

**Palladium-Catalyzed Conjugate Addition Type Reaction  
of 5-Iodopyrimidines with  $\alpha,\beta$ -Unsaturated Ketones**  
Akimori Wada\* [1], Kazuhiro Ohki, Sotou Nagai and Shōichi Kanatomo\*

School of Pharmacy, Hokuriku University, Ho-3, Kanagawa-machi,  
Kanazawa 920-11, Japan  
Received August 22, 1990

The reaction of various 5-iodopyrimidines with  $\alpha,\beta$ -unsaturated ketones in the presence of palladium diacetate-triphenylphosphine complex in triethylamine are investigated. In the reaction of 2,4-dialkoxy(or alkylthio)-6-methyl-5-iodopyrimidine the addition of pyrimidine to the carbon-carbon double bond of  $\alpha,\beta$ -unsaturated ketones occurs. In the case of other pyrimidines, according to the decrease of steric hindrance at the 5-position on the pyrimidine ring, the ratio of conjugate addition product was decreased and the usual olefinic substituted product was increased.

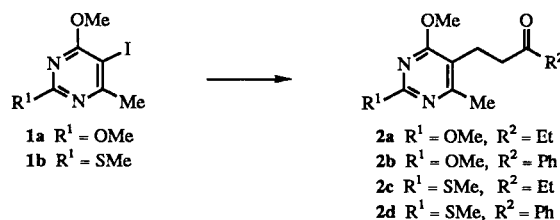
*J. Heterocyclic Chem.*, **28**, 509 (1991).

The palladium-catalyzed cross coupling reaction of aryl halides with olefins are well known to be a powerful synthetic tool in organic synthesis [2]. Recently, we found a novel reaction of 2,4-dialkoxy-5-iodo-6-methylpyrimidines with methyl vinyl ketone in the presence of palladium catalysis, in which formally the pyrimidines added to the carbon carbon double bond of methyl vinyl ketone to afford 5-(3-oxobutyl)pyrimidines [3]. Continuing this study, we describe here the reaction of various 5-iodopyrimidines with  $\alpha,\beta$ -unsaturated ketones.

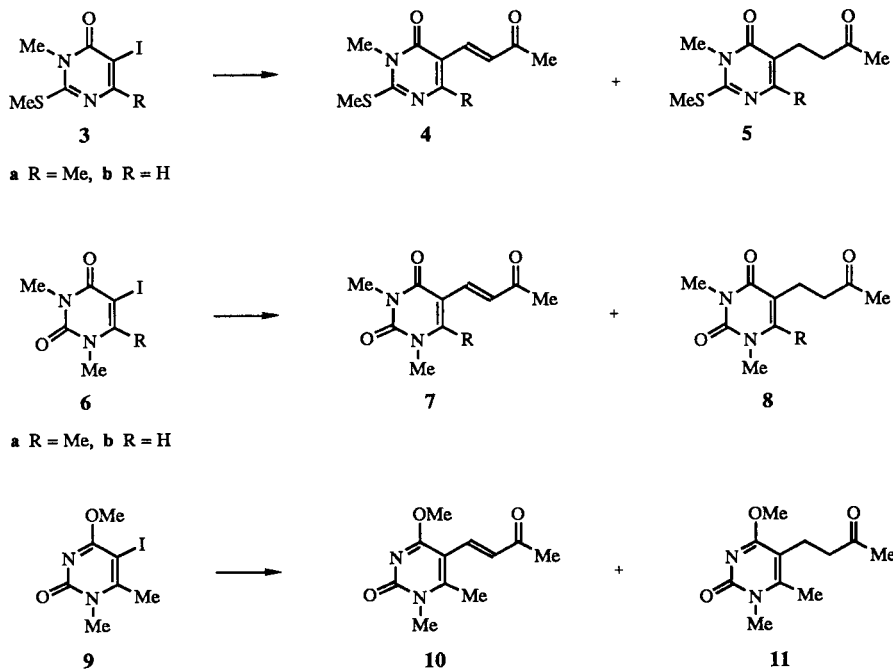
When 2,4-dimethoxy-5-iodo-6-methylpyrimidine (**1a**) was heated with ethyl vinyl ketone in the presence of palladium diacetate-triphenyl phosphine complex in triethylamine at 120° for 2 hours, the expected conjugate addition occurred to give 5-(3-oxopentyl)pyrimidine (**2a**) in 60% yield as the sole product. The <sup>1</sup>H-nmr, ir, mass spec-

tral data and elemental analysis were consistent with the indicated structure of **2a**. Similarly, reactions of **1a** with phenyl vinyl ketone, **1b** with ethyl vinyl ketone, and phenyl vinyl ketone afforded the corresponding saturated products **2b**, **2c** and **2d** in 39%, 66% and 43% yields, respectively.

