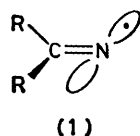


Iminyls. Part 1. Generation of Iminyls †

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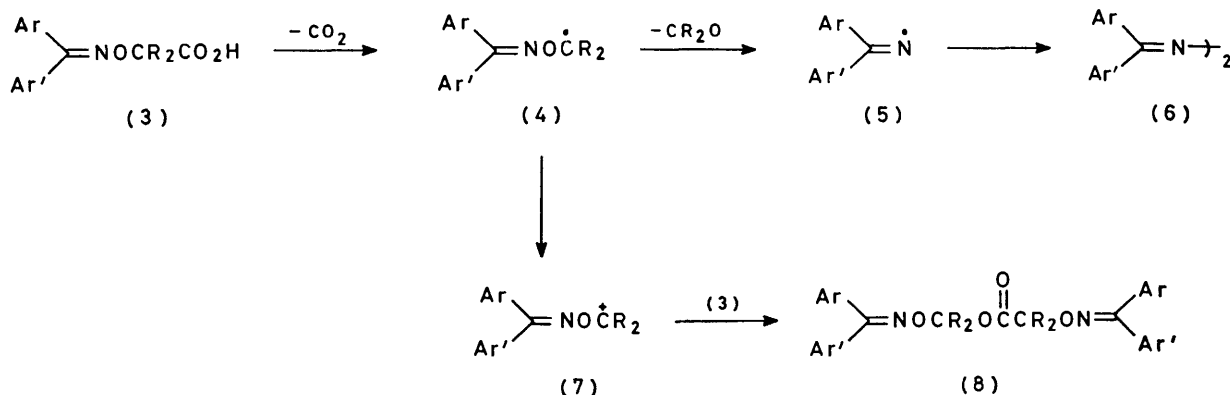
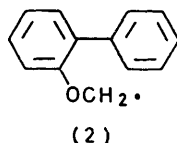
Four methods for producing iminyl radicals are described: oxidation of imino-oxyacetic acids with persulphate, thermolysis of the corresponding peresters, oxidation of oxime ethers with di-*t*-butyl peroxide, and photolysis of oxime oxalates. The first two are the most useful for chemical studies.

INTEREST in iminyl radicals has been stimulated by the recent detection and characterisation of numerous examples by e.s.r. spectroscopy.¹ The parameters derived from these spectra are consistent with a radical (1) in which the unpaired electron occupies a $2p$ orbital on nitrogen orthogonal to the $>C=N-$ π -system.^{1,2} Particularly notable are the very large a_{C-H} values of



aldiminyls, *ca.* 80 G, resulting from the strong hyperconjugative interaction implicit in the planar structure (1; R = H). At the outset of this work fragmentation³⁻⁶ to nitriles and alkyl radicals, reduction⁶ to imines, and dimerisation to azines were the only known reactions of iminyls. This was partly due to a lack of suitable methods of production since those used in the e.s.r. work are much less useful for chemical studies. We have explored several new methods of generating iminyls in both organic and aqueous solution, and report on

1 *Iminyls from Imino-oxyacetic Acids.*—Oxidation of *o*-phenylphenoxyacetic acid in boiling aqueous solution with persulphate generates *o*-phenylphenoxy-methyl radicals (2) which cyclise efficiently onto the adjacent aromatic ring to give a dibenzopyran.⁷ Similar oxidation of the imino-oxyacetic acid (3; Ar = Ar' = Ph, R = H) gave no cyclised product yielding instead the azine (6; Ar = Ar' = Ph) (97%) and formaldehyde. The corresponding fluorenyl acid (3; Ar, Ar' = fluoren-9-ylidene, R = H) behaved similarly but that from di-*t*-butyl ketoxime gave no useful result. The most likely route to these azines (6) is *via* the iminyls (5; Ar = Ar' = Ph and Ar, Ar' = fluorene-9-ylidene) formed by loss of formaldehyde from the initial imino-oxy-methyl radicals (4; R = H, Ar = Ar' = Ph and Ar, Ar' = fluorene-9-ylidene) (*cf.* ref. 8). Oxidation of the acid (3; Ar = Ar' = Ph, R = H) with persulphate in aqueous acetonitrile at 60° catalysed by silver(I) ions,^{9a} and with lead tetra-acetate^{9b} in boiling benzene [with or without addition of copper(II) acetate, pyridine, or lithium chloride] produced much lower yields of azine. A more promising alternative to persulphate was silver(II) picolinate¹⁰ in boiling benzene-pyridine



these herein. In the following papers these methods are used to produce new types of iminyl, and investigate new reactions of potential synthetic value.

