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REACTION OF 1,4-PHENYLINE DI-[BENZYLIDENE-5-(4H)-OXAZOLONE 2-YL] WITH NITROGENE NUCLEOPHILES

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Hetero ring opening of compound *1* with aliphatic amines afford cinnamid derivatives *2* and *3*, and with aniline give imidazolinone *4*, Hydrazinolysis of *1* affording triazine derivatives *5* and cinnamic acid phenylhydrazide *6*. The reaction of *1* with glycine and ammonium acetate yielded the imidazolinone derivatives *7* and *8* respectively.

Key words: Oxazolone derivatives.

Introduction

Many oxazole derivatives exhibit interesting biological as well as medicinal application [1,2]. Our interest is to study the behaviour of 1,4-phenylene di-(4-benzylidene-5-(4H)-oxazolone-2 yl) [3] *1* toward different nitrogen nucleophiles [4-6]. Thus the titled compound *1* reacted with cyclopeneylamine or diethylaine to give 1,4-phenylene di-(α-carbonylamino-N-N - cyclopentyl (or diethyl) cinnamide *2* and *3*. It seems that heteroring opening takes place by nucleophilic attack at the carbonyl group and the products formed by acyl-oxygen fission.

On the other hand, compound *1* reacted with aniline to give 1,4 phenylene di-(1-phenyl-4-benzylidene imidazolinone-2-yl) *4* through heteroring opening and subsequent cyclisation. When compound *1* is allowed to react with hydrazine hydrate in boiling toluene, the reaction product is triazine derivative *5*.

Also when compound *1* was subjected to react with phenylhydrazine in refluxing n-butanol yielded 1,4-phenyl di-[α -carbonylamino cinnamic acid phenyl hydrazide] *6*. Treatment of *1* with glycine in boiling pyridine yielded 1,4-phenylene di-[1- carboxymethyl-4-benzylidene imidazolinone-2-yl] *7*.

The reaction of 1 with ammonium acetate by fusion gave 1,4- phenylen di-[4-benzylideneimidazolinone - 2yl] 8. The assigned structure for the imidazolinone *8* is supported by its treatment with acetic anhydride or benzoylchloride or ethyl bromoacetate to give acetyl and benzoyl derivatives *9 a-b* and 1,4-phenylene di- [1-etheoxycarbonylmethyl-4-benzylidene imidazolinone-2 yl] *10*.

Experimental

Melting points reported are uncorrected. I.R. spectra in KBr were run on a Pye-Unicam No. 641749 spectrophotometer and PMR spectra on a Biumberg No. 4032 instrument.

Characterisation and physical data are listed in Table (1,2).

Reaction of compound 1 with alphatic amines : Formation of cinnamide derivatives 2 and 3. A solution of the compound *1* (0.01 mol) in (50 ml) ethanol was treated with the appropriate amine namely, cyclopentyl amine and diethylamine (0.04 mol). The solution was refluxed for 5hr. After concentration and cooling the solid product was crystallized from a suitable solvent to obtain *2* and *3* respectively.

Reaction of compound 1 with aniline : Formation of imidazolinone 4. A mixture of compound *1* (0.01 mol), anhydrous sodium acetate (0.02 mol), and aniline (0.04 mol) in acetic acid (50 ml) is heated under reflux for 3hr. After cooling, the reaction mixture was diluted with water. The solid product, separated is filtered off and washed with water, crystallized then for a suitable solvent to give *4*.

Reaction of compound 1 with hydrazines : Formation of triazine derivative 5 and cinnamic acid phenylhydrazide derivative 6. A mixture of *1* (0.01 mole), hydrazinehydrate or phenylhydrazine (0.03 mol) in toluene (40 mol) and n-butanol (40 ml) in case of phenylhydrazine was refluxed for 4hr. Then the reaction mixture is cooled. The solid products were filtered and crystallized from the proper solvent to yield *5* and *6*.

Reaction of 1 with glycine : Formation of imidazolinone 7. A solution of *1* (0.01 mol) in pyridine (40 ml) was treated with glycine (0.04 mol) and water (2 ml). Then the solution was refluxed for the 4hr. After cooling the reaction mixture is poured into ice-hydrochloric acid and the mixture allowed to stand overnight. The solid product *7* is isolated by suction and recrystallized from the proper solvent.

Reaction of 1 with ammoniumacetate : Formation of imidazolinone 8. A mixture of *1* (0.01 mol) and ammonium (6.2 g) was heated in an oil bath at 150° for 3 hr. The mixture is cooled, decomposed with water. The solid product *8* is isolated by suction and recrystallized from the suitable solvent.

