

Synthetic Studies on Fused Nitrogen-heterocycles from *N*-Amino-*N,N'*-dihydrodiazinediones (II). Condensation of *N*-Amino-*N,N'*-dihydrodiazinediones with α, β -Unsaturated Carbonyl Compounds

Sung Chul Shin[†], Kyung Ho Kang, and Youn Young Lee*

Department of Chemistry, Seoul National University, Seoul 151-742

Yang Mo Goo

Department of Pharmacy, Seoul National University, Seoul 151-742. Received September 4, 1989

The condensation of 1-amino-1,2-dihydro-3,6-pyridazinedione (**1**) and 2-amino-2,3-dihydro-1,4-phthalazinedione (**2**) with mesityl oxide or 3-penten-2-one in acetic acid-ethanol (1:1) gave 3,4,6,9-tetrahydro-6,9-dioxopyridazino[1,2-*a*][1,2,3]triazines (**9,11**) and 3,4,6,11-tetrahydro-6,11-dioxo[1,2,3]triazino[1,2-*b*]phthalazines (**10,12**), respectively. The condensation of **1** and **2** with crotonaldehyde, cinnamaldehyde or acrylaldehyde under the same reaction condition gave only *N*-alkylidene derivatives (**3-8**). When the *N*-alkylidene derivatives isolated from the reaction of **1** and **2** with crotonaldehyde and cinnamaldehyde (**3-6**) were refluxed in acetic acid, the corresponding heterocyclic compounds (**13-16**) were obtained.

Introduction

Although various fused 1,2,3-triazines have been reported¹, only a limited number of fused 1,2,3-triazines in which two nitrogen atoms are common to two adjacent ring have been synthesized.²

We previously reported³ that the condensation of 1-amino-1,2-dihydro-3,6-pyridazinedione (**1**) and 2-amino-2,3-dihydro-1,4-phthalazinedione (**2**)⁴ with acetylacetone, mesityl oxide or diethyl acetylenedicarboxylate using acidic cyclizing agents yielded the novel heterocyclic ring system, pyridazino[1,2-*a*][1,2,3]triazines and [1,2,3]triazino[1,2-*b*]phthalazines, respectively. Recently we also reported⁵ the condensation of **1** and **2** with various 1,3-dicarbonyl compounds using polyphosphoric acid as a cyclizing agent to afford 6,9-dihydro-6,9-dioxopyridazino[1,2-*a*][1,2,3]triazines and 6,11-dihydro-6,11-dioxo[1,2,3]triazino[1,2-*b*]phthalazines, respectively, in good yields. As a part of our continuing study on the construction of heterocyclic ring systems, we are examining the condensation of **1** and **2** with various bifunctional carbonyl compounds. In this report we wish to describe the synthesis of 3,4,6,9-tetrahydro-6,9-dioxopyridazino[1,2-*a*][1,2,3]triazines and 3,4,6,11-tetrahydro-6,11-dioxo[1,2,3]triazino[1,2-*b*]phthalazines from **1** and **2**, respectively, by condensation reaction with α, β -unsaturated carbonyl compounds.

Results and Discussion

When we examined various acidic cyclizing agents such as sulfuric acid, polyphosphoric acid, acetic acid etc. for the condensation of **1** or **2** with α, β -unsaturated carbonyl compounds to obtain fused 1,2,3-triazine derivatives, acetic acid was found to be the most effective. Thus, compound **1** or **2** was suspended in acetic acid-ethanol (1:1) which was maintained at 60 °C. To this mixture mesityl oxide or 3-penten-2-one was added to give homogeneous solution. It was

further stirred for 1 hr to give cyclized product, 3,4,6,9-tetrahydro-6,9-dioxopyridazino[1,2-*a*][1,2,3]triazines (**9** and **11**) or 3,4,6,11-tetrahydro-6,11-dioxo[1,2,3]triazino[1,2-*b*]phthalazines (**10** and **12**) in moderate yields (50-60 %). When **1** or **2** was reacted with crotonaldehyde, cinnamaldehyde or acrylaldehyde under the same condition, no cyclized products were obtained. Only *N*-alkylidene derivatives (**3-8**) were obtained in good yields (73-90%).

