Iminyls. Part 5.[1] Intramolecular Hydrogen Abstraction by Alkyl(aryl)-iminyls.† A New Tetralone Synthesis

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Tetralones can be synthesised by oxidation of phenylalkylideneamino-oxyacetic acids with persulphate. The iminyls formed initially abstract a γ-hydrogen from the alkyl chain and the resulting carbon radicals then cyclise onto the benzene ring. The same iminyls, when generated in benzene solution by thermolysis of imino-oxyperacetates, do not abstract γ-hydrogen unless trifluoroacetic acid is present. Hence, the hydrogen abstracting species in both cases is thought to be the protonated iminyl ($RArC=\overset{+}{N}\overset{\cdot}{H}$).

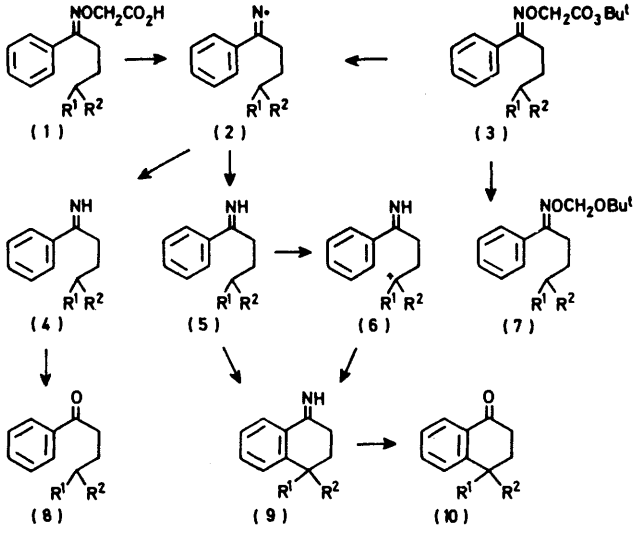
In Part 4[1] it was shown that diaryliminyls intramolecularly abstract γ-hydrogen atoms from *o*-alkyl substituents. In principle, intramolecular hydrogen abstraction from the alkyl chain of aryl(alkyl)iminyls is also possible and with this aim we investigated the reactions of several aryl[alkyl (C_3 or higher)]iminyls.

Table 1

Yields of products (%) from iminyls (2) and (12)

Iminyls	Method of generation *	Cyclic ketone (10) or (13)	Acyclic ketone (8)	Other products
(2; $R^1 = R^2 = Me$)	A	73	5	1 (19; $R^1 = R^2 = Me$)
(2; $R^1 = H$, $R^2 = Me$)	A	57	9	1 (19; $R^1 = H$, $R^2 = Me$)
(2; $R^1 = R^2 = H$)	A	32 (20) †	47 (55) †	
(2; $R^1 = R^2 = Me$)	B		12 (17) ‡	39 (38) ‡ (7; $R^1 = R^2 = Me$)
(2; $R^1 = R^2 = Me$)	B (CF_3CO_2H)	21	5	14 (7; $R^1 = R^2 = Me$)
				17 (15; $R^1 = R^2 = Me$)
(2; $R^1 = H$, $R^2 = Me$)	B		27	42 (7; $R^1 = H$, $R^2 = Me$)
(2; $R^1 = H$, $R^2 = Me$)	B (CF_3CO_2H)	21	16	18 (7; $R^1 = H$, $R^2 = Me$)
				25 (15; $R^1 = H$, $R^2 = Me$)
(2; $R^1 = R^2 = H$)	B		28	47 (7; $R^1 = R^2 = H$)
(2; $R^1 = R^2 = H$)	B (CF_3CO_2H)	6	47	18 (7; $R^1 = R^2 = H$)
				23 (15; $R^1 = R^2 = H$)
(12)	A	70	5	

* Method A, oxidation of the corresponding imino-oxyacetic acids with persulphate (yields based on isolated products); B, thermolysis of the corresponding t-butyl imino-oxyperacetates in benzene (yields based on g.l.c. measurements). † Yields based on g.l.c. measurements. ‡ Yields based on isolated products.



