

MESO-IONIC OXAZOLONES IN HETEROCYCLIC SYNTHESIS : REACTION OF 4-METHYL-2-PHENYL- Δ^2 -OXAZOLIN-5-ONE WITH ALDAZINES

Dilip Konwar, Dipak Prajapati, and Jagir Singh Sandhu*

Regional Research Laboratory, Jorhat-785006, India

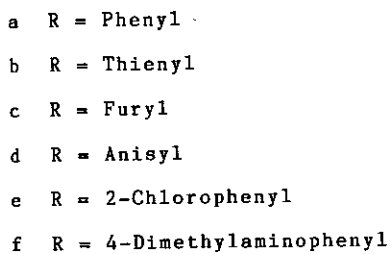
Tetsuji Kametani and Toshio Honda

Institute of Medicinal Chemistry, Hoshi University, Ebara 2-4-41, Shinagawa-ku, Tokyo 142, Japan

Abstract — Reaction of 4-methyl-2-phenyl- Δ^2 -oxazolin-5-one (**2**) with various aldazines (**1**) yielded pyridazinones (**3**) in good yields. Their structures were fully supported by spectral data.

Münchnone (2,4-diphenyl-N-methyloxazolin-5-one) is the most extensively investigated mesoionic azlactone and its reaction with a variety of multiple as well as heteromultiple bonds have been exploited.¹⁻⁶ In our investigations on 4-methyl-2-phenylazlactone (**2**) with imines and conjugated imines we obtained β -lactams⁷ and α -pyridones,^{8,9} respectively in good yields. Here we report the formation of pyridazinones (**3**) from **2** and aldazines (**1**) in good yields.

Reaction between aldazine (**1a**) and azlactone (**2**) was carried out by dissolving their equimolar quantities in dry benzene and stirring the reaction mixture at room temperature for 24 h. The white crystalline compound thus separated was filtered and recrystallized from dichloromethane to give the pyridazinone (**3a**), mp 298-300°C (decomp.) in 70% yield. The structure of **3a** is supported by high resolution mass spectrum [calculated 383.1633; found 383.1608]. The ¹H NMR (100 MHz, CDCl₃) δ : 1.85 (s, 3H, CH₃), 5.81 (s, 1H), 6.90 (s, 1H), 7.19-7.59 (m, 14H), 8.25-8.40 (m, 2H). The ir (KBr) spectrum showed absorption at 1675 and 1690 cm⁻¹ assignable to an amido carbonyl and a carbonyl group present in the 4-position of **3a**. The possibility of structure, **4** or **5**, which could have the result of 'criss-cross' cycloaddition or addition across the azomethine function is clearly ruled out as there was no absorption in ir spectrum around 1745 cm⁻¹ diagnostic for a β -lactam⁷ or any other indicating the presence of strained C=O function. All the



foregoing data supported the structural assignment for $3a$.¹⁰ Similarly were prepared $3b-f$ and their characteristics are recorded in the Table.

This new synthesis of pyridazinones using azlactones appears to be relatively simple and affords high yields. Regarding the mechanism of this reaction, we believe the ketene tautomer of 2 is not involved, since the reaction occurs at room temperature and it is reported the ketene tautomer can equilibrate only under thermal conditions.¹¹ Work is in progress to understand the mechanism as well as to further explore the scope of this new reaction.

Table. The Yields, Melting Points and Spectral Data of Pyridazinones ($3a-f$).

3^*	mp °C	Yield %	ir (KBr) cm^{-1}	MS (M^+) m/e	1H NMR
a	298-300	70	1675,1690	383	1.85 (s, 3H, CH_3), 5.81 (s, 1H), 6.90 (s, 1H), 7.19-7.59 (m, 14H), 8.25-8.40 (m, 2H)
b	315-317	63	1670,1690	395	1.50 (s, 3H, CH_3), 5.80 (s, 1H), 6.60 (s, 1H), 6.65-7.60 (m, 12H)
c	310-312	60	1675,1685	363	1.4 (s, 3H, CH_3), 5.60 (s, 1H), 5.9-7.75 (m, 13H)
d	318-320	65	1675,1695	443	1.75 (s, 3H, CH_3), 3.65 (s, 6H, OCH_3), 5.80 (s, 1H), 6.88 (s, 1H) 7.19-8.25 (m, 14H)
e	314-315	65	1675,1695	443	1.53 (s, 3H, CH_3), 5.82 (s, 1H), 6.64 (s, 1H), 7.19-8.08 (m, 14H)
f	329-330	55	1670,1685	467	1.65 (s, 3H, CH_3), 3.05 (s, 12H, CH_3), 5.80 (s, 1H), 6.90 (s, 1H), 7.19-8.05 (m, 14H)

* All the compounds reported here gave satisfactory elemental analyses.

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