Tetrahedron Vol. 26, pp. 3875 to 3882. Pergamon Press 1970. Printed in Great Britain

THE REACTION OF SOME 4-METHYLENEOXAZOLIDIN-2-ONES WITH PEROXY ACIDS

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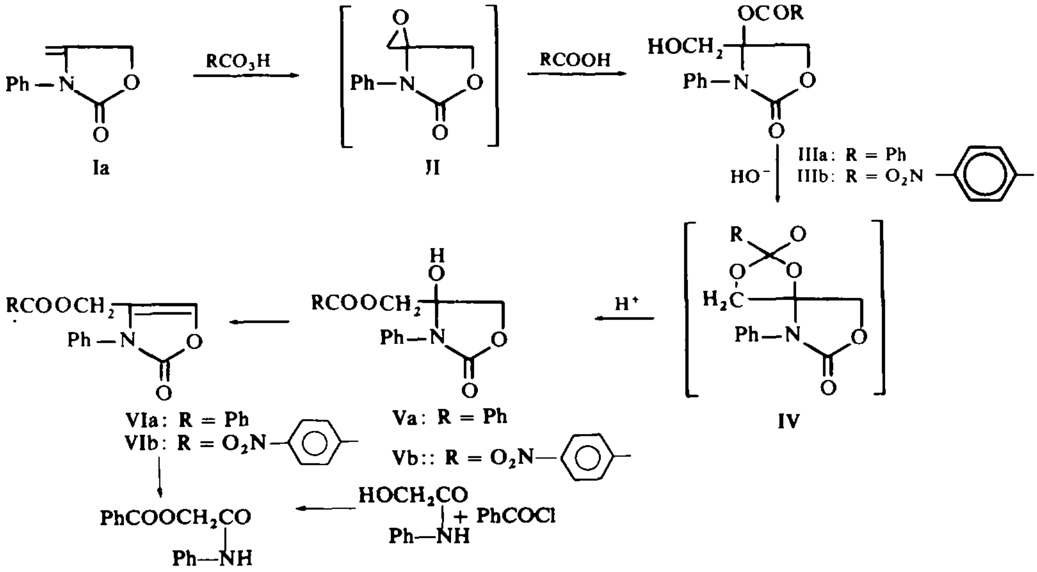
(*Received in the UK* 26 *January* 1970; *Accepted for publication* 11 *March* 1970)

Abstract—4-Methylene-3-phenyloxazolidin-2-one (Ia) reacts with peroxybenzoic (or *p*-nitroperoxybenzoic) acid to give 4-benzoyloxy- (or 4-*p*-nitrobenzoyloxy-) 4-hydroxymethyl-3-phenyloxazolidin-2-one (IIIa and IIIb). The said esters were submitted to a variety of transformations, in order to secure proof of their structure. 5,5-Dimethyl- and 5,5-pentamethylene-4-methylene-3-phenyloxazolidin-2-one (Ib and c, respectively), on treatment with the same reagents undergo oxidative fission of the double bond, and transformation into the corresponding 4-oxo derivatives XVIb and c.

IN AN earlier paper[1] we reported the preparation and biological evaluation of some 2-oxazolidones bearing an aryloxymethyl substituent at the 4 position, and chemically related to mephenesin carbamate. The interesting biological properties shown by one member of the series, namely, 4-(*o*-toloxymethyl)-4-oxazolin-2-one, prompted us to investigate new methods for the preparation of analogous 4-substituted oxazolinones. The epoxidation of an oxazolidinone bearing an exocyclic double bond at the 4 position (as e.g. Ia, Scheme I), followed by opening of the epoxide ring with a suitable reagent, was considered as a potential route leading to the desired compounds. The results obtained with three selected 4-methylenoxazolidin-2-ones (Ia, b and c), chosen as model compounds, are the subject of this paper.