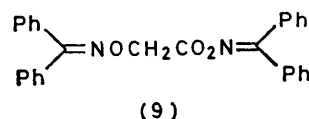
† Preliminary communication, A. R. Forrester, M. Gill, J. S. Sadd, and R. H. Thomson, *J.C.S. Chem. Comm.*, 1975, 291.

which gave the azine (6; Ar = Ar' = Ph) in 75% yield. However, other oxidations with this reagent were less effective. Hunsdiecker^{11,12} oxidation of the acids (3; Ar = Ar' = Ph, R = H, Ar = Ph, Ar' = *o*-MeC₆H₄, R = H and Ar = Ph, Ar' = 2,4,6-Me₃C₆H₂, R = Me)

in benzene gave the corresponding esters (8). These probably arise from the carbonium ion (7), formed by oxidation of the oxyalkyl radical (4), which is trapped by the anion of the acid. Ceric ammonium nitrate¹³ in aqueous acetonitrile, manganese dioxide, lead dioxide, silver(I) oxide, mercury(II) oxide in benzene, manganese tris(acetylacetonate),¹⁴ nickel peroxide¹⁵ in chloroform, oxygen (with and without palladium, platinum oxide, vanadium pentoxide or sodium tungstate) in benzene, cobalt(III) acetate¹⁶ (with and without pyridine or trifluoroacetic acid), and photolysis in the presence of the sensitizers benzoquinone and benzophenone,¹⁷ all failed to convert the acid (3; Ar = Ar' = Ph, R = H) efficiently into the azine.

2 Iminyls from Peresters of Imino-oxyacetic Acids.—The diacyl peroxides of the imino-oxyacetic acids (3) were too unstable to be used as a convenient source of iminyl radicals. Thus, when the acid chloride of (3; Ar = Ar' = Ph, R = H) was treated with sodium peroxide or hydrogen peroxide no diacyl peroxide was obtained. Instead, the azine (6; Ar = Ar' = Ph)

characterised. Some of these were prepared more efficiently by condensation of the acid with *t*-butyl hydroperoxide in the presence of di-imidazolyl ketone.^{18a}



Thermolysis of the perester (10; Ar = Ar' = Ph) in benzene gave the azine (6; Ar = Ar' = Ph) (21%), the

TABLE 1

Yields (%) of products obtained by decomposition of perester (10; Ar = Ar' = Ph) in benzene			
Concentration of perester (10) (M)	Acetal (11; Ar = Ar' = Ph)	Azine (6; Ar = Ar' = Ph)	Ph ₂ CO
1.00	25	21	40
0.10	22	20	38
0.01	24	10	37

acetal (11; Ar = Ar' = Ph) (25%), and benzophenone (40%). Other peresters gave similar results. The

TABLE 2

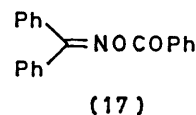
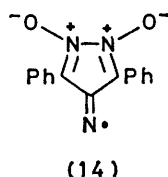
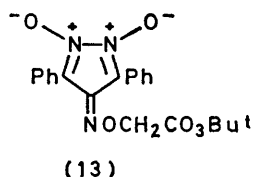
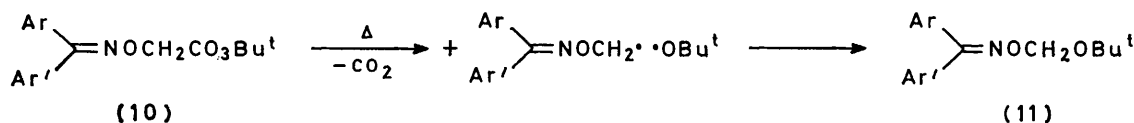
E.s.r. spectra of iminyls RR'C=N• (12)

Iminyl (12)	Source	Solvent	T/°C	g	Hyperfine coupling constants (G)
R = R' = Ph	Perester	C ₆ H ₆	75	2.0033	a _N 10.1, a _H 0.35 (8 H)
	Oxalate ester* (16)	C ₆ H ₆	75		
	Oxime ethers (15; R = Ph, R ¹ = R ² = H, Me, and Ph, R ¹ = H, R ² = Ph)	Bu ^t O ₂	25–60		
R, R ¹ = Fluoren-9-ylidene R = R ¹ = Bu ^t	Perester	Bu ^t C ₆ H ₅	95	2.0037	a _N 9.75
	Perester	C ₆ H ₆	65	2.0035	a _N 10.25, a _H 0.95 (18 H)
	Oxime methyl ether (15)	Bu ^t O ₂	–20	2.0032	a _N 10.2, a _H 1.0 (18 H)
R = H, R ¹ = Ph R = H, R ¹ = 1-C ₁₀ H ₇ (14)	Perester	C ₆ H ₆	75	2.0038	a _N 10.0, a _H 79.5 (1 H)
	Perester	C ₆ H ₆	75	2.0038	a _N 10.2, a _H 82.5 (1 H)
	Perester	C ₆ H ₆	75	2.0034	a _N 10.4

* Iminoxy, a_N 31.5 G, also detected.

