1,2,3-Benzotriazin-4-ones and Related Systems. Part IV[1]. Thermal Decomposition of 3-Imidoylated 1,2,3-Benzotriazin-4-ones. A New Synthesis of 1,2-Diaryl-1,4-dihydroquinazolin-4-ones.

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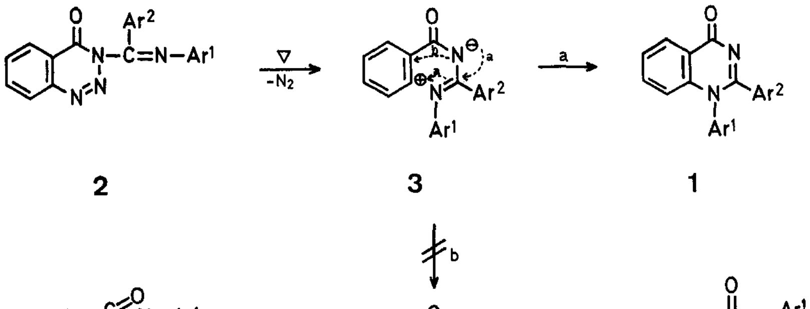
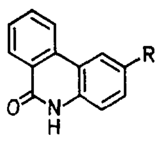
We have recently reported[1] a useful synthesis of 2-arylquinazolin-4-ones involving the thermolysis of 3-arylideneamino-1,2,3-benzotriazin-4-ones. As an extension to this work we now report a facile method of preparing the hitherto little known and difficultly accessible[2, 3, 4] 1,2-diaryl-1,4-dihydroquinazolin-4-ones (**1**), by thermolysing 3-imidoylated 1,2,3-benzotriazin-4-ones (**2**) in an inert solvent (paraffin oil).



2 **3** **1** **5** **4**



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The 3-substituted benzotriazinones (see Table 1) were readily prepared by treating a solution of 1,2,3-benzotriazin-4-one in dry dimethylformamide with sodium hydride followed by the appropriate imidoyl halide as indicated in the general method.

By analogy with previous results[1,5] it was expected that the benzotriazinone would lose nitrogen to yield the intermediate (**3**) which can either cyclise to give the 1,4-dihydroquinazolin-4-one (path a) or yield the 2,3-diaryl-quinazolin-4-one (**4**) by way of the imino-ketene⇌benzazetidinone system (**5**) (path b).

Whereas no products corresponding to route b were detected, 1,2-diaryl-1,4-dihydroquinazolin-4-ones were obtained in practicable yields (58–70%) (see Table 2). In addition and unexpectedly, a second product (20–30%) easily separable from the quinazolin-4-one, was isolated in each case. Spectroscopic evidence and unambiguous synthesis showed the by-products to be 9*H*-phenanthridones (**6**) (see Table 2), whose mode of formation is not as yet clear. Certainly they are not thermal rearrangement products of either 2,3-diaryl-quinazolin-4-ones (**4**), or of the isolated 1,4-dihydroquinazolin-4-ones (**1**) since both these systems (the former prepared by literature methods[6]) remained unchanged on heating under the reaction conditions. The origin of the phenanthridones is now under investigation.

Preparation of 3-Imidoylated 1,2,3-Benzotriazin-4-ones (2); General Procedure:

To a solution of 1,2,3-benzotriazin-4-one (2.94 g, 0.02 mol) in dry dimethylformamide (30 ml) at room temperature, was added portionwise sodium hydride (0.5 g; 0.02 mol). The mixture was stirred at room temperature until hydrogen evolution ceased. To this mixture was added dropwise a solution of the imidoyl

Table 1. 3-Imidoylated 1,2,3-Benzotriazin-4-ones (**2**)

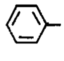
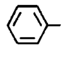
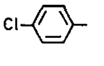
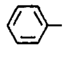
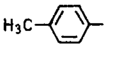
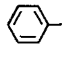
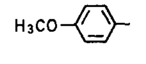
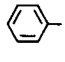
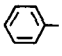
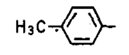
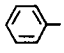
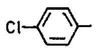
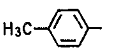
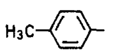
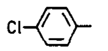
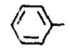
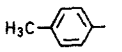
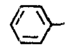
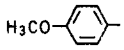
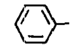
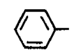
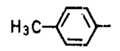
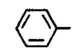
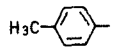
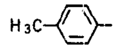
Product	Ar^1	Ar^2	M.p.	Yield (%)	Elemental	Analyses				Mass spectrum m/e ($M^{\oplus}$)
2a			134°	80	$C_{20}H_{14}N_4O$ (326.35)	found calc.	C 73.33 73.61	H 4.47 4.32	N 17.5 17.17	326
2b			125°	82	$C_{20}H_{13}ClN_4O$ (360.79)	found calc.	C 66.38 66.58	H 3.77 3.63	N 15.89 15.53	360 (362)
2c			160°	76	$C_{21}H_{16}N_4O$ (340.38)	found calc.	C 73.98 74.10	H 4.59 4.74	N 16.85 16.46	340
2d			123°	84	$C_{21}H_{16}N_4O_2$ (356.38)	found calc.	C 70.58 70.78	H 4.48 4.53	N 15.95 15.72	356
2e			164°	77	$C_{21}H_{16}N_4O$ (340.38)	found calc.	C 74.65 74.10	H 4.67 4.74	N 16.77 16.46	340
2f			171°	82	$C_{20}H_{13}ClN_4O$ (360.79)	found calc.	C 66.45 66.58	H 3.49 3.63	N 15.84 15.53	360 (362)
2g			180°	84	$C_{22}H_{18}N_4O$ (354.40)	found calc.	C 74.20 74.56	H 5.46 5.12	N 15.91 15.81	354