Scheme 1



Scheme 2

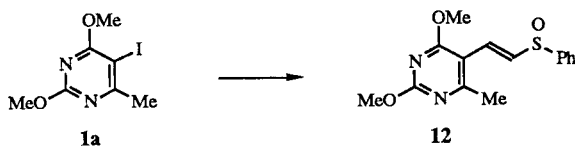


In the previous paper [3], we found that in the palladium catalyzed reaction of 6-demethylated-2,4-dialkoxy(or alkylthio)-5-iodopyrimidine with methyl vinyl ketone, a small amount of the  $\beta$ -substituted product, which is generated by the normal Heck arylation, was obtained besides the conjugate addition product. This observation suggests that the substitution patterns on the pyrimidine ring plays an important role of the reaction course. Therefore, we focused our attention on the reaction of various types of pyrimidines with methyl vinyl ketone.

Treatment of **3a** with methyl vinyl ketone under a palladium catalyzed reaction afforded the usual arylated product **4a** and the corresponding saturated product **5a** in 23% and 41% yields, respectively. In the case of **3b**, which has a demethylated structure of **3a**, **4b** and **5b** were obtained in 37% and 38% yields. The yields of the  $\alpha,\beta$ -unsaturated product **4** was increased in accordance with the decrease of steric hindrance at the 5-position on the pyrimidine ring. In the same manner, **6a** gave **7a** and **8a** in 23% and 46% yields, and **6b** afforded **7b** and **8b** in 38% and 26% yields, respectively. It was also found that a 4-methoxy group is more important for the generation of a saturated product than 2-methoxy or methylthio groups. Thus, in the reaction of 1,6-dimethyl-4-methoxy-1,2-dihydro-2-oxo-5-iodopyrimidine (**9**) with methyl vinyl ketone, the saturated product **11** was obtained as a major product (57%) and the yield of the usual arylated product **10** (12%) was decreased dramatically.

Finally, it is noteworthy that in the reaction of **1a** with phenyl vinyl sulfoxide, the usual coupling product **12** was obtained in 38% yield and the corresponding saturated product was not detected at all. These results indicate that the conjugate addition type reaction of iodopyrimidines seems to be limited only in the  $\alpha,\beta$ -unsaturated ketones.

Scheme 3



## EXPERIMENTAL

### Measurements.

All melting points were determined by using a Yanagimoto micro melting point apparatus and are uncorrected. Infrared spectra were recorded on a Hitachi 270 spectrometer. Proton magnetic resonance spectra were determined on a JEOL JNM-MH-100 instrument using tetramethylsilane as the internal standard. Mass spectra were obtained with a JEOL JMS-100 instrument.

The 5-iodopyrimidines were prepared according to the procedure described for **1a** [4].

### 3,4-Dihydro-5-iodo-3,6-dimethyl-2-methylthio-4-oxopyrimidine (**3a**).

This compound was prepared from 3,4-dihydro-3,6-dimethyl-2-methylthio-4-oxopyrimidine (1.5 g, 8.8 mmoles) [5], *N*-chlorosuccinimide (1.3 g, 10 mmoles), and sodium iodide (1.4 g, 9.9 mmoles) in 77% yield (2.0 g), mp 104-106° (dichloromethane-petroleum ether); ir (chloroform): 1650, 1555  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 2.50 (3H, s, Me), 2.54 (3H, s, Me), 3.54 (3H, s, Me) ppm; ms:  $m/z$  296 ( $\text{M}^+$ ).

*Anal.* Calcd. for  $\text{C}_7\text{H}_9\text{IN}_2\text{OS}$ : C, 28.39; H, 3.06; N, 9.46. Found: C, 28.42; H, 3.00; N, 9.34.

### 3,4-Dihydro-5-iodo-3-methyl-2-methylthio-4-oxopyrimidine (**3b**).

This compound was prepared from 3,4-dihydro-3-methyl-2-methylthio-4-oxopyrimidine (300 mg, 1.9 mmoles) [6], *N*-chlorosuccinimide (300 mg, 2.2 mmoles), and sodium iodide (320 mg, 2.1 mmoles) in 37% yield (200 mg), mp 126-128° (chloroform-petroleum ether); ir (chloroform): 1665  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 2.52 (3H, s, Me), 3.49 (3H, s, Me), 8.03 (1H, s,  $\text{C}_6\text{-H}$ ) ppm; ms:  $m/z$  282 ( $\text{M}^+$ ).