(10%), benzophenone (10%), and its oxime (2%), the ester (8; Ar = Ar' = Ph, R = H) (15%), and the oxime

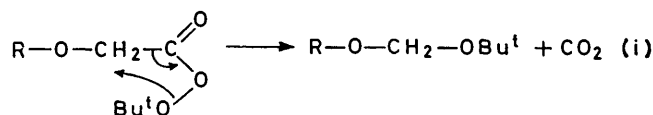
acetal (11) most probably arises by cage recombination of *t*-butoxyl and oxyalkyl radicals since in more dilute



ester (9) (2%) were isolated. Although all of these could arise by decomposition of the corresponding diacyl peroxide we have no direct evidence for its presence in the reaction mixture. However, the *t*-butyl peresters of imino-oxyacetic acids, formed by treatment of the corresponding acid chloride with *t*-butyl hydroperoxide, are normally sufficiently stable to be isolated and

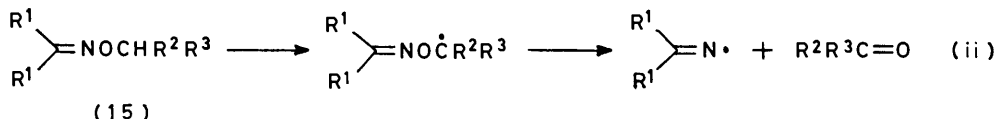
solution the yield of acetal did not decrease significantly (Table 1). The *t*-butyl peresters of α -alkoxyacetic acids are also reported to give relatively high yields of acetal by cage recombination of 'nucleophilic' alkoxyalkyl (ROCH₂•) and 'electrophilic' butoxyl (Bu^tO•) radicals.^{18b} However, the alternative concerted process [equation (i)] although less likely, has not been excluded.

Spectroscopic evidence for the mediation of iminyl radicals in the decomposition of the peresters was



obtained by heating *ca.* 1M solutions of the peresters in benzene at 75° (or at 95° in *t*-butylbenzene) in the cavity of an e.s.r. spectrometer. Strong signals were obtained from diphenyl- and di-*t*-butyl-iminyls, and weaker ones from the aldiminyls (12; R = H, R' = Ph and R = H and R' = 1-C₁₀H₇) and (12; R,R' = fluoren-9-ylidene). All had the spectroscopic parameters (*a_N* and *g*) expected¹⁻⁶ of iminyls (Table 2). Di-*t*-butyl- and diphenyl-iminyls were longer lived than the others because of steric protection³ of the nitrogen by the *t*-butyl and phenyl groups, respectively. Since no iminyl has yet been isolated (although impure samples of diadamantyliminyl have been obtained⁴) it was of interest to prepare and examine the decomposition of perester (13), the precursor of a highly hindered and potentially long-lived iminyl (14). However, only weak signals of the iminyl were observed and the products, although not fully characterised, contained no long-lived radical.

3 Iminyls from Oxime Ethers.—Hydrogen abstraction from the ethers (15) by *t*-butoxyl radicals, generated by thermolysis or photolysis of di-*t*-butyl peroxide or di-*t*-butyl peroxalate [equation (ii)], has been found to be of less value than methods 1 and 2 because yields of iminyl-derived products are usually lower.

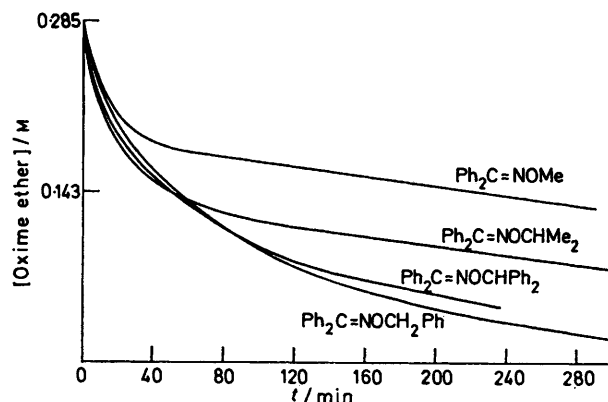


Efficient production of iminyls from oxime ethers (15) requires (a) the ready removal of an alkoxy hydrogen atom followed by (b) rapid fragmentation of the so-formed oxyalkyl radical. The effect of the structure of the alkoxy group on the first step was examined by allowing di-*t*-butyl peroxalate to decompose in solutions of the benzophenone oxime ethers (15; R¹ = Ph, R² = R³ = H; R² = R³ = Me; R² = Ph, R³ = H; R² = R³ = Ph) and monitoring the disappearance of the oxime ethers by n.m.r. The order of reactivity towards *t*-butoxyl, measured in this way, was diphenylmethyl \approx benzyl > isopropyl > methyl (Figure). Full kinetic analysis was not attempted because the fragmentation products (aldehyde or ketone) compete to differing extents with the substrate ethers for *t*-butoxyl radicals. For example, with the benzyl and methyl ethers, the formyl proton signals of benzaldehyde and formaldehyde, respectively, were never detected. In all cases benzophenone and its azine were the main products (t.l.c.).