Scheme 1

Oxidation of the series of phenylalkylideneamino-oxyacetic acids (1; $R^1 = R^2 = H$, $R^1 = H$, $R^2 = Me$, $R^1 = R^2 = Me$) with persulphate [2] gave mainly mixtures of the cyclic (10) and acyclic (8) ketones (Table 1). The parent ketones (8) are the usual products [1,2] of the oxidation of imino-oxyacetic acids and are a measure of intermolecular hydrogen abstraction by the iminyl, *i.e.* (2) ⟶ (4) ⟶ (8). Concomitant formation of the cyclic ketones (10) requires the creation of a reactive centre (radical or cation) at the γ-carbon atom of the alkyl group followed by intramolecular aromatic substitution. The most obvious route to the cyclic ketones (10) entails hydrogen transfer of γ-H to the iminyl (2), *via* a six-membered transition state, followed by cyclisation of the resulting alkyl radical (5) to the imine precursor (9) of the cyclic ketone (10) (Scheme 1). The increase in the yield of cyclic ketone (10) and complementary decrease in that of acyclic ketone (8) with increasing ease of abstraction of the γ-hydrogen (tertiary > secondary > primary) is consistent with this proposal. Intermolecular hydrogen abstraction by the iminyl or by sulphate radical-anion from the alkyl chain of the imine (4), ketone (8), or acid (1) would not have proceeded with the specificity required to give, for example, a 73% yield of the ketone (10; $R^1 = R^2 = Me$). Indeed the reaction mixtures produced from all three acids were remarkably simple consisting almost entirely of cyclic and acyclic ketones.

The abstraction step (2) ⟶ (5) is analogous to known reactions of alkoxyls (Barton reaction),[3] triplet carbonyls

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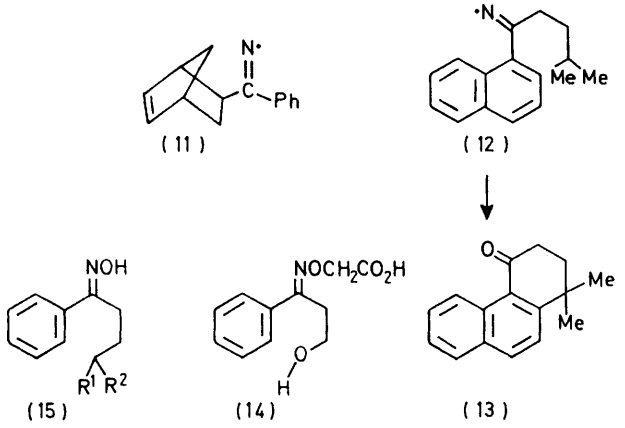
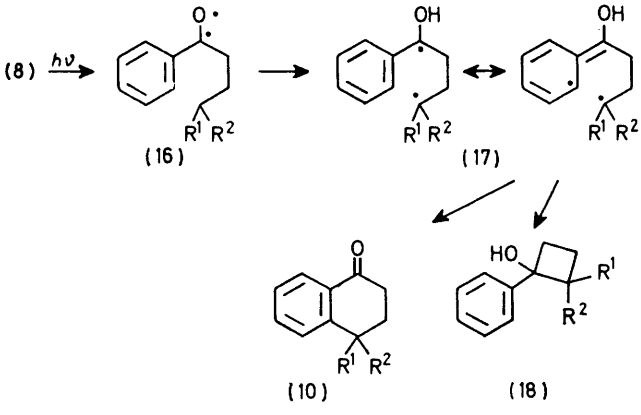
(Yang),[4] aminium ions (Hofmann–Loffler–Freytag),[5] carboxamidyls,[6] and sulphonamidyls.[6] The favoured transition state for 1,5 hydrogen transfer to alkoxyl



radicals has a chair conformation.[7] Although the iminyls (2) could adopt such a conformation phenyl-(*o*-tolyl)iminyl, which reacts similarly,[1] could not, hence the chair conformation is not essential for 1,5 hydrogen transfer in iminyls. The N–γ-H distance is clearly the critical factor (*cf.* ref. 8) since the bicyclic iminyl (11) (two stereoisomers) which have γ-H remote from N (>3 Å) only gave the corresponding ketones. Although



the hydrogen abstraction step (2) ⟶ (5) is closely analogous to known reactions [(16) ⟶ (18)] of structurally related triplet carbonyls,[7] the latter normally give cyclobutanes as final products. We know of only one example[9] where photolysis of an alkyl aryl ketone gives a tetralone derivative by the sequence (8) ⟶ (16) ⟶ (17) ⟶ (10).

