

Akira Katoh*, Yoshimori Omote and Choji Kashima

Department of Chemistry, University of Tsukuba,
Sakura-mura, Niihari-gun, Ibaraki 305, Japan
Received June 2, 1983

1-Aryl-2(1*H*)-pyrimidinones I reacted with α -haloesters in the presence of zinc to give mainly 3,4-dihydro-4-alkoxycarbonylmethyl-1-aryl-2(1*H*)-pyrimidinones IV in addition to the minor products of 3,6-dihydro-6-alkoxycarbonylmethyl-1-aryl-2(1*H*)-pyrimidinones V. Further, 3,4-dihydro derivatives IVa-c were successfully converted into the corresponding exomethylene compounds VIa-c in high yields.

J. Heterocyclic Chem., **21**, 53 (1984).

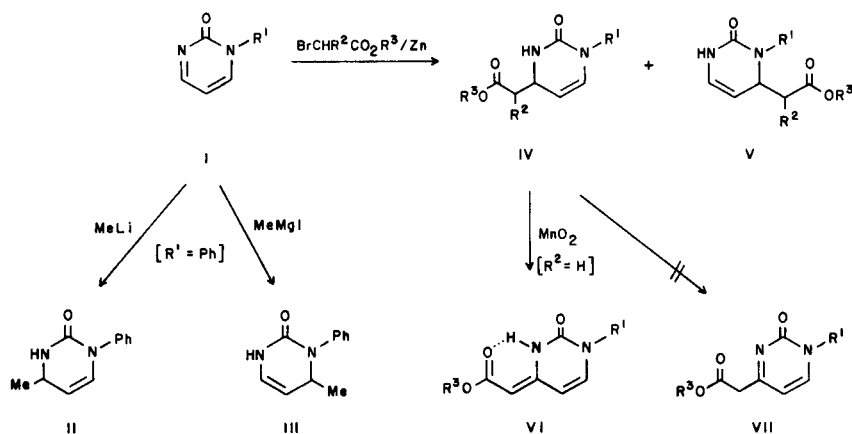
We have investigated properties [1] and reactions [2,3] of 1-substituted-2(1*H*)-pyrimidinones and their derivatives. Recently it was reported that 1-phenyl-2(1*H*)-pyrimidinone (Ia) was treated with methyllithium to give exclusively 3,4-dihydro-4-methyl-1-phenyl-2(1*H*)-pyrimidinone (II), while methylmagnesium iodide afforded only 3,6-dihydro-6-methyl-1-phenyl-2(1*H*)-pyrimidinone (III) which was isomeric with compound II [2].

As a part of an extensive study with organometallic compounds, we describe the reaction of 1-aryl-2(1*H*)-pyrimidinones with α -haloesters in the presence of zinc (Reformatsky reaction [4]).

When 1-phenyl-2(1*H*)-pyrimidinone (Ia) was treated with methyl α -bromoacetate in the presence of zinc in a dry tetrahydrofuran (THF), two products, mp 137-138°, (compound A) and mp 175-176° (compound B) were obtained. Both compounds had the same formula, C₁₃H₁₄N₂O₃, from the elemental analysis. On the basis of spectral data, compounds A and B were assumed to be structurally isomeric with each other. A comparison of the spectral characteristics with those of compounds II and III allowed A and B to be assigned the structures 3,4-dihydro-4-methoxycarbonylmethyl-1-phenyl-2(1*H*)-pyrimidinone (IVa) and 3,6-dihydro-6-methoxycarbonylmethyl-1-phenyl-2(1*H*)-pyrimidinone (Va), respectively.

These structural assignments were also confirmed by ¹H-nmr decoupling technique. While irradiating the N-H proton, the signal of an olefinic proton (dd, J = 4.9 and 7.3 Hz) at C-4 position of compound Va became a doublet (J = 7.3 Hz). The reaction of other 1-aryl-2(1*H*)-pyrimidinones with α -haloesters was examined, and the results are summarized in Tables 1 and 2. From the fact that 3,4-dihydro-2(1*H*)-pyrimidinones (IV) were the major products in all cases, it was found that α -haloester/zinc system reacted similarly to the way alkyl lithium reagents react with I.