When *N*-alkylidene derivatives were isolated and refluxed in acetic acid for 2-6 hr, the ones, **3-6** were converted to the cyclized products (**13-16**) in 13-55% yields, whereas the others, **7** and **8** were not converted to the cyclized products. Attempts to obtain these cyclized products directly from the reaction of **1** or **2** with crotonaldehyde or cinnamaldehyde by refluxing in acetic acid were failed.

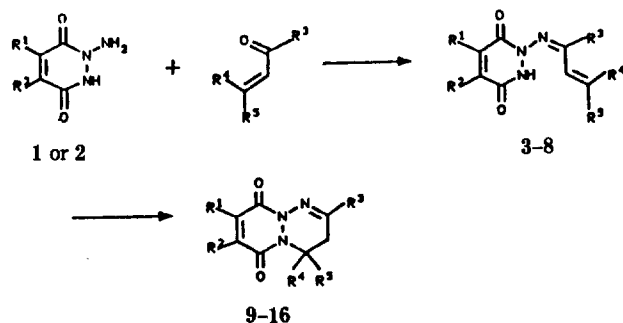
The cyclized products (**9-16**) did not show any amino or enolic hydroxy absorption in the IR spectra and showed molecular ion peaks in the mass spectra. The ¹H NMR spectra of **9** and **10** exhibited singlet at δ 2.57 and 2.50, respectively, for the geminal C-3 protons. The compound **11** and **12** showed doublets of doublets around δ 2.68-2.78 ($J = 16$ and 6 Hz) and 2.73-2.83 ($J = 16$ Hz and 6 Hz) for the geminal C-3 protons. The compound **13-16** showed triple doublets around δ 2.42-2.87 ($J = 19, 5$ and 2 Hz) and 2.84-3.17 ($J = 19, 7$ and 2 Hz) for the geminal C-3 protons. The ¹H NMR data for C-2, C-3 and C-4 protons in the compound **9-16** are summarized in Table 1.

Experimental

Melting points were recorded on a Electrothermals digital melting point apparatus and are uncorrected, ¹H NMR spectra were recorded on Varian EM-360, Bruker AC 80 or Varian XL-100 NMR spectrometer and the data were given in δ units downfield from TMS. IR spectra were obtained with Perkin-Elmer 283 infrared spectrophotometer. Mass spectra were measured with Jeol JMS-DX 303, Hewlett Packard 5945A or VG 12-250 mass spectrometer.

Analytical tlc was done on Silica gel plates, 60 F₂₅₄ (E).

[†]Present address: Department of chemistry, Gyeongsang National University, Chinju 660-300



- 1 $R^1 = R^2 = H$
- 2 $R^1 + R^2 = (CH=CH)_2$
- 3 $R^1 = R^2 = R^3 = R^4 = H, R^5 = CH_3$
- 4 $R^1 + R^2 = (CH=CH)_2, R^3 = R^4 = H, R^5 = CH_3$
- 5 $R^1 = R^2 = R^3 = R^4 = H, R^5 = Ph$
- 6 $R^1 + R^2 = (CH=CH)_2, R^3 = R^4 = H, R^5 = Ph$
- 7 $R^1 = R^2 = R^3 = R^4 = R^5 = H$
- 8 $R^1 + R^2 = (CH=CH)_2, R^3 = R^4 = R^5 = H$
- 9 $R^1 = R^2 = H, R^3 = R^4 = R^5 = CH_3$
- 10 $R^1 + R^2 = (CH=CH)_2, R^3 = R^4 = R^5 = CH_3$
- 11 $R^1 = R^2 = R^4 = H, R^3 = R^5 = CH_3$
- 12 $R^1 + R^2 = (CH=CH)_2, R^4 = H, R^3 = R^5 = CH_3$
- 13 $R^1 = R^2 = R^3 = R^4 = H, R^5 = CH_3$
- 14 $R^1 + R^2 = (CH=CH)_2, R^3 = R^4 = H, R^5 = CH_3$
- 15 $R^1 = R^2 = R^3 = R^4 = H, R^5 = Ph$
- 16 $R^1 + R^2 = (CH=CH)_2, R^3 = R^4 = H, R^5 = Ph$

