Fragmentation-rearrangement of Δ^3-Oxadiazolin-5- and 3-ones

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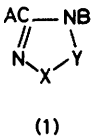
2-Phenylbenzimidazole (6) (major product) and 2-phenylbenzoxazole (10) were obtained from 2,3-diphenyl-Δ^3-1,2,4-oxadiazolin-5-one (2) by thermolysis (250 °C, diphenyl ether), and by photolysis (254 nm, dioxan). Photolysis also isomerised the oxadiazolinone (2) into 2,5-diphenyl-Δ^4-1,2,4-oxadiazolin-3-one (8), and 2,4-diphenyl-Δ^2-1,3,4-oxadiazolin-5-one (9). Similar thermolysis and photolysis of 2-benzyl-3-phenyl-Δ^3-1,2,4-oxadiazolin-5-one (3) gave cyaphenine (11) and lophine (12). The diphenylazomethine nitrene (14) can be the precursor to the imidazole (6) and the transformations (2)→(10) and (3)→(11) + (12) can proceed from the appropriate carbamic acid derivative [(16) or (23)], which are available from (2) or (3) by a 1,3-migration of oxygen from nitrogen to carbon.

To determine what the effect of an interchange of the positions of X and Y has on the ejection of XY from a heterocycle (1), a preparation of the previously unknown 2,3-diphenyl- (2) and 2-benzyl-3-phenyl-Δ^3-1,2,4-oxadiazolin-5-one (3) was undertaken in order to study their thermolysis and photolysis reactions.

A comparison of the results with those previously obtained [1,2] from 3,4-diphenyl- (4) and 3-phenyl-4-benzyl-Δ^2-1,2,4-oxadiazolin-5-one (5) was made (*a*) to ascertain any dependence of the fragmentation on the NO single bond; [3] (*b*) to appraise the intermediacy of an azomethine nitrene and/or a nitrilimine; and (*c*) to support the assignment of a fragmentation concerted with rearrangement into a carbodi-imide.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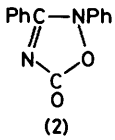
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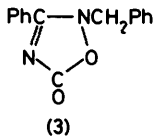
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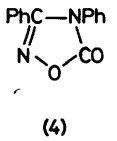
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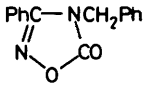
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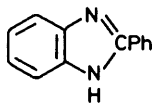
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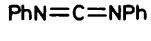
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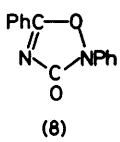
RESULTS

Table 1 summarises results from the thermolytic and photolytic fragmentation–rearrangement of heterocycles (1) (A = B = Ph), into 2-phenylbenzimidazole (6) and diphenylcarbodi-imide (7).[4a]

The preparation of oxadiazolinones (2) and (3) has been reported elsewhere.[4b] Thermolysis of the oxadiazolinone (2) gave the imidazole (6) in 71% yield based on total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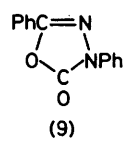
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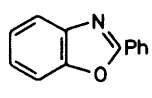
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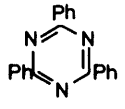
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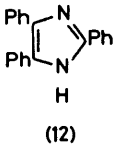
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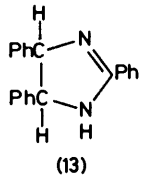
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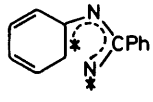
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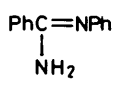

(15)

conversion of the starting material, 82% based on the conversion of starting material into carbon dioxide. The corresponding photolysis yields were 54 and 75%. Both reactions gave benzonitrile and aniline in yields ⩽1% and photolysis also gave diphenylcarbodi-imide (7) (2%), benzamide (14%), azobenzene (1%), 2,5-diphenyl-Δ^4-1,2,4-oxadiazolin-3-one (8) (trace), 2,4-diphenyl-Δ^2-1,3,4-oxadiazolin-5-one (9) (trace), and 2-phenylbenzoxazole 10 (trace). A concurrent rearrangement–fragmentation during thermolysis of the oxadiazolinone (2) gave cyanic acid (9%) and the benzoxazole (10) (12%).

