 g (71%).

9-Benzyl-3-ethyladenine Perchlorate [5f (X = ClO_4)]——A solution of $NaClO_4$ (55 mg, 0.45 mmol) in H_2O (0.5 ml) was added to a solution of **5f** (X = Br) (100 mg, 0.3 mmol) in H_2O (4.5 ml). The precipitate that resulted was filtered, washed with a little H_2O, and dried to give **5f** (X = ClO_4) (101 mg, 95%) as colorless needles, mp 256—257 °C (dec.) [lit.[4] mp 256—256.5 °C (dec.)]. This sample was identical (by comparison of IR spectrum and TLC behavior) with an authentic specimen.[4]

3-Benzyl-7-methyladenine Hydriodide [4g (X = I)] and 3-Benzyl-9-methyladenine Hydriodide [5g (X = I)]——A mixture of 3-benzyladenine (**3**)[3a,e] (4.51 g, 20 mmol) and MeI (8.52 g, 60 mmol) in $AcNMe_2$ (100 ml) was stirred at 23 °C for 8 h. Concentration of the reaction mixture under reduced pressure left a solid, which was washed with ether and recrystallized from MeOH to furnish **4g** (X = I) (5.67 g, 77%) as colorless prisms, mp 253—254 °C (dec.), identical (by comparison of IR spectrum and TLC behavior) with an analytical sample described below. A further crop from the methanolic mother liquor raised the yield of **4g** (X = I) to 88%.

The mother liquor of the second crop of **4g** (X = I) was then concentrated to a volume of *ca.* 5 ml, and the crystals that deposited were filtered, washed with a little MeOH, and dried to yield **5g** (X = I) (211 mg, 3%), mp 202—203 °C (dec.). Recrystallization from MeOH produced colorless needles, mp 204—205 °C (dec.); UV (Table I); NMR (Me_2SO-d_6) δ: 3.74 (3H, s, NMe), 5.89 (2H, s, NCH_2Ph), 7.1—7.5 (5H, m, NCH_2Ph), 8.27 [1H, s, C(8)-H],[8] 8.79 [1H, s, C(2)-H],[8] 9.34 and 9.41 (1H each, br s, NH's). *Anal.* Calcd for $C_{13}H_{14}IN_5$: C, 42.52; H, 3.84; N, 19.07. Found: C, 42.26; H, 3.76; N, 19.10.

In a separate experiment, a stirred mixture of **3**[3a,e] (3.00 g, 13.3 mmol), MeI (50 ml), and acetone (450 ml) was heated under reflux for 25 h. After cooling, the crystals that deposited were collected by filtration, washed with acetone, and recrystallized from 70% (v/v) aqueous EtOH to provide **4g** (X = I) (3.91 g, 79%) as colorless plates, mp 261—262 °C (dec.);[3a,e] UV $\lambda_{max}^{95\%\,EtOH}$ 281.5 nm (ε 17600); $\lambda_{max}^{H_2O}$ 277.5 (17600) essentially unchanged in 0.1 N aqueous HCl; $\lambda_{max}^{0.1\,N\,NaOH}$ 280 (15700); NMR (Me_2SO)[10] δ: 4.19 (3H, s, NMe), 5.72 (2H, s, NCH_2Ph), 7.48 (5H, m, NCH_2Ph), 8.75 and 9.22 (1H each, s, purine H's), 9.04 (2H, br, D, NH's). *Anal.* Calcd for $C_{13}H_{14}IN_5$: C, 42.52; H, 3.84; N, 19.07. Found: C, 42.44; H, 3.90; N, 18.89.

3-Benzyl-7-methyladenine Perchlorate [4g (X = ClO_4)]——To a hot solution of a small sample of **4g** (X = I) in H_2O was added dropwise 20% aqueous $AgClO_4$ until no further precipitation of AgI occurred. The AgI was filtered and washed with hot MeOH. The combined solution of the aqueous filtrate and methanolic washings was evaporated under diminished pressure. The residual solid was recrystallized from MeOH to give **4g** (X = ClO_4) in 86% yield as colorless pillars, mp 288—289 °C (dec.);[3e] UV (Table I); NMR (Me_2SO)[10] δ: 4.18 (3H, s, NMe), 5.70 (2H, s, NCH_2Ph), 7.54 (5H, m, NCH_2Ph), 8.69 and 9.16 (1H each, s, purine H's), 9.16 (2H, br, D, NH's). *Anal.* Calcd for

$C_{13}H_{14}ClN_5O_4$: C, 45.96; H, 4.15; N, 20.61. Found: C, 46.05; H, 4.21; N, 20.52.

