Reductive and Oxidative Cleavage of 5-Phenyl-Δ^2-isoxazoline-3-carboxylic Acid

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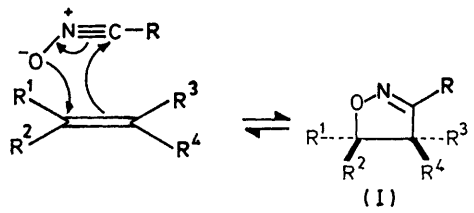
The reductive cleavage of 5-phenyl-Δ^2-isoxazoline-3-carboxylic acid (II; R = H) with zinc in acetic acid to give 4-phenyl-2-acetamido-γ-butyrolactone (III) is described. Oxidative fragmentation of the peroxy-esters t-butyl 5-phenyl-Δ^2-isoxazoline-3-peroxycarboxylate (II; R = OBu^t) and t-butyl 5-phenylisoxazole-3-peroxycarboxylate (V; R = OBu^t) parallels the mass spectral fragmentation, to give benzaldehyde and 3-hydroxy-3-phenylpropionitrile (VI), and 5-phenylisoxazole-3-carboxylic acid (V; R = H), respectively.

THE 1,3-dipolar addition ([3 + 2] cycloaddition) of a nitrile oxide to a double bond is a well known and thoroughly studied process [1] (Scheme 1). The resulting isoxazolines, in particular the acids (1; R = CO_2H), should undergo oxidative and reductive transformations that lead to synthetically useful intermediates. Reductive cleavage of isoxazolines is well known [2] but not of the acids (I; R = CO_2H). Oxidative transformations of isoazolines give isoxazoles.

We have studied 5-phenyl-Δ^2-isoxazoline-3-carboxylic acid [3] (II; R = H). The ethyl ester (II; R = Et) was prepared by 1,3-dipolar addition of ethyl cyanoformate *N*-oxide [generated *in situ* from ethyl chloro(hydroxyimino)acetate [4] by treatment with triethylamine in ether] to styrene. In this way we obtained a yield

[1] R. Huisgen, R. Grashey, and J. Sauer, 'The Chemistry of Alkenes,' ed. S. Patai, Interscience, New York, 1964, p. 739.
[2] G. W. Perold and F. V. K. von Reiche, *J. Amer. Chem. Soc.*, 1957, **79**, 465.
[3] W. R. Vaughan and J. L. Spencer, *J. Org. Chem.*, 1960, **25**, 1160.
[4] G. S. Skinner, *J. Amer. Chem. Soc.*, 1924, **46**, 731.

(85%) higher than that reported in the literature (50%) [3] and isolated the ester (II; R = Et) as a crystalline solid,

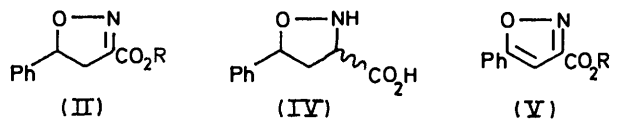


(I)

SCHEME 1

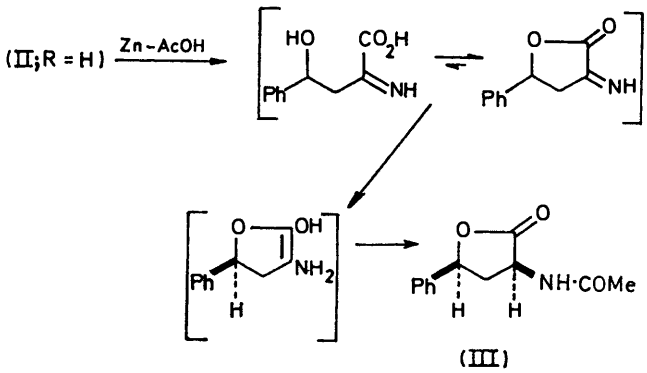
m.p. 23—27° (previous reports describe an oil). Hydrolysis of the ester (II; R = Et) gave the acid (II; R = H).

