Tetrahedron, 1964, Vol. 20, pp. 1063 to 1065. Pergamon Press Ltd. Printed in Northern Ireland

BEHAVIOUR OF THE HETEROCYCLIC RING IN 2-BENZYLIDENE-4-PHENYL-3-OXAZOLIN-5-ONE TOWARDS THE ACTION OF AMINES AND HYDRAZINES

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(*Received* 19 *November* 1963; *in revised form*, 27 *December* 1963)

Abstract—The heterocyclic ring in 2-benzylidene-4-phenyl-3-oxazolin-5-one (Ib) is opened by the action of aromatic amines in alcohol with the formation of methyl or ethyl α-arylamino-α-phenylacetamidophenylacetates. The IR spectra of the products are discussed and action of hydrazines and benzylamine on Ib has been investigated.

ALTHOUGH pseudoxazolones have been described in the literature,[1–4] only 2-benzylidene-4-methyl pseudoxazolone (Ia) has received much attention.

The light catalysed dimerization of Ia[4] and the different melting points reported for this compound,[1–3] prompted the investigation into the chemical behaviour of the relatively stable 2-benzylidene-4-phenyl pseudoxazolone(Ib), recently described by Giorgio Adembri.[5] Compound Ib does not react with the aromatic amines in xylene in the presence or absence of trimethylamine, but when a methanolic solution of Ib is heated in the presence of the trimethylamine with aromatic amines, namely, aniline, *p*-toluidine, *p*-anisidine, α-naphthylamine and/or β-naphthylamine, the amine addition to the endocyclic C=N is accompanied by the opening of the heterocyclic ring with the formation of methyl α-arylamino-α-phenylacetamidophenylacetate (IIa–e). If ethanol is used instead of methanol in the case of aniline, *p*-toluidine, *p*-anisidine, α-naphthylamine and/or β-naphthylamine, the corresponding ethyl-α-arylamine-α-phenylacetamidophenylacetates (IIf–j) are obtained. No reaction was found to take place between Ib and aniline in presence of trimethylamine on heating in boiling n-butanol. The behaviour of Ib towards aniline is similar to the formation of methyl α-aniline-α-phenylacetamidopropionate (IIk), upon heating a mixture of Ia and aniline in boiling methanol in the presence of N-ethylpiperidine. Whereas, a similar reaction has been observed between Ib and propylamine in methanol and or in ethanol in the absence of a catalyst with the formation of the methyl, or ethyl ester of α-propylamine-α-phenylacetamidophenylacetate respectively,[5] treatment of Ib with benzylamine in presence of methanol without the addition of trimethylamine yields phenylacetamide. This is also obtained upon heating a solution

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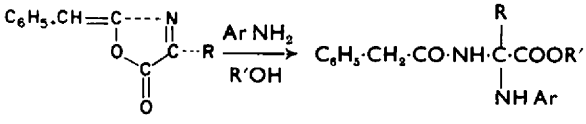
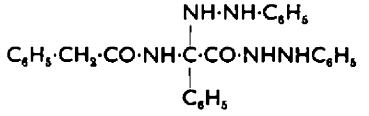


Ia, R = CH_3
b, R = C_6H_5

IIa, R = Ar = C_6H_5; R' = CH_3
b, R = C_6H_5; Ar = $C_6H_4CH_3$-p; R' = CH_3
c, R = C_6H_5; Ar = $C_6H_4OCH_3$-p; R' = CH_3
d, R = C_6H_5; Ar = $C_{10}H_7$-1; R' = CH_3
e, R = C_6H_5; Ar = $C_{10}H_7$-2; R' – CH_3
f, R = Ar = C_6H_5; R' = C_2H_5
g, R = C_6H_5; Ar = $C_6H_4CH_3$-p; R' = C_2H_5
h, R = C_6H_5; Ar = $C_6H_4OCH_3$-p; R' = C_2H_5
i, R = C_6H_5; Ar = $C_{10}H_7$-1; R' = C_2H_5
j, R = C_6H_5; Ar = $C_{10}H_7$-2; R' = C_2H_5
k, R = R' = CH_3; Ar = C_6H_5

of Ib in a saturated methanolic solution of dry ammonia. The formation of phenylacetamide resembles its formation from Ib upon treatment with dilute aqueous alkali solution.[5]

The action of hydrazine on hydrate an ethanolic solution of Ib, results in the formation of phenylacetic acid hydrazide. The latter condenses readily with benzaldehyde to give the corresponding benzal derivative. Similar treatment of Ib with *p*-nitrophenylhydrazine and or 2,4-dinitrophenylhydrazine yields phenylacetic acid *p*-nitrophenylhydrazide and phenylacetic acid, 2,4-dinitrophenylhydrazide respectively. On the other hand, when two molecules of the phenylhydrazine are added to one molecule of Ib, the reaction product probably has structure III, namely α-phenylacetamidophenylacetic acid phenylhydrazide. One molecule of the phenylhydrazine added to the C=N is accompanied by opening of the heterocyclic ring with formation of the phenylhydrazide.



$$C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}\overset{NH{\cdot}NH{\cdot}C_6H_5}{\underset{C_6H_5}{C}}{\cdot}CO{\cdot}NHNHC_6H_5 \qquad III$$

EXPERIMENTAL

All the m.ps are uncorrected. The IR spectra were measured in Nujol solution using a Perkin-Elmer model 137B. Analyses were carried out by Alfred Bernhardt, im Max-Plank Institute, Mulheim, Germany.