*Anal.* Calcd. for  $\text{C}_6\text{H}_7\text{IN}_2\text{OS}$ : C, 25.54; H, 2.54; N, 9.93. Found: C, 25.55; H, 2.50; N, 9.96.

### 1,2,3,4-Tetrahydro-5-iodo-1,3,6-trimethyl-2,4-dioxypyrimidine (**6a**).

This compound was prepared from 1,3,6-trimethyluracil (900 mg, 5.8 mmoles) [7], *N*-chlorosuccinimide (900 mg, 6.7 mmoles) and sodium iodide (990 mg, 6.6 mmoles) in 59% yield (970 mg), mp 152-153° (petroleum ether); ir (chloroform): 1690, 1640  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 2.72 (3H, s, Me), 3.49 (3H, s, NMe), 3.63 (3H, s, NMe) ppm; ms:  $m/z$  280 ( $\text{M}^+$ ).

*Anal.* Calcd. for  $\text{C}_7\text{H}_9\text{IN}_2\text{O}_2$ : C, 30.02; H, 3.24; N, 10.00. Found: C, 30.12; H, 3.12; N, 10.22.

### 1,2,3,4-Tetrahydro-5-iodo-1,3-dimethyl-2,4-dioxypyrimidine (**6b**).

This compound was prepared from 1,3-dimethyluracil (1.8 g, 13 mmoles) [8], *N*-chlorosuccinimide (2.0 g, 15 mmoles) and sodium iodide (2.1 g, 14 mmoles) in 56% yield (1.9 g), mp 184-187° (petroleum ether); ir (chloroform): 1690, 1640  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 3.26 (3H, s, NMe), 3.39 (3H, s, NMe), 8.23 (1H, s,  $\text{C}_6\text{-H}$ ) ppm; ms:  $m/z$  266 ( $\text{M}^+$ ).

*Anal.* Calcd. for  $\text{C}_6\text{H}_7\text{IN}_2\text{O}_2$ : C, 27.08; H, 2.63; N, 10.53. Found: C, 27.18; H, 2.65; N, 10.38.

### 1,2-Dihydro-5-iodo-4-methoxy-1,6-dimethyl-2-oxopyrimidine (**9**).

This compound was prepared from 5-iodo-2,4-dimethoxy-6-methylpyrimidine (700 mg, 2.5 mmoles) [3], methyl iodide (350 mg, 2.5 mmoles), and three drops of pyridine by the previous reported method [9] in 39% yield (270 mg), mp 105-106.5° (dichloromethane-petroleum ether); ir (chloroform): 1660, 1590  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 2.69 (3H, s, Me), 3.63 (3H, s, NMe), 3.96 (3H, s, OMe) ppm; ms:  $m/z$  280 ( $\text{M}^+$ ).

*Anal.* Calcd. for  $\text{C}_7\text{H}_9\text{IN}_2\text{O}_2$ : C, 30.02; H, 3.24; N, 10.00. Found: C, 30.15; H, 3.16; N, 9.89.

### General Procedure of the Coupling Reaction of Halopyrimidines with $\alpha,\beta$ -Unsaturated Ketones.

A mixture of 5-iodopyrimidine (2 mmoles),  $\alpha,\beta$ -unsaturated ketone (10 mmoles), triethylamine (4 mmoles), palladium diacetate (40 mg), and triphenylphosphine (80 mg) is heated in a sealed tube at 120° for 2 hours. After cooling, excess  $\alpha,\beta$ -unsaturated ketone is removed under the reduced pressure and the residue is

purified by the column chromatography on silica gel (dichloromethane/ethyl acetate, 9/1).

#### 2,4-Dimethoxy-6-methyl-5-(3-oxopentyl)pyrimidine (2a).

This compound was prepared from **1a** (480 mg, 1.7 mmoles) and ethyl vinyl ketone (720 mg, 8.6 mmoles) in 60% yield (242 mg), bp 140-145° (7 mm Hg); ir (chloroform): 1715, 1580  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 1.05 (3H, t,  $J = 7$  Hz, Me), 2.36 (3H, s, Me), 2.3-2.9 (6H, m,  $\text{CH}_2 \times 3$ ), 3.97 (6H, s, OMe  $\times 2$ ) ppm; ms:  $m/z$  238 ( $M^+$ ).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_3$ : C, 60.48; H, 7.61; N, 11.76. Found: C, 60.29; H, 7.80; N, 11.64.