SCHEME I



(A) *4-Methylene-3-phenyloxazolidin-2-one* (Ia). When the title compound was treated with an equimolar amount of peroxybenzoic acid, a single, rather unstable compound was obtained. Analytical and spectral data indicated the structure of a diol monobenzoate, possibly resulting from ring opening of the presumed epoxide intermediate II by benzoic acid. This finding was not surprising, since many olefins are known to give rise to 1,2-diol monoesters on treatment with peroxy acid solutions.[2] Two structures, IIIa and Va, resulting from attack on either C atom of the epoxide ring, were possible for the compound. Evidence favouring the former structure, *viz.*, 4-benzoyloxy-4-hydroxymethyl-3-phenyloxazolidin-2-one, was adduced as follows.

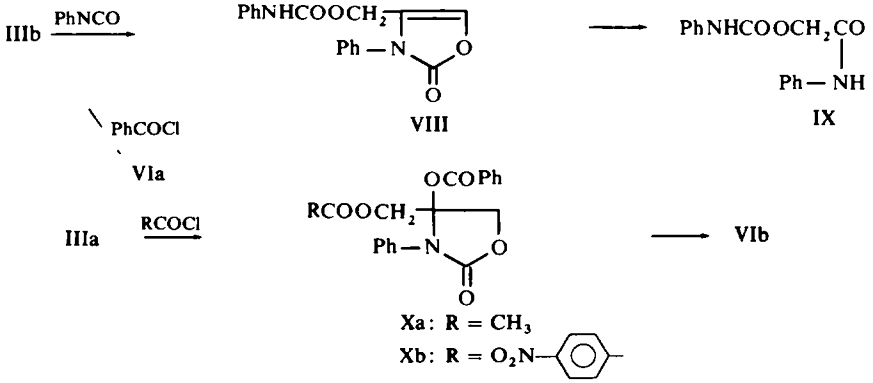
The reaction product was soluble in cold 10% sodium hydroxide. Acidification of the solution caused precipitation of an isomeric product, which was formulated as Va on account of its greater stability. Similar cases of base-catalyzed conversions of tertiary (or secondary) to primary diol monoesters have been reported,[3] and have been assumed to occur through the intermediacy of cyclic structures of type IV.

Treatment of Va with boiling acetic acid caused conversion of the compound into the corresponding Δ^4 unsaturated derivative VIa. Similar dehydrations of 4-hydroxyazolidinones have been described.[1, 4] A proof for the endocyclic position of the double bond in VIa was secured through *p*-nitroperoxybenzoic acid oxidation[1] of the compound to glycolanilide benzoate (VII), also prepared independently as shown in Scheme I.

Quite analogous results were obtained when epoxidation of Ia with *p*-nitroperoxybenzoic acid was attempted. In this case, the tertiary *p*-nitrobenzoate IIIb resulting from the reaction was very unstable, and every attempt at crystallization resulted in decomposition. Treatment of the compound with cold 10% sodium carbonate caused conversion into the stable isomer Vb, whose subsequent dehydration, carried out as indicated for Va, afforded the 4-oxazolin-2-one VIb.

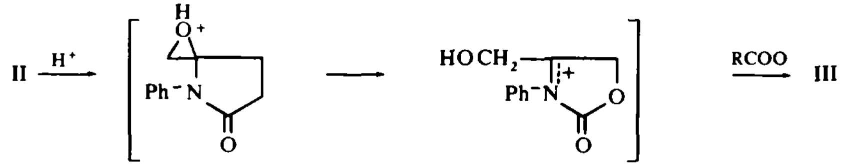
The structural proofs for IIIb rest on spectral data, and on the following reactions of the free primary OH group. Treatment of the compound with benzoyl chloride in pyridine resulted in esterification and contemporary elimination of *p*-nitrobenzoic acid to give the benzoate VIa (Scheme II). Similarly, treatment of IIIb with phenyl isocyanate gave 4-carbaniloxymethyl-3-phenyl-4-oxazolin-2-one (VIII), whose structure was proved through oxidation to the known[4] glycolanilide carbanilate (IX).