Treatment of the acid (II; R = H) with zinc in acetic acid gave a mixture of two components. The major



(II) (IV) (V)

component was isolated as a crystalline solid. The absence of a band at 940 cm^{-1} in the i.r. spectrum suggested that the weak N–O bond had been cleaved. This together with the n.m.r. spectrum (see Experimental section) enables the compound to be formulated as the lactone (III) (see Scheme 2). Since a new asymmetric



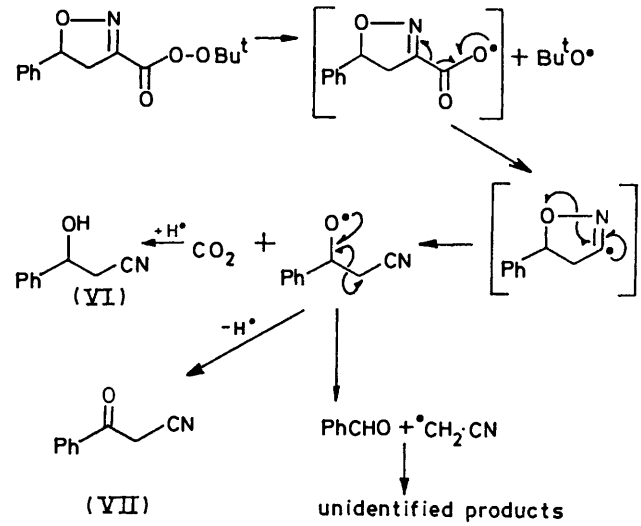
(III)

SCHEME 2

centre is created in this reduction, diastereoisomers are possible. But the lactone (III) is a single crystalline compound (the minor component is present in less than 5%). Mechanistically, protonation of the intermediate enol should take place on the least hindered side of the γ-lactone ring, giving the *cis*-relative configuration of phenyl and acetamido-groups. This represents a two step conversion of an alkene into an α-amino-γ-lactone (4-hydroxy-*allo*-proline [5]).

Reduction of the acid (II; R = H) with sodium borohydride gave a single product, a water-soluble oil (IV) with a band in the i.r. at 960 cm^{-1}. It is interesting to note that the weak N–O bond is resistant to attack by borohydride, whereas lithium aluminium hydride readily cleaves the N–O bond in isoxazolidines.[6]

Since oxidative degradation of the acid (II; R = H) produces the isoxazole (V; R = H), we required a method of oxidative fragmentation that was not attended by concomitant dehydrogenation. The t-butyl peroxy-ester (II; R = OBu^t) was prepared *via* the acid chloride of (II; R = H) and isolated as a crystalline solid. The peroxy-ester (II; R = OBu^t) was surprisingly stable: heating in benzene under reflux did not cause decomposition. However, when heated under reflux in toluene containing a trace of copper(II) hexanoate, the peroxy-ester decomposed [CO_2 evolved (90%)] to give a mixture of products. The i.r. spectrum of the product indicated the presence of 3-hydroxy-3-phenylpropionitrile (VI), 3-oxo-3-phenylpropionitrile



(VI) (VII)

SCHEME 3

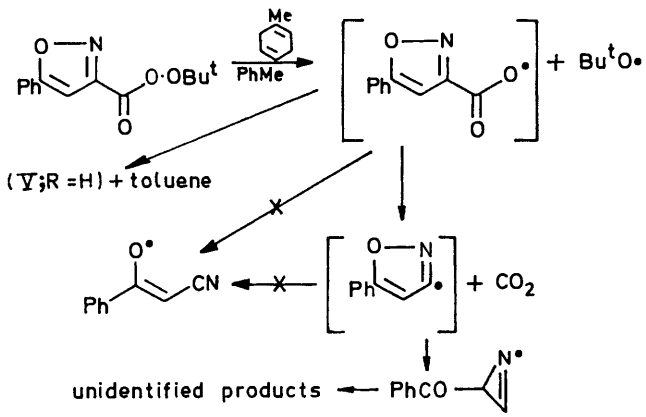
(VII), and another compound having a carbonyl group. The hydroxy-nitrile (VI) was isolated as its *p*-nitrobenzoate ester and compared with an authentic sample [7] (see Experimental section). The ketone (VII) was only formed in very low yield (<5%) and its identity confirmed by comparison (i.r. and n.m.r.) with an authentic sample. The other carbonyl compound was shown to be benzaldehyde by isolation and identification of the 2,4-dinitrophenylhydrazone (20%). This decomposition in toluene was carried out with no special precautions to exclude oxygen (traces of di-t-butyl peroxide were also present). With purified peroxy-ester (II; R = OBu^t) and exclusion of oxygen, the decomposition gave only the hydroxy-nitrile (VI) and benzaldehyde. If the decomposition of the peroxy-ester was carried out in toluene containing 1-methylcyclohexa-1,4-diene, again only two products were formed: nitrile (VI) (25%) and benzaldehyde (25%). To establish that benzaldehyde was not derived from oxidation of the solvent, the

[5] T. Wieland and U. Wintermeyer, *Chem. Ber.*, 1957, **90**, 1721.

