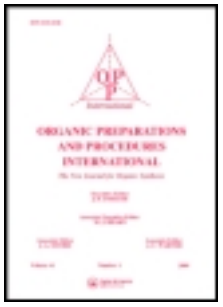

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CONDENSATION REACTION OF ACYLOINS WITH UREA WITHOUT SOLVENT UNDER MICROWAVE IRRADIATION

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OPPI BRIEFS

CONDENSATION REACTION OF ACYLOINS WITH UREA WITHOUT SOLVENT UNDER MICROWAVE IRRADIATION

Submitted by (10/07/96)

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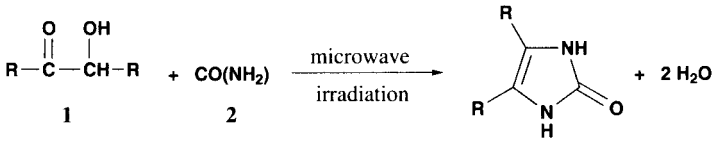
Acyloins react with urea in the presence of an acid to give 4-imidazolin-2-ones, which can be used as polyamide stabilizers, cotton fabrics crease resistants and synthetic intermediates.[1] The typical reaction conditions involve refluxing a mixture of an acyloin, urea in solvent with an acid as catalyst for 1-6 hrs.[2-4] Recently, application of microwave irradiation in organic chemistry has been developing rapidly.[5-7] We report herein the condensation of various acyloin with urea under microwave irradiation in the absence of solvent, to give 4,5-disubstituted-4-imidazolin-2-ones.



1 2 3

a) R = C_6H_5 b) R = 2-furyl c) R = *p*-$CH_3OC_6H_4$ d) R = *p*-ClC_6H_4
e) R = *m*-ClC_6H_4 f) R = C_2H_5 g) R = C_3H_7 h) R, R = $(CH_2)_8$

Irradiation of a mixture of the acyloin and urea in a microwave oven for 3-5 minutes, followed by removal of the excess urea by washing with water gave after purification, pure products in yields of 30-80%.

EXPERIMENTAL SECTION

Mps were measured on a Yanaco Mp-500 apparatus and were uncorrected. IR spectra are recorded on a Nicolet FT-IR 5DX FT spectrometer with KBr pellets, ^1H NMR spectra were determined on a JEOL JNM-PMX-60 spectrometer for solution in DMSO-d_6 with TMS as an internal reference. Ms spectra were obtained by VG-ZAB-HS spectrometer with 70ev and elemental analyses were performed by Perkin-Elmer 240C analyzer. Microwave irradiation was carried out with a modified domestic microwave oven (2450 MHz, 500W).

TABLE 1. 4,5-Disubstituted-4-imidazolin-2-ones under Microwave Irradiation

Entry	R	Time (min.)	Yieid[a] (%)	mp. (°C)	^{1}H NMR (δ)
a	C_6H_5-	4	65	>300	10.51 (s, 2H), 7.35 (m, 10H)
b	2-Furyl	3	44	>300	10.72 (s, 2H, 7.77 (s, 2H), 6.83 (s, 2H), 6.64 (s, 2H)
c	*p*-$CH_3OC_6H_4$-	3	80	290(d)	10.19 (s, 2H), 7.13 (s, 4H), 6.88 (s, 4H), 3.73 (s, 6H)
d	*p*-ClC_6H_4-	4	61	>300	9.80 (s, 2H), 7.32 (m, 8H)
e	*m*-ClC_6H_4-	5	30	>300	9.78 (s, 2H), 7.31 (m, 8H)
f	C_2H_5-	5	54	290(d)	9.28 (s, 2H), 2.11 (q, 4H), 1.01 (t, 6H)
g	*n*-C_3H_7-	5	51	210	9.43 (s, 2H), 2.26 (t, 4H), 1.52 (m, 4H), 0.87 (t, 6H)
h	-$(CH_2)_{8-}$[b]	5	40	>300	

a) Yield of pure isolated product. b) This compound has not been reported. MS: m/z 194 (78,M^+), 151 (95),137 (81), 123 (100). *Anal.* Calcd for $C_{11}H_{18}N_2O$: C, 68.04, H, 9.28; N, 14.43. Found: C, 68.18; H, 9.24; N, 14.30.

Acyloins **1a** and **1b** are commercially available, while **1c**, **1d** and **1e** were prepared according to Org. Syn. Coll. Vol.**1**, 94; **1f** and **1g** were prepared according to Org. Syn. Coll. Vol. **2**, 114; **1h** was prepared according to Org. Syn. Coll. Vol. **4**, 840.

Typical Procedure.- Benzoin (**1a**) 2.0g (9.4mmol) and urea (**2**) 2.0g (33mmol) were carefully mixed in a mortar and transferred to a flask (50mL) in the center of a microwave oven. The flask was connected to an air condenser, which passed through a metallic tube to the side of the oven and was then connected to the water reflux condenser at outside the oven. After irradiation for 4 minutes, the mixture was cooled to room temperature, and the solid was washed with 15mL water and 15mL ether respectively; the pale yellow solid was collected, recrystallized from 95% ethanol to afford 1.44g (65%) 4,5-diphenyl-4-imidazolin-2-one (**3a**), as a white solid.

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CHEMICAL TRANSFORMATION OF DIHYDRO- AND TETRAHYDRO-1,5-BENZODIAZEPIN-2-ONES INTO AMIDINES

Submitted by (10/15/96) Benedikta Dale Puodziunaite*, Lina Vertelyte, Regina Janciene and Zita Stumbreviciute

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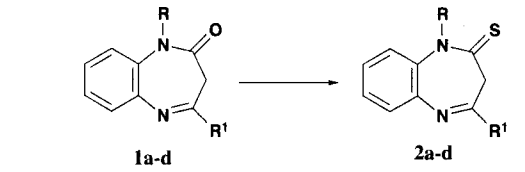
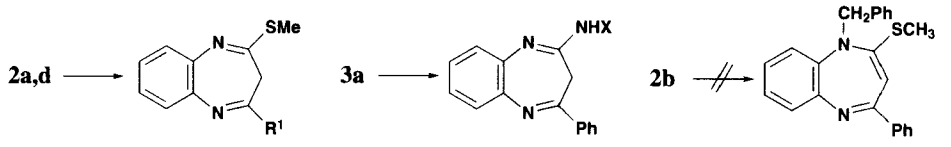
As a result of our interest in the chemistry of 1,5-benzodiazepines, we have investigated the synthesis of cyclic amidines. The present paper describes the preparation of new diversely substituted 3H- and 2,3-dihydro-1H-1,5-benzodiazepine amidines.



	R	R^1
1a, 2a	H	Ph
1b, 2b	CH_2Ph	Ph
1c, 2c	CH_2-CH=CH_2	Ph
1d, 2d	H	Me



3a R^1 = Ph
3b R^1 = Me

4a X = NHCOPh
4b X = NHCOMe
4c X = NH_2

3b

The desired hydrazino amidines **4a-c** were obtained from dihydro-1,5-benzodiazepinone derivatives **1a-d** *via* the route shown in the Scheme. Compounds **1a-d** were prepared according to the literature methods.[1] Lactams **1a-c** were transformed into the corresponding thiolactams **2a-c** using Lawesson's reagent. The interaction of **1d** with thionation agents did not proceed smoothly. The variation of the reaction temperature, time, solvents and agents led to the formation of **2d**, albeit in low yield (Table 1) which may be explained by the fact that compound **1d** is thermally less stable than **1a**.[2]