SCHEME II



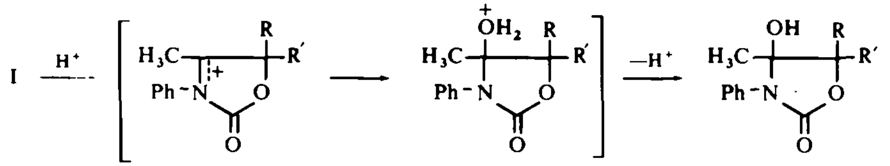
Similar esterifications of the primary OH group were also possible for the benzoate IIIa. The higher stability of the latter compound allowed esterification to be carried out without contemporary elimination of the tertiary benzoyl group. The diesters Xa and Xb were obtained on treatment with acetyl and *p*-nitrobenzoyl chloride, respectively: both compounds could be satisfactorily crystallized from DMSO–water. An attempt at crystallization of Xb from ethanol resulted in elimination of benzoic acid and formation of VIb, besides unidentified tarry by-products.

The formation of the less stable tertiary esters III in the reaction of Ia with peroxy acids might be rationalized assuming initial epoxidation of Ia, followed by protonation of the resulting epoxide II to give the conjugate acid XI. This would undergo preferential collapse to give the ion XII, stabilized by the 3-nitrogen atom. Attack to XII by the acid anion would lead to the tertiary ester.



XI XII

Strong support to the above proposed mechanism comes from a particular reaction of compounds I, which very probably proceeds *via* stable cations similar to XII. When compounds I were treated with dilute acids at room temperature, hydration of the double bond to give the 4-hydroxy-4-methyloxazolidinones XV occurred in good yield. The structure of the latter compounds was confirmed by their NMR spectra (Table 1). Formation of the said 4-hydroxy-4-methyl (instead of the isomeric 4-hydroxymethyl) derivatives can best be explained assuming preferential protonation of the starting products to give the nitrogen-stabilized cations XIII. Attack to XIII by H_2O to give XIV and proton elimination would lead to the final products XV, as indicated in the scheme.

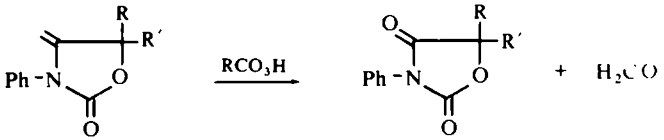


XIII XIV

XVa: $R = R' = H$
XVb: $R = R' = CH_3$
XVc: $R - R' = -(CH_2)_5-$
XVd: $R = H; R' = Ph$

(**B**) *5,5-Dimethyl- and 5,5-pentamethylene-4-methylene-3-phenyloxazolidin-2-one* (Ib *and* c). Treatment of the title compounds with one molar equivalent of peroxybenzoic or *p*-nitroperoxybenzoic acid gave entirely different results. In both cases, mixtures containing approximately equal amounts of starting materials and of the corresponding 4-oxo derivatives, XVIb and c, were obtained. When Ib and c were treated with two molar equivalents of peroxy acid, conversion into the oxazolidin-2,4-diones XVI was practically quantitative. In all cases formaldehyde, the other product resulting from oxidative fission of the double bond, was isolated as the dimedone derivative.

Compound XVIb, not described in the literature, was prepared independently by ozonolysis of Ib; compound XVIc was identical with an authentic sample.[5]



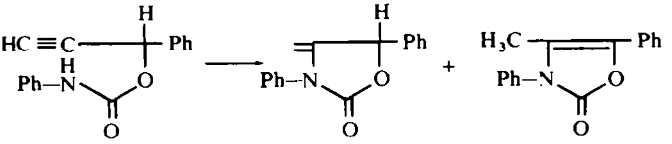
Ib: $R = R' = CH_3$
Ic: $R = R' = -(CH_2)_5$

XVIa: $R = R' = H$
XVIb: $R = R' = CH_3$
XVIc: $R - R' = -(CH_2)_5$

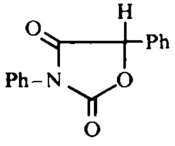
The results obtained with Ib and c prompted us to reinvestigate the reaction between Ia and peroxy acids, in search of the 4-oxo derivative of Ia, the known[6] 3-phenyloxazolidin-2,4-dione (XVIa). Evaporation of the mother liquors of IIIa (or IIIb) afforded a syrupy residue, shown by TLC to contain at least six components. None of these, however, had the same R_f of an authentic sample of XVIa, whose presence among the said reaction products seems to be excluded.