#### 2,4-Dimethoxy-6-methyl-5-(3-oxo-3-phenylpropyl)pyrimidine (2b).

This compound was prepared from **1a** (500 mg, 1.8 mmoles) and phenyl vinyl ketone (1.1 g, 8.9 mmoles) [10] in 39% yield (200 mg), bp 160-165° (7 mm Hg); ir (chloroform): 1720, 1580  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 2.41 (3H, s, Me), 2.8-3.3 (4H, m,  $\text{CH}_2 \times 2$ ), 4.03 (6H, s, OMe  $\times 2$ ), 7.4-8.3 (5H, m, Ph) ppm; ms:  $m/z$  286 ( $M^+$ ).

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_3$ : C, 67.11; H, 6.34; N, 9.78. Found: C, 67.31; H, 6.47; N, 9.98.

#### 4-Methoxy-6-methyl-2-methylthio-5-(3-oxopentyl)pyrimidine (2c).

This compound was prepared from **1b** (1 g, 3.4 mmoles) [3] and ethyl vinyl ketone (1.4 g, 17 mmoles) in 66% yield (560 mg), bp 140-145° (5 mm Hg); ir (chloroform): 1715, 1565  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 1.06 (3H, t,  $J = 7$  Hz, Me), 2.2-2.9 (6H, m,  $\text{CH}_2 \times 3$ ), 2.39 (3H, s, Me), 2.51 (3H, s, Me), 3.96 (3H, s, OMe) ppm; ms:  $m/z$  254 ( $M^+$ ).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$ : C, 56.68; H, 7.14; N, 11.02. Found: C, 56.76; H, 6.97; N, 10.89.

#### 4-Methoxy-6-methyl-2-methylthio-5-(3-oxo-3-phenylpropyl)pyrimidine (2d).

This compound was prepared from **1b** (500 mg, 1.8 mmoles) and phenyl vinyl ketone (1.2 g, 9.2 mmoles) in 43% yield (222 mg), mp 111-113° (chloroform-petroleum ether); ir (chloroform): 1685, 1560  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 2.41 (3H, s, Me), 2.51 (3H, s, SMe), 2.9-3.4 (4H, m,  $\text{CH}_2 \times 2$ ), 3.93 (3H, s, OMe), 7.4-8.2 (5H, m, Ph) ppm; ms:  $m/z$  302 ( $M^+$ ).

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$ : C, 63.56; H, 6.00; N, 9.27. Found: C, 63.68; H, 6.11; N, 9.21.

#### 3,4-Dihydro-3,6-dimethyl-2-methylthio-4-oxo-5-(3-oxo-1-butenyl)pyrimidine (4a) and 3,4-Dihydro-3,6-dimethyl-2-methylthio-4-oxo-5-(3-oxobutyl)pyrimidine (5a).

These compounds were prepared from **3a** (1 g, 3.4 mmoles) and methyl vinyl ketone (1.2 g, 17 mmoles).

Compound **4a** was obtained in 23% yield (183 mg), mp 89-92° (methanol-hexane); ir (chloroform): 1685, 1665, 1595, 1560  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 2.32 (3H, s, Me), 2.48 (3H, s, Me), 2.60 (3H, s, Me), 3.55 (3H, s, NMe), 7.57 (2H, s, =CH  $\times 2$ ) ppm; ms:  $m/z$  238 ( $M^+$ ).

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ : C, 55.45; H, 5.92; N, 11.76. Found: C, 55.14; H, 5.92; N, 11.52.

Compound **5a** was obtained in 41% yield (327 mg), mp 81-82° (dichloromethane-hexane); ir (chloroform): 1715, 1650, 1580  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 2.17 (3H, s, Me), 2.30 (3H, s, Me), 2.55 (3H, s, Me), 2.69 (4H, br s,  $\text{CH}_2 \times 2$ ), 3.47 (3H, s, NMe) ppm;

ms:  $m/z$  240 ( $M^+$ ).

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ : C, 54.99; H, 6.70; N, 11.66. Found: C, 54.84; H, 6.36; N, 11.59.