Action of aromatic amines on 2-benzylidene-4-phenyl-3-oxazolin-5-one (Ib)

General procedure. A methanolic or ethanolic solution of equimolar amounts of the pseudoxazolone and the aromatic amine was treated with a few drops trimethylamine and refluxed 2 hr. After concentration, the solution was chilled to give the colourless reaction products (IIa–j; Table 1). These, obtained in almost quantitative yield, readily crystallized from dil. alcohol. The intense IR absorption of IIa exhibits bands at 1650 cm^{-1} and at 1590 cm^{-1} (amide I and II bands), 1745 cm^{-1} (>C=O of the ester group stretching frequency) and 3330 cm^{-1} (—NH stretching frequency).

Action of hydrazine hydrate on IIb. Hydrazine hydrate (50%) (5 ml) in 10 ml warm ethanol was added to a solution of 1 g IIb in 10 ml ethanol and the mixture refluxed 1 hr. The solution was evaporated to dryness and the residue crystallized from water as colourless crystals (85% yield), identified as phenylacetic acid hydrazide, m.p. and mixture m.p. 116°. (Found: C, 64·26; H, 7·05; N, 18·12. $C_8H_{10}N_2O$ requires: C, 63·98; H, 6·71; N, 18·65%).

TABLE 1. ACTION OF AROMATIC AMINES ON 2-BENZYLIDINE-4-PHENYL-3-OXAZOLIN-5-ONE

Reaction product	m.p.	Formula	Analyses %					
			Carbon		Hydrogen		Nitrogen	
			Calc	Found	Calc	Found	Calc	Found
IIa	141°	$C_{23}H_{22}N_2O_3$	73·78	74·62	5·92	6·14	7·48	7·41
IIb	150°	$C_{24}H_{24}N_2O_3$	74·20	73·40	6·23	6·31	7·21	7·30
IIc	146°	$C_{24}H_{24}N_2O_4$	71·27	71·13	5·98	6·05	6·93	6·87
IId	157°	$C_{27}H_{24}N_2O_3$	76·39	76·98	5·70	5·85	6·60	6·70
IIe	166°	$C_{27}H_{24}N_2O_3$	76·39	76·92	5·70	5·90	6·60	6·75
IIf	126°	$C_{24}H_{24}N_2O_3$	74·20	74·42	6·23	6·57	7·21	6·79
IIg	141°	$C_{25}H_{26}N_2O_3$	74·62	74·41	6·40	6·29	6·96	6·87
IIh	151°	$C_{25}H_{26}N_2O_4$	71·75	72·05	6·26	6·22	6·69	6·98
IIi	147°	$C_{28}H_{26}N_2O_3$	76·69	76·72	5·98	6·07	6·39	6·87
IIj	126°	$C_{28}H_{26}N_2O_3$	76·69	77·00	5·98	6·07	6·39	6·84

The hydrazide on treatment with the calculated amount of benzaldehyde, yields the benzylidine derivative of phenylacetic acid hydrazide which crystallized as yellow crystals from ethanol m.p. 165°. (Found: C, 76·07; H, 5·69; N, 11·25. $C_{15}H_{14}N_2O$ requires: C, 75·60; H, 5·92; N, 11·76%).

Action of ammonia on IIb. A saturated alcoholic solution of dry ammonia was added to an alcoholic solution of IIb and the mixture refluxed 2 hr. The reaction mixture was evaporated and the residue (83% yield) crystallized from water as colourless crystals; identified as phenylacetamide, m.p. and mixture m.p. 156°. (Found: C, 71·10; H, 6·75; N, 10·33. C_8H_9NO, requires: C, 71·09; H, 6·71; N, 10·36%).

Action of benzylamine on IIb. An alcoholic solution of equimolar amounts of IIb and benzylamine was refluxed 2 hr. On evaporation phenylacetamide was obtained (75% yield), m.p. and mixture m.p. 156°. (Found: C, 71·53; H, 7·05; N, 10·10. C_8H_9NO, requires: C, 71·09; H, 6·71; N, 10·36%).

Action of 2,4-dinitrophenylhydrazine on IIb. An alcoholic solution of equimolar amounts of IIb and 2,4-dinitrophenylhydrazine was refluxed 3 hr; yielding (60%) phenylacetic acid 2,4-dinitrophenylhydrazide, m.p. 185°. (Found: C, 53·62; H, 3·45; N, 17·62. $C_{14}H_{12}N_4O_5$, requires: C, 53·16; H, 3·82; N, 17·72%).

Action of p*-nitrophenylhydrazine on* IIb. An alcoholic solution of equimolar amounts of IIb and *p*-nitrophenylhydrazine was refluxed 3 hr, yielding (65%) phenylacetic acid *p*-nitrophenylhydrazide, m.p. 145°. (Found: C, 62·12; H, 4·98; N, 15·87. $C_{14}H_{13}N_3O_3$, requires: C, 61·98; H, 4·83; N, 15·49%).

Action of phenylhydrazine on IIb. Equimolar amounts of IIb and phenylhydrazine in ethanol were heated under reflux 3 hr. The product (90% yield), α-phenylhydrazino-α-phenylacetamidophenylacetic acid phenylhydrazide (III), crystallizes as colourless crystals from ethanol, m.p. 250°. (Found: C, 72·22; H, 5·60; N, 14·84. $C_{28}H_{27}N_5O_2$, requires: C, 72·23; H, 5·85; N, 15·04%). The intense IR absorption of III exhibits bands at 1650 cm^{-1} and 1600 cm^{-1} (amide I and II bands), 3440 cm^{-1} (—NH stretching frequency) and the absence of carbonyl absorption of a carboxylic ester or lactone carbonyl group).