A smooth oxidative fission of the Δ^4 endocyclic double bond under the influence of peroxy acids has been observed many times during our investigations on 4-oxazolin-2-ones, and is probably favoured by the enamide-like structure of the compounds in question. The oxidations of VIa to VII, of VIII to IX and of XVIII to acetanilide, reported in the present paper, are one such example. It now appears that an exocyclic double bond may undergo, in some oxazolones, a similar facile oxidation. The different behaviour of Ia is rather difficult to explain, and is probably to be put in connexion with the lack of substituents at the 5 position.

(C) *Attempted preparation of 4-methylene-3,5-diphenyloxazolidin-2-one* (Id). The preparation of Id by cyclization of the known[7] α-ethynylbenzyl carbanilate (XVII) was attempted in the hope of obtaining information of the behaviour of a 5-monosubstituted 4-methyleneoxazolidin-2-one in the reaction with peroxy acids. Treatment of XVII with sodium ethoxide under mild conditions, known to favour conversion of ethynyl carbamates into 4-methyleneoxazolidinones,[8] led to an oily mixture, shown by TLC to contain approximately 60% 4-methyl-3,5-diphenyl-4-oxazolin-2-one (XVIII), and 40% of another compound, presumably Id.



XVII Id XVIII



XIX

The presence of Id was confirmed by the isolation of 4-hydroxy-4-methyl-3,5-diphenyloxazolidin-2-one (XVd) on treatment of the mixture with dilute acids. Treatment of XVd with acids under somewhat stronger conditions resulted in dehydration to XVIII. The latter compound failed to undergo double bond hydration under various experimental conditions. It was thus excluded that XVd might originate from XVIII present in the mixture.

The structure of XVIII, which could be obtained in good yield on treatment of the mixture with hot acids, was confirmed by the isolation of acetanilide as the product of *p*-nitroperoxybenzoic acid oxidation. The NMR spectrum was also in agreement with the proposed structure.

Peroxy acid oxidation of the mixture Id–XVIII, which resisted several attempts at separation or crystallization, led to a more complex oily mixture, shown by TLC to contain four components. One of these had the same R_f of an authentic sample of 3,5-diphenyloxazolidin-2,4-dione (XIX), independently prepared by the method of Lambling,[9] and another the same R_f of acetanilide.

Formation of XVIII as the major product of the cyclization of XVII under mild conditions is clearly due to the tendency of the exocyclic double bond of Id to conjugate with the 5-phenyl group. An identical shift of the exocyclic double bond has been reported to occur in Ia under somewhat stronger conditions.[10] Because of the impossibility of obtaining pure Id, non definite assessment of the behaviour of a 5-monosubstituted 4-methyleneoxazolidinone in the presence of peroxy acids could be made. Some evidence supports the hypothesis, for Id, of a reactivity essentially similar to that of the 5,5-disubstituted 4-methyleneoxazolidinones Ib and c.

In conclusion, the present work has shown that, in some 4-methyleneoxazolidin-2-ones, (a) the double bond shows an unusual kind of reactivity towards peroxy acids; and, (b) this reactivity can be influenced by the presence of substituents at the 5 position of the ring. Additional data are needed for a clear understanding of this phenomenon. It is hoped that further work, now in progress on a wider series of 4-methyleneoxazolidinones, may yield information as to the mechanism and the preparative value of this reaction.

Pharmacological data for some of the compounds described herein will be the object of a separate communication.