Scheme 1

Table 1. 1H NMR Data for C-2, C-3 and C-4 Protons in the Compounds 9-16

Compounds	C ₂ -H	C ₃ -H	C ₄ -H
9		2.57(s)	
10		2.50(s)	
11		2.68(dd, $J = 16$ and 6 Hz)	4.00(sext, $J = 6$ Hz)
12		2.73(dd, $J = 16$ and 6 Hz)	4.00 (sext, $J = 6$ Hz)
13	7.37(dd, $J = 5$ and 2 Hz)	2.83(dd, $J = 16$ and 6 Hz)	5.48(dquintet, $J = 7$ and 2 Hz)
14	7.38(dd, $J = 5$ and 2 Hz)	2.42(ddd, $J = 19, 5$ and 2 Hz)	5.63(dquintet, $J = 7$ and 2 Hz)
15	7.43(dd, $J = 5$ and 2 Hz)	2.84(ddd, $J = 19, 7$ and 2 Hz)	6.31(dd, $J = 7$ and 2 Hz)
16	7.54(dd, $J = 5$ and 2 Hz)	2.43(ddd, $J = 19, 5$ and 2 Hz)	6.61(dd, $J = 7$ and 2 Hz)
		2.79(ddd, $J = 19, 5$ and 2 Hz)	
		3.06(ddd, $J = 19, 7$ and 2 Hz)	
		2.92(ddd, $J = 19, 7$ and 2 Hz)	
		3.17(ddd, $J = 19, 7$ and 2 Hz)	

Merck). Column chromatography was done on a column packed with Silica gel 60 (70-230 mesh ASTM, E. Merck). 1-Amino-1,2-dihydro-3,6-pyridazinedione and 2-amino-2,3-dihydro-1,4-phthalazinedione were prepared by the method described in the literature^{4,5}. Other chemicals and solvents were purchased from commercial sources and used without further purification.

3,4,6,9-Tetrahydro-2,4,4-trimethyl-6,9-dioxopyridazino[1,2-*a*][1,2,3]triazine(9). To a stirred suspension of 1-amino-1,2-dihydro-3,6-pyridazinedione (1, 1.0g, 7.8 mmol) in 20 ml of acetic acid-ethanol(1:1) preheated to 60 °C was added mesityl oxide (0.76g, 7.8 mmol) in small portions, producing a green solution. After stirring for 1 hr at 60 °C, the solvent was evaporated to give a residue. To the residue was added diethyl ether (50 ml) and the mixture was allowed to stand at room temperature, yielding a solid product which was recrystallized from ethyl acetate to give 0.80g(57%) of pure 9: mp 162 °C; 1H NMR(CDCl₃) δ 1.80(s, 6H, N-C(CH₃)₂), 2.36(s, 3H, N=CCH₃), 2.57(s, 2H, CH₂), 6.87(d, 1H, $J = 10.8$ Hz, CH=), 7.10(d, 1H, $J = 10.8$ Hz, CH=); IR(KBr) 1630, 1370, 1250 cm⁻¹; MS m/e 207(M⁺, 28.6), 192(3.5), 164(5.3), 138(11.5), 136(3.5), 110(3.5), 82(100), 56(49.1), 54(64.5), 41(67.1).

3,4,6,11-Tetrahydro-2,4,4-trimethyl-6,11-dioxo[1,2,3]triazino[1,2-*b*]phthalazine(10). Compound 10 was prepared from 2-amino-2,3-dihydro-1,4-phthalazinedione (2, 1.0g, 5.6 mmol) and mesityl oxide(0.59g, 6.0 mmol) by a similar method. The major product was isolated by column chromatography using chloroform-ethanol (1:1) as an eluent and recrystallized from ethyl acetate-ether (0.85g, 50%): mp 124 °C; 1H NMR(CDCl₃) δ 1.73(s, 6H, N-C(CH₃)₂), 2.27(s, 3H, N=CCH₃), 2.50(s, 2H, CH₂), 7.66-8.43(m, 4H, C₆H₄); IR(KBr) 1630, 1370 cm⁻¹; MS m/e 257(M⁺, 100), 2.42(11), 214(10), 188(80.3), 186(3), 160(9), 132(12), 104(65), 56(49.1), 41(36).

