Thermolysis of Diphenyl-Δ^3- and Diphenyl-Δ^4-1,2,4-oxadiazolinones

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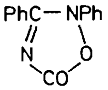
Summary Thermolysis gave 2-phenylbenzoxazole from 2,3-diphenyl-Δ^3-1,2,4-oxadiazolin-5-one and from 2,5-diphenyl-Δ^4-1,2,4-oxadiazolin-3-one and also gave benzoxazolinone from the latter by new ring transformations which accompanied the formation of 2-phenylbenzimidazole and 2,4-diphenyl-Δ^2-1,3,4-oxadiazolin-5-one as respective major products.

FRAGMENTATION–REARRANGEMENT produced 2-phenyl-benzoxazole (**2**) by a new ring-transformation and 2-phenylbenzimidazole (**3**) from 2,3-diphenyl-Δ^3-1,2,4-oxadiazolin-5-one (**1**).[1]† The imidazole (**3**) was previously obtained by a similar thermolysis of 3,4-diphenyl-Δ^2-1,2,4-oxadiazolin-5-one (**4**).[2] Other new ring transformations accounted for the formation of the oxazole (**2**) and benzoxazolinone (**6**) which accompanied the thermal isomerisation of 2,5-diphenyl-Δ^4-1,2,4-oxadiazolin-3-one (**5**)[3]† into 2,4-diphenyl-Δ^2-1,3,4-oxadiazolin-5-one (**7**).[4]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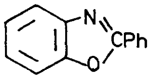
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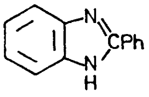
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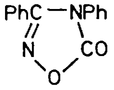
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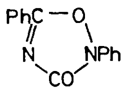
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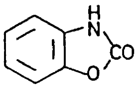
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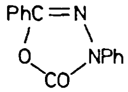
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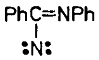
(8)

$$\mathrm{PhC(=NPh)\text{-}\ddot{N}\!:}$$

The new oxadiazolinones (**1**) and (**5**) were prepared by thermolysis of bis- and mono-condensates [(A) and (B), respectively] of thiobenzoyl isocyanate with phenylhydroxylamine.

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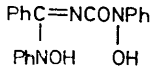
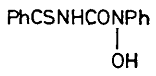
† Satisfactory elemental analyses and compatible spectroscopic characterisations were obtained for these new compounds.



$\underset{\text{PhNOH}}{\text{PhC}}{=}\text{NCO}\underset{\text{OH}}{\text{NPh}}$

(A)



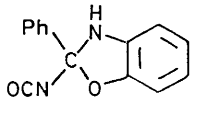
$\text{PhCSNHCO}\underset{\text{OH}}{\text{NPh}}$

(B)

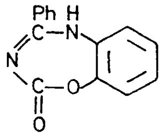
Thermolysis at 257 °C of (**1**) in diphenyl ether gave (**3**) (70%) and (**2**) (12%) together with carbon dioxide (87%) and cyanic acid [isolated as cyanuric acid, $(HOCN)_3$, 9%]. Similar treatment transformed (**5**) into (**2**) (6%), (**6**) (4%), and (**7**) (42%) together with cyanic acid (10%) and benzonitrile (7%).

An easy rupture of an N–O single bond[5] concerted or not with other bond cleavages and formations, can initiate the thermal fragmentation–rearrangements of (**1**), (**4**), and (**5**). The formation of (**3**) from (**1**) and (**4**) and that of (**2**) from (**1**) and (**5**) can be accounted for by the azomethine nitrene (**8**) and 2-isocyano-2-phenylbenzoxazoline (**9**) as appropriate common intermediates.

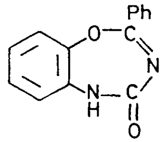
An initial isomerisation of each oxadiazolinone into a corresponding oxadiazepinone (**10**) and (**11**) is preferred to an initial ring contraction giving the oxaziridine (**12**).



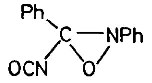
(9)



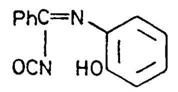
(10)



(11)



(12)



(13)

Each of the intermediates (**10**), (**11**), and (**12**) can lead directly to (**9**); however, (**11**) but not (**12**) can also account for the direct formation of (**6**) and benzonitrile.[6] A ready ring–chain tautomerism (**10**)$\rightleftharpoons$(**13**)$\rightleftharpoons$(**9**) and elimination of cyanic acid from (**9**) pre-empts the dissociation of (**10**) into (**6**) and benzonitrile.

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[1] Seven other 2,3-disubstituted-Δ^3-1,2,4-oxadiazolin-5-ones have been reported: P. W. Seale and W. K. Warburton, ***J.C.S. Perkin I***, 1974, 85; R. M. Moriarty and P. Serridge, *J. Amer. Chem. Soc.*, 1971, **93**, 1534.

[2] J. H. Boyer and P. J. A. Frints, *J. Heterocyclic Chem.*, 1970, **7**, 59.

[3] One other 2,5-disubstituted-Δ^4-1,2,4-oxadiazolin-3-one has been reported [B. W. Nash, R. A. Newberry, R. Pickles, and W. K. Warburton, *J. Chem. Soc.* (*C*), 1969, 2794] and three with substitution only at the 5-position (B. G. Baccar and F. Mathis, *Compt. rend.*, 1965, **261**, 174).

[4] W. Reichen, *Helv. Chim. Acta*, 1976, **58**, 1636.

[5] H. C. Van Der Plas, 'Ring Transformations of Heterocycles,' Vol. 1, Academic Press, London, 1973, p. 280.

[6] Ref. 5, Vol. 2, p. 315 describes a related ring contraction of a 1,4,5-oxadiazepine into an indazole.