Reaction of 8 with acetic anhydride : Formation of 9a. A solution of *8* (0.01 mol) in acetic anydride (20 ml) is heated at reflux temperaturre of 2hr. The mixture is the cooled and poured into water (70 ml) and allowed to stand overnight. Product *9a* is isolated by suction and recrystal-

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Table 1. Characterisation and Physical Data of Synthesised Compounds.

Compd. No.	Melting point°C Colour	Solvent yield %	Molecular formula (m.w.)		Analyses % Found	Required
2	>300 white	Acetic Acid 75	$C_{36}H_{38}N_4O_4$ (590)	C	73.55	73.22
				H	6.34	6.44
				N	9.63	9.49
3	263-5 white	Methanol 62	$C_{34}H_{38}N_4O_4$ (566)	C	72.03	72.08
				H	6.50	6.71
				N	9.93	9.89
4	236-8 white	*n*-Butanol 67	$C_{38}H_{26}N_4O_2$ (570)	C	79.81	80.00
				H	4.45	4.56
				N	9.93	9.82
5	208-9 white	*n*-Butanol 65	$C_{26}H_{20}N_6O_2$ (448)	C	69.49	69.64
				H	4.43	4.46
				N	18.97	18.75
6	266-8 pale yellow	AceticAcid 56	$C_{38}H_{32}N_6O_4$ (636)	C	71.51	71.69
				H	5.09	5.03
				N	13.56	13.20
7	250-1 white	*n*-Butanol 52	$C_{30}H_{22}N_4O_6$ (534)	C	67.50	67.41
				H	4.23	4.11
				N	10.53	10.48
8	264-6 pale yellow	Metanol 47	$C_{26}H_{18}N_4O_2$ (418)	C	74.11	74.64
				H	4.58	4.30
				N	13.33	13.39
9a	245-6 pale yellow	Toluene 82	$C_{30}H_{22}N_4O_4$ (502)	C	71.68	71.71
				H	4.31	4.38
				N	10.97	11.15
9b	205-7 yellow	Benzene 77	$C_{40}H_{26}N_4O_4$ (626)	C	76.60	76.67
				H	4.03	4.15
10	211-2 white	Benzene 45	$C_{34}H_{30}N_4O_6$ (590)	C	69.35	69.15
				H	5.22	5.08

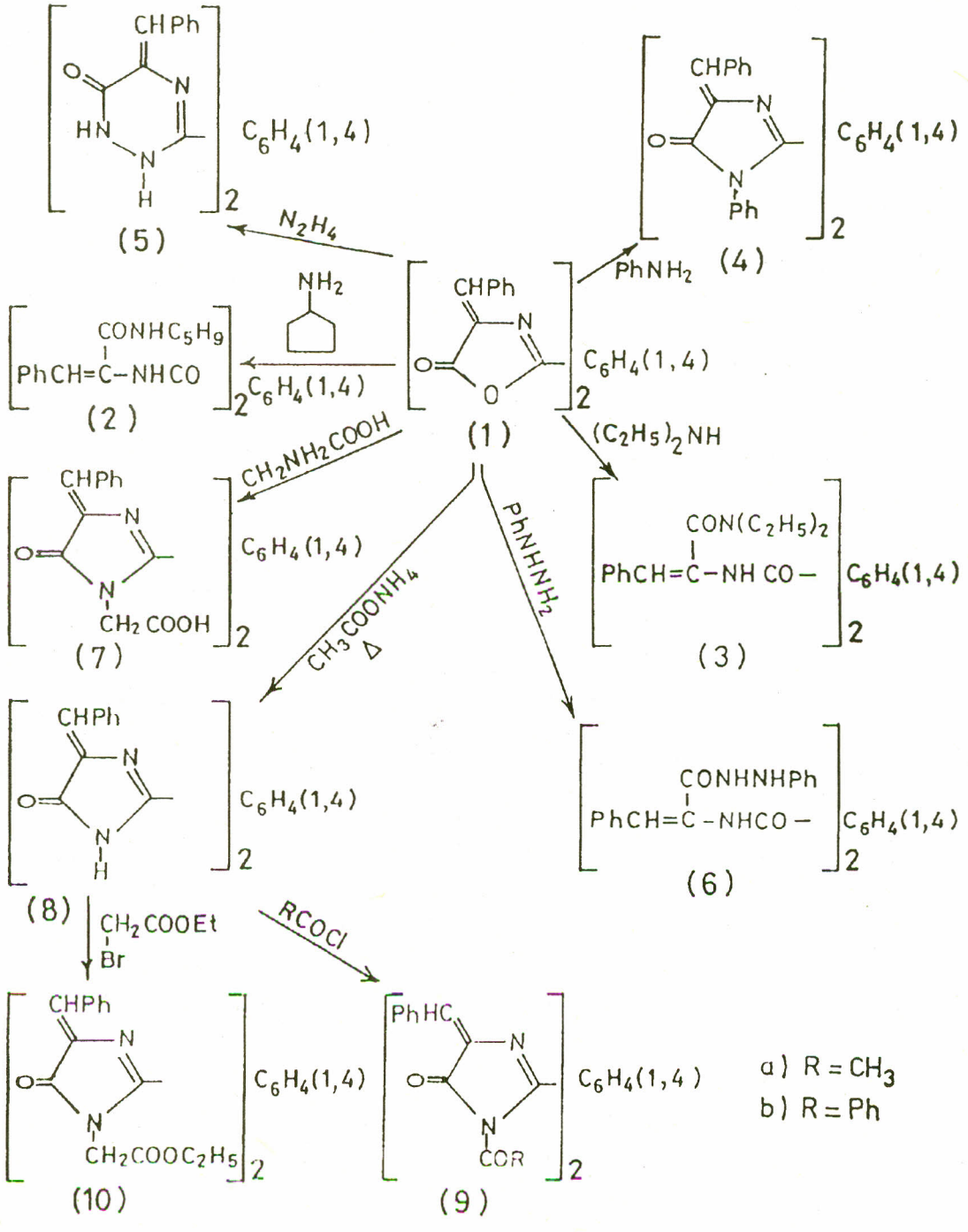
Table 2. Spectral Data of the Prepared Compounds.