3,4,6,9-Tetrahydro-2,4-dimethyl-6,9-dioxopyridazino[1,2-*a*][1,2,3]triazine(11). Compound 11 was prepared from 1 (1.0g, 7.8 mmol) and 3-penten-2-one (0.66g, 7.9 mmol) by a similar method. The major product was isolated by column chromatography using ethyl acetate as an eluent and recrystallized from ethyl acetate (1.0g, 66%): mp 112 °C; 1H NMR(CDCl₃) δ 1.17(d, 3H, $J = 6$ Hz, N-CCH₃) 2.18 (s, 3H, N=CCH₃), 2.68 (dd, 1H, $J = 16$ and 6 Hz, C₃-H), 2.73(dd, 1H, $J = 16$ and 6 Hz, C₃-H), 4.00(sext, 1H, $J = 6$ Hz, C₄-H), 7.10(d, 1H, $J = 10$ Hz, =CH), 7.27(d, 1H, $J = 10$ Hz, =CH); IR(KBr) 3000, 1720, 1660 cm⁻¹; MS m/e 193 (M⁺, 8.1), 178(5.3), 150(1.3), 124(3.1), 122(2.2), 96(5.5), 82(70.3), 54(76.5), 41(38.8).

3,4,6,11-Tetrahydro-2,4-dimethyl-6,11-dioxo[1,2,3]triazino[1,2-*b*]phthalazine(12). Compound 12 was prepared from 2 (1.0g, 5.6 mmol) and 3-penten-2-one (0.48g, 5.80 mmol) by a similar method. The major product was isolated by column chromatography using chloroform-ethanol (20:1) as an eluent (0.70g, 51%): mp 133 °C; 1H NMR (CDCl₃) δ 1.22(d, 3H, $J = 6$ Hz, N-CCH₃), 2.18(s, 3H, N=CCH₃), 2.70(dd, 1H, $J = 16$ and 6 Hz, C₃-H), 2.83(dd, 1H, $J = 16$ and 6 Hz, C₃-H), 4.00(sext, 1H, $J = 6$ Hz, C₄-H), 7.78-8.50(m, 4H, C₆H₄); IR(KBr) 3000, 1720, 1600 cm⁻¹; MS m/e 243(M⁺, 0.6), 174(1.3), 132(2.7), 104(91.5), 76(100), 41(9.0).

1-(2-Butenylidenamino)-1,2-dihydro-3,6-pyridazinedione(3). Compound 3 was prepared from 1 (2.00g, 15.7 mmol) and crotonaldehyde (3.31g, 47.2 mmol) in 40 ml of acetic acid-ethanol (1:1) by a similar method. The crude product was recrystallized from ethyl acetate (2.38g, 85%): mp 177 °C; $^1\text{H NMR}$ ($\text{CDCl}_3 + \text{DMSO}-d_6$) δ 1.96(d, 3H, $J=6$ Hz, CH_3), 6.42(m, 2H, $\text{NC}-\text{CH}=\text{CH}$), 7.00(d, 1H, $J=10$ Hz, $=\text{CH}$), 7.17(d, 1H, $J=10$ Hz, $=\text{CH}$), 8.58(m, 1, $\text{N}=\text{CH}$); IR(KBr) 3000, 1660, 1600, 1000 cm^{-1} .

2-(2-Butenylidenamino)-2,3-dihydro-1,4-phthalazinedione(4). Compound 4 was prepared from 2 (2.00g, 11.5 mmol) and crotonaldehyde (1.59g, 22.5 mmol) in 40 ml of acetic acid-ethanol (1:1) by a similar method. The crude product was recrystallized from ethyl acetate-ethanol (1.93g, 73%): mp 193-195 °C; $^1\text{H NMR}$ ($\text{CDCl}_3 + \text{DMSO}-d_6$) δ 2.00(d, 3H, $J=6$ Hz, CH_3), 6.49(m, 2H, $\text{NC}-\text{CH}=\text{CH}$), 7.79-8.56(m, 4H, C_6H_4), 8.67(m, 1H, $\text{N}=\text{CH}$); IR(KBr) 3000, 1650, 1590, 980 cm^{-1} .

