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Reaction of 2-Aryl-4-arylazo-2-oxazolin-5-ones with Amines

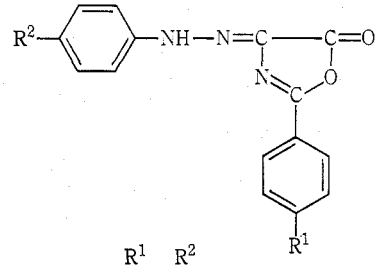
A. M. Khalil,[A,B] *I. I. Abd El-Gawad*[A] *and H. M. Hassan*[A]

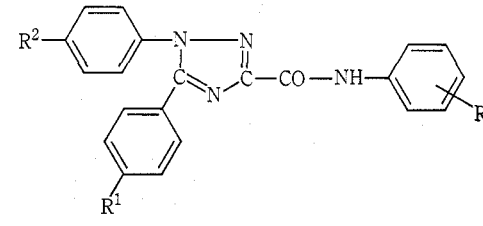
[A] Chemistry Department, Al-Mansoura Faculty of Science, Al-Mansoura, A.R.E. (Egypt).
[B] Present address: Department of Chemistry, Faculty of Science, King Abdulaziz University, P.O. Box 1540, Jeddah, Saudi Arabia.

Abstract

1,5,N_α-Triaryl-1,2,4-triazole-3-carboxamides have been prepared by the interaction of primary aromatic amines with 4-arylazo-2-*p*-chlorophenyl-2-oxazolin-5-ones.

The reaction of 4-arylazo-2-*p*-chlorophenyl-2-oxazolin-5-ones (1b–e) with some primary aromatic amines was carried out to obtain the expected triazoles (2).[1] Acetic acid containing sodium acetate was found useful for the conversion of (1) into (2). Although the acyclic intermediates postulated[2] or isolated[1] by other authors could not be obtained, a transient colour change indicated their occurrence.





	R^1	R^2
(1a)	H	H
(1b)	Cl	H
(1c)	Cl	Cl
(1d)	Cl	Me
(1e)	Cl	NO_2

	R^2	R^3
(2a)	H	H
(2b)	H	H
(2c)	H	*o*-Cl
(2d)	H	*m*-Cl
(2e)	H	*p*-Cl
(2f)	H	*o*-Me
(2g)	H	*m*-Me

	R^2	R^3
(2h)	H	*p*-Me
(2i)	Cl	H
(2j)	Cl	*p*-Cl
(2k)	Cl	*p*-Me
(2l)	Me	H
(2m)	Me	*o*-Cl
(2n)	Me	*m*-Cl

	R^2	R^3
(2o)	Me	*p*-Cl
(2p)	Me	*m*-Me
(2q)	Me	*p*-Me
(2r)	NO_2	H
(2s)	NO_2	*p*-Cl
(2t)	NO_2	*p*-Me

(2a; $R^1 = H$) (2b–t; $R^1 = Cl$)

The identity of 1,5,N_α-triphenyl-1,2,4-triazole-3-carboxamide obtained by direct interaction of (1a) with aniline in acetic acid solution containing a catalytic amount of sodium acetate with the compound obtained by the reaction of (1a) with aniline in boiling methanol was established by comparison with an authentic sample prepared by the method of Browne and Polya.[1]

[1] Browne, E. J., and Polya, J. B., *J. Chem. Soc.*, 1962, 575.
[2] Sawdey, G. W., *J. Amer. Chem. Soc.*, 1957, **79**, 1955.

Experimental

Analytical data were determined by the Microanalytical Unit, Cairo University. Infrared spectra were recorded on a SP1000 Pye–Unicam spectrophotometer.

2-Aryl-4-arylazo-2-oxazolin-5-ones (1a–e)

These compounds were prepared according to the method of Browne and Polya[1] (see Table 1).

The products (1a–e) were characterized by analysis and i.r. measurements which showed stretching frequencies at 1790 cm^{-1} characteristic for the carbonyl group of the lactone, and at 1620 cm^{-1} characteristic for –C=N–.

Table 1. 2-Aryl-4-arylazo-2-oxazolin-5-ones (1a–e)

Benzoyl-glycine	Phenylazo compound	Product	Colour	M.p. (°C)	Yield (%)	Formula	Found (%) C	H	N	Calc. (%) C	H	N
unsubst.	unsubst.	(1a)	yellow[A]	203[B]	72	$C_{15}H_{11}N_3O_2$	67·9	4·2	15·6	67·9	4·2	15·8
p-Cl	unsubst.	(1b)	orange[A]	251	75	$C_{15}H_{10}ClN_3O_2$	60·0	3·0	14·0	60·1	3·1	14·0
p-Cl	*p*-Cl	(1c)	orange[C]	245	82	$C_{15}H_9Cl_2N_3O_2$	52·8	2·6	12·5	52·9	2·7	12·6
p-Cl	*p*-Me	(1d)	orange[A]	238	85	$C_{16}H_{12}ClN_3O_2$	61·1	3·7	13·4	61·2	3·8	13·4
p-Cl	*p*-NO_2	(1e)	yellow[C]	235	78	$C_{15}H_9ClN_4O_4$	52·3	2·6	16·1	52·3	2·6	16·3

[A] Recrystallized from acetone. [B] Lit.[1] m.p. 201–203°. [C] Recrystallized from ethanol.