The effect of structure on the fragmentation step could not be estimated because the intermediate oxyalkyl

radicals could not be detected by e.s.r. when the oxime ethers (15; R¹ = Ph, R² = R³ = H; R² = R³ = Me;

R² = R³ = Ph; R² = H, R³ = Ph) in di-*t*-butyl peroxide or in di-*t*-butyl peroxide-toluene were irradiated at or below room temperature. In each case the spectrum of diphenyliminyl only was detected. However,



Reaction of benzophenone oxime ethers with *t*-butoxyl radicals from di-*t*-butyl peroxalate

it is known that the ease of fragmentation of alkoxy-alkyl radicals increases with increasing size of substituents attached to the trigonal carbon¹⁹ and so for the radicals derived from the oxime ethers, the expected

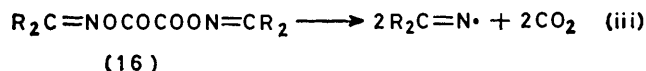
order would be Ph₂C=NOĊPh₂ > Ph₂C=NOĊHPh \approx Ph₂C=NOĊMe₂ > Ph₂C=NOĊH₂.

Hence for product studies, the methyl ether is not sufficiently reactive towards *t*-butoxyl radicals and the benzyl ether is likely to give additional products derived from benzoyl radicals (PhCHO + Bu^tO•). Although the diphenylmethyl is more reactive than the isopropyl ether, the latter is usually easier to prepare and gives acetone at the fragmentation step which is easier than benzophenone to separate from the other products.

The most intense e.s.r. spectra of diphenyliminyl were obtained from the benzyl ether. Its apparent superiority to the diphenylmethyl ether in this respect is due to its greater solubility in di-*t*-butyl peroxide which allowed more concentrated solutions to be examined. However, the intensity of the e.s.r. spectrum observed also depends on the lifetime of the iminyl and this is mainly determined by the size of the substituents attached to the imino carbon, *e.g.*, an intense spectrum of di-*t*-butyliminyl (15; R¹ = Bu^t, R² = R³ = H) was produced when the corresponding oxime *methyl* ether was irradi-

ated in di-*t*-butyl peroxide in the cavity at -20° . To date we have not been able to establish conditions under which iminyls can be generated from the acetals (11) by photolysis in the presence of di-*t*-butyl peroxide.

4 *Iminyls from Oxime Esters*.—Generation of iminyls by photolysis of oxime esters suffers from the disadvantage that the geminate acyloxy radicals also formed may determine the course of the subsequent iminyl reactions.²⁰ Oxalate esters (16) are superior in this respect [equation (iii)] and are readily available from oxalyl chloride and oxime. Photolysis of the oxalate



(16) in benzene caused rapid decomposition of the ester and formation of benzophenone (13%), its azine (21%), and oxime (14%). Benzophenone was formed by hydrolysis of the imine during isolation and is clearly an iminyl-derived product but formation of the oxime suggests that C–O competes with N–O bond fission during photolysis. E.s.r. measurements support this view since iminyl and iminoxyl spectra (both weak) were detected on irradiation of the oxalate ester in the cavity. By comparison, the benzoate ester (17) on irradiation in benzene gave only the iminoxyl [a_N 31.6, a_H 1.35 (2 H), g 2.006 6]. The esters (8) were unaffected by irradiation despite their ready fragmentation in the mass spectrometer with loss of carbon dioxide and formaldehyde.

EXPERIMENTAL

I.r. spectra were measured as KBr discs and n.m.r. spectra using deuteriochloroform as solvent, unless stated otherwise. Petrol refers to light petroleum, b.p. $60-80^\circ$ Merck silica gel GF₂₅₄ was used for chromatographic separations.

General Procedure for the Preparation of Imino-oxycetic Acids.—A solution of the oxime (0.12 mol), chloroacetic acid (0.2 mol), and sodium hydroxide (0.36 mol) in water (100 ml) and ethanol (50 ml) was heated under reflux for 16 h. The cooled reaction mixture was poured onto ice, and acidified with hydrochloric acid. The precipitate was collected, washed with water, and then dissolved in *m* aqueous hydrogencarbonate solution (100 ml). This solution was extracted with ether and then acidified. The resulting acid which precipitated was collected, washed with water, and crystallised.

