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Reaction of 4-Arylmethylene-2-Phenyl-2-Oxazolin-5-Ones with Schiff bases and Benzalazine

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4-Arylmethylene-2-phenyl-2-oxazolin-5-ones (**1**) react with schiff bases in benzene to give the arylamides of α-carboxamido-β-arylacrylic acids (**2**). However the reaction of **1** with schiff bases in acetic acid containing catalytic amounts of fused sodium acetate gave 1, 2-diaryl-4-arylmethylene-2-imidazolin-5-ones (**3**). Reaction of benzalazine with **1a** in benzene or in the absence of solvent involved cleavage of one of the imino groups yielding **4** and **5** respectively. The structures of the products were confirmed by analytical and spectral data and also by synthesis of authentic samples in most cases.

INTRODUCTION

Oxazolin-5-ones can be considered as semiacid anhydrides and they undergo many of reactions of true acid anhydrides, e.g., reactions with amines[1,2], hydrazines[3] and aromatic hydrocarbons[4] under Friedel-Crafts conditions. Acid anhydrides react with schiff bases and azines, and the products of reactions were depends upon reaction conditions[5–10]. The reaction in many cases involved the displacement of arylidene group of the imino molecule.

EXPERIMENTAL

All melting points are uncorrected, IR spectra were measured on a Perkin-Elmer 398 infrared spectrophotometer using the KBr pellet technique. Analyses were carried out in the Research Microanalytical Laboratory of Cairo University.

Reaction of oxazolin-5-ones (1) with schiff bases
General procedure

(*A*) *In benzene*: A mixture of **1** (0.01 mol) and schiff base (0.01 mol) were dissolved in benzene (50 ml). The mixture was refluxed for 2–5 hrs. The product separated out which was filtered and crystallized from the proper solvent to give **2**.

Compound **2c**: m.pt. 245°C. yield 85%, $C_{22}H_{17}N_3O_4$ calcd. (%) C 68.21; H 4.39; N 10.85. Found (%) C 68.00; H 4.60; N 10.70.

IR : νC = O (1650), νNH (1240) br cm^{-1}.

Compound **2f**: m.pt. 185°C, yield 80%, $C_{23}H_{19}N_3O_4$ calcd. (%) C68.82; H 4.73; N 10.47. Found (%) C 69.00; H 4.50; N 10.00.

IR: νC = O (1645), νNH (3230) cm^{-1}.

(*B*) *In sodium acetate and acetic acid*: A mixture of **1** (0.05 mol), and schiff base (0.05 mol), freshly fused sodium acetate (0.05 mol) and acetic acid (20 ml) was heated under reflux for 5h. The reaction mixture was concentrated. After cooling the solid product filtered, washed with water and crystallized from the suitable solvent to give **3**.

Compound **3c**: m.p. 191–2°C, yield 80%, $C_{22}H_{15}N_3O_3$ calcd. (%) C 71.54; H 4.06; N 11.38. Found (%) C 71.80; H 4.50; N 11.00.

IR : νC = O (1715), νC = N (1630) cm^{-1}.

Compound **3f**: m.p. 228°C, yield 85%, (%) $C_{23}H_{12}N_3O_3$ calcd. C 72.06; H 4.43; N 10.96. Found (%) C 72.20; H 4.20; N 10.80.

IR : νC = O (1720), νC = N (1630) cm^{-1}.