Persulphate oxidation of the imino-oxyacetic acid precursor of the iminyl (12) gave the cyclic ketone (13) in high yield. There was no evidence, from product analysis, for the competing cyclisation at the 8-position of the naphthalene ring. Persulphate readily oxidises primary alcohols[10] and hence hydrogen transfer from –OH to >C=Ṅ (*cf.* ref. 11) could not be studied using this method of iminyl production and oxidation of the hydroxy-acid (14) gave no useful result.

Thermal decomposition of the homologous series of peresters (3; $R^1 = R^2 = H$; $R^1 = H$, $R^2 = Me$; $R^1 = R^2 = Me$) in benzene gave mainly the acyclic ketones (8) and acetals (7) (Table 1). This was an unexpected result from which we initially concluded that cyclisation (5) ⟶ (9) required prior oxidation of the alkyl radical (5) to the carbonium ion (6) and that this oxidation could be achieved with persulphate[12] ($S_2O_8^{2-}$ or $SO_4^{-\cdot}$) but not with the perester. Related cyclisations of both alkyl radicals[13] and carbonium ions[14] have been reported. In some cases, where the alkyl radical is generated using a transition metal ion (Mn^{III}) it is not certain which is the reacting species.[15] However, addition of catalytic amounts of Cu^{I} or Cu^{II} or an excess of Cu^{II} ions to the perester decompositions to ensure efficient oxidation of the alkyl radicals to the corresponding carbonium ions (or to an organocopper intermediate which would behave similarly)[16] had little effect on the product mixture. However, conversion into the cyclic ketones was achieved by addition of trifluoroacetic acid to the perester decompositions. The difference in reactivity between aminyls ($R_2N\cdot$) and aminium ions ($R_2\overset{+}{N}H$) as hydrogen abstractors is well known[5,17] and we now submit that a similar difference exists between iminyls and iminium radical-cations [equation (i)], the latter

$$R_2C{=}N\cdot + H^+ \rightleftharpoons R_2C{=}\overset{+}{N}H \qquad \text{(i)}$$

being the better hydrogen abstractors. To our knowledge iminium radical-ions were previously unknown and this is the first report of their behaviour.

The basicity of iminyls will be less than that of the corresponding imines due to the increased *s* character of the unshared electron pair.[18] A similar difference, and for the same reasons, has been established[19] for dialkylaminyls and dialkylamines [pK_a of $Me_2\overset{+}{N}H$ and $Me_2\overset{+}{N}H_2$ is 7.0 (±0.5) and 10.7, respectively]. Since imines are generally less basic than dialkylamines[20] (pK_a of cyclo-$C_6H_{10}{=}\overset{+}{N}H_2$ is 9.13), iminyls will be less basic than aminyls and the pK_a of $R_2C{=}\overset{+}{N}H$ will be <7.0. Aminium ions cannot be detected by e.s.r.[19] in solutions of pH >5.2 and generally reactions of aminium ions are conducted[5,17] in strongly acidic media of pH <1.0.

Hot aqueous solutions of persulphate become acidic (pH ≈3.7) due to formation of hydrogen sulphate [equation (ii)] and iminyls generated in such solutions

$$SO_4^{-\cdot} \longrightarrow HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \qquad \text{(ii)}$$

will be in equilibrium with their iminium radical-ions. Although it is clear from the above discussion that the equilibrium concentration of iminium radical-ions will be low they could still play a key role in the formation of the tetralones (10). If this were so then the ratio of cyclic (10) to acyclic (8) ketone should be dependent on the pH of the medium. Accordingly, the iminyl (2; $R^1 = R^2 = H$) was generated in aqueous or aqueous acetonitrile solutions of different pH and the ratio [(8)] : [(10)] determined by g.l.c. measurement of the product mixtures. The ratios given in Table 2 show

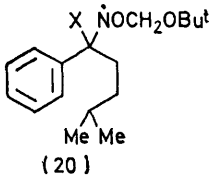
clearly how tetralone (10) formation increases as the pH decreases and lends further support to the notion that iminium radical-ions are the principal hydrogen abstracting species in these oxidations.