[6] J. E. Baldwin, D. H. R. Barton, N. J. A. Gutterridge, and R. J. Martin, *J. Chem. Soc.* (*C*), 1971, 2184.

[7] C. J. Eby and C. R. Hauser, *J. Amer. Chem. Soc.*, 1957, **79**, 723.

decomposition was carried out in decalin: benzaldehyde and the hydroxy-nitrile (VI) were again formed. The rate-determining step for the homolytic decomposition of a peroxy-ester may be either a single or a multiple bond breaking process. Simultaneous two-bond cleavage occurs when the acyloxyl radical readily decarboxylates.[8] This would appear to be a most apposite description of the decomposition of the peroxy-ester (II; R = OBu^t). The radical decomposition to a β-hydroxy-nitrile parallels the base cleavage of isoxazoles. A similar fragmentation was examined in the isoxazole series for the peroxy-ester (V; R = OBu^t). Treatment of the isoxazoline (II; R = Et) with *N*-bromosuccinimide,[9,10] followed by base hydrolysis, gave the isoxazole (V; R = H). The t-butyl peroxy-ester (V; R = OBu^t) was prepared *via* the acid chloride of (V; R = H) in the usual way.[11] Decomposition of (V; R = OBu^t) under reflux in decalin or toluene in the presence of traces (<1%) copper(II) hexanoate gave an intractable mixture containing no nitriles (i.r.). The peroxy-ester (V; R = OBu^t) readily decomposed under reflux in toluene containing 20% 1-methylcyclohexa-1,4-diene.[12] A single product was isolated and identified as the acid (V; R = H) by comparison with an authentic sample. Apparently the isoxazol-3-yl radical is not formed. Presumably its formation would be attended by fragmentation, a high-energy process involving disruption of the isoxazole aromaticity (50 kcal mol^{-1}; although this value may be high).[13] In the absence of an



SCHEME 4

hydrogen atom donor, carbon dioxide (76%) is evolved when the peroxy-ester (V; R = OBu^t) is thermally decomposed. If the isoxazol-3-yl radical is formed, its subsequent fate does not involve fragmentation to the oxo-nitrile (VII). The decomposition of (V; R = OBu^t) shows similarities to the decomposition of t-butyl perbenzoate to give benzoic acid.[14]

The mass spectra of both peroxy-esters (II; R = OBu^t) and (V; R = OBu^t), and the ethyl esters (II; R = Et) and (V; R = Et) for comparison, were recorded (see Tables 1 and 2). The metastable ions were investigated by the defocusing technique.

TABLE 1

Mass spectrum of (II; R = Et), T = 170 °C			Mass spectrum of (II; R = OBu^t), T = 110 °C		
m/e	%	Assignment	*m/e*	%	Assignment
219	46	$M^{+\cdot}$	263		$M^{+\cdot}$
218	30	$(M - 1)^+$	174	11	$(M - C_4H_8 - OOH)^+$
202	4	$(M - OH)^+$			
190	8	$(M - H - C_2H_4)^+$	146	2	$(174 - CO)^+$
174	8	$(M - OEt)^+$	129	10	$(146 - OH)^{+\cdot}$
172	5	$(M - H - EtOH)^+$	128	16	$(146 - H_2O)^+$
156	8	$(M - H_2O - OEt)^+$	107	42	$(PhCH_2O)^+$
146	15	$(M - CO_2Et)^+$	106	53	$(PhCHO)^{+\cdot}$
129	19	$(M - CO_2Et - OH)^{+\cdot}$	105	76	$(PhCO)^+$
			77	90	Ph^+
128	34	$(M - CO_2Et - H_2O)^+$	73	89	Me_2COMe^+
			59	100	Me_2COH^+
115	26	$\cdot O\cdot\overset{+}{N}{:}C\cdot CO_2Et\cdot$	57	82	$C_4H_9^+$
105	44	$PhCO^+$	51	41	
104	100	$PhCH_2\cdot CH^{+\cdot}$	41	45	$(CH_2\cdot CNH)^+$
77	37	Ph^+			