Reaction of p-nitrophenylmethylene-2-phenyl-2-oxazolin-5-one with amines

(*A*) *In Benzene*: A mixture of **1c** (0.01 mol) and the primary aromatic amine (0.01 mol) were dissolved in benzene (50 ml). The mixture was refluxed for 1h. The product separated was filtered and crystallized from the proper solvent to give **2c,f.**

(*B*) *In sodium acetate and acetic acid*: A mixture of **1c** (0.05 mol) and the primary aromatic amine (0.05 mol) in acetic acid (20 ml) containing freshly fused sodium acetate (0.05 mol) was refluxed for 5 hrs. The reaction mixture was concentrated and cooled. The crude product was filtered, washed with water and crystallized from acetic acid to give **3c,f.**

Reaction of 1a with benzalazine

(*A*) *In benzene*: A mixture of **1a** (0.01 mol) and benzalazine in benzene (50 ml) was heated under reflux for 20h. The reaction mixture was evaporated till dryness, and the residue was crystallized from ethanol to give **4.**

Compound **4**: m.p. 158°C, yield 10%, $C_{23}H_{19}N_3O_2$ calcd. (%) C74.79, H 5.14, N 11.38. Found (%) C 75.00; H 5.5; N 11.10.

IR : νC = O.(1660), νNH(3260) br cm^{-1}.

(*B*) *By fusion*: Equimolar mixture of **1a** and benzalazine was heated in an oil bath at 140–150°C for 1h. The resultant solid was crystallized from benzene to give **5.**

Compound **5**: m.p. 170°C; yield 50%. $C_{23}H_{17}N_3O$ calcd. (%) C 78.63, N 11.96. Found (%) H 4.84; C 76.70; H 5.00; N 12.20.

IR : νC = O (1760) cm^{-1}.

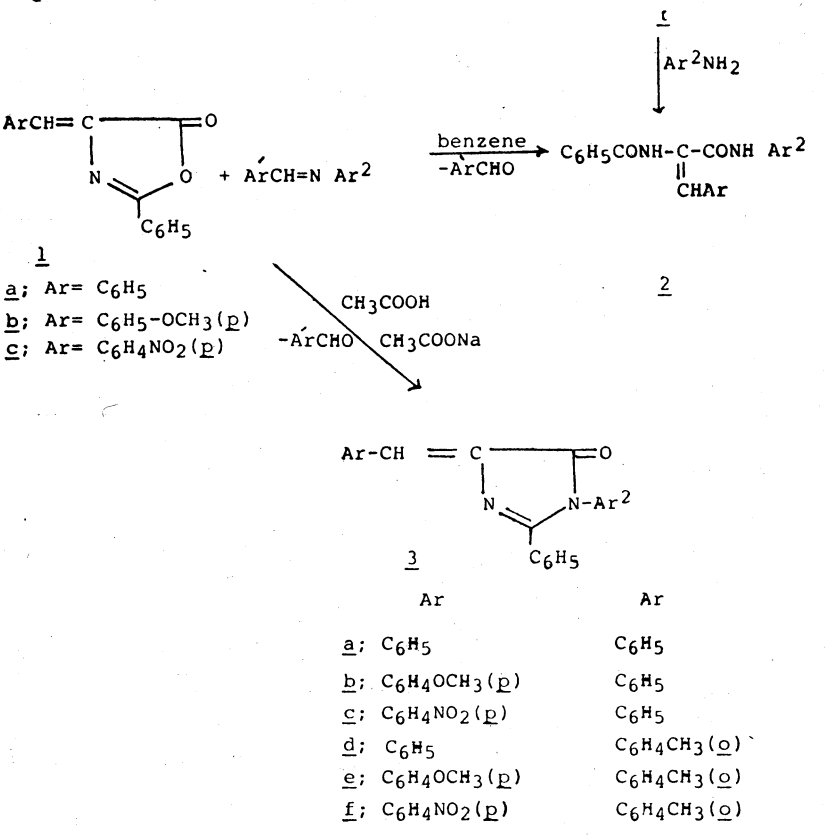
Reaction of p-methoxybenzylideneaniline with 8

Equimolar mixture of *p*-methoxybenzylideneaniline and **8** was heated in an oil bath at 160°C for 1 hr. The resultant solid was crystallized from benzene to give **1b** and **2b**.

RESULTS AND DISCUSSION

The present investigation deals with the reaction of 4-arylmethylene-2-phenyl-2-oxazolin-5-one (**1a-c**) with schiff bases and the reaction of **1a** with benzalazine.