TABLE 2

Ratio of cyclic to acyclic ketone obtained from the acid (1; $R^1 = R^2 = H$) with persulphate

Medium	pH	Ketone ratio [(8) : (10)]
CH_3CN–H_2O (1 : 1)	6.05	25.1
CH_3CN–H_2O (9 : 1)	5.2	11.1
CH_3CN–H_2O (1 : 1)	4.7	5.5
H_2O	3.5	2.7
CH_3CN–H_2O (1 : 1)	0.9	2.5

E.s.r. Spectra.—The spectra of the iminyls (2; $R^1 = R^2 = Me$, $R^1 = Me$, $R^2 = H$, and $R^1 = R^2 = H$) were detected when the corresponding t-butyl peresters (3) were thermolysed in benzene solution in the spectrometer. All had a_N 10.0 G and g 2.003 0; the proton hyperfine splitting could not be resolved. In one case (2; $R^1 = R^2 = Me$) the spectrum of the alkoxyaminyl



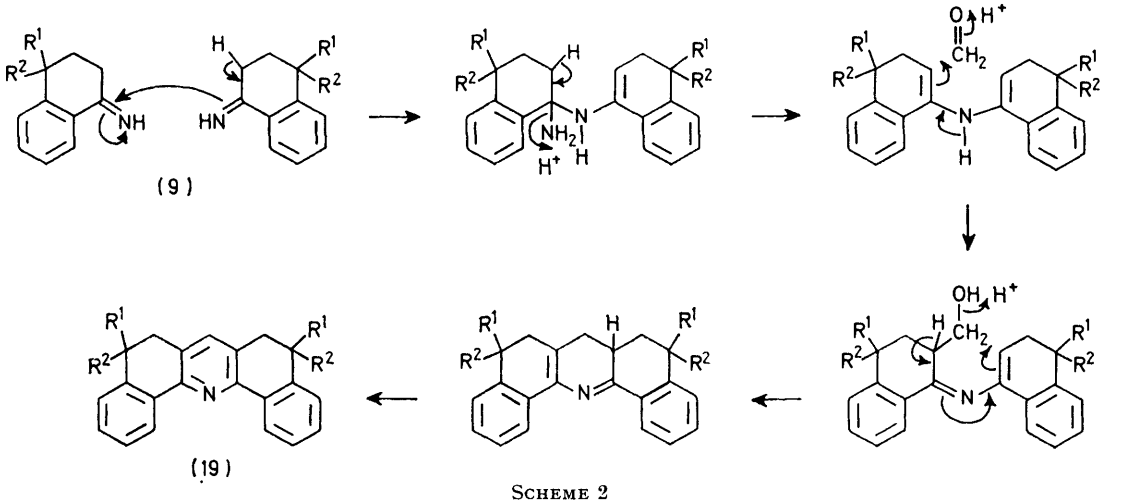
(20)

(20) (a_N 14.0 G, g 2.005 3) was also detected. When the peresters (3) and t-butyl diphenylmethyleneamino-oxyperacetate were decomposed in benzene containing trifluoroacetic acid (2 drops) the spectra of the corresponding iminyls faded and signals (a_N 30.0 G) attributed to the corresponding iminoxyls emerged. On further addition of trifluoroacetic acid the iminyl spectra disappeared leaving only the iminoxyl spectra. Spectra attributable to the iminium radical ions $R_2C{=}\dot{\overset{+}{N}}H$ were not detected irrespective of the amount of acid added. The iminoxyl radicals arise by reaction of the oxime (15) and t-butoxyl radicals. The latter are produced on decomposition of the peresters (3) and the former by acid catalysed hydrolysis of the acetals (7) [equation (iii)]. The oximes (15) are formed in 20—25% yield on decomposition of the peresters (3), in the presence of acid at

$$R_2C{=}NOCH_2OBu^t \longrightarrow R_2C{=}NOH + CH_2O + Bu^tOH \quad \text{(iii)}$$

the expense of the acetal (7) (Table 1). The small amount of water required to effect hydrolysis of the acetals must be present in the trifluoroacetic acid added.

Minor Products.—The imino-oxyacetic acids (1; $R^1 = H$, $R^2 = Me$, and $R^1 = R^2 = Me$) each gave, in very low yield, a further colourless oxidation product which fluoresced strongly on u.v. irradiation. That from the former acid had molecular formula $C_{23}H_{21}N$, showed n.m.r. signals arising from two identical $(Me)CHCH_2$ groups [δ 1.27 (3 H, d) and multiplets centred around



SCHEME 2

δ 2.72 (3 H) and 3.14 (3 H)], and a ratio of aryl to alkyl H of 9 : 12. The other, $C_{25}H_{25}N$, showed signals from two identical $(Me)_2CCH_2$ groups [singlets at δ 1.31 and 2.84 (ratio 3 : 1)]. Neither absorbed in the i.r. in the range 3 050—3 500 cm^{-1}. To these products we assign structures (19; $R^1 = H$, $R^2 = Me$, and $R^1 = R^2 = Me$).