The following acids were prepared in this way: diphenylmethyleneamino-oxycetic acid,²¹ benzylideneamino-oxycetic acid,²² fluoren-9-ylideneamino-oxycetic acid,²³ 1-naphthylmethyleneamino-oxycetic acid.²⁴ All showed ν_{max} 1 715–1 730 cm^{-1} sometimes accompanied by a shoulder at 1 710–1 700 cm^{-1} and δ 4.70–4.95 (OCH_2).

(1,2-Dioxido-3,5-diphenylpyrazol-4-ylidene)amino-oxycetic acid, prepared as above from the corresponding oxime²⁵ but using dimethylformamide as solvent, formed deep red rods, m.p. $202-205^\circ$ (from methanol–acetone–water) (Found: C, 60.2; H, 4.0; N, 12.3. $C_{17}H_{13}N_3O_5$ requires C, 60.2; H, 3.85; N, 12.4%), ν_{max} 1 764 and 1 737 cm^{-1} , δ 4.80 (CH_2).

*Di-*t*-butylmethyleneamino-oxycetic acid*. Pivalonitrile

(0.02 mol) was added slowly with stirring to 2*m-t*-butyllithium in petrol (10 ml) under nitrogen. After 1 h at room temperature ethanol (2 ml), acetic acid (1.2 ml), amino-oxycetic acid hemihydrochloride (2.2 g), and ethanol were added in sequence. The mixture was heated under reflux for 5 h and water was then added. Next day the bulk of the solvent was removed *in vacuo* and water was added to the residual oil. The solid which formed was collected, washed, and dried. The *oxycetic acid* (1.6 g, 38%) had m.p. $83-86^\circ$ (Found: C, 61.1; H, 9.6; N, 6.5. $C_{11}H_{21}NO_3$ requires C, 61.4; H, 9.8; N, 6.5%), ν_{max} (Nujol) 3 400–2 600, and 1 730 cm^{-1} , δ 4.55 (2 H, s, OCH_2), 1.39 (9 H, s,

Bu^t), and 1.23 (9 H, s, Bu^t), *m/e* 215 (M^+ , 1%), 173 (5), 140 (4), 84 (28), 68 (13), and 57 (100).

*Preparation of *t*-Butyl Peresters of Amino-oxycetic Acids*.—Diphenylmethyleneamino-oxycetyl chloride was obtained from the corresponding acid and thionyl chloride in the usual way. It formed needles, m.p. $59-62^\circ$ (from petrol) (Found: C, 65.9; H, 4.5; Cl, 13.2; N, 5.0. $C_{15}H_{12}ClNO_2$ requires C, 65.8; H, 4.4; Cl, 13.0; N, 5.1%), ν_{max} 1 796 cm^{-1} , δ 4.92 (CH_2). Similarly prepared were di-*t*-butylmethyleneamino-oxycetyl chloride as a colourless liquid, ν_{max} 1 818 cm^{-1} , and fluoren-9-ylideneamino-oxycetyl chloride as pale yellow needles, m.p. $125-127^\circ$ (from petrol) (Found: C, 66.1; H, 3.5; Cl, 13.4; N, 5.3. $C_{15}H_{10}ClNO_2$ requires C, 66.3; H, 3.7; Cl, 13.1; N, 5.15%), ν_{max} 1 809 cm^{-1} , δ 5.18 (CH_2).

t-Butyl diphenylmethyleneamino-oxycperacetate. To an ice-cold solution of the acid chloride (94 g, 0.35 mol) and *t*-butyl hydroperoxide (60.4 g, 0.67 mol) in a mixture of benzene (600 ml) and pentane (1 300 ml), an ice-cold solution of pyridine (30.2 g, 0.39 mol) in benzene–pentane (600 ml) was added. The mixture was stirred for 12 h before the pyridinium chloride was collected. The solvent was removed from the filtrate at room temperature, and the residue was dissolved in ether and washed with dilute hydrochloric acid, dilute sodium hydroxide, and water, and then dried. Evaporation of solvent and crystallisation of the residue from chloroform–petrol gave the *perester* (84 g, 74%) as needles, m.p. $71-72^\circ$ (Found: C, 69.8; H, 6.7; N, 4.4. $C_{19}H_{21}NO_4$ requires C, 69.7; H, 6.45; N, 4.3%), ν_{max} 1 783 cm^{-1} , δ 4.77 (2 H, s, CH_2), 1.30 (9 H, s, Bu^t). Similarly prepared were *t*-butyl fluoren-9-ylideneamino-oxycperacetate as needles, m.p. $55-57^\circ$ (from pentane) (Found: C, 70.5; H, 6.0; N, 4.6. $C_{19}H_{19}NO_4$ requires C, 70.15; H, 5.9; N, 4.3%), ν_{max} 1 786 cm^{-1} , δ 4.97 (2 H, s, CH_2) and 1.28 (9 H, s, Bu^t) and *t*-butyl di-*t*-butylmethyleneamino-oxycperacetate as a liquid (Found: C, 62.6; H, 10.4. $C_{15}H_{29}NO_4$ requires C, 62.7; H, 10.15%), ν_{max} 1 777 cm^{-1} , δ 4.61 (2 H, s, CH_2), 1.39 (9 H, s, Bu^t), 1.33 (9 H, s, Bu^t), and 1.23 (9 H, s, Bu^t).