#### 3,4-Dihydro-3-methyl-2-methylthio-4-oxo-5-(3-oxo-1-butenyl)pyrimidine (4b) and 3,4-Dihydro-3-methyl-2-methylthio-4-oxo-5-(3-oxobutyl)pyrimidine (5b).

These compounds were prepared from **3b** (500 mg, 1.7 mmoles) and methyl vinyl ketone (800 mg, 11 mmoles).

Compound **4b** was prepared in 37% yield (145 mg), mp 154-156° (methanol-hexane); ir (chloroform): 1685 sh, 1675, 1595, 1560  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 2.29 (3H, s, Me), 2.60 (3H, s, Me), 3.59 (3H, s, NMe), 7.37 (2H, s, =CH  $\times 2$ ), 8.04 (1H, s,  $\text{C}_\alpha\text{-H}$ ) ppm; ms:  $m/z$  224 ( $M^+$ ).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$ : C, 53.57; H, 5.39; N, 12.50. Found: C, 53.56; H, 5.36; N, 12.12.

Compound **5b** was prepared in 38% yield (152 mg), mp 92-93° (dichloromethane-hexane); ir (chloroform): 1715, 1665, 1590  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 2.13 (3H, s, Me), 2.56 (3H, s, Me), 2.68 (4H, br s,  $\text{CH}_2 \times 2$ ), 3.53 (3H, s, NMe), 7.69 (1H, s,  $\text{C}_\alpha\text{-H}$ ) ppm; ms:  $m/z$  226 ( $M^+$ ).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ : C, 53.09; H, 6.04; N, 12.38. Found: C, 52.84; H, 6.11; N, 12.14.

#### 1,2,3,4-Tetrahydro-1,3,6-trimethyl-2,4-dioxo-5-(3-oxo-1-butenyl)pyrimidine (7a) and 1,2,3,4-Tetrahydro-1,3,6-trimethyl-2,4-dioxo-5-(3-oxobutyl)pyrimidine (8a).

These compounds were prepared from **6a** (600 mg, 2.1 mmoles) and methyl vinyl ketone (1.0 g, 14 mmoles).

Compound **7a** was obtained in 23% yield (110 mg), mp 115-116° (dichloromethane-petroleum ether); ir (chloroform): 1710, 1690, 1655, 1585  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 2.31 (3H, s, Me), 2.48 (3H, s, Me), 3.39 (3H, s, NMe), 3.55 (3H, s, NMe), 7.43 (2H, s, =CH  $\times 2$ ) ppm.

Exact mass Calcd. for  $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_3$ : 222.1004. Found: 222.1009.

Compound **8a** was obtained in 46% yield (220 mg), mp 102-105° (dichloromethane-petroleum ether); ir (chloroform): 1710 sh, 1700, 1645, 1590  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 2.15 (3H, s, Me), 2.35 (3H, s, Me), 2.69 (4H, s,  $\text{CH}_2 \times 2$ ), 3.35 (3H, s, NMe), 3.46 (3H, s, NMe) ppm; ms:  $m/z$  224 ( $M^+$ ).

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_3$ : C, 58.91; H, 7.19; N, 12.49. Found: C, 58.89; H, 6.99; N, 12.32.

#### 1,2,3,4-Tetrahydro-1,3-dimethyl-2,4-dioxo-5-(3-oxo-1-butenyl)pyrimidine (7b) and 1,2,3,4-Tetrahydro-1,3-dimethyl-2,4-dioxo-5-(3-oxobutyl)pyrimidine (8b).

These compounds were prepared from **6b** (800 mg, 3.0 mmoles) and methyl vinyl ketone (1.1 g, 15 mmoles).

Compound **7b** was obtained in 38% yield (237 mg), mp 159-161° (ethyl acetate); ir (chloroform): 1715, 1680 sh, 1665, 1595  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 2.34 (3H, s, Me), 3.39 (3H, s, NMe), 3.52 (3H, s, NMe), 7.43 (2H, s, =CH  $\times 2$ ), 7.59 (1H, s,  $\text{C}_\alpha\text{-H}$ ) ppm; ms:  $m/z$  208 ( $M^+$ ).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$ : C, 57.68; H, 5.81; N, 13.46. Found: C, 57.55; H, 5.77; N, 13.46.