The interaction of equimolecular amounts of **1** and benzylideneaniline in refluxing benzene yielded arylcarboxamide of α-phenylcarboxamido-β-acrylic acids (**2a-c**). The reaction evidently involved the displacement of the arylidene group of the schiff base. This was further evidenced by the fact that the same products were obtained by the reaction of **1a,c** with



p-methoxybenzylideneaniline. Futhermore it was possible to detect the aromatic aldehydes in the reaction mixture.

Similarly, when the oxazolinones (**1a-c**) were allowed to react with benzylidene-2-methylaniline, arylamides of α-arylcarboxamido-β-arylacrylic acids (**2d-f**), respectively were obtained.

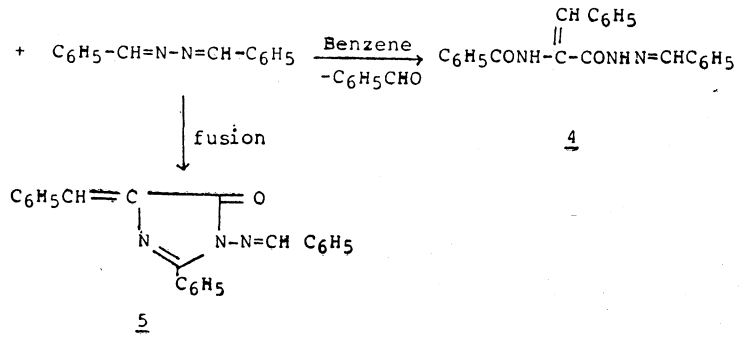
When the above reactions were conducted in glacial acetic acid containing fused sodium acetate, 1,2-diaryl-4-arylmethylene-2-imidazoline-5-ones (**3a-f**), which are the cyclization products of **2a-f**, were formed in good yields. The aromatic aldehydes were also detected in the reaction media.

However, when these reactions were carried out at elevated temperature in the absence of solvent, a mixture of **2** and **3** was obtained with the former predominating.

Compounds **2a,b,d,e** and **3a,b,d,e** were characterised by their identity (mp, and superimposable IR spectra) with authentic sample[I,II] prepared by direct interaction of **1** with amines in benzene and in glacial acetic acid containing a catalytic amount of sodium acetate respectively.

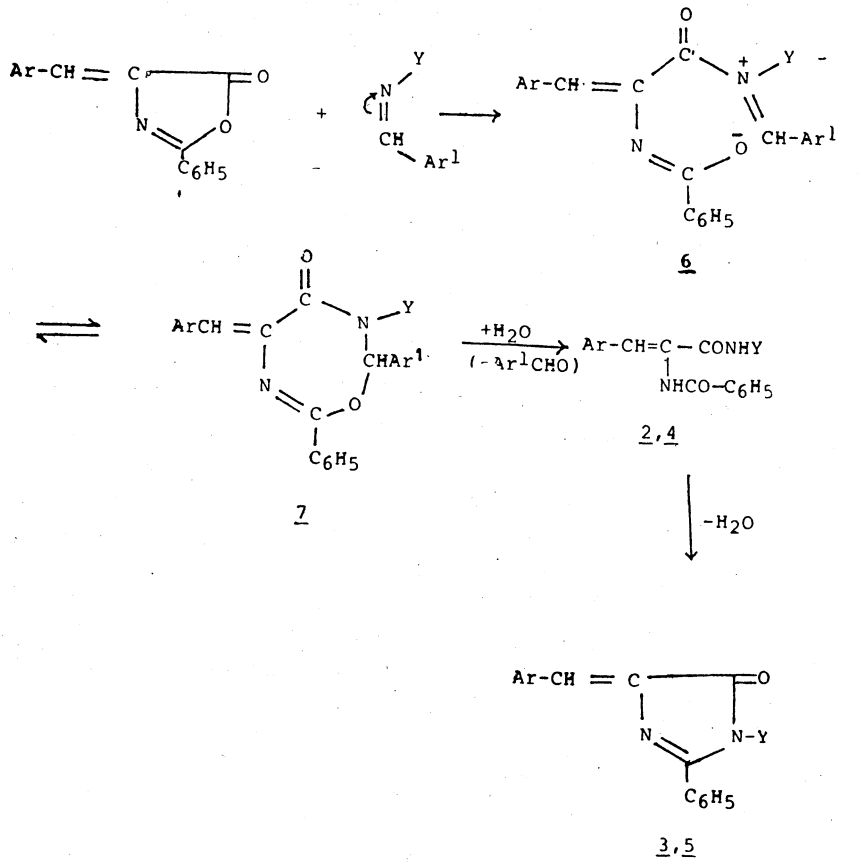
The structural assignments of **2c,f** and **3c,f** were based on microanalytical data and from the fact that their infrared spectra are similar to these previously reported (cf. exp. part), Morever, compounds **2c,f** and **3c,f** were found to be similar to the products obtained by the action of **1c** with aniline and *o*-toluidine in benzene and glacial acetic acid respectively.

