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# Purines. VII.[1] Hydration and Methoxylation of Alkynyl-9*H*-purines

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Coupling of 6- and 2-halo-9-phenyl-9*H*-purines (**1**, **2**, and **5**) with terminal acetylenes in dimethylformamide (DMF) was well catalyzed by bis(triphenylphosphino)palladium chloride [$PdCl_2(PPh_3)_2$] to give the corresponding alkynyl-9-phenyl-9*H*-purines (**3** and **4**).

Conversion of alkynyl-9-phenyl-9*H*-purines (**3** and **4**) into the corresponding purinylmethyl ketones (**6** and **7**) was achieved by treatment with an aqueous solution of mercuric sulfate and sulfuric acid (method A) or with piperidine and oxalic acid dihydrate (method B). On the other hand a trimethylsilylethynyl group on the 9*H*-purine ring was converted into an acetyl group by hydration using method A.

Addition of sodium methoxide to 6-(trimethylsilylethynyl)-9-phenyl-9*H*-purine (**3d**) took place to give 6-(2,2-dimethoxyethyl)-9-phenyl-9*H*-purine (**10**), while 2-(trimethylsilylethynyl)-9-phenyl-9*H*-purine (**4c**) reacted with sodium methoxide under the same conditions to give 2-(2-methoxyethenyl)-9-phenyl-9*H*-purine (**11**).

**Keywords**——halo-9*H*-purine; alkynyl-9*H*-purine; cross-coupling; palladium catalyst; acetylenic bond hydration; acetylenic bond methoxylation

Recently we have reported the introduction of functionalized carbons at the 2-[1] and 6-positions[2,3] on the 9*H*-purine ring by the substitution of chloro- and methylsulfonyl-9-phenyl-9*H*-purines with carbanions generated from active methylene compounds and ketones. Since an alkynyl group attached to *N*-heteroarenes can be converted easily into several functionalized carbon chains, alkynyl-*N*-heteroarenes were expected to be useful intermediates in organic synthesis. For example, it was reported that the hydration of alkynylpyrimidines[4a] with an aqueous solution of mercuric sulfate and sulfuric acid gave pyrimidinylmethyl ketones, and the addition of $H_2O$ and MeOH to ethynylpyrimidines[5] proceeded to give acetyl- and dimethoxyethylpyrimidines, respectively. Then our interest was focused on the preparation of 9*H*-purine derivatives having an acetylenic side chain and on the conversion of alkynyl groups on the 9*H*-purine ring into various functionalized carbon chains.

It is well known that the preparation of alkynyl-*N*-heteroarenes[4] from halogenated *N*-heteroarenes by cross-coupling with terminal acetylenes is effectively catalyzed by bis-(triphenylphosphino)palladium chloride [$PdCl_2(PPh_3)_2$]. For example, 2-iodoadenosine[4e]

reacted with terminal acetylenes in the presence of $PdCl_2(PPh_3)_2$ and CuI in $Et_3N$ and dimethylformamide (DMF) to give 2-alkynyladenosine, and cross-coupling of 6-halo-9*H*-purine[4f] with terminal acetylenes under the same conditions proceeded to give 6-alkynyl-9*H*-purines.

The present paper deals with the preparation of alkynyl-9-phenyl-9*H*-purines (**3** and **4**) from halo-9-phenyl-9*H*-purines (**1**,**2** and **5**) by cross-coupling and the transformation of alkynyl-9-phenyl-9*H*-purines (**3** and **4**) into the corresponding 9-phenyl-9*H*-purinylmethyl ketones (**6** and **7**), acetyl- (**8** and **9**), 2-methoxyethenyl- (**11**), and (2,2-dimethoxyethyl)-9-phenyl-9*H*-purines (**10**) by means of hydration and addition of methanol.