Table 2. 1,2-Diaryl-1,4-dihydroquinazolin-4-ones (**1**) and Penanthridones (**6**) from Pyrolysis of Benzotriazinones (**2**)

Product **1**	Ar^1	Ar^2	M.p.	Lit.[2] m.p.	Yield (%)	Mass spectrum m/e (M$^{\oplus}$)	Product **6** R	M.p.	Yield (%)
a			270°	273°	70	298	H	293°	20
b			243°	243°	63	332 (334)	Cl	329°	25
c			232°	— [a]	65	312	CH_3	257° [e]	20
d			239°	241°	70	328	H_3CO	230°	25
e			228°	— [b]	65	312	H	293°	28
f			265°	— [c]	61	332 (334)	H	293°	29
g			193°	— [d]	58	326	CH_3	257°	24

[a] New compound: $C_{21}H_{16}N_2O$ (312.36)	calc.	C 80.75	H 5.16	N 8.97
	found	80.53	5.09	8.81
[b] New compound: $C_{21}H_{16}N_2O$ (312.36)	calc.	C 80.75	H 5.16	N 8.97
	found	80.37	5.25	8.61
[c] New compound: $C_{20}H_{13}ClN_2O$ (332.77)	calc.	C 72.18	H 3.94	N 8.42
	found	72.02	4.31	8.41
[d] New compound: $C_{22}H_{18}N_2O$ (326.38)	calc.	C 80.96	H 5.56	N 8.58
	found	80.69	5.68	8.60
[e] New compound: $C_{14}H_{11}NO$ (209.23)	calc.	C 80.36	H 5.30	N 6.69
	found	80.34	5.29	6.52

chloride (prepared from the appropriate anilide and thionyl chloride via literature method[7]) (0.02 mol) in dry dimethylformamide (10 ml). The mixture was stirred for 5 h at room temperature then poured into cold water (200 ml) and stirred for a further hour. The product was filtered off, dried by suction, and then crystallised from ethyl acetate/light petrol (b.p. 60–80°) mixture. (See Table 1).

Thermolysis of the 3-Imidoylated 1,2,3-Benzotriazin-4-ones (2) in Paraffin Oil; General Procedure:

A slurry of the 3-imidoylated 1,2,3-benzotriazin-4-one (2.5 g) in liquid paraffin (20 ml) was added dropwise to liquid paraffin (20 ml) maintained at 300 ± 10°. The mixture was held at this temperature until nitrogen evolution ceased (3–5 min.), then allowed to cool whereupon a solid mass of products was deposited. Precipitation was completed by the addition of an excess of light petrol (b.p. 60–80°). The products were filtered off, washed free of paraffin oil using petrol ether and then slurried with cold chloroform. The chloroform insoluble phenanthridone was filtered off, and the filtrate evaporated to dryness to yield the 1,2-diaryl-1,4-dihydroquinazolin-4-one which was purified by crystallisation from ethanol. Yields and physical data are given in Table 2.

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[1] Part III. T. McC. Paterson, R. K. Smalley, H. Suschitzky, *Synthesis* **1975**, 187.

[2] H. M. Blatter, H. Lukaszewski, G. DeStevens, *J. Org. Chem.* **30**, 1020 (1965).

[3] G. DeStevens, H. M. Blatter, R. W. J. Carney, *Angew. Chem.* **78**, 125 (1966); *Angew. Chem. Internat. Edit.* **5**, 35 (1966).

[4] E. C. Taylor, Y. Shvo, *J. Org. Chem.* **33**, 1719 (1968).

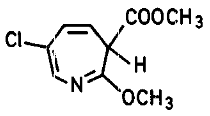
[5] H. E. Crabtree, R. K. Smalley, H. Suschitzky, *J. Chem. Soc.* [C] **1968**, 2730.

[6] P. R. Levy, H. Stephen, *J. Chem. Soc.* **1966**, 985.

[7] I. Ugi, F. Beck, U. Fetzer, *Chem. Ber.* **95**, 126 (1962).

Errata

R. K. Smalley, W. A. Strachan, H. Suschitzky, *Synthesis* **1974**, 503–504; The formula for compound **4** (p. 504) should be:



4

The last paragraph of the experimental procedure (p. 503) should be:

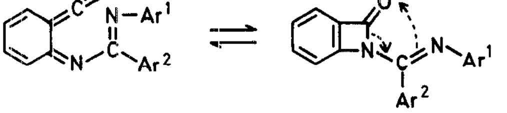
The method was applicable to the preparation of the phenyl ester (**3**; $R^1 = C_6H_5$, $R^2 = CH_3$) and to further substituted 3*H*-azepines. For example, photolysis of methyl 2-azido-4-chlorobenzoate in methanol gave 6-chloro-2-methoxycarbonyl-3*H*-azepine (**4**); yield 69%, b.p. 120°/0.2 torr.

$C_9H_{10}ClNO_3$	calc.	C 50.13	H 4.67	N 6.50	Cl 16.44
(215.64)	found.	50.24	4.66	6.46	16.41

^{1}H-N.M.R. (CCl_4): $\delta = 2.95$ (dd, 1H, H-3), 3.70, 3.75 (2s, 3H, 3H $COOCH_3$, OCH_3), 5.65 (dd, 1H, H-4), 6.25 (dm, 1H, H-5), 7.10 ppm (broad s, 1H, H-7).

Mass spectrum: $m/e = 215, 217$ ($M^{\oplus}$).

T. McC. Paterson, R. K. Smalley, H. Suschitzky, *Synthesis* **1975**, 709–710; The formula for compound **5** should be:



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