The most likely route to these heterocycles is *via* the cyclic imine (9) the additional carbon atom being provided by the formaldehyde [from (1)] in a type of Hantzsch synthesis [21] as indicated in Scheme 2. In view of the ease of hydrolysis of the imine and oxidation of the formaldehyde in the boiling aqueous (acidic) persulphate solution the low yields are not surprising.

EXPERIMENTAL

I.r. spectra were measured as KBr discs and n.m.r. spectra in deuteriochloroform, unless stated otherwise. Petrol refers to light petroleum, b.p. 60—80°, and silica to the Merck product GF_{254}.

Preparation of Ketones and Oximes.—Ketones were either purchased or prepared from the appropriate alkylmagnesium bromide and arenecarbonitrile using standard procedures.[22] 1-Phenylbutan-1-one, 4-methyl-1-phenylpentan-1-one, and 1-phenylpentan-1-one are known compounds. *4-Methyl-1-(1-naphthyl)pentan-1-one* is an oil, b.p. 206—208° at 0.5

mmHg (Found: C, 84.9; H, 8.3. $C_{16}H_{18}O$ requires C, 84.9; H, 8.0%), $\nu_{max.}$ 1 680 cm^{-1}, δ 0.93 (6 H, d, *J* 4 Hz, Me_2CH), 1.69 (3 H, m, CH_2CHMe_2), 3.03 (2 H, t, *J* 7.2 Hz, $COCH_2$), 8.59 (1 H, m, *peri*-ArH) whose 2,4-*dinitrophenylhydrazone* gave orange needles, m.p. 170—172° (from acetic acid) (Found: C, 65.0; H, 5.7; N, 13.5. $C_{22}H_{22}N_4O_4$ requires C, 65.0; H, 5.45; N, 13.8%). 3-Hydroxy-1-phenylpropan-1-one was prepared by hydrolysis of 3-bromopropiophenone.[23] *endo*- and *exo*-5-benzoyl-2-norbornenes were obtained by chromatographic separation (p.l.c.) of a commercial mixture of the isomers on silica in chloroform–petrol (6 : 4). Their identities were confirmed by their n.m.r. spectra.[24]

Oximes were prepared from the ketone (0.1 mol), hydroxylamine hydrochloride (0.22 mol), and potassium hydroxide (0.5 mol) in aqueous ethanol under reflux. 4-*Methyl*-1-(1-*naphthyl*)*pentan*-1-*one oxime* was an oil (Found: C, 79.7; H, 8.1; N, 5.9. $C_{16}H_{19}NO$ requires C, 79.65; H, 7.95; N, 5.8%).

Norborn-2-*en*-5-*yl phenyl ketone oximes*. A solution of commercial 5-benzoylnorborn-2-ene (1.98 g) and hydroxylamine hydrochloride (1.4 g) and ethanol (20 ml) in 2M-sodium hydroxide (20 ml) was refluxed for 3 h. On cooling norborn-2-en-5-yl phenyl ketone oxime (700 mg) separated as needles, m.p. 142—146° (from aqueous ethanol) (Found: C, 78.6; H, 7.1; N, 6.7. Calc. for $C_{14}H_{15}NO$: C, 78.85; H, 7.1; N, 6.55%). Dilution of the mother liquors and purification of the product on silica (p.l.c.) in chloroform gave two isomers, one (higher R_F) (600 mg) identical with that described above and the other (lower R_F) (900 mg), m.p. 102—106° [with difficulty from petrol (b.p. 30—40°)] (Found: C, 79.1; H, 7.1; N, 6.4%). Similar oximation of the pure *endo*- and *exo*-ketones gave mixtures of oximes.