t-Butyl benzylideneamino-oxycperacetate. To a stirred cold solution of the oxycetic acid (0.02 mol) in tetrahydrofuran (40 ml) under nitrogen, di-imidazolyl ketone¹⁸ (0.037 mol) was added in one portion. The mixture was stirred for 1 h before *t*-butyl hydroperoxide (0.025 mol) was added dropwise, at 0° . After stirring for a further 1 h ether was added and the resulting solution was washed successively with water, dilute hydrochloric acid, dilute sodium hydrogencarbonate solution, and water. Evaporation of the dried

(MgSO₄) solution yielded a crude product. Elution through a short column of silica GF₂₅₄ with petrol-chloroform (2 : 3) gave the *perester* as a liquid (Found: C, 61.9; H, 7.0; N, 5.7. C₁₃H₁₇NO₄ requires C, 62.15; H, 6.8; N, 5.5%), ν_{\max} 1 785 cm⁻¹, δ 1.31 (9 H, s, Bu^t), 4.73 (2 H, s, CH₂), 7.23—7.76 (5 H, m, ArH), and 8.22 (1 H, s, CH=N). Similarly prepared were *t*-butyl 1-naphthylmethyleamino-oxyperacetate as an oil (Found: C, 67.9; H, 6.6; N, 4.4. C₁₇H₁₉NO₄ requires C, 67.75; H, 6.35; N, 4.65%), ν_{\max} 1 785 cm⁻¹, δ 1.33 (9 H, s, Bu^t), 4.86 (2 H, s, CH₂), 7.45—7.98 (7 H, m, ArH), and 8.84 (1 H, s, CH=N) and *t*-butyl (1,2-dioxido-3,5-diphenylpyrazol-4-ylidene)amino-oxyperacetate (13) as orange needles, m.p. 105—107° (from chloroform-pentane) (Found: C, 61.0; H, 5.3; N, 10.2. C₂₁H₂₁N₃O₆ requires C, 61.3; H, 5.15; N, 10.2%), ν_{\max} 1 778 cm⁻¹, δ 1.30 (9 H, s, Bu^t), 4.76 (2 H, s, CH₂), 7.42 (6 H, m, ArH), 7.73 (2 H, m, ArH), and 8.16 (2 H, m, ArH).

Oxime Methyl Ethers (15).—2,2,4,4-Tetramethylpentan-3-one oxime *O*-methyl ether. This was prepared as described for the corresponding oxyacetic acid from pivalonitrile and *t*-butyl-lithium followed by reaction with *O*-methylhydroxylamine. It had b.p. 80—81° at 15 mmHg (Found: C, 70.2; H, 12.4%; M⁺, 171.162 1. C₁₀H₂₁NO requires C, 70.1; H, 12.4%; M, 171.162 3), δ (neat) 3.70 (3 H, s, Me), 1.32 (9 H, s, Bu^t), and 1.20 (9 H, s, Bu^t).

Benzophenone oxime O-isopropyl ether was prepared from benzophenone oxime, sodium ethoxide, and isopropyl bromide in a manner similar to that described²⁶ for the known *O*-methyl, *O*-benzyl, and *O*-diphenylmethyl ethers of benzophenone oxime. It had b.p. 125—130° (air bath temp.) at 0.05 mmHg (Found: C, 80.0; H, 6.9; N, 5.5%; M⁺, 239.130 7. C₁₆H₁₇NO requires C, 80.3; H, 7.2; N, 5.9%; M, 239.131 0), δ 1.20 (6 H, d, J 6 Hz, CHMe₂), 1.45 (1 H, m, J 6 Hz, OCHMe₂).

OO'-Bis(diphenylmethyleamino) Oxalate (16).—Oxaloyl chloride (2 g, 0.075 mol) in tetrahydrofuran (5 ml) was added dropwise to a stirred solution of benzophenone oxime (6 g, 0.03 mol) in tetrahydrofuran at 0° under nitrogen. Stirring was continued for 4 h at room temperature before the precipitate was collected; the filtrate was concentrated to give a further quantity of solid. The combined solids were crystallised from chloroform-petrol to give the *oxalate* (4.9 g, 69%), m.p. 165—166° (Found: C, 74.7; H, 4.5; N, 6.2. C₂₈H₂₀N₂O₄ requires C, 75.0; H, 4.5; N, 6.3%), ν_{\max} 1 792 and 1 750 cm⁻¹.