TABLE 1. 4-HYDROXY-4-METHYLOXAZOLIDINONES

Compd	M.p., °C	Crystn solvent[a]	Empirical formula	Analysis			NMR Data	
					Calcd, %	Found, %	Solvent	δ
XVa	119–120	B-PE	$C_{10}H_{11}NO_3$	C	62·16	62·30	$CDCl_3$	1·41 (s, 3, CH_3); 4·31 (s, 2, CH_2); 5·11 (broad s, 1, OH); 7·51 (m, 5, C_6H_5)
				H	5·74	5·95		
				N	7·25	7·25		
XVb	133–135	M-W	$C_{12}H_{15}NO_3$	C	65·14	64·96	$CDCl_3$	1·23 (s, 3, CH_3); 1·35 (s, 3, CH_3); 1·42 (s, 3, CH_3); 4·92 (broad s, 1, OH); 7·26 (m, 5, C_6H_5)
				H	6·83	6·62		
				N	6·33	6·40		
XVc	156–158	B	$C_{15}H_{19}NO_3$	C	68·94	68·88	$CDCl_3$	1·15 (s, 3, CH_3); 1·70 (m, 11, OH and C_5H_{10}); 7·52 (s, 5, C_6H_5)
				H	7·33	7·45		
				N	5·36	5·19		
XVd	170–172	E	$C_{16}H_{15}NO_3$	C	71·36	71·19	$(CD_3)_2SO$	1·41 (s, 3, CH_3); 5·58 (s, 1, 5H); 6·33 (broad s, 1, OH); 7·51 (m, 10, 3 and 5C_6H_5)
				H	5·61	5·39		
				N	5·20	5·11		

[a] B = benzene; PE = light petroleum, boiling range 60–80°; M = MeOH; E = EtOH; W = water.

EXPERIMENTAL

M.ps (Kofler block) are uncorrected. Light petroleum refers to the fraction of boiling range 60–80°. NMR spectra were recorded on a JEOL C 60 HL spectrometer, using TMS as internal standard. IR spectra were recorded on nujol mulls on a Perkin–Elmer Infracord Mod. 137 spectrophotometer. "Kiesel gel F_{254}" (Merck) plates were used for TLC; the eluant was a benzene–ethanol (90–10 v/v) mixture.

4-Benzoyloxy-4-hydroxymethyl-3-phenyloxazolidin-2-one (IIIa)

A 9% soln of peroxybenzoic acid in $CHCl_3$ (80 ml, 52 mmoles) was slowly added to a soln of Ia* (7·0 g, 40 mmoles) in $CHCl_3$ (30 ml), while stirring and cooling with a salt–ice mixture. After the addition, stirring at low temp was continued 30 min, then cold n-hexane (150 ml) was added to the mixture. This caused slow separation of practically pure IIIa (4·6 g, 38%), which was crystallized from cold DMSO–H_2O to give the analytical sample, m.p. 95–96°, λ_{OH} 2·89; λ_{CO} 5·72, 5·80 μ. (Found: C, 64·96; H, 5·00; N, 4·26. $C_{17}H_{15}NO_5$ requires: C, 65·17; H, 4·82; N, 4·47%).

Evaporation of the initial mother liquors from IIIa gave a thick oily residue, containing at least six components, besides IIIa (TLC). This was not further investigated.

4-Benzoyloxymethyl-4-hydroxy-3-phenyloxazolidin-2-one (Va)

A sample of IIIa (1·0 g) was dissolved in cold 10% NaOH (2·0 ml). Slow acidification of the soln with cold 10% H_2SO_4 caused separation of a white ppt, which was collected, washed with 10% Na_2CO_3, water, and crystallized from EtOH–H_2O to afford Va (0·8 g, 80%), m.p. 151–153°, λ_{OH} 2·98; λ_{CO} 5·24, 5·80 μ. (Found: C, 65·31; H, 4·87; N, 4·37. $C_{17}H_{15}NO_5$ requires: C, 65·17; H, 4·82; N, 4·47%).

4-Benzoyloxymethyl-3-phenyl-4-oxazolin-2-one (VIa)

A soln of Va (1·5 g) in glacial AcOH (5·0 ml) was heated 1 hr under reflux. Evaporation of the solvent under reduced press followed by trituration of the oily residue with Na_2CO_3 gave a solid, which was crystallized from EtOH to afford pure VIa (1·0 g, 71%), m.p. 135–137°, λ_{CO} 5·14, 5·81 μ. (Found: C, 68·95; H, 4·63; N, 4·67. $C_{17}H_{13}NO_4$ requires: C, 69·14; H, 4·44; N, 4·74%).