Thermolysis and photolysis of the oxadiazolinone (3) gave (respective yields) cyaphenine (11) (43 and 1%), lophine (12) (12 and 2%), benzonitrile (10 and 3%), and benzaldehyde (7 and 3%). Thermolysis also gave isoamarine (13) (2%).

TABLE 1

2-Phenylbenzimidazole (6) and diphenylcarbodi-imide (7) from heterocycles (1) (A = B = Ph)

(1)	Thermolysis					Photolysis				
X–Y	T/°C	Solvent	(6) (%)	(7) (%)	Ref.	λ/nm	Solvent	(6) (%)	(7) (%)	Ref.
N=N	>200		23	76	*a*—*f*	<300	benzene	66	0	*a*—*f*
O–SO	75		0	100	*g*	<300	AcOEt	3	62	*e*, *g*
O–PPh_3 [h]	80	benzene	0	66	*i*					
O–CO	257	Ph_2O	90 [j]	0	*k*	254	dioxan	86 [j]	2 [j]	1
OC–O	257	Ph_2O	82 [j]	0	*l*	254	dioxan	75 [j]	2 [j]	*l*

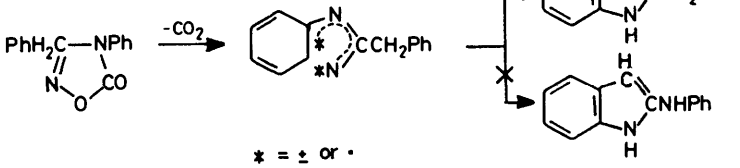
[a] T. Bacchetti and A. Alemagna, *Red. Ist. Lombardo Sci., Classe Sci. Mat. e Nat.*, 1960, **94A**, 247, 267, 351 (*Chem. Abs.*, 1961, **55**, 16 527). [b] P. A. S. Smith and E. Leon, *J. Amer. Chem. Soc.*, 1958, **80**, 4647. [c] W. Kirmse, *Angew. Chem.*, 1969, **71**, 537. [d] R. M. Moriarty and J. M. Kliegman, *J. Amer. Chem. Soc.*, 1967, **89**, 5959. [e] J. Sauer and K. K. Mayer, *Tetrahedron Letters*, 1968, 325. [f] T. Bacchetti and A. Alemagna, *Gazzetta*, 1961, **91**, 1475 (*Chem. Abs.*, 1962, **57**, 7252). [g] R. Rajagopolan and B. G. Advani, *J. Org. Chem.*, 1965, **30**, 3369. [h] This heterocycle was a postulated intermediate. [i] R. Huisgen and J. Wulff, *Tetrahedron Letters*, 1967, 921. [j] The percentage yields shown are based on conversion of starting material into carbon dioxide. [k] T. Bacchetti and A. Alemagna, *Atti acca. nazl. Lincei, Rend. Classe si. fis., mat. e nat.*, 1957, **22**, 637 (*Chem. Abs.*, 1958, **52**, 15 511. [l] This work.

Analysis of the thermolysis crude product mixtures from oxadiazolinones (3) and (5) by low-voltage mass spectrometry revealed the heterocycles (11) and (12) to be the

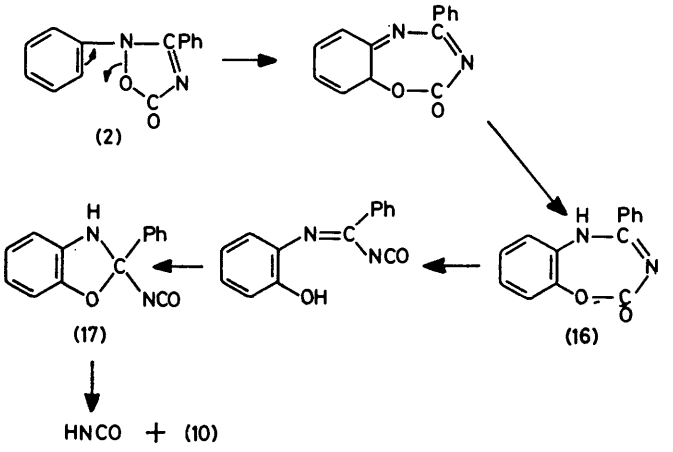
principal products in ratios of 45 : 46 and 27 : 62 (Table 2).