Further, the oxidation of dihydro-2(1*H*)-pyrimidinones was attempted. When compound IVa was treated with manganese dioxide in dry benzene under reflux for 30 hours, the product, mp 195-195.5°, formula C₁₃H₁₂N₂O₃, was obtained. The ir absorption band at 3220 cm⁻¹ attributable to N-H stretching was observed. In the ¹H-nmr spectrum the methine and methylene protons disappeared and a new olefinic proton at δ 4.78 ppm was observed. From these data the product was assigned to be not 4-methoxycarbonylmethyl-1-phenyl-2(1*H*)-pyrimidinone (VII) but 3,4-dihydro-4-methoxycarbonylmethylidene-1-phenyl-2(1*H*)-pyrimidinone (VIa) [5]. Although the isomeric 3,6-dihydro-2(1*H*)-pyrimidinone (Va) was treated with manganese di-



a, R¹ = Ph, R² = H, R³ = Me

b, R¹ = Ph, R² = H, R³ = Et

c, R¹ = 4-MeC₆H₄, R² = H, R³ = Et

d, R¹ = 4-MeC₆H₄, R² = H, R³ = Me

e, R¹ = Ph, R² = Me, R³ = Et.

Table 1

Compound No.	Mp (°C)	Yield (%)	Formula	Analysis (%)		
				Calcd.	(Found)	
IVa	137-138	34	C ₁₃ H ₁₄ N ₂ O ₃	C	H	N
				63.40 (63.18)	5.73 (5.74)	11.37 (11.25)
Va	175-176	10	C ₁₃ H ₁₄ N ₂ O ₃	63.40 (63.18)	5.73 (5.74)	11.37 (11.25)
IVb	110-111	52	C ₁₄ H ₁₆ N ₂ O ₃	64.60 (64.69)	6.19 (6.26)	10.76 (10.72)
Vb	158-159	11	C ₁₄ H ₁₆ N ₂ O ₃	64.60 (64.46)	6.19 (6.12)	10.76 (10.72)
IVc	113.5-114.5	47	C ₁₅ H ₁₈ N ₂ O ₃	65.67 (65.71)	6.61 (6.65)	10.21 (10.17)
Vc	132-133	16	C ₁₅ H ₁₈ N ₂ O ₃	65.67 (65.70)	6.61 (6.61)	10.21 (10.30)
IVd	113-114	33	C ₁₄ H ₁₆ N ₂ O ₃	64.60 (64.60)	6.19 (6.20)	10.76 (10.75)
Vd	163-164	12	C ₁₄ H ₁₆ N ₂ O ₃	64.60 (64.33)	6.19 (6.16)	10.76 (10.67)
IVe	106-107	37	C ₁₅ H ₁₈ N ₂ O ₃	65.67 (65.52)	6.61 (6.61)	10.21 (10.16)
VIa	195-195.5	82	C ₁₃ H ₁₂ N ₂ O ₃	63.92 (63.92)	4.95 (5.03)	11.46 (11.31)
VIb	170-171	85	C ₁₄ H ₁₄ N ₂ O ₃	65.10 (65.18)	5.46 (5.46)	10.84 (10.85)
VIc	187-187.5	86	C ₁₅ H ₁₆ N ₂ O ₃	66.16 (66.21)	5.92 (5.96)	10.28 (10.19)