1,5,N_2-Triaryl-1,2,4-triazole-3-carboxamides (2a–t)

A mixture of 2-aryl-4-arylazo-2-oxazolin-5-ones (1a–e), prepared as described above (0·01 mol in each case), and the appropriate primary aromatic amine (0·01 mol) in acetic acid (50 ml) containing freshly fused sodium acetate (1·5 g) was heated under reflux for 1 h. The mixture was cooled, and the crude product was collected by suction filtration. Recrystallization from ethanol gave 1,5,N_2-triaryl-1,2,4-triazole-3-carboxamides (2a–t) as white crystals (see Table 2).

Table 2. 1,5,N_2-Triaryl-1,2,4-triazole-3-carboxamides (2a–t)

Oxazol-inone	R in $RC_6H_4NH_2$	Prod-uct	M.p. (°C)	Yield (%)	Molecular formula	Found (%) C	H	N	Calc. (%) C	H	N
(1a)	unsubst.	(2a)	256[A]	75	$C_{21}H_{16}N_4O$	74·0	4·6	16·4	74·1	4·7	16·5
(1b)	unsubst.	(2b)	240	70	$C_{21}H_{15}ClN_4O$	67·3	4·0	14·8	67·3	4·0	15·0
(1b)	*o*-Cl	(2c)	213	68	$C_{21}H_{14}Cl_2N_4O$	61·6	3·3	13·7	61·6	3·4	13·7
(1b)	*m*-Cl	(2d)	179	74	$C_{21}H_{14}Cl_2N_4O$	61·5	3·4	13·5	61·6	3·4	13·7
(1b)	*p*-Cl	(2e)	172	80	$C_{21}H_{14}Cl_2N_4O$	61·5	3·5	13·6	61·6	3·4	13·7
(1b)	*o*-Me	(2f)	205	76	$C_{22}H_{17}ClN_4O$	67·9	4·4	14·4	68·0	4·4	14·4
(1b)	*m*-Me	(2g)	196	71	$C_{22}H_{17}ClN_4O$	68·0	4·3	14·3	68·0	4·4	14·4
(1b)	*p*-Me	(2h)	160	83	$C_{22}H_{17}ClN_4O$	67·8	4·2	14·5	68·0	4·4	14·4
(1c)	unsubst.	(2i)	208	71	$C_{21}H_{14}Cl_2N_4O$	61·6	3·3	13·5	61·6	3·4	13·7
(1c)	*p*-Cl	(2j)	180	83	$C_{21}H_{13}Cl_3N_4O$	56·7	3·0	12·4	56·8	2·9	12·6
(1c)	*p*-Me	(2k)	191	84	$C_{22}H_{16}Cl_2N_4O$	62·4	3·6	13·1	62·4	3·5	13·2
(1d)	unsubst.	(2l)	210	71	$C_{22}H_{17}ClN_4O$	68·0	4·2	14·2	68·0	4·4	14·4
(1d)	*o*-Cl	(2m)	165	74	$C_{22}H_{16}Cl_2N_4O$	62·3	3·6	13·1	62·4	3·5	13·2
(1d)	*m*-Cl	(2n)	170	69	$C_{22}H_{16}Cl_2N_4O$	62·4	3·6	13·0	62·4	3·5	13·2
(1d)	*p*-Cl	(2o)	185	78	$C_{22}H_{16}Cl_2N_4O$	62·5	3·5	13·2	62·4	3·5	13·2
(1d)	*m*-Me	(2p)	205	73	$C_{23}H_{19}ClN_4O$	68·5	4·6	14·0	68·6	4·7	13·9
(1d)	*p*-Me	(2q)	193	81	$C_{23}H_{19}ClN_4O$	68·7	4·7	13·8	68·6	4·7	13·9
(1e)	unsubst.	(2r)	157	67	$C_{21}H_{14}ClN_5O_3$	60·0	3·2	16·5	60·1	3·3	16·7
(1e)	*p*-Cl	(2s)	239	83	$C_{21}H_{13}Cl_2N_5O_3$	55·4	2·9	15·2	55·5	2·9	15·4
(1e)	*p*-Me	(2t)	187	80	$C_{22}H_{16}ClN_5O_3$	60·9	3·5	16·0	60·9	3·7	16·1

[A] Lit.[1] m.p. 255–256°C.

These products were characterized by analysis, and i.r. measurements which showed stretching frequencies at 1680, and 3300 cm^{-1} characteristic for the monosubstituted amides, and at 1610 cm^{-1} characteristic for –C=N–.

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