When a solution of 6-chloro-9-phenyl-9*H*-purine (**1**) and phenylacetylene in the presence of catalytic amounts of $PdCl_2(PPh_3)_2$ and CuI in $Et_3N$ and DMF as cosolvent was refluxed for 5 h, 9-phenyl-6-phenylethynyl-9*H*-purine (**3a**) was obtained in 62% yield. Similarly, compound **1** reacted with 1-hexyne and propargyl alcohol to give 6-(1-hexynyl)-9-phenyl-9*H*-purine (**3b**) and 3-(9-phenyl-9*H*-purin-6-yl) propargyl alcohol (**3c**), respectively. Compound **1** did not react with trimethylsilylacetylene under the same conditions as described above, but the reaction at 120°C in a sealed tube for 5 h gave 9-phenyl-6-[2-(trimethylsilyl)ethynyl]-9*H*-purine (**3d**). Thus, the reaction of 2-chloro-9-phenyl-9*H*-purine (**2**) with phenylacetylene, 1-hexyne, and trimethylsilylacetylene under the same conditions as in the case of **1** resulted in the formation of 2-alkynyl-9-phenyl-9*H*-purines (**4**). However, compound **2** did not react with propargyl alcohol.

It is well known[4a,b,e] that an iodine atom is more easily coupled with terminal acetylenes than a chlorine atom on *N*-heteroarenes. Thus, we investigated cross-coupling of 6-iodo-9-phenyl-9*H*-purine (**5**), prepared from **1** by substitution with NaI, with terminal acetylenes at room temperature to give 6-alkynyl-9-phenyl-9*H*-purines (**3a—d**). The yields of the products exceeded those observed in the case of **1**. However, we could not examine cross-coupling of the 2-iodo derivatives, because the substitution of **2** with NaI did not proceed. The structures of **3a—d** and **4a—c** were supported by elemental analyses and infrared (IR) absorption and proton nuclear magnetic resonance ($^1$H-NMR) spectral data, as shown in Tables I and II.

Then we examined the conversion of alkynyl-9-phenyl-9*H*-purines (**3** and **4**) into (9-