3-Benzyl-9-methyladenine Perchlorate [5g (X=ClO$_4$)]——A solution of 70% aqueous $HClO_4$ (20 mg, 0.14 mmol) in MeOH (0.3 ml) was added to a solution of **5g** (X=I) (37 mg, 0.1 mmol) in hot MeOH (1 ml). After cooling, the precipitate that resulted was filtered, washed with a little MeOH, and dried to give **5g** (X=ClO$_4$) (23 mg, 67%), mp 207—209 °C (dec.). Recrystallization from MeOH furnished colorless prisms, mp 220—221 °C, identical (by comparison of IR spectrum and TLC behavior) with authentic **5g** (X=ClO$_4$).[11]

3-Benzyl-7-ethyladenine Perchlorate [4h (X=ClO$_4$)]——A mixture of **3**[3a,e] (3.38 g, 15 mmol) and EtI (7.02 g, 45 mmol) in $AcNMe_2$ (120 ml) was stirred at 50 °C for 8 h. The resulting solution was concentrated *in vacuo*, and the residue was washed with ether and then dissolved in H_2O (30 ml). The aqueous solution was mixed with a solution of $NaClO_4$ (2.45 g, 20 mmol) in H_2O (5 ml). The precipitate that resulted was filtered, washed with a little H_2O, and dried to give **4h** (X=ClO$_4$) (3.07 g, 58%), mp 191—196 °C (dec.). Recrystallization from 70% (v/v) aqueous EtOH produced an analytical sample as colorless needles, mp 201.5 °C (dec.); UV (Table I); NMR (Me_2SO-d_6) δ: 1.38 (3H, t, J=7 Hz, $NCH_2\underline{Me}$), 4.50 (2H, q, J=7 Hz, $NC\underline{H}_2Me$), 5.60 (2H, s, $NC\underline{H}_2Ph$), 7.25—7.6 (5H, m, $NCH_2\underline{Ph}$), 8.66 and 9.02 (1H each, s, purine H's), 8.4—8.7 and 9.2—9.5 (1H each, br, D, NH's). *Anal.* Calcd for $C_{14}H_{16}ClN_5O_4$: C, 47.53; H, 4.56; N, 19.80. Found: C, 47.35; H, 4.46; N, 19.74.

3,7-Dibenzyladenine Hydrobromide [4i (X=Br)]——A stirred mixture of finely powdered **3**[3a,e] (2.25 g, 10 mmol), $PhCH_2Br$ (10.5 g, 61.4 mmol), and acetone (500 ml) was heated under reflux for 75 h. After cooling, the reaction mixture was filtered, and the crystals collected were washed with acetone and dried to yield **4i** (X=Br) (3.06 g, 77%). Recrystallization from 70% (v/v) aqueous EtOH and drying over P_2O_5 *in vacuo* (0.3 mmHg) at 78 °C for 12 h and then at 140 °C for 12 h furnished an analytical sample as a hygroscopic, colorless powder, mp 205—207 °C (lit.[3b] mp 145 °C); UV (Table I); NMR (Me_2SO)[10] δ: 5.92 [2H, s, N(3)-$C\underline{H}_2Ph$], 6.14 [2H, s, N(7)-$C\underline{H}_2Ph$], 7.48 (10H, m, $NCH_2\underline{Ph}$'s), 9.2 (2H, br, D, NH's), 9.22 and 9.44 (1H each, s, purine H's). *Anal.* Calcd for $C_{19}H_{18}BrN_5$: C, 57.59; H, 4.58; N, 17.67. Found: C, 57.56; H, 4.67; N, 17.48.

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References and Notes

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