Preparation of Imino-oxyacetic Acids.—These were prepared from the oxime, chloroacetic acid, and alkali as previously described.[1,2] The following are new. 1-*Phenylbutylideneamino-oxyacetic acid* formed needles, m.p. 64—68° (from hexane) (Found: C, 65.0; H, 6.9; N, 6.6. $C_{12}H_{15}NO_3$ requires C, 65.15; H, 6.85; N, 6.35%), $\nu_{max.}$ 1 726 and 1 707 cm^{-1}, δ 4.75 (2 H, s, OCH_2); 1-*phenylpentylideneamino-oxyacetic acid* gave needles, m.p. 44—48° (from hexane) (Found: C, 66.2; H, 7.4; N, 6.1. $C_{13}H_{17}NO_3$ requires C, 66.35; H, 7.3; N, 5.95%), $\nu_{max.}$ 1 727 cm^{-1}, δ 4.75 (2 H, s, OCH_2); 4-*methyl*-1-*phenylpentylideneamino-oxyacetic acid* afforded plates, m.p. 56—58° (from hexane) (Found: C, 67.5; H, 7.6; N, 5.7. $C_{14}H_{19}NO_3$ requires C, 67.45; H, 7.7; N, 5.6%), $\nu_{max.}$ 1 732 cm^{-1}, δ 4.73 (2 H, s, OCH_2); 4-*methyl*-1-(1-*naphthyl*)*pentylideneamino-oxyacetic acid* gave rosettes, m.p. 96—98° (from hexane) (Found: C, 72.5; H, 7.1; N, 4.6. $C_{18}H_{21}NO_3$ requires C, 72.2; H, 7.05; N, 4.7%), $\nu_{max.}$ 1 728 cm^{-1}, δ 4.78 (2 H, s, CH_2); α-*norborn*-2-*en*-5-*ylbenzylideneamino-oxyacetic acid* yielded needles, m.p. 84—92° (from chloroform–petrol) (Found: C, 70.7; H, 6.6; N, 5.3. $C_{16}H_{17}NO_3$ requires C, 70.85; H, 6.3; N, 5.15%), $\nu_{max.}$ 1 720 cm^{-1}, δ 4.52 and 4.59 (total 4 H, each s, OCH_2) (two geometrical isomers); α-*norborn*-2-*en*-5-*ylbenzylideneamino-oxyacetic acid*, needles, m.p. 97—101° (from petrol) (Found: C, 70.6; H, 6.5; N, 5.2. $C_{16}H_{17}NO_3$ requires C, 70.85; H, 6.3; N, 5.15%), $\nu_{max.}$ 1 720 cm^{-1}, δ 4.55 and 4.48 (total 4 H, each s, OCH_2) (two geometrical isomers).

3-*Hydroxy*-1-*phenylpropylideneamino-oxyacetic acid* was prepared from the ketone (1 mol), amino-oxyacetic acid hemihydrochloride (1 mol), and sodium acetate in ethanol–water (9 : 1) under reflux for 3 days. It gave an oil (Found: M^+, 223.084 3. $C_{11}H_{13}NO_4$ requires *M*, 223.084 4) $\nu_{max.}$ 1 730 cm^{-1}, δ 3.10 (2 H, t, *J* 5.4 Hz, CH_2OH), 3.90 (2 H, t, *J* 5.4 Hz, $CH_2C{=}N$), 4.73 (2 H, s, OCH_2), and 8.23br (2 H, s, 2OH).

Preparation of t-Butyl Peresters of Imino-oxyacetic Acids.—These were prepared from the corresponding acid, diimidazolyl ketone, and t-butyl hydroperoxide as previously described.[2,26] *t-Butyl* 1-*phenyl*-4-*methylpentylideneamino-oxyperacetate* gave an oil (Found: C, 67.5; H, 8.5; N, 4.6. $C_{18}H_{27}NO_4$ requires C, 67.25; H, 8.45; N, 4.35%), $\nu_{max.}$ 1 795 cm^{-1}, δ 0.93 (6 H, d, *J* 5.5 Hz, Me_2CH), 1.32 (9 H, s, Bu^t), 1.42 (3 H, m, CH and CH_2), 2.82 (2 H, m, CH_2CO), 4.79 (2 H, s, OCH_2), and 7.14—7.73 (5 H, m, ArH); *t-butyl* 1-*phenylpentylideneamino-oxyperacetate* gave an oil (Found: C, 66.1; H, 8.4; N, 4.3. $C_{17}H_{25}NO_4$ requires C, 66.4; H, 8.2; N, 4.6%), $\nu_{max.}$ 1 785 cm^{-1}, δ 0.95 (3 H, t, Me), 1.30 (9 H, s, Bu^t), 1.30—1.60 (4 H, m, CH_2CH_2), 2.82 (2 H, t, CH_2CO), 4.80 (2 H, s, OCH_2), and 7.2—7.7 (5 H, m, ArH); *t-butyl* 1-*phenylbutylideneamino-oxyperacetate* gave an oil (Found: C, 65.2; H, 7.8; N, 4.5. $C_{16}H_{23}NO_4$ requires C, 65.5; H, 7.9; N, 4.8%), $\nu_{max.}$ 1 785 cm^{-1}, δ 0.98 (3 H, t, Me), 1.30 (9 H, s, Bu^t), 1.3—1.7 (2 H, m, CH_2), 2.80 (2 H, t, CH_2CO), 4.80 (2 H, s, OCH_2), and 7.2—7.8 (5 H, m, ArH).