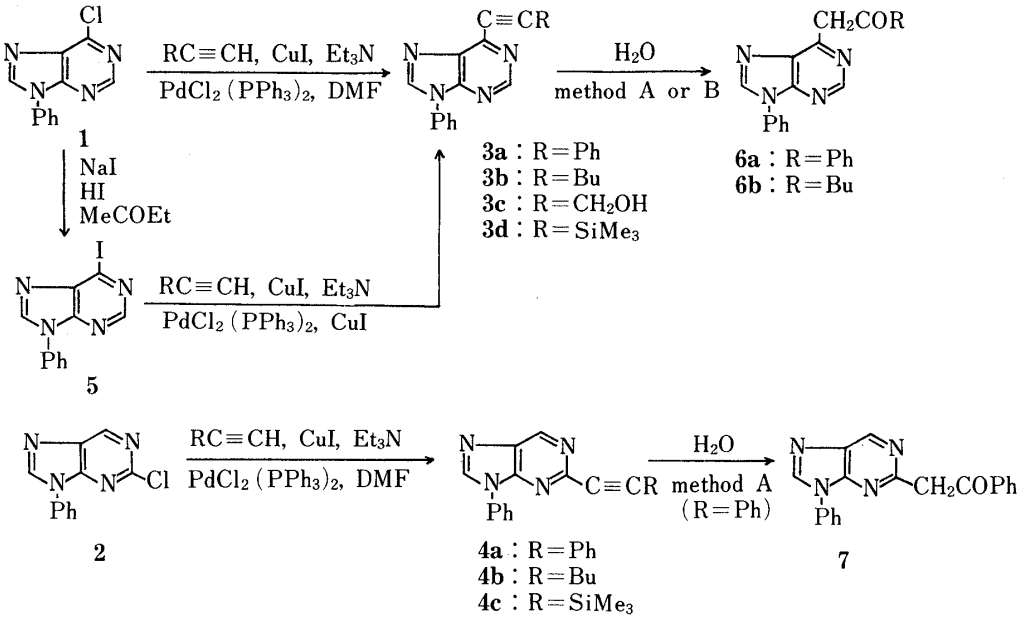


Chart 1

phenyl-9*H*-purinyl)methyl ketones (**6** and **7**) by hydration. It was reported that the phenylethynyl group on the quinoline,[6] pyridine,[7] and pyrimidine[4a] rings was converted into the phenacyl group by treatment with aqueous solution of mercuric sulfate and sulfuric acid (method A). Moreover, phenylethynylpyrimidines[4a] were transformed into phenyl pyrimidinylmethyl ketones by treatment with piperidine followed by hydrolysis of the resulting enamines with oxalic acid dihydrate (method B). The hydration of 6-(1-hexynyl)-9-phenyl-9*H*-purine (**3b**) by method A resulted in the formation of butyl (9-phenyl-9*H*-purin-6-yl)methyl ketones (**6b**) in 16% yield, and the same product (**6b**) was obtained in 87% yield by method B. Similarly, phenyl (9-phenyl-9*H*-purin-6-yl)methyl ketone (**6a**) was obtained by methods A and B in 31% and 85% yields, respectively, as shown in Table I. We conclude from the results described above that method B is more appropriate than method A for hydration of 6-alkynyl-9-phenyl-9*H*-purines (**3a** and **b**). In the case of alkynyl group at the 2-position, hydration of **4a** by method A proceeded to give phenyl (9-phenyl-9*H*-purin-2-yl)methyl ketone (**7**), although the yield was low. However, the hydration of **4a** by method B did not proceed and **4a** was recovered. Moreover, the hydration of **4b** by methods A and B failed to give the desired product. In the $^1$H-NMR spectra of **6a,b** and **7**, the existence of a highly stabilized enolic form due to intramoleculor hydrogen bonding was recognized, indicating that an acylmethyl group is attached directly to the 9*H*-purine ring, as shown in Table III.

Hydration[5] of the ethynyl group on pyridine, quinoline, isoquinoline, and pyrimidine rings by method A to give acetyl derivatives has been reported. In connection with the hydration of an ethynyl group, we examined the conversion of a trimethylsilylethynyl group on the 9*H*-purine ring into an acetyl group by hydration using method A.

When a solution of 6-(trimethylsilylethynyl)-9-phenyl-9*H*-purine (**3d**), mercuric sulfate, and sulfuric acid in aqueous acetone was refluxed for 5 h, 6-acetyl-9-phenyl-9*H*-purine (**8**) was obtained in 48% yield. Similarly, hydration of **4c** was found to occur under the same conditions, resulting in the formation of 2-acetyl-9-phenyl-9*H*-purine (**9**) in 41% yield.

It was reported[5] that ethynyl-*N*-heteroarenes having the ethynyl group at an active position, that is, 2-ethynylpyridine, 4-ethynylquinoline, 1-ethynylisoquinoline, and 4-ethynyl-

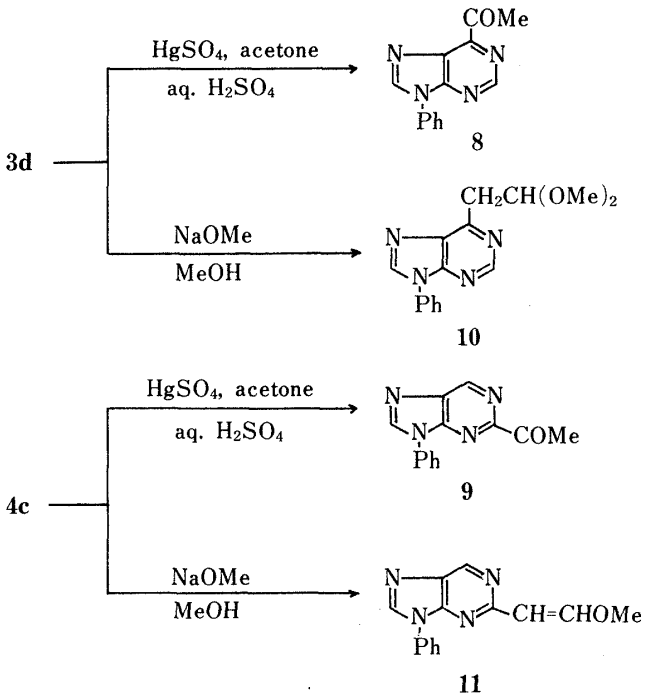


Chart 2

TABLE I. Yields, IR Spectral Data, Melting Points, and Elemental Analyses for **3**, **4**, and **6**—**11**