DISCUSSION

An intermediate delocalised diphenylazomethine nitrene (14) [1,2,*] for both thermolysis and photolysis of the isomeric oxadiazolinones (2) and (4) accounts for the conversion into the imidazole (6) and the formation of *N*-phenylbenzamidine (15) by abstraction of hydrogen atoms from the solvent.[1,2] A minor photo-transformation of each oxadiazolinone (2) and (4) into diphenylcarbodi-imide (7) is presumed to be an extension of a similar fragmentation of related heterocycles (Table 1).



Cleavage of the weak NO single bond can facilitate both a fragmentation of the oxadiazolinone (2) into the nitrene (14) and an isomerisation (Scheme 1) into a benzoxadiazepinone (16).[3] Ring-chain tautomerisation of the latter into 2-isocyanato-2-phenylbenzoxazoline (17) is assumed to account for dissociation into the benzoxazole (10), and the absence of the formation of benzoxazolone,[4a] since both products should be available from the heterocycle (16) by extrusion.

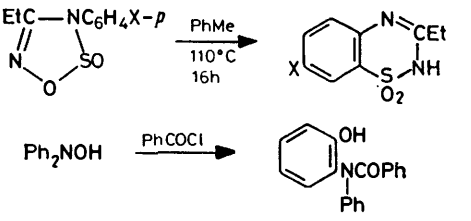


SCHEME 1

Expansion of the oxadiazolinone ring by a 1,3-migration is similar to the thermal ring-expansion of 3-aryl-4-ethyl-Δ^4-1,2,3,5-oxathiadiazolin-2-one into a 4-thiaquinazoline-4,4-dioxide.[5] The formation of *N*-phenyl-*N*-benzoyl-*o*-aminophenol on treating *NN*-diphenylhydroxylamine with benzoyl chloride is also related.[6]

* The previous observation that 2-benzylbenzimidazole but not 2-anilinoindole was obtained from 3-benzyl-4-phenyl-Δ^2-1,2,4-oxadiazolin-5-one by both thermolysis and photolysis also indicates that a delocalised orientated nitrene rather than an indiscriminate localised nitrene was predominant as an intermediate.[1]

Chromatographic separation of mixtures obtained by thermolysis of each oxadiazolinone (3) or (5) [1] gave



cyaphenine (11) and lophine (12) in percentage yield ratios of 43 : 12 and 45 : 6 respectively. Analysis of each mixture, after solvent removal but before further separation, by low-voltage mass spectrometry [7] (Table 2) revealed these principal products in the ratios of 45 : 46 and 27 : 62 respectively. Incomplete thermal aromatisation of the precursor(s) (see below) into the heterocycles (11) and (12) and their breakdown by expected chemical changes during chromatography can be assumed.

TABLE 2

Low-voltage (3 ev) mass spectrometry for Δ^3- (3) and Δ^2-oxadiazolinone (5); structure assignments

			% of total ions from	
m/e	Formula	Assignment	(3) [a]	(5) [b]
309	$C_{21}H_{15}N_3$	(11)	44.7	27.0
298	$C_{21}H_{18}N_2$	(13) [c]	3.4	5.7
296	$C_{21}H_{16}N_2$	(12)	45.7	61.6

