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Some 1-Aroyl-4,4-dialkylsemicarbazides and Their Cyclization to Afford 5-Aryl-1,3,4-oxadiazol-2(3*H*)-ones

Short Communication

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Some 1-aroyl-4,4-dialkylsemicarbazides have been prepared by reacting aroylhydrazides with dimethyl- or diethyl-carbamoyl chloride. In boiling *DMF* they lose dimethylamine or diethylamine to give 5-aryl-1,3,4-oxadiazol-2(3*H*)-ones.

(Keywords: 1-Aroyl-4,4-dialkylsemicarbazides; Oxadiazolones)

Einige 1-Aroyl-4,4-dialkylsemicarbazide und ihre Cyclisierung zu 5-Aryl-1,3,4-oxadiazol-2(3H)-onen (Kurze Mitteilung)

Es wurden mittels Reaktion von Aroyl-hydraziden mit Dimethyl- oder Diethyl-carbamidsäure-chlorid einige 1-Aroyl-4,4-dialkylsemicarbazide dargestellt. Diese verlieren in kochendem *DMF* Dimethylamin bzw. Diethylamin und geben 5-Aryl-1,3,4-oxadiazol-2(3*H*)-one.

Dornow and *Lüpfert* [1] cyclized 1-benzoylsemicarbazide by heating a solution in diphenyl to 230–240 °C for a few minutes. Recently [2] it was found that 1-*o*-aminophenyl-4,4-dimethylsemicarbazide is readily cyclized in boiling dimethylformamide and this cyclization appears to be general for 1-aroyl-4,4-dialkylsemicarbazides. Previous workers [3, 4] have prepared some 5-aryl and 5-heterocyclic derivatives of 1,3,4-oxadiazol-2(3*H*)-one from the acid hydrazide and dialkylcarbamoyl chloride in pyridine without isolation (except in one case) of the intermediate semicarbazide, but yields were generally poor. The following procedure has been found useful.

The aroyl-hydrazine (0.03 mol) was dissolved in pyridine (15 cm^3) with gentle warming and then the dialkylcarbamoyl chloride (0.033 mol) added. After some

Table 1

		2		3		4		
	Ar	Yield (%)	m.p. (°C)	Yield (%)	m.p. (°C)	Yield (%)	m.p. (°C)	Lit. m.p. (°C)
a	*Ph*	78	212	45	163–164	82	138–139	138–139 [6]
b	*o*-*Me*C_6H_4			85*	175	84	144–145	
c	*m*-*Me*C_6H_4	74	181–182	85	158–159	85	113–114	
d	*p*-*Me*C_6H_4	50	200–201	73	172–173	98	162–163	161 [7]
e	*o*-*Me*OC_6H_4			36*	137–138	92	174–175	
f	*m*-*Me*OC_6H_4	62	177–178			92	147–148	
g	*p*-*Me*OC_6H_4	58	202–204	79	150–151	95	186–187	185 [7]
h	*o*-ClC_6H_4	70	182–183	78	188–189	90	163–164	165–166 [6]
i	*m*-ClC_6H_4	90	194–195			90	160–161	158–159 [8]
j	*p*-ClC_6H_4	73	195–196	93	177–178	92	228–229	234–235 [6]
k	*o*-O_2NC_6H_4	50*	197–198	81*	186–187	89	158–159	159–161 [2]
l	*m*-O_2NC_6H_4	97	198–199	44	183–184	94	194–195	190–192 [6]
m	*p*-O_2NC_6H_4	79	202–203			86	250–251	251–253 [6]
n	*o*-HOC_6H_4	75	177–178			75	197–198	199–200 [4]
o	2,5-HO(*Me*O)C_6H_3	60	194–195			70	188–189	
p	2,5-HO(Cl)C_6H_3	82	217–219	46	173–174	46	237–239	236–239 [4]

* These yields of **2k**, **3b**, **3e**, and **3k** were obtained when the reaction time was extended to 3–4 weeks

1 2 (R = Me) 3 (R = Et) 4

hours, conveniently overnight, water was added and the precipitated 1-aroyl-4,4-dialkylsemicarbazide filtered off, washed with water and dried. The dried products **2** or **3** were quite pure and could be cyclized without further purification. Analytical specimens were recrystallised from ethanol. *Stempel* [5] obtained **3a** by heating **4a** with diethylamine in a sealed tube. Samples of **3e** and **3l** were also made by *Stempel*'s method.

To accomplish cyclization to the oxadiazolone (**4**), the semicarbazide (**2** or **3**) was dissolved in dimethylformamide (5 to 10 parts) and heated under reflux for several hours till evolution of dialkylamine ceased. Addition of water afforded the 5-aryl-1,3,4-oxadiazol-2(3*H*)-one which was recrystallised from ethanol or aqueous ethanol. Yields of **4** obtained from **2** or **3** were so similar that it is unnecessary to quote both (Table 1).

Satisfactory analyses for C, H, and N were obtained for all novel compounds. Infra-red spectra of compounds **2** and **3** showed absorption around 1 640 cm^{-1}, whereas the oxadiazolones (**4**) absorbed around 1 780 cm^{-1}. The mass spectrum of **4a** was similar to that in the literature [9]. For **2a**, **2d**, **2h**, **2i**, **3a**, and **3g** peaks were observed corresponding to M^+, $ArCO^+$, Ar^+, and R_2NCO^+.

Although 5-(2-aminophenyl)-1,3,4-oxadiazol-2(3*H*)-one readily rearranges to 3-amino-2,4(1*H*,3*H*)-quinazolinedione [2] when heated above its melting point, no analogous rearrangement of **4n** to 3-amino-2*H*-1,3-benzoxazine-2,4(3*H*)-dione [10] was observed.

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