| Compd. | Yield (%) | | $\nu_{max}^{KBr}$ ($cm^{-1}$) | mp (°C) | Formula | Analysis (%) Calcd (Found) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | N |
| **3a** | 62[a] | 81[b] | 2220 (C–C) | 154—156 | $C_{19}H_{12}N_4$ | 77.01 | 4.08 | 18.91 |
| | | | | | | (76.98 | 4.06 | 18.91) |
| **3b** | 54[a] | 75[b] | 2320 (C–C) | 92—94 | $C_{17}H_{16}N_4$ | 73.89 | 5.84 | 20.28 |
| | | | | | | (73.75 | 5.78 | 20.20) |
| **3c** | 22[a] | 64[b] | 2320 (C–C) | 200—202 | $C_{14}H_{10}N_4O$ | 67.19 | 4.03 | 22.39 |
| | | | 3400 (NH) | | | (66.94 | 4.00 | 22.31) |
| **3d** | 28[a] | 79[b] | 2110 (C–C) | 136—137 | $C_{16}H_{16}N_4Si$ | 65.72 | 5.52 | 19.16 |
| | | | | | | (65.70 | 5.42 | 19.02) |
| **4a** | 52[a] | | 2310 (C–C) | 115—117 | $C_{19}H_{12}N_4$ | 77.01 | 4.08 | 18.91 |
| | | | | | | (76.59 | 4.15 | 18.44) |
| **4b** | 47[a] | | 2320 (C–C) | 90—93 | $C_{17}H_{16}N_4$ | 73.89 | 5.84 | 20.28 |
| | | | | | | (73.88 | 5.89 | 20.25) |
| **4c** | 46[a] | | | 100—101 | $C_{16}H_{16}N_4Si$ | 65.72 | 5.52 | 19.16 |
| | | | | | | (65.72 | 5.52 | 19.12) |
| **6a** | 31[c] | 85[d] | 1660 (C=O) | 222—223[e] | | | | |
| **6b** | 16[c] | 87[d] | 1660 (C=O) | 131—132 | $C_{17}H_{18}N_4O$ | 69.37 | 6.16 | 19.04 |
| | | | | | | (69.21 | 6.14 | 19.10) |
| **7** | 19[c] | | 1635 (C=O) | 163—164[f] | | | | |
| **8** | 48[c] | | 1700 (C=O) | 206—208 | $C_{13}H_{10}N_4O$ | 65.53 | 4.23 | 23.53 |
| | | | | | | (65.17 | 4.21 | 23.54) |
| **9** | 41[c] | | 1700 (C=O) | 147—148 | $C_{13}H_{10}N_4O$ | 65.53 | 4.23 | 23.53 |
| | | | | | | (65.29 | 4.26 | 23.10) |
| **10** | 58 | | | 59—61 | $C_{15}H_{16}N_4O_2$ | 63.36 | 5.67 | 19.17 |
| | | | | | | (63.40 | 5.68 | 19.72) |
| **11** | 17 | | | 104—105 | $C_{14}H_{12}N_4O$ | 66.65 | 4.79 | 22.21 |
| | | | | | | (66.77 | 4.81 | 22.00) |

*a*) Yield from cross-coupling of 2- and 6-chloro-9-phenyl-9*H*-purines. *b*) Yield from cross-coupling of 6-iodo-9-phenyl-9*H*-purine. *c*) Yield from hydration using method A. *d*) Yield from hydration using method B. *e*) Lit.[3] mp 223.5—224.5 °C. *f*) Lit.[1] mp 164—165 °C.

pyrimidine reacted with sodium methoxide to give 2,2-dimethoxyethyl-*N*-heteroarenes, whereas ethynyl-*N*-heteroarenes having the ethynyl group at an inactive position, that is, 3-ethynylpyridine, 3-ethynylquinoline, 4-ethynylisoquinoline, and 5-ethynylpyrimidine reacted with sodium methoxide to give 2-methoxyethenyl-*N*-heteroarenes. Moreover, addition of sodium methoxide to trimethylsilylethynylpyridinecarbonitriles[8] was reported to give 2,2-dimethoxyethylpyridinecarbonitriles. Thus, we investigated the reaction of 2-(**4c**) and 6-(trimethylsilylethynyl)-9-phenyl-9*H*-purines (**3d**) with sodium methoxide. Addition of sodium methoxide to **3d** in MeOH smoothly proceeded in the same way as observed for ethynyl-*N*-heteroarenes having the ethynyl group at an active position, giving 6-(2,2-dimethoxyethyl)-9-phenyl-9*H*-purine (**10**). The $^1$H-NMR spectrum showed a characteristic singlet due to two methoxy groups (3.36 ppm) and signals of a $CH_2$-CH moiety (3.55 and 5.20 ppm), and is consistent with the assigned structure. On the other hand, the trimethylsilylethynyl group at the 2-position of the 9*H*-purine ring was converted the 2-methoxyethenyl group by addition of methanol in the same way as observed for the ethynyl-*N*-heteroarenes having the ethynyl group at an inactive position, resulting in the formation of 2-(2-methoxyethenyl)-9-phenyl-9*H*-purine (**11**). Based on the $^1$H-NMR spectrum, the side chain of **11** has the *E* configuration (see Table III).