1-(3-Phenyl-2-propenylidenamino)-1,2-dihydro-3,6-pyridazinedione(5). Compound 5 was prepared from 1 (2.00g, 15.7 mmol) and cinnamaldehyde (4.10g, 31.5 mmol) in 40 ml of acetic acid-ethanol (1:1) by a similar method (reaction time, 30 min). The precipitated solid was filtered and recrystallized from ethanol (3.42g, 90%): mp 236 °C (dec); $^1\text{H NMR}$ ($\text{CDCl}_3 + \text{DMSO}-d_6$) δ 7.10-7.67 (m, 9H, $\text{CH}=\text{CH}$ and $\text{CH}=\text{CH}-\text{C}_6\text{H}_5$), 8.77(m, 1H, $\text{N}=\text{CH}$), 11.40(br s, 1H, enolic OH); IR(KBr) 3000, 1660, 1580, 980 cm^{-1} .

2-(3-Phenyl-2-propenylidenamino)-2,3-dihydro-1,4-phthalazinedione(6). Compound 6 was prepared from 2 (2.00g, 11.5 mmol) and cinnamaldehyde (1.94g, 14.5 mmol) in 40 ml of acetic acid-ethanol (1:1) by a similar method (reaction time, 30 min). The precipitated solid was filtered and recrystallized from ethanol (2.84g, 85%): mp 228 °C (dec); $^1\text{H NMR}$ ($\text{CDCl}_3 + \text{DMSO}-d_6$) δ 7.16-8.60(m, 11H, C_6H_4 and $\text{CH}=\text{CH}-\text{C}_6\text{H}_5$), 8.87 (m, 1H, $\text{N}=\text{CH}$), 11.93 (br s, 1H, enolic OH); IR(KBr) 3000, 1650, 1590, 900 cm^{-1} .

1-(2-Propenylidenamino)-1,2-dihydro-3,6-pyridazinedione(7). Compound 7 was prepared from 1 (1.50g, 11.8 mmol) and acrylaldehyde (1.32g, 23.6 mmol) in 30 ml of acetic acid-ethanol (1:1) by a similar method (reaction time, 20 min). The crude product was recrystallized from chloroform-methanol (1.42 g, 73%): mp 191 °C (dec); $^1\text{H NMR}$ ($\text{CDCl}_3 + \text{DMSO}-d_6$) δ 5.86(m, 2H, $=\text{CH}_2$), 6.74(m, 1H, $\text{NC}-\text{CH}=\text{CH}$), 7.00(d, 1H, $J=10$ Hz, $=\text{CH}$), 7.19(d, 1H, $J=10$ Hz, $\text{CH}=\text{CH}$), 8.57(d, 1H, $J=9$ Hz, $\text{N}=\text{CH}$), 11.20 (br s, 1H, enolic OH); IR(KBr) 3000, 1660, 1600 cm^{-1} .

2-(2-Propenylidenamino)-2,3-dihydro-1,4-phthalazinedione(8). Compound 8 was prepared from 2 (2.50g, 14.1 mmol) and acrylaldehyde(1.58g, 28.2 mmol) in 50 ml of acetic acid-ethanol (1:1) by a similar method (reaction time, 20 min). The crude product was recrystallized from chloroform-methanol(2.58g, 85%): mp 190 °C; $^1\text{H NMR}$ ($\text{CDCl}_3 + \text{DMSO}-d_6$) δ 5.75(m, 2H, $=\text{CH}_2$), 6.91(m, 1H, $\text{NC}-\text{CH}=\text{CH}$), 7.67-8.47(m, 4H, C_6H_4), 8.64(d, 1H, $J=9$ Hz, $\text{N}=\text{CH}$); IR(KBr) 3000, 1650, 1590 cm^{-1} .

3,4,6,9-Tetrahydro-4-methyl-6,9-dioxypyridazino[1,2-a][1,2,3]triazine(13). The compound 3 (0.50g, 2.80 mmol) was added to 40 ml of acetic acid and the mixture was heated to 70-80 °C to give a clear solution. The resultant solution was refluxed for 2 hr. After the reaction mixture

was cooled to room temperature, it was evaporated under reduced pressure to give a residue. The residue was suspended in aqueous 10% NaHCO_3 solution and it was extracted with chloroform (3 \times 20 ml). The organic layer was dried over MgSO_4 and evaporated under reduced pressure to give a pale green solid product 13 (83mg, 16%): mp 126 °C; $^1\text{H NMR}$ (CDCl_3) δ 1.30(d, 3H, $J=7$ Hz, CH_3), 2.42(ddd, 1H, $J=19, 5$ and 2 Hz, C_3-H), 2.84(ddd, 1H, $J=19, 7$ and 2 Hz, C_3-H), 5.48(dquint, 1H, $J=7$ and 2 Hz, C_4-H), 6.97(d, 1H, $J=10$ Hz, $\text{CH}=\text{CH}$), 7.08(d, 1H, $J=10$ Hz, $\text{CH}=\text{CH}$), 7.37(dd, 1H, $J=5$ and 2 Hz, C_2-H); IR(KBr) 1700, 1660 cm^{-1} ; MS m/e 179(M^+ , 29.3), 124(19.8), 96(5.2), 82(57.6), 54(16.2).