Oxidation of Oxyacetic Acids.—(i) *With persulphate*. To a solution of the oxyacetic acid (0.012 mol) in 0.1M-sodium hydroxide solution (120 ml, 0.012 mol) under reflux a solution of potassium persulphate (0.013 mol) in water (180 ml) was added dropwise. Heating was continued until either the solution darkened or precipitation of solid appeared to be complete (*ca.* 5—15 min). The mixture was diluted with water, cooled, and then extracted with ether. The ethereal extracts were shaken successively with 2M-hydrochloric acid, 2M-alkali, and water, and then dried. The residue obtained on removal of solvent was either crystallised or chromatographed on silica (GF₂₅₄) using chloroform-petrol (3 : 2) as eluant.

Diphenylmethyleamino-oxyacetic acid gave benzophenone azine²⁷ (97%), identical with an authentic sample. Fluoren-9-ylideneamino-oxyacetic acid gave fluorenone azine²⁸ (85%), identical with an authentic sample, and traces of fluorenone.

(ii) *Hunsdiecker oxidations*. (a) Diphenylmethyleamino-oxyacetic acid (25 mg) in carbon tetrachloride was

heated under reflux with mercury(II) oxide (20 mg) and iodine (13 mg) under nitrogen for 2 h. On cooling a crystalline solid separated which was recrystallised from methanol to give *diphenylmethyleamino-oxyethyl diphenylmethyleamino-oxyacetate* (8; Ar = Ar' = Ph, R = H) (10 mg, 45%) as needles, m.p. 154—157° (Found: C, 74.8; H, 5.3; N, 5.8. C₂₉H₂₄N₂O₄ requires C, 75.0; H, 5.2; N, 6.05%), ν_{\max} 1 756 cm⁻¹, δ 4.81 (2 H, s, =NOCH₂CO₂), 5.95 (2 H, s, CO₂CH₂O), and 7.1—7.7 (20 H, m, ArH).

This ester, with benzophenone, was also produced from reaction of (a) the mercury(II) salt of diphenylmethyleamino-oxyacetic acid (50 mg) with bromine (16 mg) in benzene under reflux, (b) the acid (25 mg) with bromine (16 mg) and mercury(II) oxide (20 mg) in carbon tetrachloride under reflux, (c) the silver(II) salt of the acid (18 mg) with bromine (8 mg) in carbon tetrachloride under reflux, and (d) the silver(II) salt of the acid (18 mg) with iodine (6 mg) in carbon tetrachloride under reflux for 2 days.

(b) Treatment of *o*-methylphenyl(phenyl)methyleamino-oxyacetic acid (269 mg) as described in (a) gave *o*-methylphenyl(phenyl)methyleamino-oxyethyl *o*-methylphenyl(phenyl)methyleamino-oxyacetate (8; Ar = Ph, Ar' = *o*-C₆H₄Me, R = H) (21 mg) as needles, m.p. 109—111° (from ethanol) (Found: C, 75.3; H, 5.7; N, 5.6. C₃₁H₂₈N₂O₄ requires C, 75.6; H, 5.75; N, 5.7%), ν_{\max} 1 758 cm⁻¹, δ 2.10 (3 H, s, Me), 2.20 (3 H, s, Me), 4.72 (2 H, s, =NOCH₂CO₂), 5.86 (2 H, s, CO₂CH₂ON), and 6.9—8.0 (18 H, m, ArH).

(c) Similarly 2-[mesityl(phenyl)methyleamino-oxy]-2-methylpropanoic acid (325 mg) gave [mesityl(phenyl)methyleamino-oxy-1-methylethyl 2-[mesityl(phenyl)methyleamino-oxy]-2-methylpropanoate (8; Ar = Ph, Ar' = 2,4,6-Me₃C₆H₂, R = Me) (40 mg) as needles, m.p. 187—190° (from methanol) (Found: C, 77.7; H, 7.8; N, 4.4. C₃₉H₄₄N₂O₄ requires C, 77.45; H, 7.35; N, 4.65%), ν_{\max} 1 700 cm⁻¹, δ 1.84 (6 H, s, Me₂C), 1.91 (9 H, s, 3Me), 2.05 (6 H, s, CMe₂), 2.15 (9 H, s, 3 Me), 6.49 (2 H, s, *m*-ArH), 6.69 (2 H, s, *m*-ArH), and 7.13—7.30 (10 H, m, ArH).

(iii) *With silver picolinate*. Diphenylmethyleamino-oxyacetic acid (50 mg) in benzene (5 ml) and pyridine (80 mg) was heated under reflux with silver(I) picolinate (40 mg) for 2 h. The mixture was filtered, and the filtrate was evaporated. Crystallisation of the residue gave benzophenone azine (40 mg, 75%). In the absence of pyridine, and when trifluoroacetic acid was present benzophenone was also produced and the yield of azine decreased (*t.l.c.*).