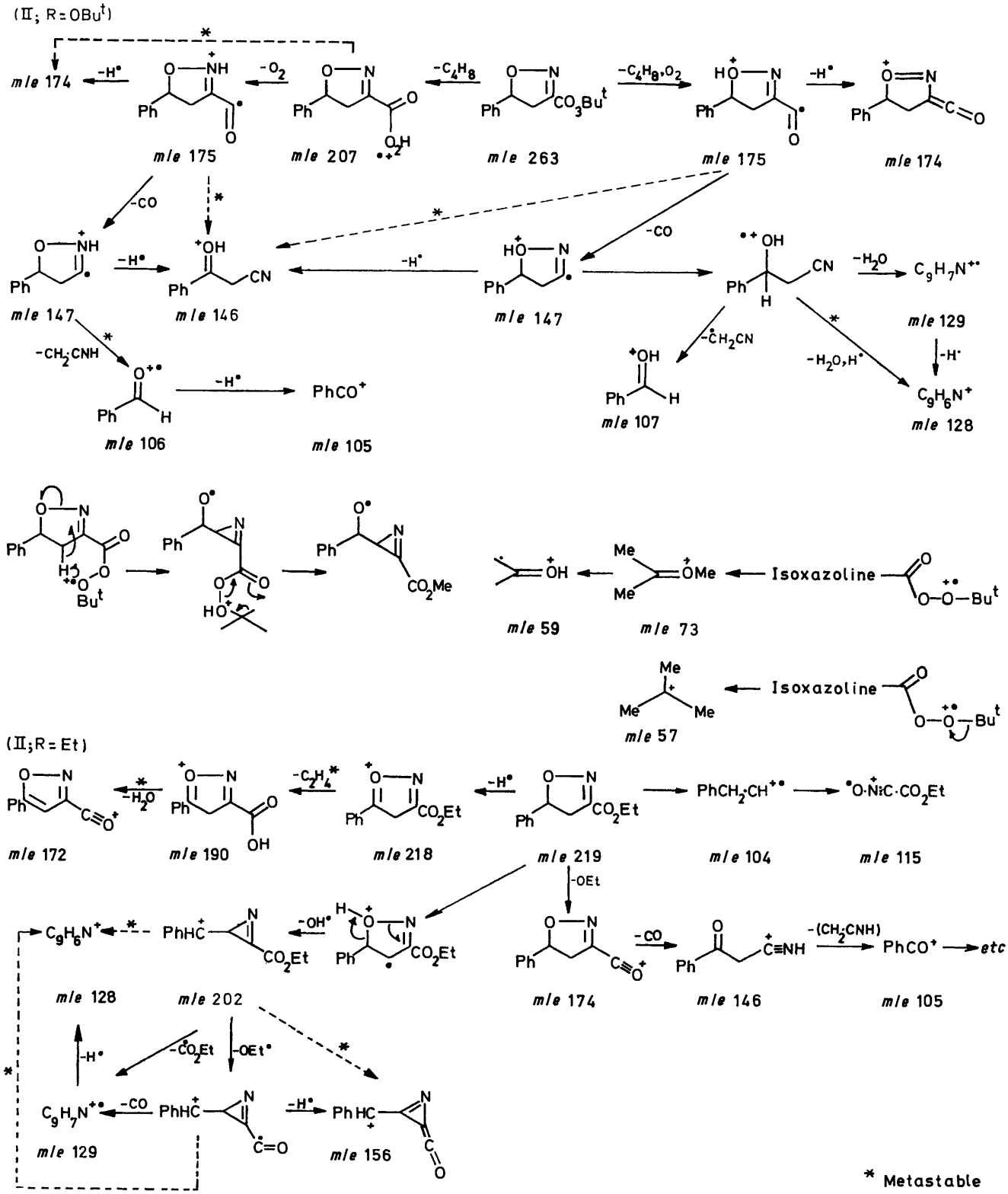
Metastable peaks correspond to	Metastable peaks correspond to
218 → 190	207 → 174
190 → 172	146(7) → 128
174 → 156	146(7) → 106
174 → 146	
156(7) → 128	174(5) → 146
	174(5) → 128
219 → 174	146(7) → 105
218 → 172	
202 → 156	
219 → 146	
146 → 105	

TABLE 2

Mass spectrum of (V; R = Et), T = 140 °C			Mass spectrum of (V; R = OBu^t), T = 120 °C		
m/e	%	Assignment	*m/e*	%	Assignment
217	89	$M^{+\cdot}$	261	8	$M^{+\cdot}$
189	2	$(M - C_2H_4)^{+\cdot}$	205	23	$(M - C_4H_8)^{+\cdot}$
173	5	$(M - CO_2)^{+\cdot}$	189	4	$(M - C_4H_8O)^{+\cdot}$
172	20	$(M - OEt)^+$	172	24	$(M - C_4H_8 - OOH)^+$
145	24	$(M - CO_2 - C_2H_4)^{+\cdot}$	145	10	$(205 - OOH - CO)^+$
105	100	$(PhCO)^+$	105	79	$(PhCO)^+$
77	30	Ph^+	77	64	Ph^+
51	17		73	6	Me_2COMe^+
			59	66	Me_2COH^+
Metastable peaks correspond to			57	100	$C_4H_9^+$
217 → 172			51	26	
217 → 145			41	20	$(CH_2CNH)^+$
217 → 105					
172 → 105					