The reaction of **1a** with benzalazine involved the displacement of one benzylidene group only. Thus when **1a** was allowed to react with benzalazine in benzene a poor yield of **4** was obtained while their reaction at elevated temperature in the absence of solvent yielded **5**.



The structure of **4** was substantiated from microanalytical data and a study of its infrared spectrum which shows the carbonyl stretching frequencies of amides at 1660 cm^{-1}, in addition to νNH at 3260 cm^{-1}. The structure of **5** was confirmed, other than from microanalytical data, from

the fact that its infrared spectrum shows a single strong carbonyl absorption at 1760 cm^{-1} while it lacks the significant absorption of NH group. A possible explanation for the reaction of **1** with schiff bases and azine is that the reaction in each case proceeds via the formation of the intermediate **6** which would be stabilised by cyclization to **7** that can give rise to the products **2–5** and indicated in scheme 1.

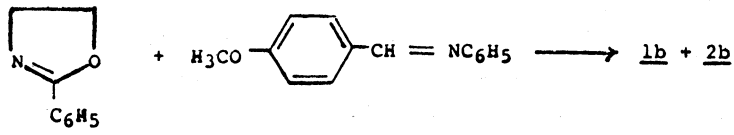


Scheme 1

It is important to mention that intermediates of related nature to **7** have been proposed for the reaction products of imines with succinic and maleic anhydrides.[8,9]

It was reported earlier[12,13] that 2-phenyl-2-oxazolin-5-one (**8**) reacts with schiff bases for short periods to give 4-arylmethylene-2-phenyl-2-oxazolin-5-ones.[12,13] However in the present work when **8** was allowed to react with *p*-methoxybenzylideneaniline, a mixture of **1b** to **2b** was obtained with the former perdominating. This presents an

important method for introducing both arylidene and amino groups in the oxazolinone molecule in one step.



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The products **1b** and **2b** were characterised by their identity with authentic samples.

TABLE 1

Compound	Yield %	M.pt., °C (Lit.)	IR, (Cm^{-1})
2a	70	230–1 (230, 234)[a,b]	νC = O (1660), νNH (3230) br
2b	30	248–90 (255)[b]	νC = O (1645), νNH (3240) br
2d	75	173 (175)[b]	νC = O (1650), νNH (3240) br
2c	25	184 (185)[b]	νC = O (1640), νNH (3240) br
3a	80	179 (175)[b]	νC = O (1720), νC = N (1640)
3b	30	154 (150)[b]	νC = O (1710), νC = N (1630)
3d	70	200 (195)[b]	νC = O (1710), νC = N (1635)
3e	25	189 (190)[b]	νC = O (1710), ν C = N (1640)

(a) Ref. [1], (b) Ref. [11].

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