Table 2

The IR, ¹H-NMR and ¹³C-NMR Spectra of Dihydro-2(1H)-pyrimidinones IVa-e and Va-e

Compound No.	IR Spectra (cm ⁻¹)	NMR Chemical Shift (δ, ppm)			
IVa	3220, 1730, 1670	2.42-2.85 (2H, ABX, J = 5.4, 7.9 and 16.7 Hz), 3.68 (3H, s), 4.52-4.68 (1H, m), 4.75-4.89 (1H, m), 5.94 (1H, broad s), 6.21-6.29 (1H, dd, J = 1.0 and 7.8 Hz) and 7.1-7.4 (5H, m), 42.80 (t), 49.19 (d), 51.84 (q), 101.27 (d), 126.11 (d), 126.52 (d), 128.81 (d), 129.81 (d), 140.55 (s), 152.35 (s) and 171.08 (s)	IVc	3220, 1725, 1665	1.25 (3H, t, J = 7.0 Hz), 2.32 (3H, s), 2.42-2.83 (2H, ABX, J = 5.3, 7.7 and 16.6 Hz), 4.15 (2H, q, J = 7.0 Hz), 4.43-4.97 (2H, m), 5.87 (1H, broad s), 6.20-6.33 (1H, dd, J = 1.0 and 7.8 Hz) and 7.1-7.3 (4H, m)
Va	3230, 1725, 1660	2.58 (2H, d, J = 5.6 Hz), 3.56 (3H, s), 4.66-4.77 (1H, m), 4.83-5.0 (1H, m), 6.06-6.18 (1H, dd, J = 4.9 and 7.3 Hz), 7.2-7.5 (5H, m) and 7.97 (1H, broad s), 39.86 (t), 51.66 (q), 57.36 (d), 100.09 (d), 125.57 (d), 127.22 (d), 128.11 (d), 129.28 (d), 140.49 (s), 153.58 (s) and 170.66 (s)	Vc	3230, 1725, 1655	1.18 (3H, t, J = 7.0 Hz), 2.32 (3H, s), 2.55 (2H, d, J = 6.0 Hz), 4.05 (2H, q, J = 7.0 Hz), 4.56-5.07 (2H, m), 5.93-6.20 (1H, dd, J = 4.9 and 7.3 Hz), 7.1-7.4 (4H, m) and 8.30 (1H, broad s)
IVb	3230, 1730, 1665	1.26 (3H, t, J = 7.3 Hz), 2.40-2.84 (2H, ABX, J = 5.3, 7.7 and 16.6 Hz), 4.15 (2H, q, J = 7.3 Hz), 4.49-4.68 (1H, m), 4.76-4.89 (1H, m), 5.86 (1H, broad s), 6.21-6.30 (1H, dd, J = 1.0 and 7.8 Hz) and 7.1-7.5 (5H, m)	IVd	3220, 1725, 1665	2.34 (3H, s), 2.43-2.90 (2H, ABX, J = 5.4, 7.9 and 16.7 Hz), 3.71 (3H, s), 4.40-5.02 (2H, m), 5.85 (1H, broad s), 6.23-6.36 (1H, dd, J = 1.0 and 7.8 Hz) and 7.1-7.3 (4H, m)
Vb	3215, 1720, 1660	1.15 (3H, t, J = 7.5 Hz), 2.54 (2H, d, J = 6.0 Hz), 4.02 (2H, q, J = 7.5 Hz), 4.53-5.07 (2H, m), 5.93-6.23 (1H, dd, J = 2.0 and 7.6 Hz), 7.2-7.6 (5H, m), and 8.28 (1H, broad s)	Vd	3220, 1730, 1655	2.35 (3H, s), 2.59 (2H, d, J = 5.9 Hz), 4.62-4.80 (1H, m), 4.87-5.01 (1H, m), 6.01-6.20 (1H, dd, J = 5.0 and 7.4 Hz), 7.2-7.3 (4H, m) and 7.43 (1H, broad s)
			IVe	3230, 1720, 1665	1.25 (3H, t, J = 7.0 Hz), 1.32 (3H, d, J = 7.0 Hz), 2.27-2.80 (1H, m), 4.15 (2H, q, J = 7.0 Hz), 4.40-4.87 (2H, m), 5.80 (1H, broad s), 6.28-6.42 (1H, dd, J = 1.0 and 7.8 Hz) and 7.2-7.5 (5H, m)
			Ve	3230, 1730, 1670	1.15 (3H, d, J = 6.9 Hz), 1.26 (3H, t, J = 6.8 Hz), 1.73 (1H, broad s), 2.52-2.77 (1H, dq, J = 4.4 and 6.9 Hz), 4.04 (2H, q, J = 6.8 Hz), 4.62-4.87 (1H, m), 4.97 (1H, t, J = 4.4 Hz), 6.15-6.28 (1H, dd, J = 4.4 and 7.8 Hz) and 7.2-7.4 (5H, m)