TABLE II. $^1$H-NMR Spectral Data for **3a—d** and **4a—c**

| Compd. | $^1$H-NMR ($CDCl_3$) $\delta$ ppm | | | | |
|---|---|---|---|---|---|
| | C(2)-H | C(6)-H | C(8)-H | N–Ph | Others |
| **3a** | 8.95 (s) | | 8.37 (s) | 7.26—7.86 (10H, m, Ph×2) | |
| **3b** | 8.88 (s) | | 8.30 (s) | 7.38—7.84 (m) | 0.83—1.20 (3H, m, $(CH_2)_3C\underline{H}_3$)<br>1.45—2.00 (4H, m, $CH_2(C\underline{H}_2)_2CH_3$)<br>2.50—2.83 (2H, m, $C\underline{H}_2(CH_2)_2CH_3$) |
| **3c**[a] | 9.17 (s) | | 9.06 (s) | 7.15 (s) | 4.82 (2H, s, $C\underline{H}_2OH$) |
| **3d** | 8.94 (s) | | 8.38 (s) | 7.39—7.82 (m) | 0.35 (9H, s, $Si(CH_3)_3$) |
| **4a** | | 8.99 (s) | 8.19 (s) | 7.35—7.95 (10H, m, Ph×2) | |
| **4b** | | 9.10 (s) | 8.29 (s) | 7.35—7.95 (m) | 0.74—1.16 (3H, m, $(CH_2)_3C\underline{H}_3$)<br>1.34—2.00 (4H, m, $CH_2(C\underline{H}_2)_2CH_3$)<br>2.29—2.67 (2H, m, $C\underline{H}_2(CH_2)_2CH_3$) |
| **4c** | | 9.18 (s) | 8.38 (s) | 7.40—7.86 (m) | 0.30 (9H, s, $Si(CH_3)_3$) |

*a*) In $CF_3COOH$.

TABLE III. $^1$H-NMR Spectral Data for **6—11**

| Compd. | $^1$H-NMR ($CDCl_3$) $\delta$ ppm | | | | |
|---|---|---|---|---|---|
| | C(2)-H | C(6)-H | C(8)-H | N–Ph | Others |
| **6a** | 8.43 (s) | | 8.13 (s) | 7.28—7.81 (8H, m, Ph) | 6.80 (1H, s, CH=C–OH)<br>7.81—8.12 (2H, m, Ph)<br>14.70—16.13 (1H, br, CH=C–O$\underline{H}$) |
| **6b** | 7.23 (s) | | 8.03 (s) | 7.27—7.90 (m) | 0.71—1.12 (3H, m, $(CH_2)_3C\underline{H}_3$)<br>1.35—2.02 (4H, m, $CH_2(C\underline{H}_2)_2CH_3$)<br>2.25—2.80 (2H, m, $C\underline{H}_2(CH_2)_2CH_3$)<br>4.38 (0.6H, s, $CH_2C=O$)<br>6.01 (0.7H, s, $C\underline{H}$=C–OH)<br>14.45—15.66 (0.7H, br, CH=C–O$\underline{H}$) |
| **7** | | 8.94 (s) | 8.15 (s) | 7.21—7.98 (10H, m, Ph×2) | 4.68 (0.4H, s, $CH_2C=O$)<br>6.31 (0.8H, s, $C\underline{H}$=C–OH)<br>13.86—14.78 (0.8H, br, CH=C–O$\underline{H}$) |
| **8** | 9.16 (s) | | 8.57 (s) | 7.42—7.96 (m) | 2.92 (3H, s, $CH_3C=O$) |
| **9** | | 9.10 (s) | 8.32 (s) | 7.31—7.77 (m) | 2.77 (3H, s, $CH_3C=O$) |
| **10** | 8.82 (s) | | 8.20 (s) | 7.27—7.96 (m) | 3.36 (6H, s, $OCH_3$×2)<br>3.55 (2H, d, $C\underline{H}_2$–CH)[a]<br>5.20 (1H, t, $CH_2$–C$\underline{H}$)[a] |
| **11** | | 8.91 (s) | 8.10 (s) | 7.21—7.85 (m) | 3.68 (3H, s, $OCH_3$)<br>6.02 (1H, d, CH=CH)[b]<br>7.86 (1H, d, CH=CH)[b] |