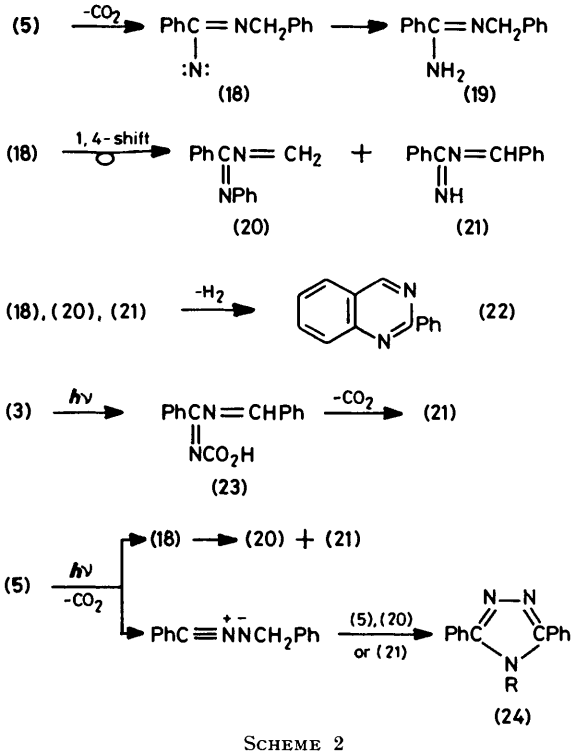
[a] The products not listed account for 6.2% of the total ions. The ion *m/e* 206 (0.4%) can be assigned to 2-phenylquinazoline ($C_{14}H_{10}N_2$). [b] The products not listed account for 5.7% of the total ions. Quantitative i.r. analysis of the crude thermolysis product mixture from the oxadiazolinone (5) showed the presence of products (11) and (12) in a molar ratio of 2.4 : 1 (see Experimental section). [c] Ring tautomers, *e.g.* isoamarine, are included in this assignment. A t.l.c. examination of the thermolysis product mixture from the oxadiazolinone (5) revealed the presence of isoamarine (not detected in the earlier investigation [1]).

Several indistinguishable pathways based on the generation of benzaldimine in monomeric or oligomeric form [8,†] can lead to the formation of the heterocycles (11) and (12). A cyclic head-to-tail trimer of benzaldimine at 257 °C affords cyaphenine (11) by dehydrogenation and lophine (12) by dehydrogenation with elimin-

† B. Coffin and R. F. Robbins (*J. Chem. Soc. Suppl. no.* 1, 1964, 5901) describe the formation of the heterocycles (11) and (12) by thermolysis of benzyl azide in diphenyl ether at 250 °C and in *p*-xylene at 280 °C (autoclave). The respective percentage yield ratios were 6 : 42 and 20 : 24. The products were attributed to benzyl nitrene and its isomerisation into benzaldimine.

ation of ammonia.* After an alternative trimerisation of benzaldimine, elimination of ammonia produced hydrobenzamide, $C_6H_5CH(N{=}CHPh)_2$,[8] whose cyclisation into amarine (13) or an isomer which can undergo thermal dehydrogenation into lophine (12) is known.

The isolation of benzaldehyde revealed the presence of benzaldimine in the product mixture from either (3) or (5). Since benzaldimine is the principal initial rearrangement product of benzyl nitrene,* the latter together with carbon dioxide and benzonitrile can account for a dissociation pattern for oxadiazolinones (3) or (5). In addition an initial dissociation of the heterocycle into the nitrene (18) (Scheme 2) can be contemplated since the amidine (19), produced by



SCHEME 2

hydrogen abstraction, was isolated in trace amount after thermolysis of the oxadiazolinone (5).[1]

The minor thermolytic and photolytic formation of 2-phenylquinazoline (22) (Scheme 2) from the oxadiazolinone (5) was attributed to dehydrogenation following ring closure from the nitrene (18), either directly or after isomerisation into an imine [(20) or (21)] by a 1,4-migration.† The quinazoline was barely detected as a thermolytic product from the oxadiazolinone (3) by low-voltage mass spectrometry of the crude product mixture (Table 2).