Table 3

The IR, UV and NMR Spectra of Exo-methylene Compounds (VIa-c)

Compound No.	IR Spectra (cm ⁻¹)	UV Spectra nm (log ϵ)	NMR Chemical Shift (δ , ppm)
VIa	3220, 1685, 1660	268 (3.99), 323 (4.83)	3.73 (3H, s), 4.78 (1H, s), 5.67 (1H, dd, J = 1.8 and 7.8 Hz), 6.85 (1H, d, J = 7.8 Hz), 7.3-7.6 (5H, m) and 10.95 (1H, d, J = 1.8 Hz)
VIb	3220, 1690, 1665	268 (4.00), 323 (4.39)	1.25 (3H, t, J = 7.5 Hz), 4.12 (2H, q, J = 7.5 Hz), 4.68 (1H, s), 5.57 (1H, dd, J = 1.8 and 7.8 Hz), 6.72 (1H, d, J = 7.8 Hz), 7.1-7.5 (5H, m) and 10.94 (1H, d, J = 1.8 Hz)
VIc	3240, 1695, 1665	266 (3.99), 323 (4.26)	1.27 (3H, t, J = 7.5 Hz), 2.35 (3H, s), 4.15 (2H, q, J = 7.5 Hz), 5.56 (1H, s), 5.61 (1H, dd, J = 1.8 and 7.8 Hz), 6.77 (1H, d, J = 7.8 Hz), 7.1-7.3 (4H, m) and 10.98 (1H, d, J = 1.8 Hz)

oxide in the same fashion, the starting material was completely recovered. The oxidation of other 3,4-dihydro-2(1H)-pyrimidinones was tried, and the results are listed in Table 1 and 3.

It is concluded that 1-aryl-2(1H)-pyrimidinones react with α -haloesters in the presence of zinc to give mainly 3,4-dihydro-2(1H)-pyrimidinones similar to the products from the reaction of I with alkyl lithium reagents. Furthermore, 3,4-dihydro-2(1H)-pyrimidinones are easily oxidized to yield the corresponding exo-methylene compounds in high yields.

EXPERIMENTAL

Melting points were uncorrected. The ir spectra were recorded on a

Jasco IRA-1 spectrophotometer. The ¹H- and ¹³C-nmr spectra were taken on a Hitachi R-24 or a JEOL-100 spectrometer using TMS as an internal standard. The uv spectra were obtained on a Shimadzu UV-365 UV-VIS-NIR spectrophotometer.

General Procedure for the Preparation of Dihydro-2(1H)-pyrimidinones (IV and V).

Zinc was purified *in situ* by washing with 2% hydrochloric acid, then with water, ethanol, acetone, and dry ether. Zinc was then warmed at 100° for an hour under reduced pressure. α -Haloesters (2 mmoles) in dry THF (5 ml) was added dropwise to the suspension of 1-aryl-2(1H)-pyrimidinones (2 mmoles) and zinc (2 mmoles) in dry THF (5 ml) under an argon atmosphere. The mixture was warmed at 60° for 3 hours, then refluxed for an hour. The reaction mixture was poured onto ice, and worked up with aqueous ammonia. The organic layer was dried over anhydrous magnesium sulfate, then evaporated off. Products IV and V were purified by column chromatography with chloroform/acetone/ethanol (100:20:4) on silica gel and then recrystallized from benzene/hexane mixture.

General Procedure for the Preparation of Compounds VIa-c by Manganese Dioxide Oxidation.

A mixture of equal weights (130 mg) of compounds IVa-c and manganese dioxide in dry benzene (20 ml) was refluxed for 8 hours. An additional equivalent weight of manganese dioxide was added in 8 hours intervals (3 times), and the mixture was further refluxed for 6 hours. The solids were filtered off, and the filtrate was evaporated under reduced pressure. The resulting products VIa-c were recrystallized from benzene/hexane mixture.

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