*a*) $J$=6 Hz. *b*) $J$=13 Hz.

We concluded that the transformation of alkynyl groups into acylmethyl, acetyl, 2,2-dimethoxyethyl, and 2-methoxyethenyl groups is a useful method for the introduction of functionalized carbons at the 2- and 6-positions of the 9*H*-purine ring.

## Experimental

All melting points are uncorrected. IR spectra were measured with a Jasco A-102 diffraction grating IR

spectrophotometer. $^1$H-NMR spectra were taken at 60 MHz and 23 °C with a Hitachi R-24B high-resolution $^1$H-NMR spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane as an internal standard. The following abbreviations are used; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

**General Procedure for Cross-Coupling of 6-Chloro-9-phenyl-9*H*-purine (1) with Terminal Acetylenes**——A mixture of **1** (0.5 g, 2.2 mmol), a terminal acetylene (2.4 mmol), CuI (8 mg, 0.044 mmol), $PdCl_2$ $(PPh_3)_2$ (31 mg, 0.044 mmol), $Et_3N$ (4 ml), and DMF (3 ml) was refluxed for 5h. The solvent was removed under reduced pressure. The residue was diluted with $H_2O$ and extracted with $CHCl_3$. The crude product obtained from the $CHCl_3$ extract was purified by $SiO_2$ column chromatography using $CHCl_3$ as an eluant and recrystallized from petroleum benzin–benzene to give **3a**—**c**.

**Cross-Coupling of 1 with Trimethylsilylacetylene**——A mixture of **1** (0.5 g, 2.2 mmol), trimethylsilylacetylene (0.23 g, 2.4 mmol), CuI (8 mg, 0.044 mmol), $PdCl_2(PPh_3)_2$ (31 mg, 0.044 mmol), $Et_3N$ (1 ml), and DMF (3 ml) was heated at 120 °C for 5 h in a sealed tube. The solvent was removed under reduced pressure. The residue was purified by $SiO_2$ column chromatography using benzene–$CHCl_3$ (1 : 1) as an eluant, and recrystallized from petroleum benzin–benzene to give 9-phenyl-6-trimethylsilylethynyl-9*H*-purine (**3d**) as colorless needles.

**General Procedure for Cross-Coupling of 2-Chloro-9-phenyl-9*H*-purine (2) with Terminal Acetylenes**——A mixture of **2** (0.3 g, 1.3 mmol), a terminal acetylene (1.5 mmol), CuI (5 mg, 0.026 mmol), $PdCl_2$ $(PPh_3)_2$ (20 mg, 0.026 mmol), $Et_3N$ (3 ml), and DMF (2 ml) was refluxed for 5h. The same work-up of the reaction mixture as for **3a**—**c** gave **4a**,**b** from the first fraction eluted with benzene–$CHCl_3$ (1 : 1) and **2** from the second fraction.

**Cross-Coupling of 2 with Trimethylsilylacetylene**——A mixture of **2** (0.5 g, 2.2 mmol), trimethylsilylacetylene (0.23 g, 2.4 mmol), CuI (8 mg, 0.044 mmol), $PdCl_2$ $(PPh_3)_2$ (31 mg, 0.044 mmol), $Et_3N$ (1 ml), and DMF (2 ml) was heated at 120 °C in a sealed tube. The same work-up of the reaction mixture as for **3d** gave **4c** as colorless needles from petroleum benzin–benzene.