The evidence permits the conclusion that thermolysis and photolysis of the oxadiazolinone (3) can proceed without the intermediacy of either an azomethine nitrene or its isomeric nitrilimine, whereas similar treatment of the oxadiazolinone (5) must produce both intermediates (Scheme 2). An initial isomerisation of the oxadiazolinone (3) into *N*-benzylidene-*N'*-carboxybenzamidine (23) is related to the 1,3-rearrangement (2)→(16). Decarboxylation of the carbamic acid (23) can lead to *N*-benzylidenebenzamidine (21), a possible precursor to the heterocycles (11), (12), and (22).

Thermolysis of the oxadiazolinone (5) may require the intermediacy of the azomethine nitrene (18) for the formation of N-benzylbenzamidine [1] [not obtained from the oxadiazolinone (3)] and the formation of the quinazoline (22). Photolysis products,[1] 3,5-diphenyl-1,2,4-triazole (24; R = H) and its 4-phenyl derivative, from the oxadiazolinone (5), support the intermediacy of both the nitrene (18) and *N*-benzylbenzonitrilimine (Scheme 2).

EXPERIMENTAL

Instruments used; Cary 14 and Perkin-Elmer 237B grating i.r. spectrometers; a Varian 1800 gas chromatograph equipped with a flame-ionisation detector and a Varian 20 recorder with disc integrator, and either a 182.9 × 0.32-cm stainless steel column packed with 15% carbowax 20 M on 80—100 mesh chromosorb W, or a 182.9 × 0.32-cm stainless steel column packed with 2.5% silicon rubber SE 30 on 80—100 mesh chromosorb G AWDMCS, with helium as the carrier gas at a flow rate of 30—40 ml min^{-1}. Temperature of the injection port was 240 °C, and of the detector 285 °C. Yields of small quantities of volatile products were determined by gas chromatography with an internal standard.[9] Preparative thin-layer chromatography was carried out on glass plates (20 × 20 cm) coated with 1 mm of silica gel PF254 (Merck). Low-voltage mass spectra were recorded on a modified Consolidated 20-102 mass spectrometer with an inlet system and ionisation chamber at 250 °C. Spectra were measured at 70, 9.5, and 7.5 eV nominal. For the low-voltage measurements, the repellers were maintained at an average of 3 eV, the exact value being selected to give maximum sensitivity. The following compounds were commercially available: cyanuric acid, benzonitrile, aniline, benzaldehyde, naphthalene, lophine, benzamide, 2-benzoxazolinone, biphenyl, azobenzene, *NN'*-diphenylurea, benzanilide, and isoamarine. The following compounds were prepared: 2-phenylbenzimidazole,[10] m.p. 294—295 °C; 2-phenylbenzoxazole,[11] m.p. 101—102 °C; cyaphenine,[12] m.p. 234—234.5 °C; 2-phenylquinazoline,[13] m.p. 99—100 °C; 2,4-diphenyl-Δ^2-1,3,4-oxadiazolin-5-one,[14] m.p. 111—112 °C; 3-phenyl-4-benzyl-Δ^2-1,2,4-oxadiazolin-5-one,[1] m.p. 80—82 °C; 3,4-diphenyl-1,2,4-oxadiazolin-5-one,[1] m.p. 166—168 °C; *NN'*-diphenylcarbodi-imide,[1] n_D^{24} 1.636 2; *N*-phenylbenzamidine,[15] m.p. 114—115 °C; *N*-benzyl-*N*-phenylcyanamide,[16] m.p. 56—58 °C; 3,5-diphenyl-1,2,4-triazole,[17] m.p. 190—191 °C; 3,4,5-triphenyl-1,2,4-triazole,[18] m.p. 298—299 °C; and *N*-benzylbenzamidine,[19] m.p. 69—70 °C. Elemental analyses were provided by Micro-Tech Laboratories, Inc. Each previously known compound was identified by comparison with authentic data for m.p., t.l.c., g.c., i.r., n.m.r., and mass spectrometry as appropriate.