Compound **8b** was obtained in 26% yield (162 mg), mp 91-92° (dichloromethane-hexane); ir (chloroform): 1705, 1665, 1640, 1600  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 2.13 (3H, s, Me), 2.59 (2H, t,  $J = 6.5$  Hz,  $\text{CH}_2$ ), 2.68 (2H, t,  $J = 6.5$  Hz,  $\text{CH}_2$ ), 3.33 (3H, s, NMe), 3.41 (3H, s, NMe), 7.21 (1H, s,  $\text{C}_\alpha\text{-H}$ ) ppm; ms:  $m/z$  210 ( $M^+$ ).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_3$ : C, 57.13; H, 6.71; N, 13.33.

Found: C, 57.09; H, 6.62; N, 13.24.

1,2-Dihydro-3-methoxy-1,6-dimethyl-2-oxo-5-(3-oxo-1-butenyl)pyrimidine (**10**) and 1,2-Dihydro-3-methoxy-1,6-dimethyl-2-oxo-5-(3-oxobutyl)pyrimidine (**11**).

These compounds were prepared from **9** (600 mg, 2.1 mmoles) and methyl vinyl ketone (1.0 g, 14 mmoles).

Compound **10** was obtained in 12% yield (58 mg), mp 175-177° (methanol-hexane); ir (chloroform): 1700 sh, 1670, 1605  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 2.36 (3H, s, Me), 2.51 (3H, s, Me), 3.61 (3H, s, NMe), 4.04 (3H, s, OMe), 6.79 (1H, d, J = 16 Hz, =CH), 7.47 (1H, d, J = 16 Hz, =CH) ppm.

Exact mass Calcd. for  $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_3$ : 222.1004. Found: 222.1006.

Compound **11** was obtained in 57% yield (270 mg), mp 100-102° (dichloromethane-hexane); ir (chloroform): 1715, 1660, 1620  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 2.16 (3H, s, Me), 2.35 (3H, s, Me), 2.64 (4H, br s,  $\text{CH}_2 \times 2$ ), 3.51 (3H, s, NMe), 3.98 (3H, s, OMe) ppm.

Exact mass Calcd. for  $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_3$ : 224.1161. Found: 224.1155.

2,4-Dimethoxy-6-methyl-5-(2-phenylsulfinyl-1-ethenyl)pyrimidine (**12**).

This compound was prepared from **1a** (600 mg, 2.1 mmoles) and phenyl vinyl sulfoxide (600 mg, 4.0 mmoles) in 38% yield

(245 mg), mp 114-116° (petroleum ether); ir (chloroform): 1610, 1580, 1480, 1045  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): 2.55 (3H, s, Me), 3.97 (6H, s, OMe  $\times 2$ ), 7.05 (1H, d, J = 16 Hz, =CH), 7.42 (1H, d, J = 16 Hz, =CH), 7.3-8.0 (5H, m, Ph) ppm; ms: m/z 304 ( $\text{M}^+$ ).

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$ : C, 59.20; H, 5.30; N, 9.21. Found: C, 59.33; H, 5.18; N, 9.18.

#### REFERENCES AND NOTES

- [1] Present address: Faculty of Pharmaceutical Sciences, Kanazawa University, 13-1, Takara-machi, Kanazawa 920, Japan.
- [2] For reviews: R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, Orlando, FL, 1985, p 179; *Org. React.*, **27**, 345 (1982); *Acc. Chem. Res.*, **12**, 146 (1979).
- [3] A. Wada, H. Yasuda and S. Kanatomo, *Synthesis*, 771 (1988).
- [4] A. Wada, J. Yamamoto, T. Hase, S. Nagai and S. Kanatomo, *Synthesis*, 555 (1986).
- [5] S. Senda, M. Honda, K. Maeno and H. Fujimura, *Chem. Pharm. Bull.*, **6**, 490 (1958).
- [6] D. J. Brown, E. Hoergen and S. F. Mason, *J. Chem. Soc.*, 211 (1955).
- [7] B. Kurtev and M. Kirilov, *Bulgarska Akad. Nauk., Otdel. Geol. Geograf. Khim. Nauk., Izvest. Khim. Inst.*, **1**, 277 (1951); *Chem. Abstr.*, **47**, 1607f (1953).
- [8] D. Davidson and O. Baudish, *J. Am. Chem. Soc.*, **48**, 2379 (1926).
- [9] J. L. Rabinowitz and S. Gurin, *J. Am. Chem. Soc.*, **75**, 5758 (1953).
- [10] C. S. Marvel and D. J. Casey, *J. Org. Chem.*, **24**, 957 (1959).