**General Procedure for Cross-Coupling of 5 with Terminal Acetylenes**——A mixture of **5** (0.5 g, 1.6 mmol), a terminal acetylene (1.9 mmol), CuI (6 mg, 0.03 mmol), $PdCl_2$ $(PPh_3)_2$ (21 mg, 0.03 mmol), $Et_3N$ (4 ml), and DM (3 ml) was stirred for 5 h at room temperature. The same work-up of the reaction mixture as for cross-coupling of **1** with terminal acetylenes gave **3a**—**c**.

**Cross-Coupling of 5 with Trimethylsilylacetylene**——A mixture of **5** (0.5 g, 1.6 mmol), trimethylsilylacetylene (0.16 g, 1.7 mmol), CuI (6 mg, 0.03 mmol), $PdCl_2$ $(PPh_3)_2$ (21 mg, 0.03 mmol), $Et_3N$ (4 ml), and DMF (3 ml) was stirred for 5 h at room temperature. The same work-up as for cross-coupling of **1** with trimethylsilylacetylene gave **3d**.

**General Procedure for Hydration of Alkynyl-9-phenyl-9*H*-purines (3a, b, d, and 4a, c)**——Method A : A solution of an alkynyl-9-phenyl-9*H*-purine (**3a**, **b**, **d** or **4a**, **c**) (0.68 mmol) and $HgSO_4$ (0.68 mmol) in 70% aqueous acetone (5 ml) containing 98% $H_2SO_4$ (0.5 g) was refluxed for 6 h. The solvent was removed under reduced pressure. The residue was diluted with $H_2O$, made alkaline with $Na_2CO_3$, and extracted with $CHCl_3$. The crude procuct obtained from the $CHCl_3$ extract was purified by $SiO_2$ column chromatography using $CHCl_3$ as an eluant and recrystallized from benzene to give **6a**, **b**, **7**, **8**, and **9**.

Method B : A solution of an alkynyl-9-phenyl-9*H*-purine (**3a** or **3b**) (0.68 mmol) and piperidine (1.36 mmol) in toluene (5 ml) was refluxed for 60 h. The solvent was removed under reduced pressure. The residue was dissolved in a mixture of oxalic acid dihydrate (0.81 mmol), ether (5 ml), and EtOH (3 ml), and the whole was refluxed for 6 h. After removal of the solvent by evaporation, the residue was diluted with $H_2O$, made alkaline with $Na_2CO_3$, and extracted with $CHCl_3$. The crude product obtained from the $CHCl_3$ extract was purified by $SiO_2$ column chromatography using $CHCl_3$ as an eluant and recrystallized from benzene to give **6a**, **b**.

**General Procedure for the Reaction of Trimethylsilylethynyl-9-phenyl-9*H*-purine (3d and 4c) with Sodium Methoxide**——A solution of trimethylsilylethynyl-9-phenyl-9*H*-purine (**3d** or **4c**) (0.5 g, 1.7 mmol) and NaOMe (0.2 g, 3.7 mmol) in MeOH (10 ml) was refluxed for 2 h. The solvent was removed under reduced pressure. The residue was diluted with $H_2O$ and extracted with $CHCl_3$. The crude product obtained from the $CHCl_3$ extract was purified by $SiO_2$ column chromatography using $CHCl_3$ as an eluant and recrystallized from petroleum benzin–benzene to give **10** or **11**.

**6-Iodo-9-phenyl-9*H*-purine (5)**——A solution of **1** (0.5 g, 0.22 mmol), NaI (0.97 g, 0.65 mmol), and 57% HI (5 ml) in ethyl methyl ketone (30 ml) was stirred at room temperature for 1 h. The solvent was removed under reduced pressure. The residue was diluted with $H_2O$, made alkaline with $Na_2CO_3$, and extracted with $CHCl_3$. The crude product obtained from the $CHCl_3$ extract was purified by $SiO_2$ column chromatography using $CHCl_3$ as an eluant and recrystallized from benzene to give **5** as colorless needles, mp 196—198 °C. Yield 0.63 g (90%). *Anal.* Calcd for $C_{11}H_7IN_4$: C, 41.01; H, 2.19; N, 17.39. Found: C, 41.30; H, 2.23; N, 17.56. $^1$H-NMR ($CDCl_3$) $\delta$: 7.31—7.73 (5H, m, Ph), 8.29 (1H, s, C(8)-H), 8.54 (1H, s, C(2)-H).

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