Thermolysis of 1,2,4-*Oxadiazolinones*.—An oxadiazolinone in diphenyl ether in a 100-ml two-necked flask, equipped

* Thermolysis of a hydrogenated cyaphenine gave lophine.[8,*] A similar thermolysis of dibenzylaminde gave ammonia and stilbene.[8]

† A 1,4-rearrangement in an azomethine nitrene has been proposed.[1]

with a condenser, gas inlet and outlet tubes, and a heating mantle, was treated with a slow stream of nitrogen for six hours before and then during thermolysis. As nitrogen swept carbon dioxide through a saturated solution of barium hydroxide, barium carbonate was collected.

A solution of 2,3-diphenyl-Δ^3-1,2,4-oxadiazolin-5-one (2) (300 mg, 1.26 mmol) in diphenyl ether (50 ml) was heated at reflux for 14 h. Carbon dioxide was collected as barium carbonate (215 mg, 1.09 mmol, 86.5%). From the walls of the condenser cyanuric acid $(HOCN)_3$ (5 mg, 0.039 mmol, 9%) was removed. A distillation (0.10 mm) forerun was collected in a receiver cooled in a liquid-nitrogen bath and showed by g.c. (2.5% SE30, 125 °C) a barely detectable peak at 1.35 m which was assigned to benzonitrile and/or aniline (identical retention times of 1.35 m). After distilling off diphenyl ether (85—87 °C, 0.90 mmHg), the residue was triturated with dry ether (3 ml) and the mixture cooled in an ice-bath for 15 min to induce precipitation. The precipitate was filtered off to give 2-phenylbenzimidazole (168 mg, 0.87 mmol, 80%). A g.c. (2.5% SE30, 200 °C) peak at 2.70 m was assigned to 2-phenylbenzoxazole, a component of the ether-soluble fraction (53 mg). This fraction in ethyl acetate was streaked onto a preparative t.l.c. plate of silica gel, and developed in chloroform–acetone (19 : 1). The band at R_F 0.20 was collected, extracted with chloroform, and filtered. Removal of the solvent left 2-phenylbenzimidazole (4 mg, 0.021 mmol, total yield 82%). The band at R_F 0.69 gave a yellow solid which was then eluted by carbon tetrachloride from a column of silica gel (3 g) to give 2-phenylbenzoxazole (30 mg, 0.154 mmol, 12%).

A solution of 2-benzyl-3-phenyl-Δ^3-1,2,4-oxadiazolin-5-one (3) (500 mg, 1.98 mmol) in diphenyl ether (60 ml) was heated at reflux for 12 h. Carbon dioxide was collected as barium carbonate (277 mg, 1.40 mmol, 71%). A distillation forerun was taken up in chloroform and gave g.c. peaks (15% carbowax, column temperature 155 °C) at 2.60, 3.50, and 16.00 m for benzaldehyde, benzonitrile, and diphenyl ether, respectively. Fractions containing benzaldehyde and benzonitrile were combined, concentrated, and mixed with naphthalene (69.98 mg) and 6N hydrochloric acid (20 ml). The mixture was thoroughly stirred for 15 min and the organic layer was separated and treated with a stream of hydrogen chloride gas. G.c. analysis of the diphenyl ether solution showed that the peak at 2.60 m had increased and a new peak at 6.00 m (naphthalene) had appeared. With relative sensitivities of 1.35 and 1.11 for standard solutions of naphthalene and benzaldehyde and benzonitrile respectively, the ratio of peak areas (3.5 : 26.5 : 144) indicated the presence of benzaldehyde (2.3 mg, 0.022 mmol, 1.5%) and benzonitrile (14.3 mg, 0.14 mmol, 10%).

A light yellow residue (346 mg), after diphenyl ether had distilled off, was treated with chloroform (4 ml), and cyaphenine (88 mg, 0.284 mmol, 30%) separated on cooling. The chloroform solution was then extracted with 6N hydrochloric acid (2 × 25 ml), treated with a stream of hydrogen chloride gas, and thoroughly extracted with water. The combined acid extracts were dried ($MgSO_4$), filtered, and the solvent removed *in vacuo*. After naphthalene (7.98 mg) was added to a chloroform solution of the residue, g.c. analysis gave a ratio of peak areas of 20 : 30 which showed the presence of benzaldehyde (7.2 mg, 0.068 mmol, total yield 6.5%).