Glycolanilide benzoate (VII)

(a) *From* VIa. A soln of VIa (0·5 g) in $CHCl_3$ (5·0 ml) was slowly added to a stirred cold (0°) suspension of *p*-nitroperoxybenzoic acid (86%, 0·7 g) in $CHCl_3$ (5·0 ml). After 6 hr the mixture was poured into excess 10% Na_2CO_3, the organic layer was separated, washed with H_2O, dried and evaporated. The residue (0·2 g) was crystallized from benzene to afford VII, m.p. 151–153°.

(b) *From glycolanilide.* A soln of glycolanilide[12] (1·0 g) in pyridine (3·0 ml) was treated with benzoyl chloride (1·0 g). The mixture was heated 3 hr at 100°, then was poured into excess cold 10% Na_2CO_3. The solid which separated was crystallized from benzene to afford 1·1 g (65%) VII, identical with the previously obtained material. (Found: C, 70·41; H, 5·12; N, 5·32. $C_{15}H_{13}NO_3$ requires: C, 70·58; H, 5·13; N, 5·49%).

4-p-*Nitrobenzoyloxy-4-hydroxymethyl-2-phenyloxazolidin-2-one* (IIIb)

A soln of Ia (1·75 g, 10 mmoles) in $CHCl_3$ (30 ml) was slowly added to a suspension of 86% *p*-nitroperoxybenzoic acid (2·13 g, 10 mmoles) in $CHCl_3$ (100 ml), while stirring and cooling with a salt–ice mixture. Stirring at low temp was continued 1 hr, then the white solid was collected, washed with three 50 ml portions of $CHCl_3$ and dried: 2·2 g (63%). The product showed no definite m.p., and every attempt at further purification failed; it decomposed slowly even on standing in a vacuum desiccator over $CaCl_2$. IR: λ_{OH} 2·92; λ_{CO} 5·80 μ; the main absorption bands of Ia and of *p*-nitrobenzoic acid were absent. (Found: N, 7·12. $C_{17}H_{14}N_2O_7$ requires: N, 7·82%).

4-p-*Nitrobenzoyloxymethyl-4-hydroxy-3-phenyloxazolidin-2-one* (Vb)

A sample of IIIb (2·2 g) was triturated with 10% Na_2CO_3 (15 ml). The product was then collected, washed with H_2O and crystallized from EtOH to give Vb (1·9 g, 86%), m.p. 158–160°, λ_{OH} 3·01; λ_{CO} 5·80 μ. (Found: C, 56·75; H, 3·75; N, 7·60. $C_{17}H_{14}N_2O_7$ requires: C, 56·98; H, 3·94; N, 7·82%).

4-p-*Nitrobenzoyloxymethyl-3-phenyl-4-oxazolin-2-one* (VIb)

Treatment of Vb with glacial AcOH, as described for the preparation of VIa, resulted in conversion (65%) into VIb, m.p. 137–139° after crystallization from EtOH, λ_{CO} 5·64, 5·81 μ. (Found: C, 59·61; H, 3·32; N, 8·23. $C_{17}H_{12}N_2O_6$ requires: C, 59·53; H, 3·55; N, 8·23%).

* Prepared from phenyl isocyanate and propargyl alcohol by the sodium acetate method.[11]

Reactions of IIIb

(a) ***Reaction with benzoyl chloride.*** To a soln of IIIb (0·7 g) in pyridine (2·0 ml) was added a soln of benzoyl chloride (0·4 g) in pyridine (1·5 ml), while stirring and cooling at 0–5°. The mixture was allowed to stand overnight at room temp, then was poured into 10% Ba_2CO_3. The oil which separated solidified on treatment with EtOH, and was crystallized from the same solvent to afford 0·4 g (70%) VIa, identical with the previously obtained material.