3,4,6,11-Tetrahydro-4-methyl-6,11-dioxo[1,2,3]-triazino[1,2-b]phthalazine(14). Compound 14 was prepared from 4 (0.50g, 2.18 mmol) by a similar method; yield: 0.16g (32%); mp 193 °C; $^1\text{H NMR}$ (CDCl_3) δ 1.35(d, 3H, $J=7$ Hz, CH_3), 2.43 (ddd, 1H, $J=19, 5$ and 2 Hz, C_3-H), 2.92(ddd, 1H, $J=19, 7$ and 2 Hz, C_3-H), 5.63(dquint, 1H, $J=7$ and 2 Hz, C_4-H), 7.38(dd, 1H, $J=5$ and 2 Hz, C_2-H), 7.76-8.56(m, 4H, C_6H_4); IR(KBr) 1690, 1650 cm^{-1} ; MS m/e 229 (M^+ , 15.0), 174(71.8), 146(3.3), 132(5.8), 104(75.2), 76(100).

3,4,6,9-Tetrahydro-4-phenyl-6,9-dioxypyridazino[1,2-a][1,2,3]triazine(15). Compound 15 was prepared from 5 (1.0g, 4.14 mmol) by a similar method (refluxed for 6 hr). The major product was isolated by column chromatography using ethyl acetate-hexane (3:1) as an eluent (0.13g, 13%): mp 156 °C; $^1\text{H NMR}$ (CDCl_3) δ 2.79(ddd, 1H, $J=19, 5$ and 2 Hz, C_3-H), 3.06(ddd, 1H, $J=19, 7$ and 2 Hz, C_3-H), 6.31 (dd, 1H, $J=7$ and 2 Hz, C_4-H), 6.89(d, 1H, $J=10$ Hz, $=\text{CH}$), 7.00(d, 1H, $J=10$ Hz, $=\text{CH}$), 7.29(s, 5H, C_6H_5), 7.43(dd, 1H, $J=5$ and 2 Hz, C_2-H); IR(KBr) 1700, 1660 cm^{-1} ; MS m/e 241(M^+ , 81.6), 186(86.7), 158(11.2), 82(100), 54(70.7).

3,4,6,11-Tetrahydro-4-phenyl-6,11-dioxo[1,2,3]-triazino[1,2-b] phthalazine(16). Compound 16 was prepared from 6(0.50g, 1.72 mmol) by a similar method (refluxed for 6hr). The crude product was recrystallized from ethanol (0.28g, 55%): mp 214 °C; $^1\text{H NMR}$ (CDCl_3) δ 2.87(ddd, 1H, $J=19, 5$ and 2 Hz, C_3-H), 3.17(ddd, 1H, $J=19, 7$ and 2 Hz, C_3-H), 6.61(dd, 1H, $J=7$ and 2 Hz, C_4-H), 7.31(s, 5H, C_6H_5), 7.54(dd, 1H, $J=5$ and 2 Hz, C_2-H), 7.74-8.50 (m, 4H, C_6H_4); IR(KBr) 1690, 1660 cm^{-1} ; MS m/e 291 (M^+ , 26.2), 236(70.4), 208(1.7), 132(15.0), 104(91.9), 76(100).

Acknowledgement. This research was supported by a grant from Korea Science and Engineering Foundation.