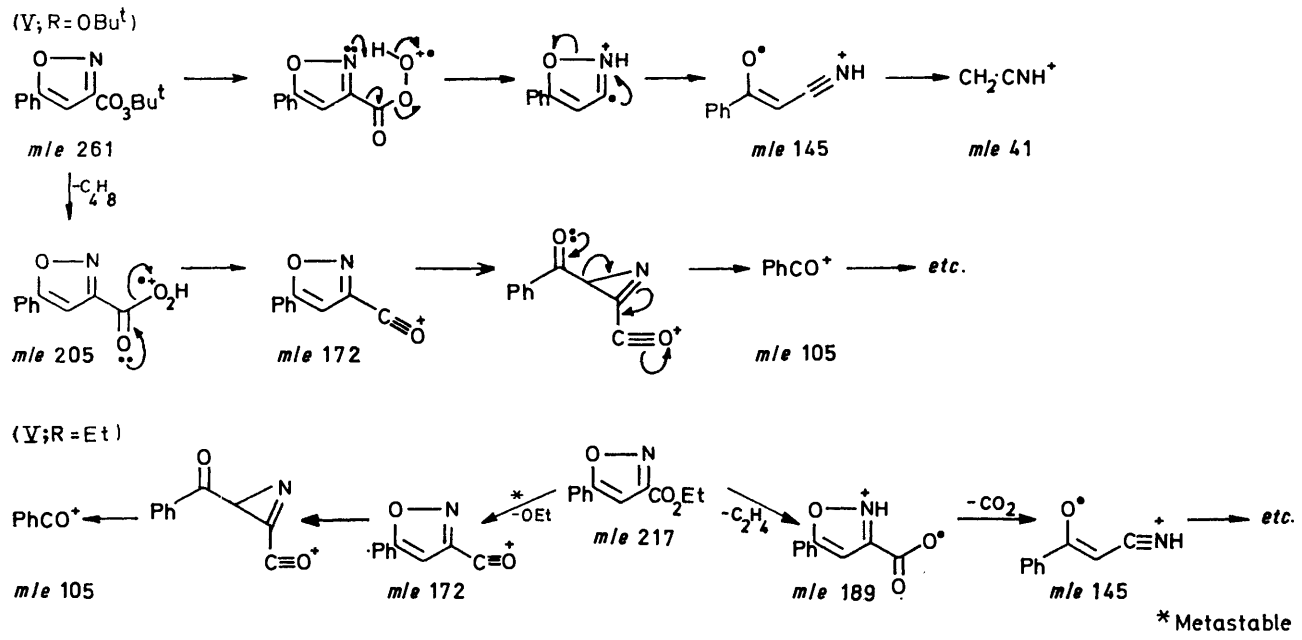
The peroxy-esters fragment by processes which correspond to the loss of isobutene followed by ·O·OH (or O_2 + H·), but the molecular and $(M - C_4H_8)^{+\cdot}$ ion of the peroxy-ester (II; R = OBu^t) are considerably less abundant than these ions in the peroxy-ester (V; R = OBu^t) spectrum. The fragmentation processes thought to occur in the four esters examined are given in Scheme 5. Distinct similarities may be seen between the thermal decomposition of the peroxy-ester (II;

[8] P. D. Bartlett, ' Aspects of the Chemistry of Perester,' in ' Peroxide Reaction Mechanisms,' ed. J. O. Edwards, Interscience, New York, 1962, p. 1.
[9] G. Bianchi and P. Grunanger, *Tetrahedron*, 1965, **21**, 817.
[10] P. V. Finzi and M. Arbasino, *Ricerca Sci.*, 1965, **8**, 1484.
[11] N. A. Milas and D. M. Surgenor, *J. Amer. Chem. Soc.*, 1946, **68**, 642.
[12] A. J. Birch, *J. Chem. Soc.*, 1944, 430.
[13] G. Tappi, *Gazzetta*, 1940, **70**, 114.
[14] M. S. Kharasch, G. Sosnovsky, and N. C. Yang, *J. Amer. Chem. Soc.*, 1959, **81**, 5819.