Oxidations of Imino-oxyacetic Acids with Persulphate.—These were carried out as previously described.[1,2]

1-*Phenylpentylideneamino-oxyacetic acid* (2.35 g) gave (i) 1-phenylpentan-1-one (128 mg, 9%) identical with authentic material; (ii) 4-methyl-1-tetralone (788 mg, 57%) as an oil, $\nu_{max.}$ 1 685 cm^{-1}, δ 1.31 (3 H, d, *J* 7.5 Hz, MeCH), 1.6—3.3 (5 H, m, CH_2CH_2CHMe), 7.0—7.6 (3 H, m, ArH), and 7.97 (1 H, dd, ArH *peri* to CO); its 2,4-dinitrophenylhydrazone gave orange leaflets, m.p. 218—221° (from acetic acid) (lit.,[27] 218°) (Found: N, 16.6. Calc. for $C_{17}H_{16}N_4O_4$: N, 16.45%); (iii) 5,6,8,9-*tetrahydro*-5,9-*dimethyldibenz*[c,h]*acridine* (one isomer) (10 mg, 0.75%) as rhombs, m.p. 193—195° (from petrol) (Found: M^+, 311.167 6. $C_{23}H_{21}N$ requires *M*, 311.167 3), δ 1.27 (6 H, d, *J* 6 Hz, 2MeCH), 2.72 and 3.14 (6 H, m, $2CH_2CH$), 7.22—7.49 (7 H, m, ArH), and 8.56 (2 H, dd, ArH adjacent to N); and (iv) unchanged acid (333 mg).

4-Methyl-1-phenylpentylideneamino-oxyacetic acid (2.5 g) gave (i) 4-methyl-1-phenylpentan-1-one (100 mg, 5%) identical with an authentic specimen; (ii) 4,4-dimethyl-1-tetralone (1.1 g, 73%) as an oil, $\nu_{max.}$ 1 685 cm^{-1}, δ 1.38 (6 H, s, Me_2), 2.01 (2 H, t, *J* 6 Hz, CH_2CMe_2), 2.73 (2 H, t, *J* 6 Hz, CH_2CO), 7.2—7.6 (3 H, m, ArH), and 8.04 (1 H, dd, ArH *peri* to CO); its 2,4-dinitrophenylhydrazone gave red plates, m.p. 223—224° (from acetic acid) (lit.,[28] 217—218°) (Found: N, 15.7. Calc. for $C_{18}H_{18}N_4O_4$: N, 15.8%); (iii) 5,6,8,9-*tetrahydro*-5,5,9,9-*tetramethyldibenz*[c,h]*acridine* (12 mg, 0.8%) as prisms, 250—252° (from chloroform–petrol or methyl ethyl ketone); the analytical sample was sublimed at 230° and 0.4 mmHg (Found: C, 88.2; H, 7.3; N, 4.4%; M^+, 339. $C_{25}H_{25}N$ requires C, 88.45; H, 7.4; N, 4.15%; *M*, 339), δ 1.31 (12 H, s, $2Me_2C$), 2.84 (4 H, s, $2CH_2$), 7.26—7.43 (7 H, m, ArH), 8.61 (2 H, m, ArH adjacent to N); and (iv) unchanged acid (330 mg).

1-Phenylbutylideneamino-oxyacetic acid (44 mg) gave (i) 1-phenylbutan-1-one (13.8 mg, 47%) and (ii) 1-tetralone (9.2 mg, 32%) both identical with authentic samples.