Comp. No.	IR in KBr (υ in cm^{-1})	^{1}H-NMR (DMSO-d_6) solvent (σ ppm)
2	1670-1690 (C=O abd 3200-3300 (NH).	1.8-2.7 (M, 9H; cyclopentan-H), 6.5 (s, 2H; =CH), 7.1-8.2 (m,32H; arom-H) and 7.8-9.0 (broad, 4H; NH).
3	1670-1685 (C=O) and 3200-3300 (NH).	1.2 (t, 12H; CH_3CH_2), 2.1(q, 8H; CH_3CH_2), 6.3 (s, 2H;=CH), 7.1-8.3 (m,14H; arom-H) and 8,6-9.1 (broad, 2H; NH).
4	1635 (C=N) and 1690 (C=O).	6.6 (s, 2H; = CH) and 7.5-8.2 (m, 24H; arom-H).
5	1640 (C=N), 1664 (C=O) and 3200-3400 (NH).	4.4 (broad, 2H; NH), 6.6 (s, 2H; =CH), 7.1-8.0 (m, 4H; arom-H) and 8.6-8.8 (broad, 2H; *NH*CO).
6	1650-1670 (amidic C=O and 3100-3200 (NH).	6.5 (s, 2H; =CH), 7.3-8.1 (m, 24H; arom H) and 8.5-9.0 (broad, 6H; NH).
7	1650 (C=N), 1670 (C=O of cyclic carboxamide), 1700 (C=O of acid and 3200 (broad chelated OH).	2.4 (s, 4H;CH2), 6.3 (s, 2H; = CH), 7.4-8.2 (m, 14 H; arom-H) and 10.4 (broad, 2H; COO*H*).
8	1640 (C=N), 1700 (C=O) and 3300 (NH).	6.3 (s, 2H; =CH), 7.2-8.1 (m, 14H; arom H)and 8.3 (broad, 2H; NH).
9a	1640 (C=N) and 1685 (C=O).	2.8 (s, 6H; CH_3), 6.4 (s, 2H; =CH) and 7.1-8.2 (m, 14H; arom-H).
10	1645 (C=N), 1690 (C=O cyclic carboxamide) and 1740 (C=O of ester).	1.2 (t, 6H;-CH_2-CH_3), 4.3 (q, 4H; CH_2-CH_3); 4.8 (s, 4H;-CH_2 COO), 6.3 (s, 2H; =CH) and 7.1-8.3 (m, 14H; arom-H).

lized from the suitable solvent.

Reaction of 8 with benzoylchloride : Formation of 9b. A mixture of *8* (0.01 mol) and benzoychloride (0.04 mol) in pyridine (30 ml) is heated on water bath for 3 hr. The mixture is then cooled and poured into ice-hydrochloric acid. The pricipitated product is isolated by suction and recrystallized from the proper solvent to give *9b*.

Reaction of 8 with ethylbromoacetate : Formation of 10. A mixture of *8* (0.01 mol) and ethylbromacetate (0.06 mol) in pyridine (30 ml) is heated on steam bath for 5 hr. The mixture is then cooled and poured into ice-hydrochloric acid, and the whole extracted with ether. The ether extract is washed with water and is dried with sodium sulphate. The solvent is slow evaporated. The solid product left is washed with light petrol and collected with suction, and recrystallized from the suitable solvent to give *10*.



Scheme I

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