(iv) *With hydrogen peroxide*. Hydrogen peroxide (30% aqueous solution; 0.125 ml, 1.1 mol) was added to a solution of pyridine (316 mg) in ether (0.5 ml) cooled to -10°. To this solution diphenylmethyleamino-oxyacetyl chloride (540 mg, 2 mmol) in ether (1 ml) was added, and the mixture was stirred at 0° for 2 h. The organic phase was separated, washed with water, dried, and evaporated. Chromatography (*p.l.c.*) of the residue on silica using chloroform-petrol (6 : 4) gave benzophenone (40 mg, 10%), benzophenone azine (80 mg, 10%), benzophenone oxime (8 mg, 2%), diphenylmethyleamino-oxyethyl diphenylmethyleamino-oxyacetate (66 mg, 14%), diphenylmethyleamino-oxyacetic acid (40 mg, 8%) all identical with authentic specimens, and *diphenylmethyleamino diphenylmethyleamino-oxyacetate* (9) (10 mg, 2%), m.p. 113—114° (from methanol) (Found: C, 76.7; H, 5.6%; M⁺, 434.163 0. C₂₈H₂₂N₂O₃ requires C, 76.7; H, 5.05%;

M, 434.163 0), ν_{\max} , 3 060, 2 930, and 1 782 cm^{-1} , δ 4.85 (2 H, s, OCH_2CO_2) and 7.36 (20 H, m, ArH).

Thermolysis of Peresters.—(a) *t*-Butyl diphenylmethylenamino-oxyperacetate (327 mg) in benzene [(a) 1 ml, (b) 10 ml, and (c) 100 ml] was heated under reflux under nitrogen for 0.5 h. The solvent was removed, and the residue was crystallised from methanol to give benzophenone azine. The mother liquors were chromatographed on silica (p.l.c.) to give benzophenone and *diphenylmethylenamino-oxy-t-butoxymethane* as needles, m.p. 32–35° (after short path distillation) (Found: C, 76.16; H, 7.3 N, 4.8. $\text{C}_{18}\text{H}_{21}\text{NO}_2$ requires C, 76.3; H, 7.45; N, 4.95%), δ 1.22 (9 H, s, Bu^t), 5.34 (2 H, s, CH_2), and 7.37 (10 H, m, ArH). Yields of products at the three dilutions are given in Table 1. In a further experiment the nitrogen gas which was bubbled through the solution of the perester during decomposition was passed into a 10% ethanolic solution of dimedone. Leaflets of the formaldehyde–dimedone condensation product (20%) separated, m.p. 177° (lit.,²⁹ 187–188°).

(b) A solution of *t*-butyl fluoren-9-ylideneamino-oxyperacetate (400 mg) in benzene (25 ml) was heated under reflux for 1 h. Work-up as in (a) gave fluorenone (84 mg, 38%), fluorenone azine (20 mg, 9%), and *fluoren-9-ylideneamino-oxy-t-butoxymethane* (76 mg, 22%) as a pale yellow oil (Found: C, 76.7; H, 6.6; N, 5.1. $\text{C}_{18}\text{H}_{19}\text{NO}_2$ requires C, 76.85; H, 6.8; N, 5.0%), 1.34 (9 H, s, Bu^t), 5.59 (2 H, s, CH_2), and 7.1–7.9 (8 H, m, ArH).

Oxidation of Oxime Ethers.—The n.m.r. spectrum of the oxime ether (0.000 1 mol) in deuteriobenzene (0.35 ml) was measured using a Perkin-Elmer R12A spectrometer. Di-*t*-butyl peroxalate (0.000 2 mol) was added, the solution was shaken, and the alkoxy proton resonance measured at regular intervals during 5 h. After the initial shaking the solution was kept in the cavity between measurements.

Photolysis of Oxalate (16).—The oxalate (2.5 g) in benzene (400 ml) was photolysed in a 'falling curtain reactor'³⁰ with a 500 W medium pressure mercury vapour lamp. When reaction was complete (t.l.c.) (*ca.* 10 min) the solvent was evaporated, and the residue was chromatographed on silica with chloroform–petrol (6:4) as eluant to give (a) benzophenone (0.380 g, 18%), (b) benzophenone azine (0.420 g, 22%), (c) benzophenone oxime (0.150 g, 7%), and the starting oxalate (0.381 g, 17%).

E.s.r. Measurements.—(a) A thoroughly degassed *ca.* 1M solution of the *t*-butyl perester in benzene was heated rapidly to 75° in the cavity of a Varian E3 spectrometer.

(b) A saturated solution of the oxime ether or oxalate in di-*t*-butyl peroxide or di-*t*-butyl peroxide–toluene was photolysed with a 1 kW high pressure mercury lamp in the cavity of the spectrometer in the temperature range –20 to 60°.

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