(II; R = OBu^t)
m/e 174
m/e 175
m/e 207
m/e 263
m/e 175
m/e 174
m/e 147
m/e 146
m/e 147
m/e 129
m/e 106
m/e 105
m/e 107
m/e 128
m/e 59
m/e 73
Isoxazoline
m/e 57
(II; R = Et)
m/e 172
m/e 190
m/e 218
m/e 219
m/e 104
m/e 115
m/e 128
m/e 202
m/e 174
m/e 146
m/e 105
m/e 129
m/e 156
* Metastable

Scheme 5

SCHEME 5 (*continued*)

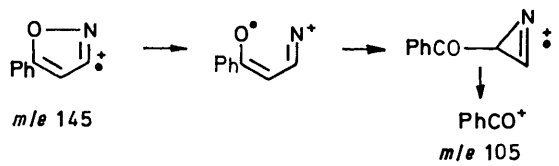


SCHEME 5

R = OBu^t) and the mass-spectral fragmentation, especially with regard to the ion at *m/e* 146.

Comparison of the fragmentations of the ethyl ester (II; R = Et) and the peroxy-ester (II; R = OBu^t) shows that the t-butoxy-group has a strong directing effect for fragmentation along two very similar pathways. Of particular interest are the suppression of the ' retro ' 1,3-dipolar processes (*m/e* 104—105) and of ions at *m/e* 218, 202, 172, 156, and 129. The appearance of strong peaks at *m/e* 107 and 106 is of particular significance in that the thermal decomposition of the peroxy-ester (II; R = OBu^t) gives benzaldehyde as one of the products.

The similarity of the fragmentation of the ester (V; R = Et) and the peroxy-ester (V; R = OBu^t) rather than their difference is striking; the resemblance to that of 5-phenylisoxazole (Scheme 6) is evident. If the



SCHEME 6

thermal decomposition of the peroxy-ester (V; R = OBu^t) follows this pathway, an intractable mixture would not be unexpected. It is of interest that the peroxy-ester (V; R = OBu^t) does not give an ion at *m/e* 106, unlike (II; R = OBu^t).

Although the oxidative fragmentation of the isoxazoline peroxy-ester (II; R = OBu^t) offers no viable synthetic use it does illustrate a homolytic degradation for isoxazolines. Furthermore the close parallel between the thermal decomposition of (II; R = OBu^t) and its mass spectral fragmentation might be of use in studying the decomposition of peroxy-esters in general.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. I.r. spectra were recorded for Nujol mulls. N.m.r. spectra were measured for solutions in carbon tetrachloride with tetramethylsilane as internal standard. U.v. spectra were measured for solutions in cyclohexane. Mass spectra were obtained on a A.E.I. MS9 spectrometer (direct inlet) operating at 70 eV.

Ethyl Chloro(hydroxyimino)acetate [4] was prepared from ethyl glycinate hydrochloride (48%), m.p. 70—75° (from benzene).

Ethyl 5-Phenyl-Δ²-isoxazoline-3-carboxylate [3] (II; R = Et).—To a solution of styrene (10·3 g) and triethylamine (3·3 g) in dry ether (50 ml) was added at −5° a solution of ethyl chloro(hydroxyimino)acetate (5·2 g) in ether (40 ml) with stirring during 40 min. After 15 h at room temperature the mixture was filtered and the filtrate was evaporated. Distillation of the residue at 160—165° and 0·6 mmHg gave the *ester* (II; R = Et) (85%), m.p. 23—27°, $\nu_{max.}$ 1725, 1590, 1020, and 940 cm^{-1}; n.m.r. data are given in Table 3; $\lambda_{max.}$ 243 nm (ε 2430).

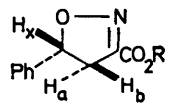
5-Phenyl-Δ²-isoxazoline-3-carboxylic Acid (II; R = H).—The ester (II; R = Et) was hydrolysed at room temperature in aqueous 10% potassium hydroxide. Acidification and extraction with chloroform gave the *acid* (II; R = H) (90%) (lit.,[3] 49%), m.p. 100—102° (from benzene), $\nu_{max.}$ 1695, 1590, and 927 cm^{-1}, n.m.r. data are given in Table 3.