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Syntheses and Properties of the High-Tc Superconductive $\text{Bi}_{2-x}\text{Mo}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ System

Keu Hong Kim^{*}, Jong Tae Lim, Seung Koo Cho, Byoung Chan Kwak, Don Kim[†], and Jae Shi Choi

Department of Chemistry, Yonsei University, Seoul 120-749. Received September 11, 1989

The superconducting properties have been studied for high-Tc superconductors of the $\text{Bi}_{2-x}\text{Mo}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ system ($x = 0.03-0.30$). The crystal structure is pseudo tetragonal with the average lattice parameters $a = 5.38 \text{ \AA}$, $b = 5.44 \text{ \AA}$ and $c = 30.6 \text{ \AA}$. All samples exhibit superconductivity with Tc offset at 79 K and Tc onset at 90-115 K. The Tc onset point decreases with increasing x , but the Tc offset points are nearly the same for all samples. Scanning electron micrographs show a special growth behavior of the grains with a plate shape. It is suggested that the decrease in Tc onset points with substitution of Mo for Bi is due to the decrease in lattice parameters and to the p -orbital of Mo. It is concluded that Mo does not play a crucial role in the superconducting transition of the $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ system.

Introduction

Maeda *et al.*¹ were the first to synthesize a superconducting composition of $\text{BiSrCaCu}_2\text{O}_x$ (1112) which had a Tc of about 105 K, but with a low-temperature tail extending to 80 K. They reported that the composition must contain both Sr and Ca in order to have a high-Tc phase. The $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (2223) phase² has been synthesized by D. Kim *et al.*³ and it exhibits superconductivity with Tc onset at 120 K and Tc offset at 79 K. They report that the 2223 composition can easily contain a low-Tc phase depending on thermal treatment condition.

Recently, K. H. Kim *et al.*⁴ have synthesized 1111, 1112 and 1113 compositions and studied their Raman spectra. They have found that the Raman line at 630 cm^{-1} is the most intense, corresponds to the (zz) configuration and is assigned to Cu-O stretching vibration along the c axis. However, this strong band at 630 cm^{-1} is split into at least two components, 629 and 655 cm^{-1} , indicating the presence of distinct Cu-O bonds along the c axis, especially for the samples with a low-Tc phase.

To study a possible structure ordering effect in the Bi-Sr-Ca-Cu-O system with a low-Tc phase, high-Tc superconducting materials, $(\text{Bi}_{1-x}\text{Pb}_x)_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_{16-\delta}$ with a variable amount of Pb ($x = 0.1-0.5$) have been synthesized and studied by electron microprobe analysis, x-ray diffraction, resistivity measurement and micro-Raman spectroscopy⁵. They have found that the optimum effective Pb amount for the best high-Tc superconductivity, with a single phase (high-Tc phase), is around 12 percent. They have also ob-

served that the intensity of the 655 cm^{-1} (Cu-O stretching vibration) line decreases with increasing Pb content, and finally disappears at $x = 0.5$, where the intensity of the 630 cm^{-1} line is maximum. Based on the Raman data, they have suggested that the Cu-O bond in $(\text{Bi}_{1-x}\text{Pb}_x)_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_{16-\delta}$ becomes more homogeneous, a low-Tc phase disappears, and onset Tc increases due to the substitution of Pb for Bi.

In this study, Mo has been substituted for Bi in the superconducting 2223 phase with a variable amount of Mo at a nominal Mo mol percent of $x = 0.03-0.30$ to see if Mo eliminates the low-Tc phase, enhances onset Tc and increases homogeneity of the Cu-O bond as Pb does in the Bi-Sr-Ca-Cu-O system.

Experimental

Sample Preparation and Analysis. A number of compositions in the $\text{Bi}_{2-x}\text{Mo}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ system were prepared from a mixture of Bi_2O_3 , MoO_3 , SrCO_3 , CaCO_3 and CuO powders (each 99.9% pure). The starting powder materials were ball mill mixed and calcined at 750°C in air for 12 h. The well-mixed powder was pressed into a pellet at a pressure of 49 MPa. The pellet was then heated at 840°C in air for three days and quenched to room temperature.

Inductive coupled plasma (ICP) analysis was performed to determine effective Mo mol percent in the sample. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed to check the change in defect concentration and phase transition and to determine the calcination and sintering temperatures. X-ray diffraction (XRD) was carried out to detect crystal structure and formation of solid solution, on a diffractometer (Philips 1710, $\text{CuK}\alpha$) equipped with a curved graphite monochromator in the scattered beam path. Scanning electron microprobe (SEM) analysis was also

^{*}Present address: General Education Department, Pusan National Institute of Technology, Yongdang-dong 100, Nam-gu, Pusan 608-080