In separate experiments, the same acid (221 mg, 0.001 mol) and sodium hydroxide (0.001 mol) were dissolved in (a) water (55 ml), (b) water (1 ml) and acetonitrile (54 ml), (c) water (25 ml) and acetonitriile (30 ml), (d) and (e) water (20 ml) and acetonitrile (30 ml) and the solutions heated

under reflux. To (a)—(c) potassium persulphate (297 mg, 0.001 1 mol) in water (5 ml), to (d) potassium persulphate (297 mg) in 0.3M-sulphuric acid (10 ml), and to (e) potassium persulphate (297 mg) in 0.31M-sodium hydroxide (10 ml) were added. After 10—15 min the solutions were cooled, their pH values measured [(a) 3.5, (b) 5.2, (c) 4.7, (d) 0.85, and (e) 6.05], and acetonitrile was removed *in vacuo*. The aqueous residues were extracted with ether and the ethereal extracts were washed with hydrochloric acid and sodium hydroxide solution. The dried ethereal extracts were evaporated and the residues analysed by g.l.c. using a column of silicone gum rubber E-301 on AN-DMCS Chromosorb G, 80—100 mesh at 150°. Results are given in Table 2.

4-Methyl-1-(1-naphthyl)pentylideneamino-oxyacetic acid (120 mg) gave *4,4-dimethyl-3,4-dihydro-1(2H)-phenanthrone* (55 mg, 70%) as an oil (Found: C, 85.5; H, 7.2%. $C_{16}H_{16}O$ requires C, 85.7; H, 7.2%), $\nu_{max.}$ 1 670 cm^{-1}, δ 1.43 (6 H, s, Me_2C), 2.05 and 2.85 (total 4 H, each t, *J* 7.2 Hz, CH_2CH_2CO), 7.41—8.01 (5 H, m, ArH), and 9.29 (1 H, dd, ArH *peri* to CO); its *2,4-dinitrophenylhydrazone* gave orange-red plates, m.p. 235—237° (from acetic acid) (Found: C, 65.6; H, 5.1; N, 13.7. $C_{22}H_{20}N_4O_4$ requires C, 65.35; H, 5.0; N, 13.85%); (ii) 4-methyl-1-(1-naphthyl)-pentan-1-one (4 mg, 5%), identical with synthetic material.

Thermolysis of the t-Butyl Peresters of Imino-oxyacetic Acids.—The peresters (3) (0.001 mol) in (a) benzene (10 ml) and (b) benzene (10 ml) containing 6 drops of trifluoroacetic acid were heated under reflux for 1 h. The solutions were extracted with sodium hydroxide solution to remove acidic material and then analysed by g.l.c. as before. The yields of products are given in Table 1.

The acetals (7) are the only new compounds produced in these decompositions. After g.l.c. analysis of the product mixtures the acetals were separated by chromatography. *(4-Methyl-1-phenylylideneamino-oxy)-t-butoxymethane* was an oil (Found: C, 74.0; H, 9.7; N, 5.0. $C_{17}H_{27}NO_2$ requires C, 73.6; H, 9.8; N, 5.05%), δ 0.94 (6 H, d, *J* 5.4 Hz, Me_2CN), 1.31 (9 H, s, Bu^t), 1.40 (3 H, m, CH_2CHMe_2), 2.75 (2 H, m, $CH_2C{=}N$), 5.40 (2 H, s, OCH_2), and 7.27 (5 H, m, ArH). *(1-Phenylpentylideneamino-oxy)-t-butoxymethane* was an oil (Found: M^+, 263.188 2. $C_{16}H_{25}NO_2$ requires *M*, 263.188 5), δ 0.90 (3 H, t, Me), 1.30 (9 H, s, Bu^t), 1.2—1.7 (4 H, m, CH_2CH_2), 2.8 (2 H, m, $CH_2C{=}N$), 5.4 (2 H, s, OCH_2), and 7.40 (5 H, m, ArH). *(1-Phenylbutylideneamino-oxy)-t-butoxymethane* was an oil (Found: M^+, 249.173 0. $C_{15}H_{23}NO_2$ requires *M*, 249.172 8), δ 1.0 (3 H, t, Me), 1.30 (9 H, s, Bu^t), 1.2—1.7 (2 H, m, CH_2CH_3), 2.07 (2 H, t, $CH_2C{=}N$), 5.42 (2 H, s, OCH_2), and 7.20—8.10 (5 H, m, ArH).

Effect of Cu^I *and* Cu^{II} *Ions.*—Solutions of t-butyl 4-methyl-1-phenylpentylideneamino-oxyperacetate (321 mg) in benzene (10 ml) containing (a) copper(I) chloride (trace), (b) copper(II) chloride (trace), and (c) copper(II) chloride (1.34 g) were heated under reflux for 1 h. The solutions were then washed with sodium hydroxide solution, dried, and evaporated. Examination of the residues by n.m.r. spectroscopy showed the absence of 4,4-dimethyl-1-tetralone in each case.

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