Chloroform was removed from the combined organic extracts and the residue was chromatographed on silica gel (50 g). Hexane eluted diphenyl ether, and hexane–benzene (3 : 1) eluted cyaphenine (36 mg, 0.117 mmol, total yield 43%). This solvent then eluted 2 mg of an unidentified blue solid whose methylene chloride solution turned colourless during four days. Benzene–chloroform (3 : 1) eluted lophine (22 mg, 0.074 mmol, 8%) and benzene–ethyl acetate (3 : 1) eluted isoamarine (5 mg, 0.017 mmol, 2%). Ethyl acetate eluted an unidentified colourless solid (8 mg), m.p. 295—296 °C.

The combined acid extracts were made basic with sodium carbonate and extracted thoroughly with chloroform. The chloroform solution was dried ($MgSO_4$), filtered, and the solvent evaporated off. The residue (34 mg) was separated by preparative t.l.c. (chloroform). The band at R_F 0.23 gave lophine (10 mg, 0.034 mmol, 4%).

A solution of 3-phenyl-4-benzyl-Δ^2-1,2,4-oxadiazolin-5-one (5) (500 mg, 1.98 mmol) in diphenyl ether (60 ml) was heated at reflux for 43 h. The evolved carbon dioxide gave barium carbonate (366 mg, 1.86 mmol, 94%). After diphenyl ether was removed, the residue was examined by low-voltage mass spectrometry (Table 2) and by quantitative i.r. analysis.[20] Absorbance peaks at 714 (lophine) and 644 cm^{-1} (cyaphenine) plotted against weight ratios gave a curve from which a weight ratio of 2.5 : 1 (mol ratio 2.4 : 1) for cyaphenine : lophine in the crude reaction mixture was obtained.

Photolysis of 1,2,4-*Oxadiazolinones*.—Irradiation of dioxan solutions at about 40 °C was carried out in a Rayonet RPR100 photochemical chamber reactor equipped with sixteen low-pressure mercury lamps. Dioxan was purified by refluxing over lithium aluminium hydride for three hours and was distilled into the quartz reaction vessel. Nitrogen was bubbled through the solution *via* a sintered glass tube for six hours prior to irradiation, and during irradiation it passed through the solution into a saturated solution of barium hydroxide. Reaction progress was monitored by the precipitation of barium carbonate.

A solution of 2,3-diphenyl-Δ^3-1,2,4-oxadiazolin-5-one (2) (300 mg, 1.26 mmol) in dioxan (125 ml) was irradiated at 254 nm for 10 h, during which time a dark yellow colour developed and barium carbonate (0.174 g, 0.88 mmol, 72%) was collected. Dioxan was removed, and 5 ml of cold ether was added to the residue to precipitate a light yellow solid (190 mg), which dissolved in chloroform and was chromatographed on silica gel (20 g). Chloroform eluted 2-phenylbenzimidazole (128 mg, 0.66 mmol, 75%), and ethyl acetate eluted a tar (55 mg).

The yellow ether solution gave g.c. peaks (15% carbowax, 155 °C) at 3.90 and 6.60 m, identical with those for benzonitrile and aniline respectively, and an unassigned peak at 7.40 m. Addition of 4.39 mg of biphenyl to the ether solution gave a ratio of peak areas of benzonitrile, aniline, and biphenyl of 18 : 3 : 98. From relative sensitivities of 1.22 and 6.10 determined from standard solutions of biphenyl and benzonitrile or aniline, respectively, the amounts in the product mixture were shown to be 1.0 mg (0.010 mmol, 1%) and 0.8 mg (0.009 mmol, 1%) respectively.

Evaporation to dryness of the ether solution, extraction of the residue with light petroleum, evaporation and g.c. analysis (2.5% SE30, 150 °C) of the residue in methylene chlorine gave peaks at 7.35 (unassigned) and 15.0 m. Since the area of the latter peak decreased after the methylene chloride solution had been treated with 6N hydrochloric acid (5 ml) with stirring for 30 min it was assigned

partially to *NN'*-diphenylcarbodi-imide. This assignment was supported by an i.r. absorption of the methylene chloride solution at 2 140 cm^{-1} (–N=C=N–) which was not present after the acid treatment.