(b) ***Reaction with phenyl isocyanate.*** A mixture of IIIb (1·0 g), phenyl isocyanate (0·5 g), pyridine (0·2 g) and benzene (8·0 ml) was heated 5 min under reflux, then was allowed to cool and filtered. The filtrate was evaporated under reduced press, and the residue was crystallized from EtOH–H_2O to afford 0·4 g (47%) *4-carbaniloxymethyl-3-phenyl-4-oxazolin-2-one* (VIII), m.p. 171–173°, λ_{NH} 3·0; λ_{CO} 5·70, 5·80 μ. (Found: C, 65·61; H, 4·67; N, 9·17. $C_{17}H_{14}N_2O_4$ requires: C, 65·80; H, 4·55; N, 9·03%).

p-Nitroperoxybenzoic acid oxidation of the above compound, carried out as described for the oxidation of VIa, gave a 70% yield of *glycolanilide carbanilate* (IX), m.p. 146–148°. (Lit.[5] m.p. 145–147°), identical with an authentic sample.

Reactions of IIIa

(a) ***Reaction with acetyl chloride.*** To a soln of IIIa (0·6 g) in pyridine (1·5 ml) was added a soln of acetyl chloride (0·2 ml) in pyridine (1·5 ml), while stirring and cooling at 0–5°. After the addition, the mixture was kept 3 hr at room temp, then was poured into excess 10% Na_2CO_3. The solid which separated was crystallized from cold DMSO–H_2O to give 0·65 g (95%) *4-acetoxymethyl-4-benzoyloxy-3-phenyloxazolidin-2-one* (Xa), m.p. 111–113°, λ_{CO} 5·65, 5·70 (sh), 5·80 μ. (Found: C, 63·98; H, 4·81; N, 3·74. $C_{19}H_{17}NO_6$ requires: C, 64·22; H, 4·82; N, 3·94%).

(b) ***Reaction with p-nitrobenzoyl chloride.*** To a soln of IIIa (0·6 g) in pyridine (1·5 ml) was added a soln of *p*-nitrobenzoyl chloride (0·4 g) in pyridine (1·0 ml), while stirring and cooling at 0–5°. After the addition the mixture was briefly heated at 60–70°, then was allowed to stand 3 hr at room temp. Addition of excess 10% Na_2CO_3 caused separation of a solid, which was collected, washed with H_2O and crystallized from cold DMSO–H_2O to afford 0·7 g (79%) *4-p-nitrobenzoyloxymethyl-4-benzoyloxy-3-phenyloxazolidin-2-one* (Xb), m.p. 140–141°, λ_{CO} 5·65, 5·80 μ. (Found: C, 62·25; H, 3·99; N, 5·83. $C_{24}H_{18}N_2O_8$ requires: C, 62·34; H, 3·92; N, 6·06%).

Crystallization of Xb from EtOH–H_2O caused conversion into VIb in 50% yield.

4-Methyl-4-hydroxyoxazolidinones XVa, b *and* c

To a soln of Ia (Ib or Ic; 1·0 g) in acetone–H_2O (90:10; 40 ml) was added 0·5 ml 2N H_2SO_4. After 24 hr at room temp the soln was neutralized with 10% Na_2CO_3. Evaporation of the solvent followed by crystallization of the residue from the appropriate solvent (cf Table 1) afforded the products in 80–85% yield. IR: XVa, λ_{OH} 2·99; λ_{CO} 5·76 μ. XVb, λ_{OH} 3·00; λ_{CO} 5·75 μ. XVc, λ_{OH} 3·00; λ_{CO} 5·76 μ.

5,5-Dimethyl-3-phenyloxazolidin-2,4-dione (XVIb) *and 5,5-pentamethylene-3-phenyloxazolidin-2,4-dione* (XVIc)

A soln of Ib (1·79 g, 10 mmoles) in $CHCl_3$ (25 ml) was slowly added, while stirring and cooling with a salt–ice mixture, to a 9% soln of peroxybenzoic acid in $CHCl_3$ (31 ml, 20 mmoles). Stirring at low temp was continued 1 hr, then the mixture was diluted with $CHCl_3$, washed with 10% Na_2CO_3, H_2O, dried ($MgSO_4$) and evaporated. The residue (1·5 g, 83%) was crystallized from MeOH to give XVIb, m.p. 106–108°, λ_{CO} 5·50 (w), 5·79 (s) μ. (Found: C, 64·21; H, 5·46; N, 6·83. $C_{11}H_{11}NO_3$ requires: C, 64·38; H, 5·40; N, 6·93%).