Treatment of 5-Phenyl-Δ²-isoxazoline-3-carboxylic Acid (II; R = H) *with Zinc in Acetic Acid.*—The acid (II; R = H) (480 mg) in glacial acetic acid (25 ml) and water (1·5 ml) was treated with zinc dust (2·0 g). The mixture

was stirred at room temperature for 0·5 h, then heated under reflux for 3 h, and left for 15 h at 25°. The mixture was filtered, water was added (80 ml) and then solid sodium carbonate until the pH was 4—5. The mixture was extracted with chloroform (5 × 10 ml); the extracts were

TABLE 3

N.m.r. data for 5-phenyl-Δ^2-isoxazoline-3-carboxylates, chemical shifts in τ values, and J in Hz [a]



	J_{ab}	J_{ax}	J_{bx}	$\tau_{a \text{ or } b}$	$\tau_{b \text{ or } a}$	τ_x
(II; R = Et)	±18·1	14·9	5·9	6·48	6·90	4·32
(II; R = H)	±19·0	13·7	8·2	($\tau_a - \tau_b$) ±0·18		
(II; R = OBu^t)	±18·0	14·1	6·8	6·40	6·78	4·27
(II; R = Bu^t)	±18·1	15·1	6·4	6·52	6·95	4·36

[a] The spectrum is an ABX system.

dried (Na_2SO_4) and evaporated to give an oil. Chromatography on silica gel with 5% methanolic chloroform as eluant gave the *lactone* (III) (110 mg), m.p. 100—101° (from benzene), $\nu_{max.}$ 3450, 1775, 1680, and 1520 cm^{-1}, τ 2·5—3·0 (6H, m), 4·5 (1H, m), 5·4 (1H, m), 7·4 (2H, m), and 8·0 (3H, s), *m/e* 219 (M^+), 191 (M − 28), 175 (M − 44), and 160 (M − 59).

Treatment of the Acid (II; R = H) *with Sodium Borohydride*.—The acid (II; R = H) (350 mg) in ethanol (1 ml) and aqueous sodium hydroxide (2N; 1 ml) was treated with sodium borohydride (400 mg) in ethanol (25 ml). After 15 h at room temperature the mixture was diluted with water (25 ml) and acidified (6N-hydrochloric acid). Continuous extraction with chloroform gave *5-phenylisoxazolidine-3-carboxylic acid* (IV) (100 mg) as an oil, $\nu_{max.}$ 3500—2500, 1710, 1590, 1340, and 960 cm^{-1}, τ 2·6 (5H, s), 4·6 (1H, m), 5·0 (1H, t), 7·2 (2H, m), and two exchangeable protons, *m/e* 193 (M^+).

t-Butyl 5-Phenyl-Δ^2-isoxazoline-3-peroxycarboxylate (II; R = OBu^t).—The acid (II; R = H) (2·0 g) in dry benzene (50 ml) was treated with thionyl chloride (1·25 g) and dimethylformamide (1 drop). After heating under reflux for 2 h, the solution was evaporated to give an oil, $\nu_{max.}$ 1740 and 940 cm^{-1}. This was dissolved in dry ether (10 ml) and added dropwise to a solution of t-butyl hydroperoxide (0·68 g) and dry pyridine (0·68 g) in dry ether (20 ml) at 0° in the dark. After 0·5 h, the mixture was filtered and evaporated below 30° to give an oil. Chromatography over Florisil with ether as eluant gave the *peroxy-ester* (II; R = OBu^t) (1·30 g), m.p. 39—40°, $\nu_{max.}$ 1760, 1588, and 935 cm^{-1} [Found: C, 63·9; H, 6·5; N, 5·3%; oxidising equiv. (iodometric [15]), 290. $C_{14}H_{17}NO_4$ requires C, 63·9; H, 6·5; N, 5·3%; oxidising equiv., 264].

Thermal Decomposition of the Peroxy-ester (II; R = OBu^t).—The peroxy-ester (II; R = OBu^t) (0·75 g) in dry toluene (30 ml) containing a trace of dry copper(II) hexanoate (3 mg) was heated under reflux (without precautions for removing oxygen) for 2 h. Evaporation of the mixture gave an oil, $\nu_{max.}$ 3450, 2260, 2220, 1730, and 1705 cm^{-1}, which was treated with *p*-nitrobenzoyl chloride–pyridine. Work-up in the usual way gave the *p*-nitrobenzoate of 3-hydroxy-3-phenylpropionitrile (VI), m.p. 109—110° (from ethanol), undepressed on admixture with an authentic sample (see later). Treatment of the crude decomposition products with 2,4-dinitrophenylhydrazine (in ethanol–sulphuric acid) gave benzaldehyde 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 237—238°.

Decomposition of the peroxy-ester (II; R = OBu^t) in the absence of oxygen gave a crude oil, $\nu_{max.}$ 3480, 2270, and 1730 cm^{-1} (80% CO_2 as barium carbonate).