In a separate experiment evaporation of the yellow ether extract left a brown oil. This was treated with 3N hydrochloric acid (10 ml) and extracted thoroughly with chloroform. The acid layer was made basic (pH 8) with sodium carbonate, extracted thoroughly with chloroform, and the extracts combined, dried ($MgSO_4$), filtered, evaporated, and the residue chromatographed on silica gel (15 g). Hexane eluted azobenzene (1 mg, 0.005 mmol, 1%); hexane–benzene (3 : 1) eluted a fraction (4 mg) which contained 2-phenylbenzoxazole [silica gel t.l.c. R_F 0.24, g.c. (2.5% SE30, 175 °C retention time 5.85 m] and 2,4-diphenyl-Δ^2-1,3,4-oxadiazolin-5-one (R_F 0.32, retention time 9.70 m); hexane–benzene (1 : 3) eluted 2,3-diphenyl-Δ^3-1,2,4-oxadiazolin-5-one (8 mg, 0.03 mmol, 3%) and a trace amount of 2,5-diphenyl-Δ^4-1,2,4-oxadiazolin-3-one. Benzene and benzene–chloroform (3 : 1) eluted a mixture (37 mg) of five components. Two were identified by t.l.c. as 2-phenylbenzimidazole and *NN'*-diphenylurea. Benzene–chloroform (1 : 1) eluted benzamide (20 mg, 0.17 mmol, 14%). Ethyl acetate eluted a dark oil (28 mg).

In a separate experiment the ether-soluble fraction was treated with 3N hydrochloric acid and the acid insoluble fraction was separated by preparative t.l.c. (chloroform). A band at R_F 0.27 gave 2-phenylbenzoxazole (1 mg, 0.005 mmol, 1%). All bands with R_F <0.27 were combined, extracted thoroughly with ethyl acetate, and separated by preparative t.l.c. [chloroform–ethyl acetate (9 : 1)]. The band at R_F 0.40 gave *NN'*-diphenylurea (3 mg, 0.014 mmol, 1.6%).

A solution of 2-benzyl-3-phenyl-Δ^3-1,2,4-oxadiazolin-5-one (3) (500 mg, 1.98 mmol) in dioxan (200 ml) was irradiated at 254 nm for 10 h; carbon dioxide was collected as barium carbonate (227 mg, 1.15 mmol, 58%). Dioxan was removed, and the residue in chloroform was shown by g.c. (15% carbowax, 155 °C) to contain benzaldehyde and benzonitrile (peaks at 2.60 and 3.50 min respectively). The chloroform solution was treated with 6N hydrochloric acid (5 ml) and stirred for 30 min; naphthalene (7.80 mg) was then added to give a ratio of peak areas for benzaldehyde, benzonitrile, and naphthalene of 14.5 : 13 : 39.5. From the relative sensitivities (1.41 and 1.26) for benzaldehyde to naphthalene and benzonitrile to naphthalene respectively, it was calculated that benzaldehyde (4 mg, 0.037 mmol, 3%) and benzonitrile (3 mg, 0.029 mmol, 2.5%) were present.

The chloroform solution was separated from the aqueous layer, dried ($MgSO_4$), and filtered. The organic solution was treated with a stream of hydrogen chloride gas for 15 min, and extracted with water. The aqueous layer was washed with chloroform and the combined chloroform solutions were dried ($MgSO_4$), filtered, and evaporated to dryness. The residue (160 mg) was chromatographed on silica gel (50 g). Hexane–benzene (3 : 1) eluted cyaphenine (2 mg, 0.006 mmol, 0.8%); benzene–chloroform (3 : 1) eluted lophine (5 mg, 0.017 mmol, 2%). Further elution gave oils. No identifiable material was found in the combined aqueous layers.

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