In another run, 1 hr after the addition of peroxy acid the mixture was treated with excess 10% Na_2CO_3 and steam-distilled. The aqueous layer of the distillate was diluted with EtOH and treated with a 10% alcoholic soln of dimedone: the ppt was identical with an authentic sample of formaldehyde–dimedone.

A treatment of Ic with peroxybenzoic acid, carried out as described for Ib, gave in 85% yield XVIc, m.p. 137–139°, λ_{CO} 5·50 (w), 5·79 (s) μ, identical with an authentic sample.[6]

Compound Ib was identical with a sample obtained in 20% yield by ozonolysis of Ib according to the method of Sisido *et al.*[6]

A treatment both of Ib and Ic with one molar equivalent of peroxy acid gave mixtures containing equal proportions of oxidation products and starting materials. The use of *p*-nitroperoxybenzoic acid gave in both cases strictly analogous results.

Cyclization of α-ethynylbenzyl carbanilate (XVII)

To a soln of XVIII (2·0 g) in EtOH (5·0 ml) was added a soln of sodium (50 mg) in EtOH (2·0 ml). After the ensuing mild exotermic reaction had subsided, the mixture was diluted with water and extracted with ether. The etheral extract was washed with H_2O, dried ($MgSO_4$) and evaporated to give an oily residue (A, 1·7 g). This gave on TLC two spots, a major one with R_f 0·61 and a minor one with R_f 0·39.

A 0·5 g sample of A was dissolved in 30 ml of acetone–H_2O (90:10), and the soln was acidified with 0·2N H_2SO_4 (0·3 ml). After 24 hr the solvent was partially evaporated, the oily ppt was collected and crystallized from EtOH to give 0·2 g *4-methyl-4-hydroxy-3,5-diphenyloxazolidin-2-one* (XVd), λ_{OH} 2·95; λ_{CO} 5·70, 5·72 μ; other data, cf Table 1.

A soln of XVd (0·2 g) in EtOH (3·0 ml) was acidified with conc H_2SO_4 (0·2 ml), then was heated to boiling and allowed to cool. The ppt was collected and crystallized from benzene–light petroleum to give 0·15 g *4-methyl-3,5-diphenyl-4-oxazolin-2-one* (XVIII), m.p. 113–115°, λ_{CO} 5·75 μ; NMR ($CDCl_3$) 2·17 δ (s, 3, CH_3); 7·50 δ (m, 10, 3 and 5 C_6H_5). (Found: C, 76·32; H, 4·94; N, 5·68. $C_{16}H_{13}NO_2$ requires: C, 76·47; H, 5·22; N, 5·57%).

A treatment of the mixture A (0·5 g) with warm ethanolic H_2SO_4 afforded 0·4 g XVIII.

Structure proof of XVIII. A sample of the title compound, on treatment with *p*-nitroperoxybenzoic acid as described for VIa gave a 70% yield of acetanilide, identical with an authentic sample.

Oxidation of A. A soln of the mixture A (1·3 g) in $CHCl_3$ (20 ml) was slowly added to a 4·8% soln of peroxybenzoic acid in $CHCl_3$ (16 ml), while stirring and cooling with a salt–ice mixture. Stirring at low temp was continued 30 min, then the soln was diluted with $CHCl_3$, washed with 10% Na_2CO_3, H_2O, dried and evaporated. The oily residue (0·9 g), which could not be induced to crystallize, gave on TLC four spots (R_f 0·21, 0·39, 0·63 and 0·68). Parallel samples of acetanilide and of 3,5-diphenyloxazolidin-2,4-dione (XIX) had R_f 0·21 and 0·68, respectively.

Acknowledgement—The authors are grateful to Professor Antonio Marsili for many helpful discussions. This work was supported in part by a grant from Consiglio Nazionale delle Richerche.

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