Decomposition of the peroxy-ester (II; R = OBu^t) in the presence of 1-methylcyclohexa-1,4-diene [12] gave a product with liberation of CO_2 (90%), $\nu_{max.}$ 3500, 2760, 2260, and 1715 cm^{-1}. Analysis of the mixture by n.m.r. indicated the presence of benzaldehyde (25%) and 3-hydroxy-3-phenylpropionitrile (VI) (25%).

Decomposition of the peroxy-ester (II; R = OBu^t) in decalin at 140° for 18 h gave CO_2 (92%), and analysis by n.m.r. indicated the presence of benzaldehyde and 3-hydroxy-3-phenylpropionitrile (VI) (35—40%).

Ethyl 5-Phenylisoxazole-3-carboxylate (V; R = Et).—The ester (II; R = Et) was treated with 1 equiv. of *N*-bromosuccinimide in carbon tetrachloride under reflux.[10] After evaporation of the solvent the residue was treated with triethylamine and left at room temperature overnight. The mixture was filtered and the filtrate was evaporated. The residue was washed with water, extracted with ether, and dried (Na_2SO_4). Evaporation of the extract gave the *ester* (V; R = Et) (86%), m.p. 48—50° (from hexane) (lit.,[3,16] 51—52°), $\nu_{max.}$ 3130, 1737, and 1612 cm^{-1}, τ 8·55 (3H, t), 5·6 (2H, q), 3·15 (1H, s), and 2·6—2·2 (5H, m).

5-Phenylisoxazole-3-carboxylic Acid (V; R = H).—The ester (V; R = Et) (2·5 g) was shaken with aqueous 20% potassium hydroxide (30 ml) at room temperature for 15 h. The crystals of the potassium salt (V; R = H) were filtered off, washed with cold water, and dissolved in boiling water (40 ml). Acidification (6N-hydrochloric acid) gave the *acid* (V; R = H) (83%), m.p. 160—161° (from water) (lit.,[16] 162°), $\nu_{max.}$ 2580, 1702, and 1607 cm^{-1}, τ ($CF_3 \cdot CO_2H$) 2·9 (1H, s), and 2·5—2·2 (5H, m).

t-Butyl 5-Phenylisoxazole-3-peroxycarboxylate (V; R = OBu^t).—The acid chloride of the foregoing acid was prepared in the usual way (see before) and converted into the *peroxy-ester* (V; R = OBu^t) (70%) in the manner previously described,[11] m.p. 30—32°, $\nu_{max.}$ 1790 and 1621 cm^{-1}, τ 8·6 (9H, s), 3·1 (1H, s), and 2·55—2·2 (5H, m) (Found: C, 64·5; H, 5·9; N, 5·5. $C_{14}H_{15}NO_4$ requires C, 64·4; H, 5·8; N, 5·4%).

Thermal Decomposition of the Peroxy-ester (V; R = OBu^t).—The peroxy-ester (V; R = OBu^t) (50 mg) was heated under reflux in toluene (3 ml) containing 20% 1-methylcyclohexa-1,4-diene with a trace (<0·5%) copper(II) hexanoate for 1 h. Cooling gave crystals of the acid (V; R = H) separated (29 mg, 81%), m.p. and mixed m.p. 159—160° (from benzene).

Decomposition of the peroxy-ester (V; R = OBu^t) under reflux in toluene gave only the acid (V; R = H) (<5%) and a complex mixture of products.

3-Hydroxy-3-phenylpropionitrile [7] (VI).—Acetonitrile was condensed with ethyl benzoate with sodamide in liquid ammonia to give 3-oxo-3-phenylpropionitrile (VII) (65%), m.p. 78—80°, $\nu_{max.}$ 2210 and 1700 cm^{-1}, τ 5·95 (2H, s) and 2·4—2·0 (5H, m).

Reduction of the ketone (VII) (2·0 g) with sodium borohydride (0·3 g) in the usual way gave the alcohol (VI) (55%), $\nu_{max.}$ 3450 and 2260 cm^{-1}, τ 7·3 (2H, d, J 7 Hz), 4·05 (1H, s), 5·02 (1H, t, J 7 Hz), and 2·62 (5H, s). The p-

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nitrobenzoate had m.p. 109—110° (from ethanol), $\nu_{max.}$ 2270, 1740, and 1615 cm^{-1}, τ 6·9 (2H, d, J 6 Hz), 3·8 (1H, t, J 6 Hz), 2·6 (5H, s), and 1·6 (4H, s) (Found: C, 64·6; H, 4·3; N, 9·5. $C_{16}H_{12}N_2O_4$ requires C, 64·9; H, 4·1; N, 9·5%).

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